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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 November 2010 (25.11.2010)

PCT

(10) International Publication Number
WO 2010/133575 A2

(51) International Patent Classification:
A61K 8/41 (2006.01) *A61Q 5/10* (2006.01)
A61K 8/58 (2006.01) *A61K 8/25* (2006.01)
A61K 8/891 (2006.01) *A61K 8/31* (2006.01)
A61K 8/898 (2006.01) *A61K 8/92* (2006.01)

(21) International Application Number:
PCT/EP2010/056784

(22) International Filing Date:
18 May 2010 (18.05.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0953319	19 May 2009 (19.05.2009)	FR
0953322	19 May 2009 (19.05.2009)	FR
61/180,196	21 May 2009 (21.05.2009)	US
61/181,775	28 May 2009 (28.05.2009)	US

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

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

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2010/133575 A2

(54) Title: DYEING COMPOSITION COMPRISING A SECONDARY PARA-PHENYLENEDIAMINE OXIDATION BASE AND A SILICONE FATTY SUBSTANCE OR A NON-SILICONE LIQUID FATTY SUBSTANCE

(57) Abstract: A subject-matter of the invention is a dyeing composition comprising at least one specific secondary para-phenylenediamine oxidation base and one fatty substance chosen from a) non-silicone liquids and b) silicones. Another subject-matter of the invention is the use of this composition for dyeing keratinous fibres and the dyeing method employing this composition. Finally, a subject-matter of the invention is multicompartment devices. The composition of the present invention makes it possible in particular to obtain a colouring with varied, intense and/or chromatic, attractive and not very selective shades which is highly resistant to the various attacks which hair may be subjected to.

DYEING COMPOSITION COMPRISING A SECONDARY PARA-PHENYLENEDIAMINE OXIDATION BASE AND A SILICONE FATTY SUBSTANCE OR A NON-SILICONE LIQUID FATTY SUBSTANCE

A subject-matter of the invention is a dyeing composition comprising at least one specific secondary para-phenylenediamine oxidation base and at least one fatty substance chosen from a) non-silicone liquid fatty substances and b) silicones. Another subject-matter of the invention is the use of this composition for dyeing keratinous fibres and the dyeing method employing this composition. Finally, a subject-matter of the invention is a multicompartment device.

It is known to dye keratinous fibres, in particular human hair, with dyeing compositions comprising oxidation dye precursors, generally known as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, in combination with oxidizing products, can give rise, by an oxidative coupling process, to coloured compounds.

It is also known that it is possible to vary the shades obtained with these oxidation bases by combining them with couplers or colouring modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds, such as indole compounds.

The variety of the molecules employed as oxidation bases and couplers makes it possible to obtain a rich palette of colours.

The “permanent” colouring obtained by virtue of these oxidation dyes furthermore has to satisfy a certain number of requirements. Thus, it must be without disadvantage toxicologically, it must make it possible to obtain shades within the desired intensity and it must behave well in the face of external agents, such as light, bad weather, washing, permanent waving,

perspiration and rubbing.

The dyes must also make it possible to cover white hair and, finally, be as non-selective as possible, that is to say make it possible to obtain the smallest possible differences in colouring along the same keratinous fibre, which is generally differently sensitized (i.e. damaged) between its tip and its root.

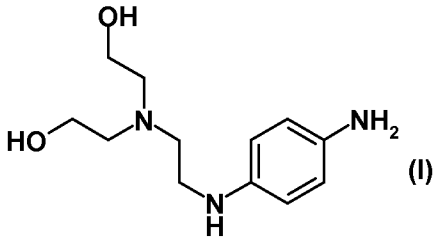
It is already known to use oxidation bases of the secondary para-phenylenediamine type of formula (I) below for dyeing keratinous fibres, especially the hair. In particular, such a base is disclosed in the documents EP 1 580 184 and EP 0 055 386. This base exhibits the disadvantages of resulting in colourings which are insufficiently intense or chromatic and/or excessively selective.

Furthermore, it is known to use oils in the field of oxidation hair dyeing (see, for example, FR 2 464 710, WO2008/020730 or US 7 458 995). It is also known to use compositions employing silicones. For example, aminated, polyoxyalkylenated silicones, or silicone gums/resins, have been used in combination with cationic direct dyes (EP 1 049 447). Other specific aminated silicones have been used in combination with oxidation dyes (EP 1 312 343). However, the colourings obtained with conventional oxidation dyes in combinations with these oils or with these silicones are not satisfactory, in particular in terms of chromaticity, of power, of selectivity and/or of resistance to external agents.

The aim of the present invention is to obtain a composition for dyeing the hair which exhibits improved dyeing properties in terms of intensity or of chromaticity, and/or of selectivity and/or of resistance to external agents.

This aim is achieved with the present invention, a subject-matter of which is a composition for dyeing keratinous fibres comprising, in an appropriate dyeing medium:

- one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid:



(I)

and

- one or more fatty substances chosen from a) non-silicone liquids and b) silicones.

Another subject-matter of the invention is a dyeing method employing this composition.

Another subject-matter of the invention is the use of the composition of the present invention for dyeing keratinous fibres, in particular human keratinous fibres, such as the hair.

Another subject-matter of the invention is a multicompartment device comprising, in one of the compartments, the dyeing composition according to the invention and, in another compartment, a composition comprising one or more oxidizing agents.

According to another alternative form of the invention, the device comprises a first compartment including one or more oxidation bases chosen from the compound of formula (I) or its salts with an acid and optionally one or more oxidation bases other than the compound of formula (I) or its salts and optionally one or more couplers, a second compartment including a composition comprising one or more fatty substances chosen from a) non-silicone liquids and b) silicones, and a third compartment including a composition comprising one or more oxidizing agents.

The composition of the present invention makes it possible in particular to obtain a composition for dyeing keratinous fibres which is suitable for use in oxidation dyeing and which makes it possible to obtain a colouring with varied, intense or chromatic,

attractive and not very selective shades which are highly resistant to the various attacks which hair may be subjected to, such as shampoos, sweat, permanent deformations and light.

It should be noted that, in that which will follow and unless otherwise indicated, the limits of a range of values are included within this range.

