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(54) **Title**: METHOD FOR THE DENSIFICATION OF KERATINOUS FIBRES BASED ON SPECIFIC ACRYLIC POLYMER AND SPECIFIC SILICONE COMPOUND

(57) **Abstract**: A subject-matter of the present invention is a method for colouring a skin region supporting keratinous fibres, which consists in applying, to the said skin region, and optionally to said keratinous fibres, a composition comprising at least one aqueous dispersion of particles of hydrophobic film-forming hybrid acrylic polymer, at least one silicone compound chosen from linear block silicone copolymers, aminated silicones and their mixtures, and at least one pigment.

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METHOD FOR THE DENSIFICATION OF KERATINOUS FIBRES BASED ON SPECIFIC ACRYLIC POLYMER AND SPECIFIC SILICONE COMPOUND

A subject-matter of the present invention is a method for the visual densification of keratinous fibres, more particularly the hair and very especially its roots, beard hairs, moustache hairs, eyelashes and eyebrows, by colouration of at least one region of the skin supporting the said keratinous fibres and optionally colouration of the said keratinous fibres. More particularly, the method consists in colouring the skin which supports the keratinous fibres using a composition comprising an aqueous dispersion of particles of specific acrylic polymer, a linear block silicone copolymer or an aminated silicone and a pigment.

For a visual densification of the eyebrows, it is known to use pencils, felt-tip pens or permanent tattoos which make it possible to trace features imitating the presence of eyelashes and to visually fill out the eyebrows, in particular when they are sparse. However, these products give a diffuse and blurred result, the pencil line becomes visible at the place where the density of keratinous fibres is lower and uneven, which leads to a rather unnatural colour result. Moreover, the pencils and felt-tip pens may not always modify the initial colour of the eyebrows and the colour introduced is not very persistent over time (feel) and not always resistant to water or sweat.

Furthermore, it is possible to permanently colour keratinous fibres, such as the hairs of the eyebrows or of the moustache, using "oxidation" dyes, which consist in applying, to the hair, one or more dye precursors and an oxidizing agent.

Furthermore, it is known to carry out coloured sheathings of keratinous fibres using a pressure-sensitive adhesive silicone copolymer, in particular a copolymer based on silicone resin and on fluid silicone. Once deposited on the fibres, these copolymers exhibit the advantage of contributing persistent colour. On the other hand, the treated fibres are somewhat harsh to the touch.

However, these methods do not result in a colouration of the skin little by little. The permanent colouration of the non-head hairs is not sufficient to contribute a sufficient densification at the place where the density of the keratinous fibres is lower and uneven.

Thus, the aim of the present invention is to provide one which makes it possible to obtain a natural effect of visual densification of keratinous fibres which holds over time.

This aim is achieved with the present invention, a subject-matter of which is a method which consists in colouring, using a specific composition, at least one region of the skin which supports keratinous fibres, in particular of the skin of the face, and optionally in also colouring said keratinous fibres.

More specifically, a subject-matter of the invention is a method for colouring a skin region supporting keratinous fibres, which consists in applying, to the said skin region, and optionally to said keratinous fibres, a composition comprising at least one aqueous dispersion of particles of hydrophobic film-forming hybrid acrylic polymer, at least one silicone compound chosen from linear block silicone copolymers, aminated silicones and their mixtures, and at least one pigment.

The term "at least one" is understood to mean "one or more".

The term "comprising a" is understood to mean "comprising at least one", unless specified to the contrary.

The term "keratinous fibres" means in particular the hair and non-head hairs, such as the eyelashes, eyebrows, beard hairs or moustache hairs.

The region of the skin which supports the keratinous fibres can be the skin of the scalp, skin at the eyebrows or eyelashes, skin of the face which carries the beard hairs, moustache hairs, locks of hair on the temples.

Preferably, the composition is applied non-continuously to the skin region concerned, for example little by little, in particular via fine lines or small points, in order to imitate the presence of non-head hairs, eyelashes or eyebrows on the skin.

The method according to the invention thus makes it possible to obtain, by the colouration of the skin close to the keratinous fibres, an effect of visual densification of the keratinous fibres.

In particular, in the case of sparse or uneven eyebrows, this method makes it possible to obtain a natural effect of thicker and more even eyebrows.

The colouration obtained withstands well shampooing or washing operations and external attacks which the fibres may be subjected to, such as blow drying and perspiration. It makes it possible in particular to obtain a smooth and uniform deposit.

Furthermore, when the keratinous fibres are also coloured, it has been found that they remain completely individualized.

The term “individualized fibres” is understood to mean fibres which, after application of the composition and drying, are not stuck together (or are all separated from one another) and thus do not form clumps.

According to a first alternative form, the method consists in colouring a region of the skin which supports keratinous fibres, in particular skin of the face, and in also colouring the said keratinous fibres supported by this skin region.

In one embodiment of this first alternative form, the skin and the keratinous fibres can be coloured in a similar colour (the colouration is such that the variation in colour ΔE, expressed in the CIE L* a* b* system, between the fibres coloured by the composition and the untreated fibres is less than or equal to 2).

In another embodiment of this first alternative form, the initial colour of the skin and keratinous fibres is modified, that is to say that the colouration is such that the variation in colour ΔE, expressed in the CIE L* a* b* system, between the fibres coloured by the composition and the untreated fibres is greater than or equal to 2.

According to a second alternative form, the method consists in colouring solely a region of the skin which supports keratinous fibres, in particular skin of the face, for example the skin region or regions between the eyebrows.

Aqueous dispersion of particles of hydrophobic film-forming hybrid acrylic polymer

The term “polymer” is understood to mean, within the meaning of the invention, a compound corresponding to the repetition of one or more units (these units resulting from compounds known as monomers). This or these unit(s) is (are) repeated at least twice and preferably at least 3 times.

The term “film-forming polymer" is understood to mean a polymer capable of forming, by itself alone or in the presence of an auxiliary film-forming agent, a macroscopically continuous film on a support, in particular on keratinous substances, and preferably a cohesive film.

The term "hydrophobic polymer" is understood to mean a polymer having a solubility in water at 25°C of less than 1% by weight.

The dispersion can be a simple dispersion in the aqueous medium of the composition.

Mention may be made, as specific case of dispersions, of latexes.

The term "hybrid acrylic polymer" is understood to mean, within the meaning of the present invention, a polymer synthesized from at least one compound (i) chosen from monomers having at least one (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers and from at least one compound (ii) different from the compounds (i), that is to say which does not comprise (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers.

The (meth)acrylic acid esters (also known as (meth)acrylates) are advantageously chosen from alkyl (meth)acrylates, in particular C_1-C_{30}, preferably C_1-C_{20} and better still C_1-C_{10} alkyl (meth)acrylates, aryl (meth)acrylates, in particular C_6-C_{10} aryl (meth)acrylates, and hydroxyalkyl (meth)acrylates, in particular C_2-C_6 hydroxyalkyl (meth)acrylates.

Mention may be made, among alkyl (meth)acrylates, of methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate or cyclohexyl methacrylate.

Mention may be made, among hydroxyalkyl (meth)acrylates, of hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxyethyl methacrylate or 2-hydroxypropyl methacrylate.

Mention may be made, among aryl (meth)acrylates, of benzyl acrylate and phenyl acrylate.

The (meth)acrylic acid esters which are particularly preferred are the alkyl (meth)acrylates.

According to the present invention, the alkyl group of the esters can be either fluorinated or perfluorinated, that is to say that a portion or all of the hydrogen atoms of the alkyl group are replaced by fluorine atoms.

Mention may be made, as amides of the acid monomers, for example, of (meth)acrylamides and in particular N-alkyl(meth)acrylamides, especially N-(C_2-C_{12} alkyl)(meth)acrylamides. Mention may be made, among the N-alkyl(meth)acrylamides, of N-ethylacrylamide, N-(t-butyl)acrylamide, N-(t-octyl)acrylamide and N-undecylacrylamide.

Mention will be made, as compounds (ii) different from the compounds (i), for example, of styrene monomers.

In particular, the acrylic polymer can be a styrene/acrylate copolymer and especially a polymer chosen from copolymers resulting from the polymerization of at least one styrene monomer and at least one C_1-C_{20} and preferably C_1-C_{10} alkyl acrylate monomer.

Mention may be made, as styrene monomer which can be used in the invention, of styrene or α-methylstyrene, and preferably styrene.

The C_1-C_{10} alkyl acrylate monomer can be chosen from methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate or 2-ethylhexyl acrylate.

Mention may be made, as acrylic polymer synthesized with styrene compound, of the styrene/acrylate copolymers sold under the name Joncryl 77 by BASF, under the name Yodosol GH41F by Akzo Nobel and under the name Syntran 5760 CG by Interpolymer.

Mention may also be made, as compound (ii), of the compounds which interact via a process other than the radical polymerization of unsaturated compounds or the compounds resulting from such a process. Such a process can, for example, be a polycondensation. Mention may be made, as polycondensation, of the formation of polyurethanes, polyesters or polyamides. In addition to the acrylic monomer or monomers, the hydrophobic film-forming hybrid polymer of the invention will then comprise the compound resulting from the condensation process or the compounds which interact in the polycondensation process.

Mention may in particular be made, as hydrophobic film-forming hybrid acrylic copolymer of this type, of that sold under the reference Hybridur 875 Polymer Dispersion by Air Products and Chemicals.

Use may also be made, as hydrophobic film-forming hybrid acrylic copolymer, of the product sold under the reference Primal HG 1000 by Dow.

The hydrophobic film-forming hybrid acrylic polymer or polymers in aqueous dispersion can be present in a content, as active materials, ranging from 0.1% to 30% by weight, more particularly from 0.5% to 20% by weight and preferably from 1% to 15% by weight, with respect to the total weight of the composition.

Silicone compounds chosen from linear block silicone copolymers and/or aminated silicones

Linear block silicone copolymer

The silicone copolymer used in the composition according to the invention is a linear block copolymer, that is to say a non-crosslinked copolymer, obtained by chain extension and not by crosslinking.

The term "block copolymer" (or "sequential copolymer") denotes a polymer comprising at least two distinct blocks (sequences). Each block of the polymer results from one type of monomer or from several different types of monomer. This means that each block can be composed of a homopolymer or a copolymer; this copolymer constituting the block which can in turn be random or alternating.

The silicone copolymer used in the composition according to the invention preferably comprises at least two distinct silicone blocks (or sequences), each block resulting from the polymerization of at least one type of silicone monomer or of several types of silicone monomer, as described below.

It should also be noted that the copolymer is "linear", in other words the structure of the polymer is neither branched, nor star-shaped, nor grafted.

The linear block silicone copolymer is advantageously provided in the form of particles in dispersion in an aqueous medium.

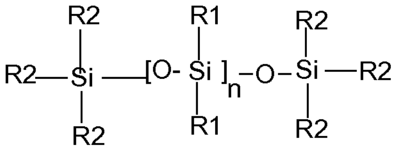
The aqueous dispersion of block copolymer particles is a silicone-in-water (Sil/W) emulsion, the oil globules of which are composed of a silicone of high viscosity, such that these globules appear to form like "flexible particles".

The size of the linear block silicone copolymer particles can vary widely. Preferably, in the present patent application, the linear block silicone copolymer particles generally exhibit a number-average size of less than or equal to 2 microns and preferably of less than or equal to 1 micron.

The aqueous dispersions of linear block silicone copolymer particles used in the composition according to the invention can be chosen in particular from those described in the document EP-A-874 017, the teaching of which is incorporated herein by reference. According to this document, it is possible in particular to obtain the silicone copolymers constituting these particles by a chain-extension reaction, in the presence of a catalyst, starting from at least:

- (a) a polysiloxane (i) having at least one reactive group and preferably one or two reactive groups per molecule; and
- (b) an organosilicone compound (ii) which reacts with the polysiloxane (i) via a chain-extension reaction.

In particular, the polysiloxane (i) is chosen from the compounds of formula (I):



$$R2-\underset{R2}{\overset{R2}{Si}}-[O-\underset{R1}{\overset{R1}{Si}}]_n-O-\underset{R2}{\overset{R2}{Si}}-R2 \qquad (I)$$

in which R_1 and R_2 represent, independently of one another, a hydrocarbon group having from 1 to 20 carbon atoms and preferably from 1 to 10 carbon atoms, such as methyl, ethyl, propyl or butyl, or an aryl group, such as phenyl, or a reactive group, and n is an integer greater than 1, provided that there are on average between one and two reactive groups per polymer.

The term "reactive group" is understood to mean any group capable of reacting with the organosilicone compound (ii) to form a block copolymer. Mention may be made, as reactive groups, of hydrogen; aliphatically unsaturated groups, in particular vinyl, allyl or hexenyl groups; the hydroxyl group; alkoxy groups, such as methoxy, ethoxy or propoxy groups; alkoxyalkoxy groups; the acetoxy group; amino groups, and their mixtures. Preferably, more than 90% and better still more than 98% of the reactive groups are at the chain end, that is to say that the R_2 radicals generally constitute more than 90% and even 98% of the reactive groups.

n can in particular be an integer ranging from 5 to 30, preferably from 10 to 30 and better still from 15 to 25.

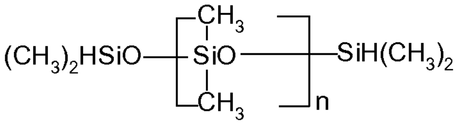
The polysiloxanes of formula (I) are linear polymers, that is to say comprising few branches and generally less than 2 mol% of siloxane units. Moreover, the R_1 and R_2 groups can optionally be substituted by amino groups, epoxy groups, groups comprising sulfur, silicon or oxygen.

Preferably, at least 80% of the R_1 groups are alkyl groups and better still methyl groups.

Preferably, the reactive R_2 group at the chain end is an aliphatically unsaturated group and in particular a vinyl group.

Mention may in particular be made, as polysiloxanes (i), of dimethylvinylsiloxypolydimethylsiloxane, compound of formula (I) in which the R_1 radicals are methyl radicals and the R_2 radicals at the chain end are vinyl radicals, whereas the two other R_2 radicals are methyl radicals.

The organosilicone compound (ii) can be chosen from the polysiloxanes of formula (I) or the compounds which act as chain extenders. If it is a compound of formula (I), the polysiloxane (i) will comprise a first reactive group and the organosilicone compound (ii) will comprise a second reactive group which will react with the first. If it is a chain extender, it can be a silane, a siloxane (disiloxane or trisiloxane) or a silazane. Preferably, the organosilicone compound (ii) is a liquid organohydropolysiloxane of formula (II):



$$(CH_3)_2HSiO-\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_n-SiH(CH_3)_2 \quad \text{(II)}$$

where n is an integer greater than 1 and preferably greater than 10, for example ranging from 2 to 100, preferably from 10 to 30 and better still from 15 to 25. According to a specific embodiment of the invention, n is equal to 20.

The silicone block copolymers used according to the invention are advantageously devoid of oxyalkylene group(s), in particular devoid of oxyethylene and/or oxypropylene group(s).

The catalyst for the reaction between the polysiloxane and the organosilicone compound can be chosen from metals and in particular from platinum, rhodium, tin, titanium, copper and lead. It is preferably platinum or rhodium.

The dispersion of silicone copolymer particles used in the composition according to the invention can in particular be obtained, for example, by mixing (a) water, (b) at least one emulsifier, (c) the polysiloxane (i), (d) the organosilicone compound (ii) and (e) a catalyst. Preferably, one of the constituents (c), (d) or (e) is added last to the mixture, in order for the chain-extension reaction to begin only in the dispersion.

Mention may be made, as emulsifiers capable of being used in the preparation process described above in order to obtain the aqueous dispersion of particles, of nonionic or ionic (anionic, cationic or amphoteric) emulsifiers. They are preferably nonionic emulsifiers which can be chosen from polyalkylene glycol ethers of a fatty alcohol comprising from 8 to 30 carbon atoms and preferably from 10 to 22 carbon atoms; polyoxyalkylenated and in particular polyoxyethylenated sorbitan alkyl esters, where the alkyl radical comprises from 8 to 30 carbon atoms and preferably from 10 to 22 carbon atoms; polyoxyalkylenated and in particular polyoxyethylenated alkyl esters, where the alkyl radical comprises from 8 to 30 carbon atoms and preferably from 10 to 22 carbon atoms; polyethylene glycols; polypropylene glycols; diethylene glycols; and their mixtures. The amount of emulsifier(s) is generally from 1% to 30% by weight, with respect to the total weight of the reaction mixture.

The emulsifier used in order to obtain the aqueous dispersion of particles is preferably chosen from polyethylene glycol ethers of fatty alcohols and their mixtures, and in particular polyethylene glycol ethers of alcohols comprising an alcohol of 12 or 13 carbon atoms and from 2 to 100 oxyethylene units and preferably from 3 to 50 oxyethylene units, and their mixtures. Mention may be made, for example, of C_{12}-C_{13} Pareth-3, C_{12}-C_{13} Pareth-23 and their mixtures.

According to a specific embodiment of the invention, the dispersion of silicone copolymer particles is obtained from dimethylvinylsiloxypolydimethylsiloxane (or divinyl dimethicone) as compound (i) and from the compound of formula (II) with preferably n = 20 as compound (ii), preferably in the presence of a catalyst of platinum type, and the dispersion of particles is preferably obtained in the presence of C_{12}-C_{13} Pareth-3 and C_{12}-C_{13} Pareth-23 as emulsifiers.

Use may in particular be made, as dispersion of silicone copolymer particles, of the product sold under the name HMW 2220 by Dow Corning (CTFA name: divinyl dimethicone/dimethicone copolymer/C_{12}-C_{13} Pareth-3/C_{12}-C_{13} Pareth-23), which is a 60% aqueous dispersion of divinyl dimethicone/dimethicone copolymer comprising C_{12}-C_{13} Pareth-3 and C_{12}-C_{13} Pareth-23, the said dispersion comprising approximately 60% by weight of copolymer, 2.8% by weight of C_{12}-C_{13} Pareth-23, 2% by weight of C_{12}-C_{13} Pareth-3 and 0,31% by weight of preservatives, the remainder to 100% being water.

Aminated silicone

According to the invention, the term "aminated silicone" denotes any silicone comprising at least one primary, secondary or tertiary amine or one quaternary ammonium and more particularly at least one primary amine.

The aminated silicones used in the cosmetic composition according to the present invention can be chosen from the silicones of following formula (I):

$$(R^1)_a(T)_{3-a}\text{-Si}[\text{OSi}(T)_2]_n\text{-}[\text{OSi}(T)_b(R^1)_{2-b}]_m\text{-OSi}(T)_{3-a}\text{-}(R^1)_a \qquad (I)$$

in which:

T is a hydrogen atom, a phenyl radical, a hydroxyl (-OH) radical, a C_1-C_8 alkyl radical, preferably a methyl radical, or a C_1-C_8 alkoxy radical, more preferably a methyl radical,

a denotes the number 0 or an integer from 1 to 3, and preferably 0,

b denotes 0 or 1, and in particular 1,

m and n are numbers such that the sum (n + m) can vary in particular from 1 to 2000 and especially from 50 to 150, n denotes a number from 0 to 1999 and in particular from 49 to 149 and m denotes a number from 1 to 2000 and in particular from 1 to 10,

R^1 is a monovalent radical of formula $-C_qH_{2q}L$ in which q is a number from 2 to 8, it being possible for one or more hydrogen atoms to be replaced by a hydroxyl group, and L is an optionally quaternized amino group chosen from the groups:

$-N(R^2)-CH_2-CH_2-N(R'^2)_2$;

$-N(R^2)_2$;

$-N^+(R^2)_3Q^-$;

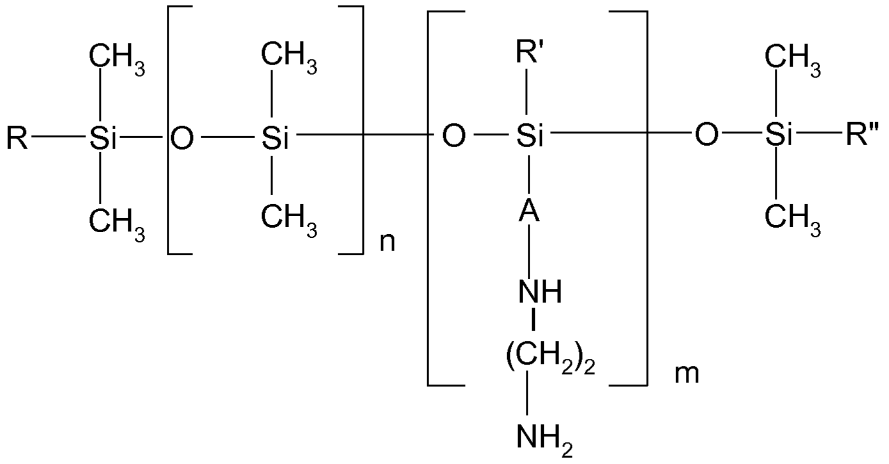
$-N^+(R^2)(H)_2Q^-$;

$-N^+(R^2)_2HQ^-$;

$-N(R^2)-CH_2-CH_2-N^+(R'^2)(H)_2Q^-$,

in which R^2 and R'^2 denote a hydrogen atom, a phenyl, a benzyl or a saturated monovalent hydrocarbon radical, for example a C_1-C_{20} alkyl radical, and Q^- represents an anion, such as, for example, fluoride, chloride, bromide or iodide.

In particular, the aminated silicones corresponding to the definition of the formula (I) are chosen from the compounds corresponding to the following formula:



(II)

in which:

R, R' and R", which are identical or different, denote a C_1-C_4 alkyl, preferably CH_3, radical, a C_1-C_4 alkoxy, preferably methoxy, radical or an OH radical;

A represents a linear or branched C_3-C_8, preferably C_3-C_6, alkylene radical, and m and n are integers which depend on the molecular weight and the sum of which is between 1 and 2000.

According to a first possibility, R, R' and R", which are identical or different, represent a C_1-C_4 alkyl, preferably methyl, radical or a hydroxyl radical, A represents a C_1-C_8, preferably C_3-C_4, alkylene radical, and m and n are such that the weight-average molecular weight of the compound is between 5000 and 500 000 approximately. The compounds of this type are named “amodimethicone” in the CTFA dictionary.