The compound of formula (I):

The compound of formula (I) can be in the form of cosmetically acceptable addition salts chosen in particular from the addition salts with an acid, such as hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzenesulphonates, phosphates and acetates.

The compound of formula (I) or its salts are generally each present in an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

a) The non-silicone liquid fatty substances:

According to a specific embodiment of the invention, the compositions comprise a) one or more non-silicone liquid fatty substances.

Within the meaning of the present invention:

- the term “liquid fatty substance” is understood to mean an organic compound which is liquid at ambient temperature (25°C) and at atmospheric pressure (760 mm of mercury), which is insoluble in water under these conditions, that is to say with a solubility of less than 5% by weight, preferably of less than 1% by weight and more preferably still of less than 0.1% by weight in water, and which exhibits, in its structure, at least one hydrocarbon chain comprising at least 6 carbon atoms, and
- the term “non-silicone liquid fatty substance” is understood to mean a liquid fatty substance as defined

above not comprising a silicon atom in its structure.

In addition, non-silicone liquid fatty substances are generally soluble in organic solvents under the same temperature and pressure conditions, such as, for example, chloroform, ethanol, benzene, liquid paraffin or decamethylcyclopentasiloxane.

The non-silicone liquid fatty substances according to the invention are chosen in particular from liquid lower C_6-C_{16} alkanes, non-silicone oils of animal, vegetable, mineral or synthetic origin, liquid fatty alcohols, liquid fatty acids or liquid fatty alcohol and/or fatty acid esters.

It should be remembered that, within the meaning of the invention, fatty alcohols, esters and acids exhibit more particularly at least one saturated or unsaturated and linear or branched hydrocarbon group comprising from 6 to 30 carbon atoms which is optionally substituted, in particular by one or more hydroxyl groups (in particular from 1 to 4 hydroxyl groups). If they are unsaturated, these compounds can comprise from one to three conjugated or nonconjugated carbon-carbon double bonds.

As regards the lower C_6-C_{16} alkanes, the latter are linear or branched or optionally cyclic. By way of example, the alkanes can be chosen from hexane, dodecane or isoparaffins, such as isohexadecane and isodecane.

Mention may be made, as non-silicone oils of animal, vegetable, mineral or synthetic origin which can be used in the composition of the invention, for example, of:

- hydrocarbon oils of animal origin, such as perhydrosqualene;
- triglyceride oils of vegetable or synthetic origin, such as liquid triglycerides of fatty acids comprising from 6 to 30 carbon atoms, such as triglycerides of heptanoic acid or octanoic acid or also, for example, sunflower oil, maize oil, soybean oil, cucumber oil,

grape seed oil, sesame oil, hazelnut oil, apricot oil, macadamia oil, arara oil, castor oil, avocado oil, camellia seed oil, olive oil, peach kernel oil, mango seed oil, argan oil, quinoa seed oil, wheat germ oil, pomegranate seed oil, camelina seed oil, blackcurrant seed oil, jojoba seed oil, coconut oil, triglycerides of caprylic/capric acids, such as those sold by Stearineries Dubois or those sold under the names Miglyol® 810, 812 and 818 by Dynamit Nobel, jojoba oil or shea butter oil;

- linear or branched hydrocarbons of mineral or synthetic origin and of more than 16 carbon atoms, such as volatile or nonvolatile liquid paraffins and their derivatives, petrolatum, liquid petrolatum, polydecenes or hydrogenated polyisobutene, such as Parleam®;
- fluorinated oils, such as perfluoromethylcyclopentane and perfluoro-1,3-dimethylcyclohexane, sold under the names "Flutec® PC1" and "Flutec® PC3" by BNFL Fluorochemicals; perfluoro-1,2-dimethylcyclobutane; perfluoroalkanes, such as dodecafluoropentane and tetradecafluorohexane, sold under the names of "PF 5050®" and "PF 5060®" by 3M, or also bromoperfluorooctyl, sold under the name "Foralkyl®" by Atochem; nonafluoromethoxybutane and nonafluoroethoxyisobutane; or perfluoromorpholine derivatives, such as 4-(trifluoromethyl)perfluoro-morpholine, sold under the name "PF 5052®" by 3M.

Preferably, the non-silicone oils of animal, vegetable, mineral or synthetic origin which can be used in the composition of the invention are chosen from oils of mineral origin, such as petrolatum or polydecenes, or oils of vegetable origin, such as camellia seed oil, olive oil, peach kernel oil, apricot kernel oil, avocado oil, mango seed oil, argan oil, quinoa seed oil, wheat germ oil, sunflower seed oil, grape seed oil, pomegranate seed oil, camelina seed oil, blackcurrant seed oil, jojoba seed oil and coconut oil.

The liquid fatty alcohols which can be used in the composition according to the invention are unsaturated and/or branched and comprise from 6 to 30 carbon atoms and more particularly from 8 to 30 carbon atoms. Mention may be made, for example, of oleyl alcohol, isocetyl alcohol, isostearyl alcohol, octyldodecanol, 2-ethylhexyl dodecanol, linoleyl alcohol, linolenyl alcohol and their mixtures.

The liquid fatty acids which can be used in the composition according to the invention can be unsaturated and/or branched carboxylic acids and they comprise from 6 to 30 carbon atoms, in particular from 9 to 30 carbon atoms. They are more particularly chosen from oleic acid, linoleic acid, isostearic acid and their mixtures.

As regards the liquid fatty alcohol and/or fatty acid esters, advantageously different from the triglycerides mentioned above, which can be used in the composition according to the invention, they can result from C_3-C_{30} carboxylic acid and from C_1-C_{30} alcohol, at least one of the acid or of the alcohol being branched and/or unsaturated and at least one of the acid or of the alcohol comprising more than 6 carbon atoms.