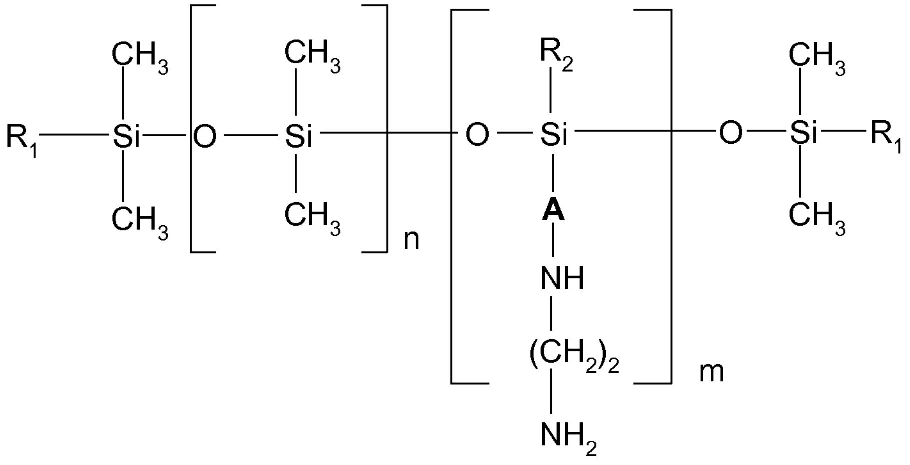
According to a second possibility, R, R' and R”, which are identical or different, represent a C_1-C_4 alkoxy or hydroxyl radical, at least one of the R or R” radicals is an alkoxy radical and A represents a C_3 alkylene radical. The hydroxyl/alkoxy molar ratio is preferably between 0.2/1 and 0.4/1 and advantageously equal to 0.3/1. Moreover, m and n are such that the weight-average molecular weight of the compound is between 2000 and 10^6. More particularly, n is between 0 and 999 and m is between 1 and 1000, the sum of n and m being between 1 and 1000.

In this category of compounds, mention may be made, *inter alia*, of the product Belsil® ADM 652 sold by Wacker.

According to a third possibility, R and R”, which are different, represent a C_1-C_4 alkoxy or hydroxyl radical, at least one of the R and R” radicals is an alkoxy radical, R’ represents a methyl radical and A represents a C_3 alkylene radical. The hydroxyl/alkoxy molar ratio is preferably between 1/0.8 and 1/1.1 and is advantageously equal to 1/0.95. Moreover, m and n are such that the weight-average molecular weight of the compound is between 2000 and 200 000. More particularly, n is between 0 and 999 and m is between 1 and 1000, the sum of n and m being between 1 and 1000.

More particularly, mention may be made of the product Fluid WR® 1300 sold by Wacker.

The aminated silicones used in the composition in accordance with the invention preferably exhibit the following general formula (III):



$$R_1-\underset{CH_3}{\overset{CH_3}{Si}}-\left[O-\underset{CH_3}{\overset{CH_3}{Si}}\right]_n-\left[O-\underset{\underset{\underset{\underset{NH_2}{|}}{(CH_2)_2}}{\underset{NH}{|}}}{\overset{R_2}{\underset{\mathbf{A}}{Si}}}\right]_m-O-\underset{CH_3}{\overset{CH_3}{Si}}-R_1$$

in which:

A denotes a linear or branched C_2-C_8 and preferably C_2-C_8, better still C_3, alkylene radical;

R_1 and R_2 denote, independently of one another, a C_1-C_4 alkyl, preferably methyl, radical or a C_1-C_4 alkoxy, preferably methoxy, radical or a hydroxyl radical, m and n are numbers such that the weight-average molecular weight (MW) is greater than or equal to 75 000.

Preferably, the R_1 radicals are identical and denote a hydroxyl radical.

Preferably, the viscosity of the aminated silicone is greater than 25 000 mm^2/s, measured at 25°C.

More preferably, the viscosity of the aminated silicone is between 30 000 and 200 000 mm^2/s at 25°C and more preferably still between 50 000 and 150 000 mm^2/s, measured at 25°C, and better still from 70 000 to 120 000 mm^2/s. The viscosities of the silicones are, for example, measured according to Standard ASTM 445, Appendix C.

Preferably, the cationic charge of the aminated silicone is less than or equal to 0.5 meq/g, preferably ranging from 0.01 to 0.1 meq/g and better still from 0.03 to 0.06 meq/g.

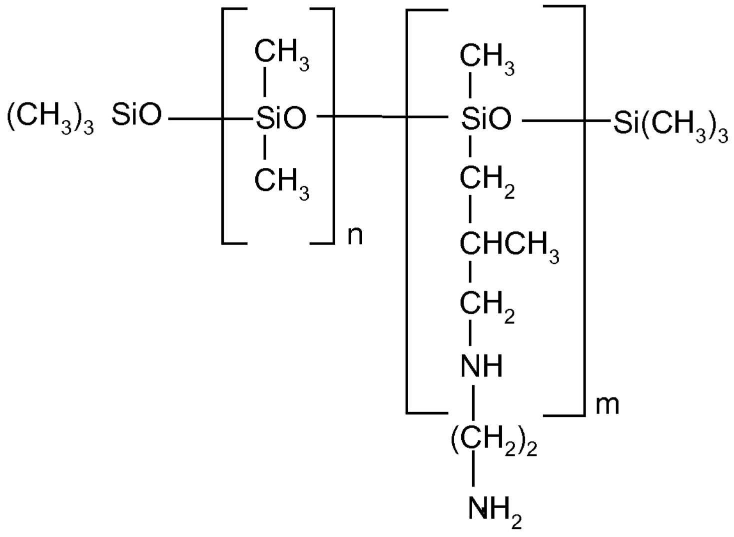
Preferably, the aminated silicone has a weight-average molecular weight ranging from 75 000 to 1 000 000 and more preferentially still ranging from 100 000 to 200 000.

The weight-average molecular weights of these aminated silicones are measured by gel permeation chromatography (GPC) at ambient temperature, as polystyrene equivalent. The columns used are µ styragel columns. The eluent is THF and the flow rate is 1 ml/min. 200 µl of a 0.5% by weight solution of silicone in THF are injected. Detection is carried out by refractometry and UV spectrometry.

A particularly preferred aminated silicone corresponding to this formula (III) is, for example, Xiameter MEM-8299 ® Emulsion from Dow Corning.

It should be noted that the molecular weight of these silicones is determined by gel permeation chromatography (ambient temperature; polystyrene standard; µ styragem columns; eluent THF; flow rate of 1 mm/m; 200 µl of a 0.5% by weight solution of silicone in THF are injected and detection is carried out by refractometry and UV spectrometry).

A product corresponding to the definition of the formula (I) is in particular the polymer called “trimethylsilylamodimethicone” in the CTFA dictionary, corresponding to the following formula (IV):



$$(CH_3)_3SiO-\left[\begin{matrix}CH_3\\|\\SiO\\|\\CH_3\end{matrix}\right]_n-\left[\begin{matrix}CH_3\\|\\SiO\\|\\CH_2\\|\\CHCH_3\\|\\CH_2\\|\\NH\\|\\(CH_2)_2\\|\\NH_2\end{matrix}\right]_m-Si(CH_3)_3$$

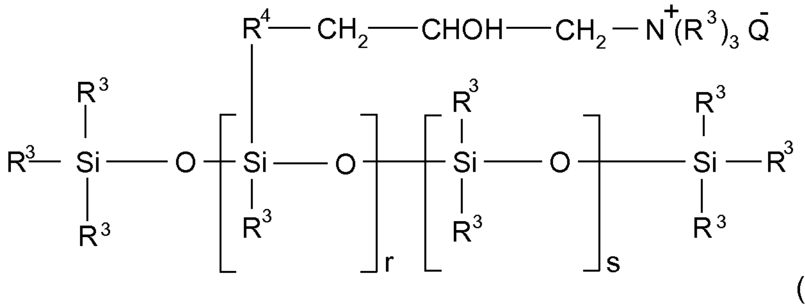
(IV)

in which n and m have the meanings given above in accordance with the formula (II).

Such compounds are described, for example, in EP 95 238; a compound of formula (III) is sold, for example, under the name Q2-8220 by OSI.

Other aminated silicones according to the invention are quaternized aminated silicones, in particular:

(a) the compounds corresponding to the following formula (V):



$$R^3-\underset{R^3}{\overset{R^3}{Si}}-O-\left[\underset{R^3}{\overset{R^4-CH_2-CHOH-CH_2-\overset{+}{N}(R^3)_3\overset{-}{Q}}{Si}}-O\right]_r-\left[\underset{R^3}{\overset{R^3}{Si}}-O\right]_s-\underset{R^3}{\overset{R^3}{Si}}-R^3$$

(V)

in which:

R^3 represents a C_1-C_{18} alkyl radical, for example methyl;

R^4 represents a divalent hydrocarbon radical, in particular a C_1-C_{18} alkylene radical;

Q^- is an anion, in particular chloride;

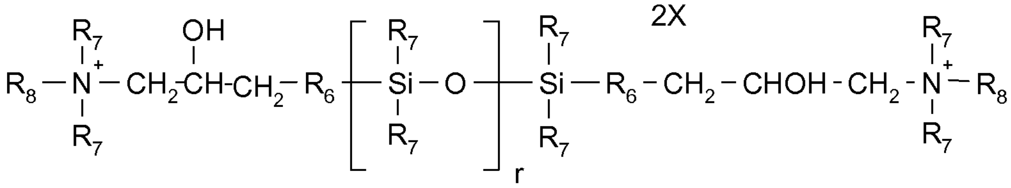
r represents a mean statistical value from 2 to 20 and in particular from 2 to 8;

s represents a mean statistical value from 20 to 200 and in particular from 20 to 50.

Such compounds are described more particularly in Patent US 4 185 087.

A compound coming within this category is that sold by Union Carbide under the name Ucar Silicone ALE 56.

(b) the quaternary ammonium silicones of formula (VI):



$$R_8-\underset{R_7}{\overset{R_7}{\overset{+}{N}}}-CH_2-\overset{OH}{CH}-CH_2-R_6-\left[\underset{R_7}{\overset{R_7}{Si}}-O\right]_r-\underset{R_7}{\overset{R_7}{Si}}-R_6-CH_2-CHOH-CH_2-\underset{R_7}{\overset{R_7}{\overset{+}{N}}}-R_8 \quad 2X$$

(VI

)

in which:

R_7, which are identical or different, represent a monovalent hydrocarbon radical having from 1 to 8 carbon atoms and in particular a C_1-C_8 alkyl radical, for example methyl;

R_6 represents a divalent hydrocarbon radical, in particular a C_1-C_{18} alkylene radical or a divalent C_1-C_{18}, for example C_1-C_8, alkylenoxy radical connected to the Si via an SiC bond;

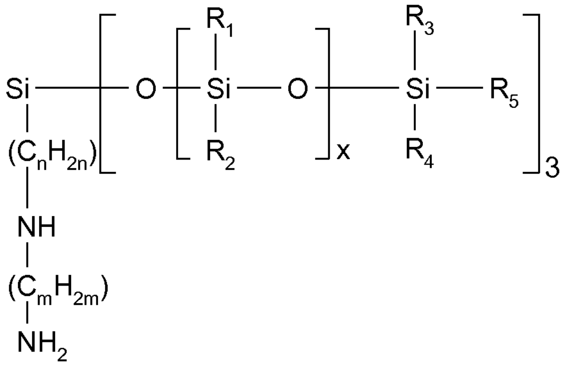
R_8, which are identical or different, represent a hydrogen atom, a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, in particular a C_1-C_{18} alkyl radical or a C_2-C_{18} alkenyl radical, or an -R_6-NHCOR_7 radical;

X^- is an anion, such as a halide ion, in particular chloride, or an organic acid salt (acetate, and the like);

r represents a mean statistical value from 2 to 200 and in particular from 5 to 100.