Mention may be made of octyldodecyl behenate, isocetyl behenate, isocetyl lactate, isostearyl lactate, linoleyl lactate, oleyl lactate, isostearyl octanoate, isocetyl octanoate, decyl oleate, isocetyl isostearate, isocetyl laurate, isocetyl stearate, isodecyl octanoate, isodecyl oleate, isononyl isononanoate, isostearyl palmitate, myristyl isostearate, octyl isononanoate, 2-ethylhexyl isononanoate, octyl isostearate, octyldodecyl erucate, isopropyl palmitate, 2-ethylhexyl palmitate, 2-octyldecyl palmitate, myristates of branched alkyls, such as isopropyl myristate, t-butyl myristate or 2-octyldodecyl myristate, hexyl isostearate, butyl isostearate, isobutyl stearate or 2-hexyldecyl laurate.

Use may also be made of esters of C_4-C_{22} di- or

tricarboxylic acids and of C_1-C_{22} alcohols and esters of mono-, di- or tricarboxylic acids and of di-, tri-, tetra- or pentahydroxy alcohols comprising from 2 to 26 carbon atoms.

Mention may in particular be made of diisopropyl sebacate, diisopropyl adipate, diisostearyl adipate, octyldodecylstearoyl stearate, pentaerythrityl tetraisononanoate, pentaerythrityl tetraisostearate, triisostearyl citrate or trioctyldodecyl citrate.

Preferably, the acid and the alcohol of the ester are saturated.

Preference is given, among the abovementioned esters, to the use of isopropyl palmitate, 2-ethylhexyl palmitate, 2-octyldecyl palmitate, myristates of branched alkyls, such as isopropyl myristate, t-butyl myristate or 2-octyldodecyl myristate, hexyl isostearate, butyl isostearate, isobutyl stearate, 2-hexyldecyl laurate and isononyl isononanoate.

Mention may also be made of esters of C_7-C_{30} aromatic acid and of C_1-C_{30} alcohol, preferably esters of C_7-C_{17} aromatic acid and of C_1-C_{20} alcohol. These esters are in particular C_{12}-C_{15} alkyl benzoates, isostearyl benzoate, octyldodecyl benzoate, behenyl benzoate or 2-ethylhexyl benzoate.

More particularly, the liquid fatty substance or substances present in the composition according to the invention are chosen from linear or branched C_6-C_{16} alkanes, hydrocarbons of more than 16 carbon atoms, liquid triglycerides of fatty acids comprising from 6 to 30 carbon atoms, liquid fatty acids or liquid fatty alcohol and/or acid esters other than the triglycerides.

More particularly, the liquid fatty substance or substances according to the invention are chosen from linear or branched hydrocarbons of more than 16 carbon atoms and of mineral or synthetic origin, such as liquid petrolatum or polydecenes, oils of vegetable origin, liquid fatty acids, liquid fatty alcohol and/or

fatty acid esters or their mixtures.

The liquid fatty substance or substances are generally each present in an amount of between 0.01 and 80% by weight approximately of the total weight of the dyeing composition, preferably between 1 and 70% by weight.

b) The silicones:

According to another specific embodiment of the invention, the compositions comprise b) one or more silicones.

The expression "silicone" is understood to mean, in conformity with what is generally accepted, any organosilicon polymer or oligomer with a linear or cyclic and branched or crosslinked structure of variable molecular weight obtained by polymerization and/or by polycondensation of suitably functionalized silanes and essentially composed of a repetition of main units in which the silicon atoms are connected to one another via oxygen atoms (siloxane –Si-O-Si- bond), optionally substituted hydrocarbon radicals being directly connected via a carbon atom to the said silicon atoms (see, for example, the encyclopaedias *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 10.1002/14356007.a24 057 (2005); or *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons Inc., updated (2009), http://mrw.interscience.wiley.com/emrw/9780471238966/kirk/article/silirich.a01/current/pdf).

The commonest hydrocarbon radicals are linear or branched C_1-C_{30} alkyl or alkenyl radicals, preferably alkyl and linear radicals, especially C_1-C_4 radicals and in particular a methyl radical, or aryl radicals and in particular a phenyl radical. These hydrocarbon radicals and in particular the alkyl radicals can be substituted by various groups. The term used is then "organomodified silicones".

The silicones used in the composition according to the invention may be volatile or nonvolatile and soluble or insoluble in the composition. They can be provided in the form of oils, waxes, resins or gums.

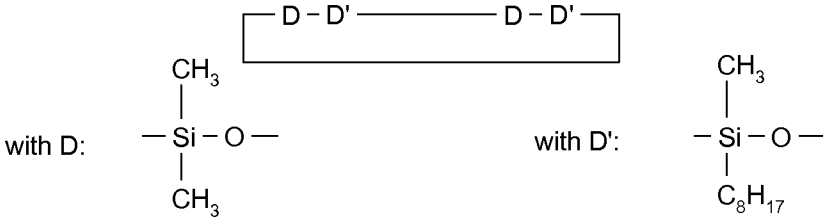
The insoluble silicones are in particular dispersed in the compositions in the form of particles generally having a number-average size of between 2 nanometres and 100 micrometres, preferably between 20 nanometres and 20 micrometres (measured with a particle sizer).

"Organopolysiloxanes" are defined in more detail in the work by Walter Noll, *Chemistry and Technology of Silicones*, Academic Press (1968). They can be volatile or nonvolatile.

When they are volatile, the silicones are chosen more particularly from those having a boiling point of between 60°C and 260°C and more particularly still from:

(i) cyclic silicones comprising from 3 to 7 silicon atoms and preferably 4 or 5. They are, for example, octamethylcyclotetrasiloxane, sold in particular under the name of "Volatile Silicone 7207" by Union Carbide or "Silbione 70045 V 2" by Rhodia, decamethylcyclopentasiloxane, sold under the name of "Volatile Silicone 7158" by Union Carbide or "Silbione 70045 V 5" by Rhodia, and their mixtures.

Mention may also be made of cyclocopolymers of the dimethylsiloxane/methylalkylsiloxane type, such as "Silicone Volatile FZ 3109", sold by Union Carbide, with the chemical structure:



Mention may also be made of mixtures of cyclic silicones with silicon-derived organic compounds, such as the mixture of octamethylcyclotetrasiloxane and of tetratrimethylsilylpentaerythritol (50/50) and the mixture of octamethylcyclotetrasiloxane and of 1,1'-oxy(hexa-2,2,2',2',3,3'-trimethylsilyloxy)bisneopentane;

(ii) linear volatile silicones having from 2 to 9 silicon atoms and having a viscosity of less than or equal to 5×10^{-6} m^2/s at 25°C. They are, for example, decamethyltetrasiloxane, sold in particular under the name "SH 200" by Toray Silicone. Silicones coming within this category are also described in the article published in Cosmetics and Toiletries, Vol. 91, Jan. 76, pp. 27-32, Todd & Byers, "Volatile Silicone Fluids for Cosmetics".

The term “nonvolatile silicone” is understood to mean, within the meaning of the present invention, any silicone having a number of silicon atoms of greater than 7.

Mention may in particular be made, among nonvolatile silicones, of poly(di)alkylsiloxanes, poly(di)arylsiloxanes, poly(di)alkyl(di)arylsiloxanes, silicone gums and resins, polyorganosiloxanes modified by organofunctional groups, polysiloxane(A)-polyoxyalkylene(B) linear block copolymers of $(A\text{-}B)_n$ type with $n > 3$, grafted silicone polymers having a non-silicone organic backbone, composed of an organic main chain formed from organic monomers not comprising silicone, to which is grafted, inside the said chain and optionally at one at least of its ends, at least one polysiloxane macromonomer, grafted silicone polymers having a polysiloxane backbone grafted with non-silicone organic monomers, comprising a polysiloxane main chain to which is grafted, inside the said chain and optionally at one at least of its ends,

at least one organic macromonomer not comprising silicone, and their mixtures.

Mention may in particular be made, as examples of poly(di)alkylsiloxanes, of polydimethylsiloxanes possessing trimethylsilyl end groups having a viscosity of 5×10^{-6} to 2.5 m^2/s at 25°C and preferably of 1×10^{-5} to 1 m^2/s. The viscosity of the silicones is, for example, measured at 25°C according to Standard ASTM 445 Appendix C.

Mention may be made, among these polyalkylsiloxanes, without implied limitation, of the following commercial products:

- Silbione oils of the 47 and 70 047 series or Mirasil oils sold by Rhône-Poulenc, such as, for example, the oil 70 047 V 500 000;
- oils of the Mirasil series sold by Rhodia;
- oils of the 200 series from Dow Corning, such as, more particularly, DC200 with a viscosity of 60 000 cSt;
- Viscasil oils from General Electric and some oils of the SF series (SF 96, SF 18) from General Electric.

Mention may also be made of polydimethylsiloxanes possessing dimethylsilanol end groups (dimethiconol according to the CTFA name), such as oils of the 48 series from Rhodia.

Mention may also be made, in this category of poly(di)alkylsiloxanes, of the products sold under the names "Abil Wax 9800" and "Abil Wax 9801" by Goldschmidt, which are poly(di)(C_1-C_{20})alkylsiloxanes; or the products sold, for example, under the name Belsil DM 300 000, DC 200 Fluid 300 000, Silbione 300 000, Mirasil DM 300 000 or 200 Fluid 350 cSt, more particularly the product DC 200 Fluid 350 cSt® from Dow Corning, which comprises polydimethylsiloxane.

The poly(di)alkyl(di)arylsiloxanes can in particular be chosen from linear and/or branched polydimethyl(methylphenyl)siloxanes or polydimethyl-

diphenylsiloxanes with a viscosity of 1×10^{-5} to 5×10^{-2} m^2/s at 25°C.

Mention may be made, among these poly(di)alkyl-(di)arylsiloxanes, by way of example, of the products sold under the following names:

- Silbione oils of the 70 641 series from Rhodia;
- oils of the Rhodorsil 70 633 and 763 series from Rhodia;
- the oil Dow Corning 556 Cosmetic Grade Fluid from Dow Corning;
- silicones of the PK series from Bayer, such as the product PK20;
- silicones of the PN and PH series from Bayer, such as the products PN1000 and PH1000;
- some oils of the SF series from General Electric, such as SF 1023, SF 1154, SF 1250 and SF 1265.

Silicone gums which can be used in accordance with the invention are in particular polydiorganosiloxanes having high number-average molecular weights of between 200 000 and 1 000 000, used alone or as a mixture in a solvent. This solvent can be chosen from volatile silicones, polydimethylsiloxane (PDMS) oils, polyphenylmethylsiloxane (PPMS) oils, isoparaffins, polyisobutylenes, methylene chloride, pentane, dodecane, tridecanes or their mixtures.

Mention may more particularly be made of the following products:

- polydimethylsiloxane gums,
- polydimethylsiloxane/methylvinylsiloxane gums,
- polydimethylsiloxane/diphenylsiloxane gums,
- polydimethylsiloxane/phenylmethylsiloxane gums,
- polydimethylsiloxane/diphenylsiloxane/methylvinyl-siloxane gums.

Mixtures of silicones can also be employed, such as:

a) mixtures formed from a polydimethylsiloxane gum hydroxylated at the chain end (named dimethiconol according to the nomenclature of the CTFA

dictionary) and from a cyclic polydimethylsiloxane (named cyclomethicone according to the nomenclature of the CTFA dictionary), such as the product Q2 1401 sold by Dow Corning;

b) mixtures formed from a polydimethylsiloxane gum with a cyclic silicone, such as the product SF 1214 Silicone Fluid from General Electric; this product is a gum SF 30, corresponding to a dimethicone, having a number-average molecular weight of 500 000, dissolved in the oil SF 1202 Silicone Fluid, corresponding to decamethylcyclopentasiloxane;

c) mixtures of two PDMSs with different viscosities and more particularly of a PDMS gum and of a PDMS oil, such as the product SF 1236 from General Electric. The product SF 1236 is the mixture of a gum SE 30 defined above, having a viscosity of 20 m^2/s, and of an oil SF 96 with a viscosity of 5×10^{-6} m^2/s. This product preferably comprises 15% of gum SE 30 and 85% of an oil SF 96.

The organopolysiloxane resins which can be used in accordance with the invention are crosslinked siloxane systems including the units: $R_2SiO_{2/2}$, $R_3SiO_{1/2}$, $RSiO_{3/2}$ and $SiO_{4/2}$, in which R represents a hydrocarbon group having from 1 to 16 carbon atoms or a phenyl group.