These silicones are described, for example, in Application EP-A-0 530 974.

(c) the aminated silicones of formula (VII):



$$\mathrm{Si}\left[\mathrm{O}\left[\mathrm{Si}(R_1)(R_2)-\mathrm{O}\right]_x-\mathrm{Si}(R_3)(R_4)-R_5\right]_3-(C_nH_{2n})-\mathrm{NH}-(C_mH_{2m})-\mathrm{NH_2}$$

(VII)

in which:

- R_1, R_2, R_3 and R_4, which are identical or different, denote a C_1-C_4 alkyl radical or a phenyl group,
- R_5 denotes a C_1-C_4 alkyl radical or a hydroxyl group,
- n is an integer varying from 1 to 5,
- m is an integer varying from 1 to 5,

and in which x is chosen so that the amine number is between 0.01 and 1 meq/g.

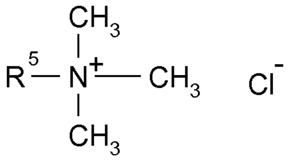
Preferably, the aminated silicones of the invention are non-quaternized, that is to say that they do not comprise a nitrogen atom having a permanent charge (quaternary ammonium group).

Preferably, the aminated silicones of the invention are not block polymers.

The silicones which are particularly preferred in accordance with the invention are the polysiloxanes comprising amino groups, such as amodimethicones or trimethylsilylamodimethicones, and in particular the compounds of formulae (II), (III) and (IV).

When the aminated silicones of the invention are used, a particularly advantageous embodiment is their joint use with cationic and/or nonionic surfactants.

Use may be made, by way of example, of the product sold under the name Cationic Emulsion DC 929 by Dow Corning, which comprises, in addition to amodimethicone, a cationic surfactant comprising a mixture of products corresponding to the formula:



$$R^5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_3 \quad Cl^-$$

in which R^5 denotes C_{14}-C_{22} alkenyl and/or alkyl radicals derived from tallow fatty acids and known under the CTFA name tallowtrimonium chloride, in combination with a nonionic surfactant of formula:

C_9H_{19}-C_6H_4-$(OC_2H_4)_{10}$-OH, known under the CTFA name Nonoxynol 10.

Use may also be made, for example, of the products sold under the names Xiameter MEM-0939 Emulsion and Xiameter MEM-0949 Emulsion by Dow Corning, which comprise, in addition to amodimethicone, a cationic surfactant which is trimethylcetylammonium chloride and a nonionic surfactant of formula: $C_{13}H_{27}$-$(OC_2H_4)_{12}$-OH, known under the CTFA name Trideceth-12.

Mention may also be made of the product sold under the reference Belsil ADM 6060 by Wacker, which comprises, in addition to amodimethicone, a nonionic surfactant Trideceth-10.

In particular, when these aminated silicones are used, a particularly advantageous embodiment is their use in the form of an oil-in-water emulsion.

The oil-in-water emulsion comprises one or more surfactants. The surfactants can be of any nature but are preferably cationic and/or nonionic.

The silicone particles in the emulsion have a volume-average diameter [D4.3] generally ranging from 10 nm to 1000 nanometres, preferably from 50 nm to 800 nanometres, more particularly from 100 nm to 600 nanometres and more particularly still from 200 nm to 500 nanometres. These particle sizes can be determined in particular using a laser particle sizer, such as, for example, the Malvern Mastersizer 2000.

According to the invention, all the silicones can also be used in the form of emulsions or microemulsions.

According to the invention, the silicone compound(s) chosen from the linear silicone block copolymers and/or the aminated silicones can represent from 0.1% to 30% by weight, preferably from 0.5% to 10% by weight and more particularly from 0.1% to 20% by weight, better still from 1% to 15% by weight, as active materials, with respect to the total weight of the composition.

According to one embodiment, the hydrophobic film-forming hybrid acrylic polymer or polymers and the silicone compound or compounds chosen from linear block silicone copolymers and/or aminated silicones are present in a weight ratio (as active materials) of hydrophobic film-forming hybrid acrylic polymer(s) to linear block silicone copolymer(s) and/or aminated silicone(s) ranging from 0.2 to 10, better still from 0.5 to 5 and even better still from 1 to 3.

According to a preferred embodiment, the hydrophobic film-forming hybrid acrylic polymer or polymers and the silicone compound or compounds chosen from linear block silicone copolymers and/or aminated silicones are present in a weight ratio (as polymer active materials) of hydrophobic film-forming hybrid acrylic polymer(s) to linear block silicone copolymer(s) and/or aminated silicone(s) greater than or equal to 1.

When the hydrophobic film-forming hybrid acrylic polymer has a glass transition temperature which is too high for the desired use, a plasticizer may be combined therewith so as to lower this temperature of the mixture used. The plasticizer can be chosen from the plasticizers normally used in the field of application and in particular from the compounds which may be solvents for the polymer.

Preferably, the plasticizer has a molecular weight of less than or equal to 5000 g/mol, preferably of less than or equal to 2000 g/mol, preferentially of less than or equal to 1000 g/mol and more preferentially still of less than or equal to 900 g/mol. The plasticizer advantageously has a molecular weight of greater than or equal to 100 g/mol.

Thus, the composition can additionally comprise at least one plasticizer. In particular, mention may be made, alone or as a mixture, of the normal plasticizers, such as:

- glycols and their derivatives, such as diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol butyl ether or diethylene glycol hexyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether or ethylene glycol hexyl ether;
- polyethylene glycols, polypropylene glycols, polyethylene glycol/polypropylene glycol copolymers and their mixtures, in particular high molecular weight polypropylene glycols, for example having a molecular weight ranging from 500 to 15 000, such as, for example,

- glycol esters;

- propylene glycol derivatives and in particular propylene glycol phenyl ether, propylene glycol diacetate, dipropylene glycol ethyl ether, tripropylene glycol methyl ether and diethylene glycol methyl ether, dipropylene glycol butyl ether. Such compounds are sold by Dow Chemical under the names Dowanol PPH and Dowanol DPnB.

- acid esters, in particular carboxylic acid esters, such as citrates, phthalates, adipates, carbonates, tartrates, phosphates or sebacates;

- esters resulting from the reaction of a monocarboxylic acid of formula $R_{11}COOH$ with a diol of formula $HOR_{12}OH$ with R_{11} and R_{12}, which are identical or different, representing a saturated or unsaturated and linear, branched or cyclic hydrocarbon chain preferably comprising from 3 to 15 carbon atoms and optionally comprising one or more heteroatoms, such as N, O or S, in particular the monoester resulting from the reaction of isobutyric acid and octanediol, such as 2,2,4-trimethyl-1,3-pentanediol, such as that sold under the reference Texanol Ester Alcohol by Eastman Chemical;

- oxyethylenated derivatives, such as oxyethylenated oils, in particular vegetable oils, such as castor oil;

- their mixtures.

More particularly, the plasticizer can be chosen from esters of at least one carboxylic acid comprising from 1 to 7 carbon atoms and of a polyol comprising at least 4 hydroxyl groups.

The polyol can be a cyclized or uncyclized monosaccharide - polyhydroxyaldehyde (aldose) or polyhydroxyketone (ketose). The polyol is preferably a monosaccharide cyclized in hemiacetal form.

The polyol can be a monosaccharide or a polysaccharide comprising from 1 to 10 monosaccharides, preferably from 1 to 4 monosaccharides and more preferably one or two monosaccharides. The polyol can be chosen from erythritol, xylitol, sorbitol, glucose, sucrose, lactose or maltose.

The polyol is preferably a disaccharide. Mention may be made, among the disaccharides, of sucrose (also known as α-D-glucopyranosyl-(1→2)-β-D-fructofuranose), lactose (also known as β-D-galactopyranosyl-(1→4)-β-D-glucopyranose) and maltose (also known as α-D-glucopyranosyl-(1→4)-β-D-glucopyranose), and preferably sucrose.

The ester can be composed of a polyol esterified by at least two different monocarboxylic acids or by at least three different monocarboxylic acids.

The ester can be a copolymer of two esters, in particular a copolymer i) of a sucrose substituted by benzoyl groups and ii) of a sucrose substituted by acetyl and/or isobutyryl groups.

The carboxylic acid is preferably a monocarboxylic acid comprising from 1 to 7 carbon atoms and preferably from 1 to 5 carbon atoms, for example chosen from acetic acid, n-propanoic acid, isopropanoic acid, n-butanoic acid, isobutanoic acid, tert-butanoic acid, n-pentanoic acid and benzoic acid.

The ester can be obtained from at least two different monocarboxylic acids. According to one embodiment, the acid is an unsubstituted linear or branched acid.

The acid is preferably chosen from acetic acid, isobutyric acid, benzoic acid and their mixtures.

According to a preferred embodiment, the ester is sucrose diacetate hexa(2-methylpropanoate), such as that sold under the name Sustane SAIB Food Grade Kosher by Eastman Chemical.

According to another embodiment, the plasticizer can be chosen from esters of an aliphatic or aromatic polycarboxylic acid and of an aliphatic or aromatic alcohol comprising from 1 to 10 carbon atoms.

The aliphatic or aromatic alcohol comprises from 1 to 10 and preferably from 1 to 8 carbon atoms, for example from 1 to 6 carbon atoms. It can be chosen from R1OH alcohols such that R1 represents methyl, ethyl, propyl, isopropyl, butyl, hexyl, ethylhexyl, decyl, isodecyl, benzyl, or benzyl substituted by an alkyl comprising from 1 to 3 carbon atoms, and their mixtures.

The aliphatic or aromatic polycarboxylic acid preferably comprises from 3 to 12 carbon atoms, preferably from 3 to 10 carbon atoms and preferably from 3 to 8 carbon atoms, for example 6 or 8 carbon atoms.

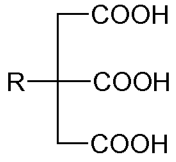
The aliphatic or aromatic polycarboxylic acid is advantageously chosen from dicarboxylic acids and tricarboxylic acids.

Mention may be made, among the aliphatic dicarboxylic acids, of those of formula $HOOC\text{-}(CH_2)_n\text{-}COOH$, in which n is an integer ranging from 1 to 10 and preferably ranging from 2 to 8, for example equal to 2, 4, 6 or 8.

Dicarboxylic acids chosen from succinic acid, adipic acid and sebacic acid are preferred.

Mention may be made, among the aromatic dicarboxylic acids, of phthalic acid.

Mention may be made, among the tricarboxylic acids, of the triacids which correspond to the formula



$$R-\left[\begin{array}{l}-COOH\\-COOH\\-COOH\end{array}\right.$$

in which R represents an -H, -OH or -OCOR’ group in which R’ represents an alkyl group having from 1 to 6 carbon atoms. Preferably, R represents a $-OCOCH_3$ group.

The tricarboxylic acid is in particular chosen from acetylcitric acid, butyroylcitric acid or citric acid.

Use may be made, among the tricarboxylic acid esters, of the esters derived from citric acid (or citrates), such as tributyl acetylcitrate, triethyl acetylcitrate, triethylhexyl acetylcitrate, trihexyl acetylcitrate, trihexyl butyroylcitrate, triisodecyl citrate, triisopropyl citrate, tributyl citrate and tri(2-ethylhexyl) citrate. Mention may be made, as commercial references of plasticizers mentioned above, of the Citroflex range sold by Vertellus, in particular Citroflex A4 and Citroflex C2.

Mention may be made, among the adipic acid esters, of dibutyl adipate and di(2-ethylhexyl) adipate.

Mention may be made, among the sebacic acid esters, of dibutyl sebacate, di(2-ethylhexyl) sebacate, diethyl sebacate and diisopropyl sebacate.

Mention may be made, among the succinic acid esters, of di(2-ethylhexyl) succinate and diethyl succinate.

Mention may be made, among the phthalic acid esters, of benzyl butyl phthalate, dibutyl phthalate, diethylhexyl phthalate, diethyl phthalate and dimethyl phthalate.

Advantageously, the plasticizer or plasticizers can be present in the composition in a content such that the weight ratio of the hydrophobic film-forming hybrid acrylic polymer or polymers to the plasticizer or plasticizers varies from 0.5 to 100, preferably from 1 to 50 and preferably from 1 to 10.

Pigments

The composition comprises one or more pigments.

Such a composition makes it possible to obtain coloured and persistent sheathings without damaging the keratinous fibres.

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

The pigments which can be used are chosen in particular from organic and/or inorganic pigments known in the art, in particular those described in Kirk-Othmer’s

Encyclopedia of Chemical Technology and in Ullmann's *Encyclopedia of Industrial Chemistry*.

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

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

The pigments can be chosen, for example, from inorganic pigments, organic pigments, lakes, special effect pigments, such as pearlescent agents or glitter, and their mixtures.

The pigment can be an inorganic pigment. The term "inorganic pigment" is understood to mean any pigment which corresponds to the definition of Ullmann's Encyclopaedia in the "Inorganic Pigments" chapter. Mention may be made, among inorganic 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) 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 aluminium 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 cosmetic compositions, provided that these compounds contribute colour or whiteness to the composition under the conditions under which they are employed.

The pigment can be an organic pigment. The term "organic pigment" is understood to mean any pigment which corresponds to the definition of Ullmann's Encyclopaedia in the "Organic Pigments" chapter.

The organic pigment can in particular be chosen from nitroso, nitro, azo, xanthene, pyrene, quinoline, anthraquinone, triphenylmethane, fluoran or phthalocyanine compounds, compounds of metal complex type, or isoindolinone, isoindoline, quinacridone, perinone, perylene, diketopyrrolopyrrole, indigo, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

Use may also be made of any inorganic or organic compound which is insoluble in the composition and which is conventional in the cosmetics field, provided that these compounds contribute colour or whiteness to the composition under the conditions under which they are employed, for example guanine, which, according to the refractive index of the composition, is a pigment.

In particular, the white or coloured organic pigments can 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 and 74160, the yellow pigments codified in the Color Index under the references CI 11680, 11710, 15985, 19140, 20040, 21100, 21108, 47000 and 47005, the green pigments codified in the Color Index under the references CI 61565, 61570 and 74260, the orange pigments codified in the Color Index under the references CI 11725, 15510, 45370 and 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 and 75470, and the pigments obtained by oxidative polymerization of indole or phenol derivatives, as are described in Patent FR 2 679 771.

Mention may also be made, as example, of pigment pastes formed of organic pigment, such as the products sold by Hoechst under the names:

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

The pigments in accordance with the invention can also be in the form of composite pigments, as are described in Patent EP 1 184 426. These composite pigments can be composed in particular of particles comprising an inorganic 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 can also be a lake. The term “lake” is understood to mean dyes adsorbed onto insoluble particles, the combination thus obtained remaining insoluble during use.

The inorganic substrates onto which the dyes are adsorbed are, for example, alumina, silica, calcium sodium borosilicate, calcium aluminium borosilicate and aluminium.

Mention may be made, among the dyes, 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) or 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 can also be a special effect pigment. The term “special effect pigments” is understood to mean pigments which generally create a coloured appearance (characterized by a certain shade, a certain vividness and a certain brightness) which is not uniform and which changes as a function of the conditions of observation (light, temperature, angles of observation, etc.). They thereby contrast with coloured pigments, which provide a conventional opaque, semi-transparent or transparent, uniform colour.

There exist several types of special effect pigments: those with a low refractive index, such as fluorescent, photochromic or thermochromic pigments, and those with a higher refractive index, such as pearlescent agents, interferential pigments or glitter.

Mention may be made, as examples of special effect pigments, of pearlescent pigments, such as mica covered with titanium oxide or with bismuth oxychloride, coloured pearlescent pigments, such as mica covered with titanium oxide and with iron oxides, mica covered with iron oxide, mica covered with titanium oxide and in particular with ferric blue or chromium oxide or mica covered with titanium oxide and with an organic pigment as defined above, and pearlescent pigments based on bismuth oxychloride. Mention may be made, as pearlescent pigments, of the following pearlescent agents: Cellini sold by Engelhard (mica-TiO_2-lake), Prestige sold by Eckart (mica-TiO_2), Prestige Bronze sold by Eckart (mica-Fe_2O_3) or Colorona sold by Merck (mica-TiO_2-Fe_2O_3).

Mention may also be made of pearlescent agents of gold colour sold in particular by Engelhard under the name Brilliant Gold 212G (Timica), Gold 222C (Cloisonne), Sparkle Gold (Timica), Gold 4504 (Chromalite) and Monarch Gold 233X (Cloisonne); bronze pearlescent agents sold in particular by Merck under the names Bronze Fine (17384) (Colorona) and Bronze (17353) (Colorona) and by Engelhard under the name Super Bronze (Cloisonne); orange pearlescent agents sold in particular by Engelhard under the name Orange 363C (Cloisonne) and Orange MCR 101 (Cosmica) and by Merck under the names Passion Orange (Colorona) and Matte Orange (17449)

(Microna); brown-coloured pearlescent agents sold in particular by Engelhard under the names Nu-Antique Copper 340XB (Cloisonne) and Brown CL4509 (Chromalite); pearlescent agents with a copper glint sold in particular by Engelhard under the name Copper 340A (Timica); pearlescent agents with a red glint sold in particular by Merck under the name Sienna Fine (17386) (Colorona); pearlescent agents with a yellow glint sold in particular by Engelhard under the name Yellow (4502) (Chromalite); red-coloured pearlescent agents with a gold glint sold in particular by Engelhard under the name Sunstone G012 (Gemtone); pink pearlescent agents sold in particular by Engelhard under the name Tan Opale G005 (Gemtone); black pearlescent agents with a gold glint sold in particular by Engelhard under the name Nu-Antique Bronze 240 AB (Timica), blue pearlescent agents sold in particular by Merck under the name Matte Blue (17433) (Microna), white pearlescent agents with a silvery glint sold in particular by Merck under the name Xirona Silver, and golden green pinkish orangey pearlescent agents sold in particular by Merck under the name Indian Summer (Xirona), and their mixtures.

Mention may also be made, still as examples of pearlescent agents, of particles comprising a borosilicate substrate coated with titanium oxide.

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

Finally, mention may also be made, as examples of pearlescent agents, of polyethylene terephthalate glitter, in particular that sold by Meadowbrook Inventions under the name Silver 1P 0.004X0.004 (silver glitter).

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

The special effect pigments can also be chosen from reflective particles, that is to say in particular particles having a size, a structure, in particular a thickness of the layer or layers of which it is composed and their physical and chemical nature, and a surface condition which allow them to reflect incident light. This reflection may, if appropriate, have an intensity sufficient to create, at the surface of 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 can be selected so as not to detrimentally affect, to a significant extent, the colouring effect generated by the colouring agents which are combined with them and more particularly so as to optimize this effect in terms of colour rendition. They can more particularly have a yellow, pink, red, bronze, orangey, brown, gold and/or coppery colour or glint.

These particles can exhibit varied forms and can in particular be in the platelet or globular form, especially the spherical form.

The reflective particles, whatever their form, may or may not exhibit a multilayer structure and, in the case of a multilayer structure, may exhibit, for example, at least one layer of uniform thickness, in particular of a reflective material.

When the reflective particles do not exhibit a multilayer structure, they can be composed, for example, of metal oxides, in particular of titanium or iron oxides obtained synthetically.

When the reflective particles exhibit a multilayer structure, they can, for example, comprise a natural or synthetic substrate, in particular a synthetic substrate, at least partially coated with at least one layer of a reflective material, in particular of at least one metal or metal material. The substrate can be made of one or more organic and/or inorganic materials.

More particularly, it can be chosen from glasses, ceramics, graphite, metal oxides, aluminas, silicas, silicates, in particular aluminosilicates and borosilicates, synthetic mica and their mixtures, this list not being limiting.

The reflective material can comprise a layer of metal or of a metal material.

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 an inorganic substrate coated with a layer of metal, of the particles comprising a borosilicate substrate coated with silver.

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 comprising a glass substrate coated with nickel/chromium/molybdenum alloy are sold under the names Crystal Star GF 550 and GF 2525 by this same company.

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

Mention may be made, as examples, of aluminium powder, bronze powder or copper powder coated with SiO_2 sold under the name Visionaire by Eckart.

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). Special effect pigments also comprise fluorescent pigments, whether these are substances which are fluorescent in daylight or which produce ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, for example sold by Quantum Dots Corporation.

Quantum dots are luminescent semiconductor nanoparticles capable of emitting, under light excitation, radiation exhibiting a wavelength of between 400 nm and 700 nm. These nanoparticles are known from the literature. In particular, they can be synthesized according to the processes described, for example, in US 6 225 198 or US 5 990 479, in the publications which are cited therein and in the following publications: Dabboussi B.O. et al., “(CdSe)ZnS core-shell quantum dots: synthesis and characterization 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. 7019-7029.

The variety of the pigments which can be used in the present invention makes it possible to obtain a rich palette of colours and also specific 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 generally between 10 nm and 200 µm, preferably between 20 nm and 80 µm and more preferentially between 30 nm and 50 µm.

The pigments can be dispersed in the product by virtue of a dispersing agent.

The dispersing agent serves to protect the dispersed particles from the agglomeration or flocculation thereof. This dispersing agent can be a surfactant, an oligomer, a polymer or a mixture of several of them carrying one or more functionalities having a strong affinity for the surface of the particles to be dispersed. In particular, they can become attached physically or chemically to the surface of the pigments. These dispersants additionally exhibit at least one functional group compatible with or soluble in the continuous medium. Use is made in particular of esters of 12-hydroxystearic acid, in particular, and of C_8 to C_{20} fatty acid and of polyol, for instance glycerol or diglycerol, such as poly(12-hydroxystearic acid) stearate with a molecular weight of approximately 750 g/mol, such as that sold under the name of Solsperse 21 000 by Avecia, polyglyceryl-2 dipolyhydroxystearate (CTFA name), sold under the reference Dehymyls PGPH by Henkel, or polyydroxystearic acid, such as that sold under the reference Arlacel P100 by Uniqema, and their mixtures.

Mention may be made, as other dispersant which can be used in the compositions of the invention, of the quaternary ammonium derivatives of polycondensed fatty acids, such as Solsperse 17 000, sold by Avecia, or polydimethylsiloxane/oxypropylene mixtures, such as those sold by Dow Corning under the references DC2-5185 and DC2-5225 C.

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

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

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

The surface-treated pigments of use in the context of the present invention can be prepared according to surface treatment techniques well known to a person skilled in the art or found as such commercially.