Among these products, those which are particularly preferred are those in which R denotes a lower C_1-C_4 alkyl radical, more particularly methyl, or a phenyl radical.

Mention may be made, among these resins, of the product sold under the name "Dow Corning 593" or those sold under the names "Silicone Fluid SS 4230" and "Silicone Fluid SS 4267" by General Electric and which are silicones with a dimethyl/trimethylsiloxane structure.

Mention may also be made of resins of the trimethylsiloxysilicate type, sold in particular under the names X22-4914, X21-5034 and X21-5037 by Shin-Etsu.

The organomodified silicones which can be used in accordance with the invention are silicones as defined above which comprise, in their structure, one or more organofunctional groups attached via a hydrocarbon group.

Mention may be made, among organomodified silicones, of the polyorganosiloxanes comprising:

- polyethyleneoxy and/or polypropyleneoxy groups optionally comprising C_6-C_{24} alkyl groups, such as the products known as dimethicone copolyol, sold by Dow Corning under the name DC Fluid 190 or DC 1248, or the Silwet® L 722, L 7500, L 77 and L 711 oils from Union Carbide, and (C_{12})alkyl methicone copolyol, sold by Dow Corning under the name Q2 5200;
- thiol groups, such as the products sold under the names "GP 72 A" and "GP 71" from Genesee;
- alkoxylated groups, such as the product sold under the name "Silicone Copolymer F-755" by SWS Silicones and Abil Wax® 2428, 2434 and 2440 by Goldschmidt;
- hydroxylated groups, such as the polyorganosiloxanes possessing a hydroxyalkyl functional group described in French Patent Application FR-A-85 16334;
- acyloxyalkyl groups, such as, for example, the polyorganosiloxanes described in Patent US-A-4 957 732;
- anionic groups of the carboxylic acid type, such as, for example, in the products described in Patent EP 186 507 from Chisso Corporation, or of the alkylcarboxyl type, such as those present in the product X-22-3701E from Shin-Etsu; 2-hydroxyalkylsulphonate; 2-hydroxyalkyl thiosulphate, such as the products sold by Goldschmidt under the names "Abil® S201" and "Abil® S255";
- hydroxyacylamino groups, such as the polyorganosiloxanes described in Application

EP 342 834. Mention may be made, for example, of the product Q2-8413 from Dow Corning;

- halogenated groups, such as polymethyltrifluoropropyldimethylsiloxane, provided under the name FL5 by Shin-Etsu.

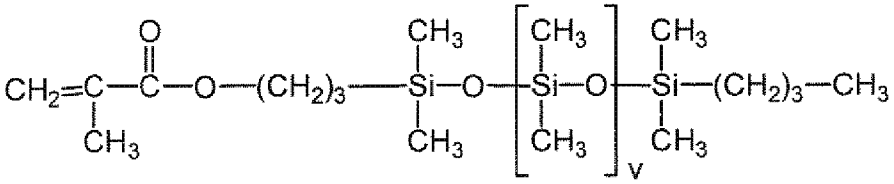
According to the invention, use may also be made of polymers of the grafted silicone type comprising a polysiloxane portion and a portion comprising a non-silicone organic chain, one of the two portions constituting the main chain of the polymer and the other being grafted to the main chain. These polymers are disclosed, for example, in the documents EP A 0 412 704, EP-A-0 412 707, EP-A-0 640 105, WO 95/00578, EP-A-0 582 152 and WO 93/23009 and Patents US Nos 4 693 935, 4 728 571 and 4 972 037. These polymers are, for example, anionic or nonionic.

Such polymers are, for example, copolymers capable of being obtained by radical polymerization starting from the mixture of monomers comprising:

a) approximately 50% to approximately 90% by weight of tert-butyl acrylate;

b) 0% to approximately 40% by weight of acrylic acid;

c) approximately 5% to approximately 40% by weight of silicone macromer of formula (**VII**):



(**VII**)

in which formula (**VII**) **v** is an integer ranging from 5 to 700 inclusive, the percentages by weight being calculated with respect to the total weight of the monomers.

Other examples of grafted silicone polymers are in particular polydimethylsiloxanes (PDMS) to which are grafted, via a connecting link of thiopropylene type,

mixed polymer units of the poly((meth)acrylic acid) type and of the poly(alkyl (meth)acrylate) type and polydimethylsiloxanes (PDMS) to which are grafted, via a connecting link of thiopropylene type, polymer units of the poly(isobutyl (meth)acrylate) type.

Preferably, the silicone is an aminated silicone.

The term "aminated silicone" is understood to mean, within the meaning of the present invention, any silicone comprising at least one primary, secondary or tertiary amine functional group or one quaternary ammonium group.

The aminated silicones used in the composition in the film form according to the present invention are chosen from:

(a) the compounds corresponding to the following formula **(II)**:

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

in which formula **(II)**:

- **T**, which are identical or different, are a hydrogen atom, a phenyl radical, a hydroxyl (-OH) radical, a linear or branched C_1-C_8 alkyl radical, preferably a methyl radical, or a C_1-C_8 alkoxy radical, preferably a methoxy radical,
- **a** denotes the number 0 or a number from 1 to 3, and preferably 0,
- **b** denotes 0 or 1, and in particular 1,
- **m** and **n**, which are identical or different, are numbers such that the sum (n + m) can vary in particular from 1 to 2000 inclusive and in particular from 50 to 150 inclusive, it being possible for n to denote a number ranging from 0 to 1999 inclusive and in particular from 49 to 149 inclusive and it being possible for m to denote a number ranging from 1 to 2000 inclusive and in particular from 1 to 10 inclusive;
- $\mathbf{R^1}$, which are identical or different, are a monovalent radical of formula $\mathbf{-C_qH_{2q}-L}$ in which q is a number of from 2 to 8 inclusive and L is an

aminated group, optionally quaternized, chosen from the groups:

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

$-N(R^2)_2$;

$-N^+(R^2)_3\ Q^-$;