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

The organic agent with which the pigments are treated can be deposited on the pigments by solvent evaporation, 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 can thus be carried out, 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 fillers. This method is described in particular in Patent US 4 578 266.

Preferably, use will be made of an organic agent covalently bonded to the pigments.

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

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

- a PEG-silicone treatment, such as the AQ surface treatment sold by LCW;
- a methicone treatment, such as the SI surface treatment sold by LCW;
- a dimethicone treatment, such as the Covasil 3.05 surface treatment sold by LCW;
- a dimethicone/trimethylsiloxysilicate treatment, such as the Covasil 4.05 surface treatment sold by LCW;
- a magnesium myristate treatment, such as the MM surface treatment sold by LCW;
- an aluminium dimyristate treatment, such as the MI surface treatment sold by Miyoshi;
- a perfluoropolymethylisopropyl ether treatment, such as the FHC surface treatment sold by LCW;
- an isostearyl sebacate treatment, such as the HS surface treatment sold by Miyoshi;
- a perfluoroalkyl phosphate treatment, such as the PF surface treatment sold by Daito;
- an acrylate/dimethicone copolymer and perfluoroalkyl phosphate treatment, such as the FSA surface treatment sold by Daito;
- a polymethylhydrosiloxane/perfluoroalkyl phosphate treatment, such as the FS01 surface treatment sold by Daito;
- an acrylate/dimethicone copolymer treatment, such as the ASC surface treatment sold by Daito;
- an isopropyl titanium triisostearate treatment, such as the ITT surface treatment sold by Daito;

- an acrylate copolymer treatment, such as the APD surface treatment sold by Daito;

a perfluoroalkyl phosphate/isopropyl titanium triisostearate treatment, such as the PF + ITT surface treatment sold by Daito.

Preferably, the pigment is chosen from inorganic pigments or inorganic/organic mixed pigments.

The amount of pigment(s) can vary from 0.01% to 30% by weight, more particularly from 0.05% to 20% by weight and preferably from 0.1% to 15% by weight, with respect to the total weight of the composition.

The composition of the invention can comprise other coloured or colouring entities, such as direct dyes or dye precursors.

Amino acid

According to one embodiment, the composition used in the process according to the invention comprises at least one amino acid or amino acid derivative.

The term "amino acid" or "amino acid derivative" is understood to mean any compound chosen from synthetic or natural and modified or unmodified amino acids, their salts, their enantiomers, synthetic or natural oligomers or polymers comprising at least two amino acids, their salts and their mixtures.

The amino acids and derivatives used in the composition according to the invention comprise at least one amine functional group and at least one acid functional group.

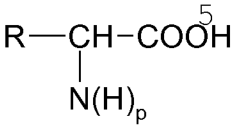
The acid functional group or groups can be carboxylic, sulfonic, phosphonic or phosphoric, preferably carboxylic.

The amino acids can in particular correspond to the following formula:

$(COOH)_x—R—(NH_2)_y$,

in which R is a linear or branched and/or cyclic, saturated or unsaturated hydrocarbon chain optionally interrupted by one or more heteroatoms or groups comprising one or more heteroatoms, the said chain and the said rings being optionally substituted, and x et y representing an integer equal to 1 or 2, preferably x=1 and y=1.

Preferably, the amino acids used in the present invention are α-amino acids, that is to say that they comprise an amine functional group and an R group which are located in the α position with respect to the acid functional group. They can be represented by the following formula (A):



$$R-\underset{N(H)_p}{CH}-COOH$$

(A)

p is equal to 1 or 2, and

when p = 2, R represents a hydrogen atom, an aliphatic group optionally comprising a heterocyclic portion, or an aromatic group,

or

when p = 1, R can form, with the nitrogen atom of $-N(H)_p$, a heterocycle. This heterocycle is preferably a saturated 5-membered ring, optionally substituted by one or more C_{1-4} alkyl or hydroxyl groups.

Preferably, the aliphatic group is a linear or branched C_1-C_4 alkyl group; a linear or branched C_1-C_4 hydroxyalkyl group; a linear or branched C_1-C_4 aminoalkyl group; a linear or branched (C_1-C_4 alkyl)thio(C_1-C_4 alkyl) group; a linear or branched carboxy(C_2-C_4 alkyl) group; a linear or branched ureidoalkyl group, a linear or branched imidazoloalkyl group or a linear or branched indolylalkyl group, the alkyl portions of these last three groups comprising from one to four carbon atoms.

The aromatic group can be a C_6 aryl or C_7-C_{10} aralkyl group, the aromatic nucleus being optionally substituted by one or more C_1-C_4 alkyl or hydroxyl groups.

Preferably, when p = 2, R represents a hydrogen atom, an aliphatic group chosen from a linear or branched (C_1-C_4 alkyl)thio(C_1-C_4 alkyl) group, a linear or branched imidazoloalkyl group or a linear or branched indolylalkyl group, the alkyl portions of these last two groups comprising from one to four carbon atoms, or a C_7-C_{10} aralkyl group, the aromatic nucleus being optionally substituted by one or more C_1-C_4 alkyl or hydroxyl groups, in particular a phenyl or hydroxyphenyl group.

Mention may in particular be made, as amino acids which can be used in the present invention, of alanine, glycine, isoleucine, leucine, methionine, proline, tyrosine, valine, cysteine, phenylalanine, preferably in their L form, tryptophan, in particular D-tryptophan, or their mixtures, and also their salts. The amino acid derivatives can also be chosen from:

- modified amino acids, in particular:

N-acylamino acids, the acyl group comprising from 10 to 30 carbon atoms and preferably from 12 to 22 carbon atoms, such as amino acids, which are preferably not polycarboxylic and/or not water-soluble (solubility of less than 1% at pH 7 and at 25°C), substituted by a lauroyl, myristoyl, palmitoyl, stearoyl, behenoyl, olivoyl or cocoyl group, such as, for example, lauroyl-L-Lysine,

amino acids substituted by a carboxyalkyl group, in particular a carboxymethyl group, such as carboxymethylcysteine,

- synthetic or natural oligomers or polymers comprising at least two amino acids. They can be homopolymers or copolymers of natural or modified amino acids.

Mention may be made, as homopolymers, of polylysines, poly-β-alanines or polyaspartic acids.

Mention may also be made, as amino acid oligomers or polymers, of proteins or protein hydrolysates, such as soybean (glycine) proteins, such as, for example, the glycine soya protein dispersion sold under the reference Eleseryl HGP LS 9874 by Laboratoires Sérobiologiques, or silk proteins, such as the silk protein powder sold by Croda.

The amino acids or their derivatives can be present in the composition as such or contributed by a compound bearing an amino acid or a derivative, for example a particle (filler, pigment) surface-treated with an amino acid or an amino acid derivative.

The amino acids or their derivatives can be present in the composition in a content ranging from 0.001% to 20% by weight, in particular from 0.01% to 10% by weight and preferentially from 0.05% to 5% by weight, with respect to the total weight of the composition.

Thickening agent

According to a preferred embodiment, the composition according to the invention comprises at least one thickening agent chosen from polymeric or non-polymeric and inorganic or organic thickening agents, and their mixtures.

The term “thickener” is understood to mean a compound which modifies the rheology of the medium in which it is incorporated.

According to a specific embodiment of the invention, the composition comprises at least one inorganic thickener.

Preferably, the thickener or thickeners are chosen from fumed silica, clays or their mixtures.

The fumed silicas can be obtained by high-temperature pyrolysis of a volatile silicon compound in an oxhydric flame, producing a finely divided silica. This process makes it possible in particular to obtain hydrophilic silicas which exhibit a large number of silanol groups at their surface. Such hydrophilic silicas are sold, for example, under the names Aerosil 130®, Aerosil 200®, Aerosil 255®, Aerosil 300® and Aerosil 380® by Degussa and Cab-O-Sil HS-5®, Cab-O-Sil EH-5®, Cab-O-Sil LM-130®, Cab-O-Sil MS-55® and Cab-O-Sil M-5® by Cabot.

It is possible to chemically modify the surface of the said silica via a chemical reaction which brings about a reduction in the number of silanol groups. It is possible in particular to replace silanol groups with hydrophobic groups: a hydrophobic silica is then obtained.

The hydrophobic groups can be:

- trimethylsiloxyl groups, which are obtained in particular by treating fumed silica in the presence of hexamethyldisilazane. Silicas thus treated are known as "Silica silylate" according to the CTFA (6th edition, 1995). They are sold, for example, under the references Aerosil R812® by Degussa and Cab-O-Sil TS-530® by Cabot.
- dimethylsilyloxyl or polydimethylsiloxane groups, which are obtained in particular by treating fumed silica in the presence of polydimethylsiloxane or dimethyldichlorosilane. Silicas thus treated are known as Silica Dimethyl Silylate according to the CTFA (6th edition, 1995). They are sold, for example, under the references Aerosil R972® and Aerosil R974® by Degussa, and Cab-O-Sil TS-610® and Cab-O-Sil TS-720® by Cabot.

The fumed silica preferably exhibits a particle size which can be nanometric to micrometric, for example ranging from approximately 5 to 200 nm.

Clays are well-known products which are described, for example, in the publication *Minéralogie des argiles* [Mineralogy of Clays], S. Caillère, S. Hénin and M. Rautureau, 2nd Edition, 1982, Masson.

Clays are silicates including a cation which can be chosen from calcium, magnesium, aluminium, sodium, potassium or lithium cations, and their mixtures.

Mention may be made, as examples of such products, of clays of the family of the smectites, such as montmorillonites, hectorites, bentonites, beidellites or saponites, and also of the family of the vermiculites, stevensites or chlorites.

These clays can be of natural or synthetic origin. Use is preferably made of clays which are cosmetically compatible with and acceptable to keratinous substances.

Mention may be made, as clay which can be used according to the invention, of synthetic hectorites (also known as laponites), such as the products sold by Laporte under the names Laponite XLG, Laponite RD and Laponite RDS (these products are sodium magnesium silicates and in particular lithium magnesium sodium silicates); bentonites, such as the product sold under the name Bentone HC by Rheox; magnesium aluminium silicates, in particular hydrated, such as the product sold by Vanderbilt Company under the name Veegum Ultra, or calcium silicates and in particular that in synthetic form sold by the company under the name Micro-Cel C.

The organophilic clay can be chosen from montmorillonite, bentonite, hectorite, attapulgite or sepiolite, and their mixtures. The clay is preferably a bentonite or a hectorite.

These clays can be modified with a chemical compound chosen from quaternary ammoniums, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulfates, alkylarylsulfonates, amine oxides and their mixtures.

Mention may be made, as organophilic clays, of quaternium-18 bentonites, such as those sold under the names Bentone 3, Bentone 38 and Bentone 38V by Rheox, Tixogel VP by United Catalyst and Claytone 34, Claytone 40 and Claytone XL by Southern Clay; stearalkonium bentonites, such as those sold under the names Bentone 27 by Rheox, Tixogel LG by United Catalyst and Claytone AF and Claytone APA by Southern Clay; and quaternium-18/benzalkonium bentonites, such as those sold under the names Claytone HT and Claytone PS by Southern Clay.

The thickener can also be chosen from organic thickeners.

Mention may be made, for example, of the following non-polymeric thickeners:

- C_{10}-C_{30} fatty amides, such as lauric acid diethanolamide.