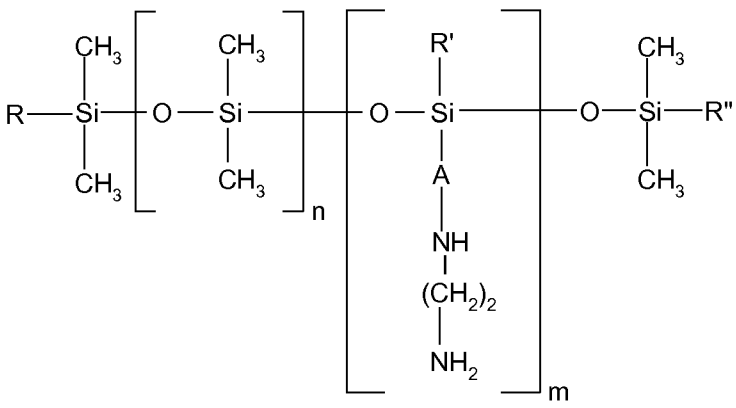
$-N^+(R^2)H_2\ Q^-$;

$-N^+(R^2)_2H\ Q^-$; and

$-N(R^2)-CH_2-CH_2-N^+(R^2)H_2\ Q^-$,

in which R^2, which are identical or different, can 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 anionic counterion of halide type, such as, for example, fluoride, chloride, bromide or iodide.

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



(III)

in which formula (**III**):

- **R**, **R'** and **R"**, which are identical or different, denote a linear or branched C_1-C_4 alkyl radical, preferably a methyl radical; a linear or branched C_1-C_4 alkoxy radical, preferably a methoxy radical; or OH;
- **A** represents a linear or branched C_3-C_8, preferably C_3-C_6, alkylene radical;
- **m** and **n** are numbers depending on the molecular weight, the sum of which is between 1 and 2000 inclusive.

According to a first possibility, R, R' and R", which are identical or different, represent a linear or branched C_1-C_4 alkyl or hydroxyl radical, A represents a C_3 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 linear or branched 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 is advantageously equal to 0.3/1.

Furthermore, m and n are such that the weight-average molecular weight of the compound is between 2000 and 1 000 000. More particularly, n is between 0 and 1500 inclusive and m is between 1 and 1000 inclusive, the sum of n and m being between 1 and 1800 inclusive.

Mention may be made, in this category of compounds, inter alia, of:

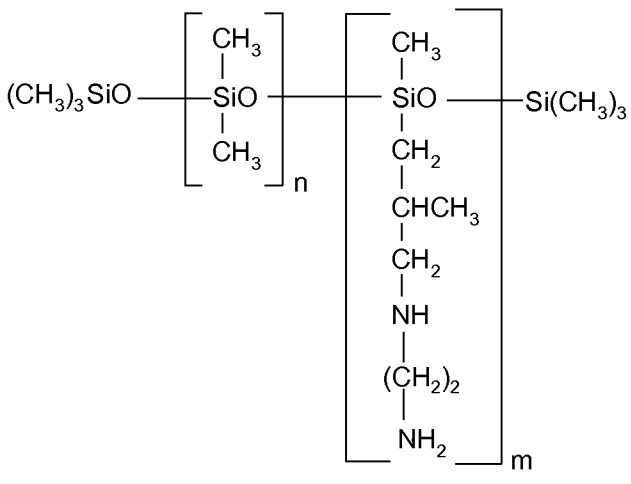
- the product Belsil® ADM 652 sold by Wacker;
- the product DC 939 emulsion sold by Dow Corning, corresponding to an emulsion of i) Amodimethicone, ii) Trideceth-12 and iii) halide, such as cetrimonium chloride;
- the product DC 2-8299 Cationic Emulsion sold by Dow Corning, corresponding to an emulsion of i) Amodimethicone, ii) Trideceth-6 and iii) halide, such as cetrimonium chloride;
- the product SME253, which corresponds to a mixture of i) Amodimethicone, ii) C11-15 Pareth-7, iii) Trideceth-12, iv) Laureth-9 and v) Glycerine;
- Wacker-Belsil ADM LOG 1, corresponding to the mixture as a microemulsion of i) Amodimethicone, ii) Trideceth-5 and iii) Trideceth-10.

According to a third possibility, R and R", which are different, represent a linear or branched C_1-C_4 alkoxy or hydroxyl radical, at least one of the R or 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. Furthermore, m and n are such that the weight-average molecular weight of the compound is between 2000 and 200 000 inclusive. More particularly, n is between 0 and 1500 inclusive and m is between 1 and 1000 inclusive, the sum of n and m being between 1 and 1800 inclusive.

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

It should be noted that the molecular weight of these silicones is determined by gel permeation chromatography (ambient temperature; polystyrene standard; styragem μ 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 (**II**) is in particular the polymer named "trimethylsilylamodimethicone" in the CTFA dictionary, corresponding to the following formula (**IV**):

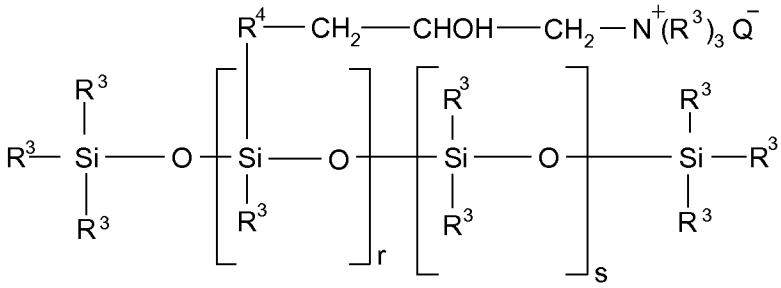


(IV)

in which formula (**IV**) 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 (**II**) is, for example, sold under the name Q2-8220 by OSI.

(**b**) the compounds corresponding to the following formula (**V**):



(V)

in which formula (**V**):

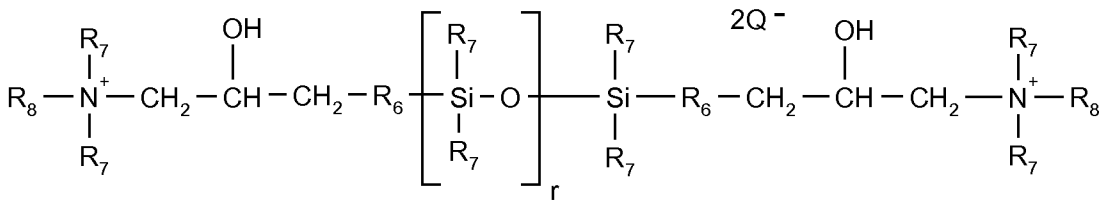
- **R^3** represents a monovalent C_1-C_{18} hydrocarbon radical and in particular a linear or branched C_1-C_{18} alkyl radical or a linear or branched C_2-C_{18} alkenyl radical, for example a methyl or ethylenyl radical;
- **R^4** represents a divalent hydrocarbon radical, in particular a linear or branched C_1-C_{18} alkylene radical, or a linear or branched divalent C_1-C_{18}, for example C_1-C_8, alkyleneoxy radical, such as $-(CH_2)_r-$, with r corresponding to an integer between 1 and 8 inclusive, or $-(CH_2=CH_2)_t-(CH_2)_u-(CH_2=CH_2)_v-$, with t, u and v, which are identical or different, representing an integer between 0 and 8 inclusive with the sum t+u+v being between 1 and 8 inclusive;
- **Q^-** is an anionic counterion, such as halide, in particular chloride;
- **r** represents a mean statistical value between 2 and 20 inclusive and in particular between 2 and 8 inclusive;
- **s** represents a mean statistical value between 20 and 200 inclusive and in particular between 20 and 50 inclusive.

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".

c) the quaternary ammonium silicones of formula (**VI**):



(VI)

in which formula (**VI**):

- **R_7**, which are identical or different, represent a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, in particular a linear or branched C_1-C_{18} alkyl radical, a linear or branched C_2-C_{18} alkenyl radical or a ring comprising 5 or 6 carbon atoms, for example a methyl or ethylenyl radical;
- **R_6** represents a divalent hydrocarbon radical, in particular a linear or branched C_1-C_{18} alkylene radical, or a linear or branched divalent C_1-C_{18}, for example C_1-C_8, alkyleneoxy 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 linear or branched C_1-C_{18} alkyl radical or a linear or branched C_2-C_{18} alkenyl radical, or an $-R_6-NHCOR_7$ radical with R_6 and R_7 as defined above;
- **Q^-**, which are identical or different, represent an anionic counterion, such as halide, in particular chloride, or an organic acid ion (acetate, and the like);
- **r** represents a mean statistical value between 2 and 200 inclusive and in particular between 5 and 100 inclusive.

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

Preferably, the silicones are liquid, i.e. liquid at ambient temperature (25°C) and at atmospheric pressure (760 mm of mercury), and insoluble in water

under these conditions, that is to say with a solubility of less than 5% by weight, preferably of less than 1% by weight and more preferably still of less than 0.1% by weight in water. More particularly, the silicones are liquids and are oils.

The silicone or silicones used in the composition according to the invention can be present in an amount varying from 0.01 to 20% by weight, preferably in an amount varying from 0.1 to 15% by weight and more preferably still in an amount varying from 0.1 to 10% by weight, with respect to the total weight of the composition.

Preferably, the ratio by weight of the compound of formula (I) or its salts to b) the silicone or silicones in accordance with the invention is between 0.005 and 20 and more preferably still between 0.01 and 10, better still between 0.05 and 1.

The other oxidation dyes:

The dyeing composition according to the invention can comprise one or more couplers conventionally used for the dyeing of keratinous fibres.

Mention may in particular be made, among these couplers, of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene couplers, heterocyclic couplers and their addition salts.

Mention may be made, as example of coupler, of 2-methyl-5-aminophenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 6-chloro-2-methyl-5-aminophenol, 3-aminophenol, 2,4-dichloro-3-aminophenol, 5-amino-4-chloro-o-cresol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diamino-benzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-(dimethylamino)benzene, sesamol, 1-(β-hydroxyethylamino)-3,4-methylenedioxy-benzene, α-naphthol, 2-methyl-1-naphthol,

1,5-dihydroxynaphthalene, 2,7-naphthalenediol, 1-acetoxy-2-methylnaphthalene, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 2,6-dihydroxy-3-4-dimethyl-pyridine, 3-amino-2-methylamino-6-methoxypyridine, 1-N-(β-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β-hydroxyethylamino)toluene, 3-methyl-1-phenyl-5-pyrazolone and their addition salts with an acid.

In the composition of the present invention, the coupler or couplers, if they are present, generally represent an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

The dyeing composition of the invention can optionally comprise one or more additional oxidation bases conventionally used for dyeing keratinous fibres other than the compound of formula (I) or its salts.

By way of example, these additional oxidation bases are chosen from para-phenylenediamines other than the oxidation base of formula (I) and its addition salts, bisphenylalkylenediamines, para-aminophenols, bis-para-aminophenols, ortho-aminophenols or heterocyclic bases.

Mention may be made, among para-phenylenediamines, by way of example, of para-phenylenediamine, para-toluenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-(β-hydroxyethyl)-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-

para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl, β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-(β-hydroxyethyloxy)-para-phenylenediamine, 2-(β-acetylaminoethyloxy)-para-phenylenediamine, N-(β-methoxyethyl)-para-phenylenediamine, 4-amino-phenylpyrrolidine, 2-thienyl-para-phenylenediamine, 2-(β-hydroxyethylamino)-5-aminotoluene, 3-hydroxy-1-(4'-aminophenyl)pyrrolidine and their addition salts with an acid.

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-toluenediamine, 2-isopropyl-para-phenylenediamine, 2-(β-hydroxyethyl)-para-phenylenediamine, 2-(β-hydroxyethyloxy)-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine, 2-(β-acetylaminoethyloxy)-para-phenylenediamine and their addition salts with an acid are particularly preferred.

Mention may be made, among bisphenylalkylenediamines, by way of example, of N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methyl-phenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane and their addition salts with an acid.