Mention may also be made of the following organic thickening polymers:

- the polyglyceryl (meth)acrylate polymers sold under the Hispagel or Lubragel names by Hispano Quimica or Guardian,
- polyvinylpyrrolidone,
- polyvinyl alcohol,
- crosslinked acrylamide polymers and copolymers, such as those sold under the names PAS 5161 or Bozepol C by Hoechst or Sepigel 305 by SEPPIC by Allied Colloid, or alternatively
- the crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymers sold under the name Salcare SC95 by Allied Colloid,
- (meth)acrylamido(C_1-C_4)alkylsulfonic acid homopolymers, which are preferably

crosslinked, in particular crosslinked poly(2-acrylamido-2-methylpropanesulfonic acid) homopolymers partially neutralized with ammonia,

- crosslinked acrylic acid homopolymers,
- acrylate/C_{10}-C_{30} alkyl acrylate copolymers,
- associative polyurethanes,
- celluloses, in particular hydroxyalkylcelluloses, such as hydroxyethylcelluloses,

and their mixtures.

The thickening polymers are preferably polymers exhibiting, in solution or in dispersion at 1% by weight of active material in water or in ethanol, at 25°C, a viscosity of greater than 0.2 poise at a shear rate of 1 s^{-1}. The viscosity is measured with a Haake RS600 viscometer from Thermo Electron. This viscometer is a controlled-stress viscometer with cone-plate geometry (for example having a diameter of 60 mm).

The thickening agent is present in the composition in a total content ranging from 0.1% to 10% by weight, with respect to the weight of the composition.

The composition according to the invention comprises water, which can preferably be present in a content ranging from 20% to 98% by weight, with respect to the weight of the composition.

The compositions can also comprise at least one agent commonly used in cosmetics, for example chosen from reducing agents, fatty substances, organic solvents or oils, softening agents, anti-foaming agents, moisturizing agents, UV screening agents, peptizing agents, solubilizing agents, fragrances, anionic, cationic, non-ionic or amphoteric surfactants, proteins, vitamins, propellants, oxyethylenated or non-oxyethylenated waxes, paraffins or C_{10}-C_{30} fatty acids, such as stearic acid or lauric acid.

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

Of course, 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.

The composition according to the invention can be provided in particular in the form of a suspension, a dispersion, a gel, an emulsion, in particular an oil-in-water (O/W), water-in-oil (W/O) or multiple (W/O/W or polyol/O/W or O/W/O) emulsion, a cream, a foam, a stick, a dispersion of vesicles, in particular of ionic or non-ionic lipids, a two-phase or multiphase lotion, a spray or a paste. The composition can also be provided in the form of a lacquer.

A person skilled in the art can choose the appropriate formulation form, and also its method of preparation, on the basis of his general knowledge, taking into account first the nature of the constituents used, in particular their solubility in the support, and secondly the application envisaged for the composition.

Application method

The composition described above can be employed on wet or dry keratinous fibres, and also on any type of fibre: light or dark, natural or dyed, or permanent-waved, bleached or straightened.

The application to the skin can be carried out using a brush, including a fine brush, or a felt.

The application to the keratinous fibres can be carried out by any conventional means, in particular by means of a comb, a brush, including a fine brush, such as a mascara brush, or with the fingers.

The application to the skin and keratinous fibres, if appropriate, can be carried out using the same application means or using a different means.

After the application of the composition, the fibres can be left to dry or can be dried, for example at a temperature of greater than or equal to 30°C. According to a specific embodiment, this temperature is greater than 40°C. According to a specific embodiment, this temperature is greater than 45°C and less than 220°C.

The drying, if it is employed, can be carried out immediately after application or after a leave-on time which can range from 1 minute to 30 minutes.

Preferably, if the fibres are dried, they are dried, in addition to a supply of heat, with a flow of air. This flow of air during the drying makes it possible to improve the individualization of the sheathing.

During the drying, a mechanical action can be exerted on the locks, such as combing, brushing or running the fingers through the hair. This operation can likewise be carried out once the fibres have been dried, naturally or unnaturally.

The drying stage of the method of the invention can be carried out with a hood dryer, a hair dryer, a smoothing iron or a Climazone.

When the drying stage is carried out with a hood dryer or a hair dryer, the drying temperature is between 40°C and 110°C and preferably between 50°C and 90°C.

When the drying stage is carried out with a smoothing iron, the drying temperature is between 110°C and 220°C and preferably between 140°C and 200°C.

Once the drying is complete, a final rinsing or shampooing can optionally be carried out.

The examples which follow serve to illustrate the invention without, however, exhibiting a limiting nature. Unless otherwise indicated, the amounts shown are as % by weight.

EXAMPLES

Example 1: Dying black and densifying a grey moustache:

The following compositions are prepared:

Composition	**A1**	**A2**	**A3**
Styrene/acrylate copolymer in aqueous dispersion, sold by BASF under the name Joncryl 77	21.2 g, i.e. 10 g of AM	21.2 g, i.e. 10 g of AM	21.2 g, i.e. 10 g of AM
Divinyl dimethicone/dimethicone copolymer as an aqueous emulsion, sold by Dow Corning under the reference HMW 2220 Nonionic Emulsion	3 g, i.e. 1.05 g of AM	3 g, i.e. 1.05 g of AM	3 g, i.e. 1.05 g of AM
Glycine, sold by Ajinomoto	-	2	-
Silk protein powder (Crosilk Powder from Croda)	-	-	2.1 g
Carbon black dispersion, sold under the name WD CB2 by Daito Kasei Kogyo	10 g, i.e. 2.5 g of	10 g, i.e. 2.5 g of	10 g, i.e. 2.5 g of

	AM	AM	AM
Water	q.s. for 100 g	q.s. for 100 g	q.s. for 100 g

The composition A1 or A2 or A3 is applied to the hairs of a grey moustache using a brush of the mascara type and, using a fine brush, faint lines are drawn on the skin at the moustache at the points where the density of hairs is lowest.

After a few seconds, the moustache hairs are dry and dyed black and the moustache appears denser visually. The colour on the moustache (hairs and skin) is persistent towards water, to the touch and towards several washing operations with soap.

Example 2: Densification of the eyebrows without dyeing or with invisible dyeing (in matching tones) of the hairs

Composition B	
Styrene/acrylate copolymer in aqueous dispersion, sold by BASF under the name Joncryl 77	21.2 g, i.e. 10 g of AM
Divinyl dimethicone/dimethicone copolymer as an aqueous emulsion, sold by Dow Corning under the reference HMW 2220 Nonionic Emulsion	8.3 g, i.e. 2.6 g of AM
Clay (magnesium aluminium silicate), sold by Vanderbilt under the name Veegum granules	2 g
Pearlescent agent, Timica Nu-Antique Copper 340 AB from BASF	2 g
Water	q.s. for 100 g

Faint points/lines are drawn on the skin, with the composition B and using a fine brush, at "chestnut" eyebrows at the points where the density of the hairs is lowest.

If the coloured composition B is deposited on the "chestnut" hairs while the faint points or lines are being drawn on the skin, the colour will not be visible to the naked eye on the hairs; it will be visible only on the skin.

The visual densification is more natural than with an eyebrow pencil and the colour is persistent to the touch, towards water and towards several washing operations.

Example 3: Densification of the eyebrows or of the head hair without dyeing or with invisible dyeing (in matching tones) of the hairs/head hair.

Composition	**C1**	**C2**	**C3**	**C4**
Styrene/acrylate copolymer in aqueous dispersion, sold by BASF under the name Joncryl 77	21.2 g, i.e. 10 g of AM	21.2 g, i.e. 10 g of AM	21.2 g, i.e. 10 g of AM	21.2 g, i.e. 10 g of AM
Polydimethylsiloxane comprising aminoethyliminopropyl groups, as a cationic emulsion comprising 35% of active materials (Xiameter MEM-0939 Emulsion from Dow Corning)	12 g, i.e. 4.2 g of AM	-	10 g, i.e. 3.5 g of AM	12 g, i.e. 4.2 g of AM
Polydimethylsiloxane comprising aminoethylaminopropyl and α,ω-silanol groups, as a cationic emulsion comprising 31% of active materials (Xiameter MEM-0949 Emulsion from Dow Corning)	-	11 g, i.e. 3.41 g of AM	-	-
Polydimethylsiloxane comprising aminoethylaminopropyl groups and comprising methoxy and/or hydroxyl and α,ω-silanol functional groups, as a cationic emulsion comprising 60% of active materials (Xiameter MEM-8299 Emulsion from Dow Corning)	-	-	8 g, i.e. 4.8 g of AM	-
Polydimethylsiloxane comprising aminoethylaminopropyl groups, as a non-ionic macroemulsion comprising 35% of active materials (Belsil ADM 6060 from Wacker)	-	-	-	13 g, i.e. 4.55 g of AM

Pearlescent agent, Timica Nu-Antique Copper 340 AB from BASF Personal Care Ingredients	2 g	2 g	2 g	2 g
Water	q.s. for 100 g	q.s. for 100 g	q.s. for 100 g	q.s. for 100 g

The composition C1 or C2 or C3 or C4 is applied in faint touches, using a fine brush, to the skin at "chestnut" eyebrows at the points where the density of the hairs is lowest.

If the coloured composition C1 or C2 or C3 or C4 is deposited on the "chestnut" hairs while the faint points or lines are being drawn on the skin, the colour will not be visible to the naked eye on the hairs; it will be visible only on the skin.

The visual densification is more natural than with an eyebrow pencil and the colour is persistent to the touch, towards water and towards several washing operations.

For the visual densification of head hair having a height of tone of 4, faint lines are drawn on the scalp with the compositions C1 or C2 or C3 or C4 and using a fine brush at the points where the density of keratinous fibres is lowest. The head hair appears denser visually and the colour is persistent to the touch and towards water.

CLAIMS

1. Method for colouring a skin region supporting keratinous fibres, which consists in applying, to the said skin region, and optionally to said keratinous fibres, a composition comprising at least one aqueous dispersion of particles of hydrophobic film-forming hybrid acrylic polymer, at least one silicone compound chosen from linear block silicone copolymers, aminated silicones and their mixtures, and at least one pigment.

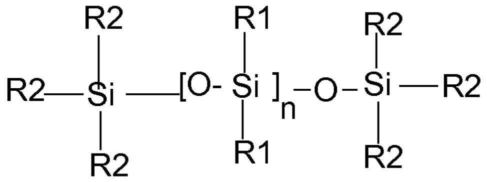
2. Method according to the preceding claim, characterized in that the composition comprises at least one linear block silicone copolymer which is provided in the form of particles in dispersion in an aqueous medium.

3. Method according to either one of the preceding claims, in which the composition comprises at least one linear block silicone copolymer obtained by a chain-extension reaction, in the presence of a catalyst, starting from at least:

(a) a polysiloxane (i) having at least one reactive group and preferably one or two reactive groups per molecule; and

(b) an organosilicone compound (ii) which reacts with the polysiloxane (i) via a chain-extension reaction.

4. Method according to the preceding claim, characterized in that the organopolysiloxane (i) is chosen from the compounds of formula (I):



$$R2-Si(R2)(R2)-[O-Si(R1)(R1)]_n-O-Si(R2)(R2)-R2 \quad (I)$$

in which R_1 and R_2 represent, independently of one another, a hydrocarbon group having from 1 to 20 carbon atoms or an aryl group or a reactive group and n is an integer greater than 1, provided that there are on average between one and two reactive groups per polymer.

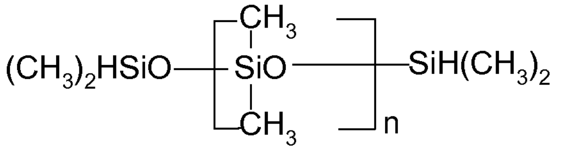
5. Method according to the preceding claim, characterized in that the reactive group is chosen from hydrogen; aliphatically unsaturated groups; the hydroxyl group; alkoxy groups; alkoxyalkoxy groups; the acetoxy group; amino groups; and their mixtures.

6. Method according to either one of Claims 4 and 5, characterized in that R_1 represents a methyl group.

7. Method according to any one of Claims 4 to 6, characterized in that R_2 at the chain end represents a vinyl group.

8. Method according to Claim 3, characterized in that the organosilicone compound (ii) is chosen from the polysiloxanes of formula (I) or the compounds which act as chain extenders.

9. Method according to the preceding claim, characterized in that the compound (ii) is a liquid organohydropolysiloxane of formula (II):



$$(CH_3)_2HSiO-\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_n-SiH(CH_3)_2 \qquad (II)$$

where n is an integer greater than 1, preferably greater than 10 and preferably equal to 20.

10. Method according to any one of Claims 3 to 9, characterized in that the aqueous dispersion of silicone copolymer particles is obtained by mixing water, at least one emulsifier, the polysiloxane (i), the organosilicone compound (ii) and a catalyst.

11. Method according to the preceding claim, characterized in that the dispersion is an aqueous dispersion of divinyl dimethicone/dimethicone copolymer.

12. Method according to one of the preceding claims, in which the aminated silicone is chosen from the compounds corresponding to the following formula (I):

$$(R^1)_a(T)_{3-a}\text{-}Si[OSi(T)_2]_n\text{-}[OSi(T)_b(R^1)_{2-b}]_m\text{-}OSi(T)_{3-a}\text{-}(R^1)_a$$

in which:

T is a hydrogen atom, a phenyl radical, a hydroxyl radical, a C_1-C_8 alkyl radical, preferably a methyl radical, or a C_1-C_8 alkoxy radical, more preferably a methyl radical,

a denotes the number 0 or an integer from 1 to 3, and preferably 0,

b denotes 0 or 1, and in particular 1,

m and n are numbers such that the sum (n + m) can vary in particular from 1 to 2000 and especially from 50 to 150, n denotes a number from 0 to 1999 and in particular from 49 to 149 and m denotes a number from 1 to 2000 and in particular from 1 to 10,

R^1 is a monovalent radical of formula $-C_qH_{2q}L$ in which q is a number from 2 to 8, it being possible for one or more hydrogen atoms to be replaced by a hydroxyl group, and L is an optionally quaternized amino group chosen from the groups:

$-N(R^2)-CH_2-CH_2-N(R^2)_2$;

$-N(R^2)_2$;

$-N^+(R^2)_3Q^-$;

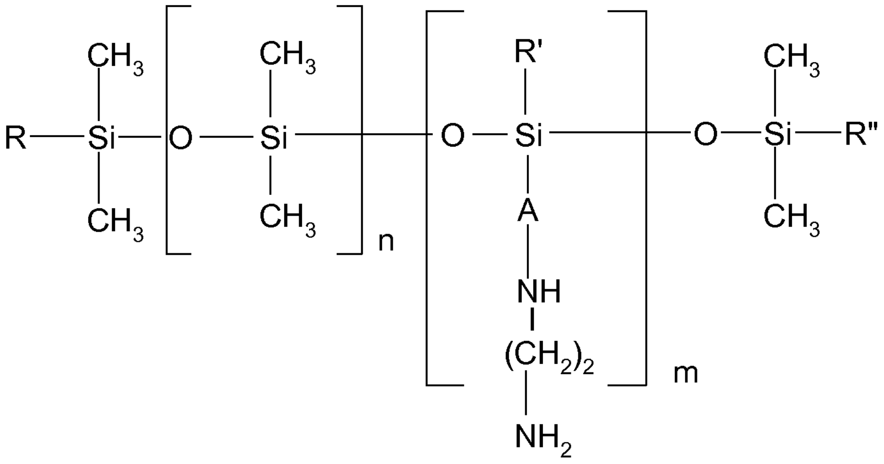
$-N^+(R^2)(H)_2Q^-$;

$-N^+(R^2)_2HQ^-$;

$-N(R^2)-CH_2-CH_2-N^+(R^2)(H)_2Q^-$,

in which R^2 denotes a hydrogen atom, a phenyl, a benzyl or a saturated monovalent hydrocarbon radical, for example a C_1-C_{20} alkyl radical, and Q^- represents an anion, such as, for example, fluoride, chloride, bromide or iodide.

13. Method according to one of the preceding claims, in which the aminated silicone is chosen from the compounds corresponding to the following formula:



(II)

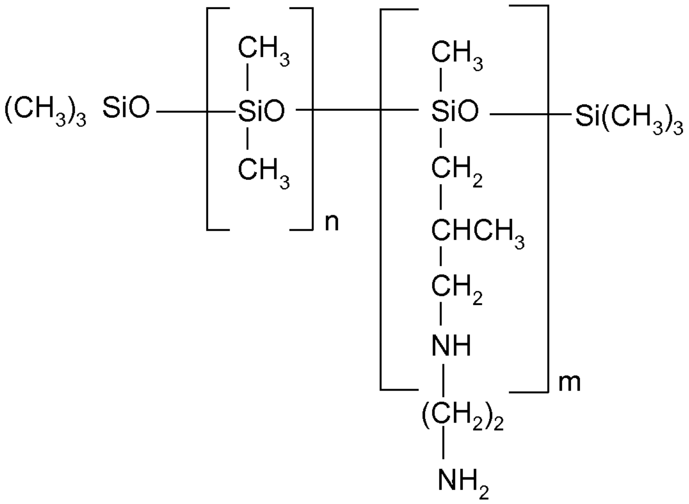
in which:

R, R' and R", which are identical or different, denote a C_1-C_4 alkyl, preferably CH_3, radical, a C_1-C_4 alkoxy, preferably methoxy, radical or an OH radical;

A represents a linear or branched C_3-C_8 and preferably C_3-C_6 alkylene radical;

m and n are integers, the sum of which is between 1 and 2000.

14. Method according to one of the preceding claims, in which the aminated silicone is chosen from the silicones of following formula (III):



$$(CH_3)_3SiO-[Si(CH_3)_2O]_n-[Si(CH_3)(CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2)O]_m-Si(CH_3)_3$$

(III)

in which n and m have the meanings indicated for the formula (I) according to Claim 12.

15. Method according to one of the preceding claims, in which the aminated silicone is not a block polymer.

16. Method according to one of the preceding claims, in which the composition exhibits a content of silicone compound(s) chosen from the linear block silicone copolymer(s) and/or the aminated silicones, as active materials, ranging from 0.1% to 30% by weight, more particularly from 0.5% to 20% by weight and preferably from 1% to 15% by weight, with respect to the total weight of the composition.

17. Method according to any one of the preceding claims, in which the colouring composition comprises at least one hydrophobic film-forming hybrid acrylic polymer synthesized from at least one compound (i) chosen from monomers having at least one (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers and from at least one compound (ii) different from the compounds (i), that is to say which does not comprise (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers.

18. Method according to any one of the preceding claims, in which the colouring composition comprises at least one hydrophobic film-forming hybrid acrylic polymer synthesized from at least one monomer having at least one (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers and from at least one styrene compound.

19. Method according to any one of the preceding claims, in which the colouring composition comprises at least one hydrophobic film-forming hybrid acrylic polymer chosen from styrene/acrylate copolymers, in particular a copolymer resulting from the

polymerization of at least one styrene monomer and at least one C_1-C_{10} alkyl acrylate monomer.

20. Method according to the preceding claim, in which the C_1-C_{10} alkyl acrylate monomer is chosen from methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate or 2-ethylhexyl acrylate.

21. Method according to any one of the preceding claims, in which the colouring composition comprises at least one hydrophobic film-forming hybrid acrylic polymer synthesized from at least one monomer having at least one (meth)acrylic acid group and/or esters of these acid monomers and/or amides of these acid monomers and from at least one compound resulting from a polycondensation process or from two or more than two compounds which interact in a polycondensation process.

22. Method according to any one of the preceding claims, in which the hydrophobic film-forming hybrid acrylic polymer or polymers in aqueous dispersion is or are present in a content, as active materials, ranging from 0.1% to 30% by weight, more particularly from 0.5% to 20% by weight and preferably from 1% to 15% by weight, with respect to the total weight of the composition.

23. Method according to any one of the preceding claims, in which the hydrophobic film-forming hybrid acrylic polymer or polymers and the silicone compound or compounds chosen from linear block silicone copolymers and/or aminated silicones are present in a weight ratio (as active materials) of hydrophobic film-forming hybrid acrylic polymer(s) to linear block silicone copolymer(s) and/or aminated silicone(s) ranging from 0.2 to 10, better still from 0.5 to 5 and even better still from 1 to 3.

24. Method according to any one of the preceding claims, in which the amount of pigment(s) ranges from 0.01% to 30% by weight, more particularly from 0.05% to 20% by weight and preferably from 0.1% to 15% by weight, with respect to the total weight of the composition.

25. Method according to any one of the preceding claims, in which the composition additionally comprises at least one inorganic thickening agent, preferably chosen from clays, preferably a smectite, and/or at least one organic thickener, preferably a polymeric organic thickener.

26. Method according to any one of the preceding claims, in which the composition additionally comprises at least one amino acid or amino acid derivative.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062803

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/81 A61K8/895 A61K8/891 A61K8/898 A61K8/22
A61Q5/06 A61Q1/10 A61Q1/02
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, CHEM ABS Data, PAJ, WPI 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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Y	claims 1-20; example 8 -----	7,9,26
Y	FR 2 947 175 A1 (OREAL [FR]) 31 December 2010 (2010-12-31) claims 1-10 page 23, line 23 - page 24, line 6 -----	1-26
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent 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

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"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 17 July 2014	Date of mailing of the international search report 28/07/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Wörth, Christian

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	ANONYMOUS: "Wacker-Belsil ADM 652, ADM 656, ADM 1100, ADM 1600, ADM 1650", INTERNET CITATION, 2000, XP002258243, Retrieved from the Internet: URL:http://www.wacker.com/internet/webcache/de_DE/PTM/TM/Wacker_Belsil/ADM/Wacker-Belsil_ADM_div_E.pdf?ts=1066372115918 [retrieved on 2003-10-17] the whole document	1-26
Y	US 2004/131577 A1 (DAVIES ALAN GLYN [GB] ET AL) 8 July 2004 (2004-07-08) paragraphs [0014], [0025], [0037]; claims 1-15	1-26
Y	FR 2 936 414 A1 (OREAL [FR]) 2 April 2010 (2010-04-02) claims 1-14	1-26
X	EP 2 070 516 A1 (OREAL [FR]) 17 June 2009 (2009-06-17)	1-6, 8-10, 16-25
Y	claims 1-11; examples 2,3	9,26
X	WO 98/51265 A1 (OREAL [FR]; CANNELL DAVID [US]; NGUYEN NGHI [US]) 19 November 1998 (1998-11-19) claims 1-15	26

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