Mention may be made, among para-aminophenols, by way of example, of para-aminophenol, 4-amino-

3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-2-methylphenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-(methoxymethyl)phenol, 4-amino-2-(aminomethyl)phenol, 4-amino-2-((β-hydroxyethyl)aminomethyl)phenol, 4-amino-2-fluorophenol, 1-hydroxy-4-(methylamino)benzene, 2,2'-methylenebis(4-aminophenol) and their addition salts with an acid.

Mention may be made, among ortho-aminophenols, by way of example, of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol and their addition salts with an acid.

Mention may be made, among heterocyclic bases, by way of example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Mention may be made, among pyridine derivatives, of the compounds described, for example, in Patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-[(4-methoxyphenyl)amino]-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-[(β-methoxyethyl)amino]-3-amino-6-methoxypyridine, 3,4-diaminopyridine and their addition salts with an acid.

Mention may be made, among pyrimidine derivatives, of the compounds described, for example, in Patents DE 2 359 399; JP 88-169571; JP 05-63124; EP 0 770 375 or Patent Application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine or 2,5,6-triaminopyrimidine, and pyrazolopyrimidine derivatives, such as those mentioned in Patent Application FR-A-2 750 048 and among which may be mentioned pyrazolo[1,5-a]-pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]-pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-amino-

pyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-amino-pyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxy-ethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]-pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 3-amino-5-methyl-7-(imidazolylpropyl-amino)pyrazolo[1,5-a]pyrimidine and their addition salts with an acid and their tautomeric forms, when a tautomeric equilibrium exists.

Mention may be made, among pyrazole derivatives, of the compounds described in Patents DE 3 843 892 and DE 4 133 957 and Patent Applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β-hydroxy-ethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenyl-pyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-(tert-butyl)-1-methylpyrazole, 4,5-diamino-1-(tert-butyl)-3-methylpyrazole, 4,5-diamino-1-(β-hydroxy-ethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methyl-pyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)-pyrazole, 4,5-diamino-1-ethyl-3-(hydroxymethyl)-pyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-tri-aminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-(methylamino)pyrazole, 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole and their addition salts with an acid.

Mention may also be made of the diaminopyrazolinones described in Patent Application

FR 2 886 137 and in particular 2,3-diamino-6,7-dihydro-1H,5H-pyrazol-1-one and its salts.

Generally, the addition salts of the oxidation bases and couplers which can be used in the context of the invention are chosen in particular from the addition salts with an acid, such as hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzenesulphonates, phosphates and acetates, and the addition salts with a base, such as sodium hydroxide, potassium hydroxide, aqueous ammonia, amines or alkanolamines.

When the composition comprises one or more additional oxidation bases, the latter more particularly represent(s) from 0.0005 to 12% by weight, with respect to the total weight of the dyeing composition, preferably from 0.005 to 8% by weight.

The direct dyes:

The dyeing composition in accordance with the invention can additionally comprise one or more direct dyes which can in particular be chosen from nitrobenzene dyes, azo direct dyes or methine direct dyes. These direct dyes can be nonionic, anionic or cationic in nature.

In the composition of the present invention, the direct dye or dyes, if they are present, generally represent an amount of between 0.001 and 20% by weight, with respect to the total weight of the dyeing composition, preferably between 0.01 and 10% by weight.

The appropriate dyeing medium of the composition:

The medium appropriate for dyeing, also referred to as dyeing vehicle, generally comprises water or a mixture of water and of one or more solvents, such as, for example, lower C_1-C_4 alkanols, such as ethanol and isopropanol, polyols, such as propylene glycol, dipropylene glycol or glycerol, and polyol ethers, such as dipropylene glycol monomethyl ether.

The solvent or solvents are generally present in proportions which can be between 1 and 40% by weight approximately, with respect to the total weight of the dyeing composition, and more preferably still between 3 and 30% by weight approximately.

The dyeing composition in accordance with the invention can also include various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or their mixtures, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or their mixtures, inorganic or organic thickening agents and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents other than fatty substances a) or b) as defined above, modified or unmodified, film-forming agents, ceramides, preservatives or opacifying agents.

The above adjuvants 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.

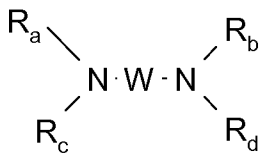
Of course, a person skilled in the art will take care to choose this or these optional additional compounds so that the advantageous properties intrinsically attached to the oxidation dyeing composition in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately. It can be adjusted to the desired value using acidifying or basifying agents commonly used in the dyeing of keratinous fibres or else by means of conventional buffering systems.

Mention may be made, among acidifying agents, by way of example, of inorganic or organic acids, such as

hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, or sulphonic acids.

Mention may be made, among basifying agents, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines, such as mono-, di- and triethanolamines and their derivatives, sodium hydroxide, potassium hydroxide and the compounds of following formula (**VIII**):



(VIII)

in which formula (**VIII**):

- **W** is a propylene residue optionally substituted by a hydroxyl group or a C_1-C_4 alkyl radical;
- R_a, R_b, R_c and R_d, which are identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl radical.

The chemical oxidizing agents:

The composition according to the invention can comprise one or more oxidizing agents.

The oxidizing agents conventionally used for the oxidation dyeing of keratinous fibres are, for example, hydrogen peroxide, urea hydrogen peroxide, persalts, such as perborates and persulphates, peracids, alkali metal bromates and oxidase enzymes, among which may be mentioned peroxidases, 2-electron oxidoreductases, such as uricases, and 4-electron oxygenases, such as laccases. Hydrogen peroxide is particularly preferred.

The dyeing composition according to the invention can be provided in various forms, such as in the form of liquids, of creams or of gels or in any other form appropriate for carrying out dyeing of keratinous fibres, in particular of human hair.

It can result from the mixing at the time of use of several compositions.

In a first specific alternative form, it results from the mixing of at least two compositions, one comprising one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid, optionally one or more additional oxidation bases other than the compound of formula (I) or its salts and optionally one or more couplers, a second composition comprising the non-silicone liquid fatty substance or substances described above and optionally a third composition comprising one or more oxidizing agents as described above.

In a second specific alternative form, it results from the mixing of two compositions, one comprising one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid, the non-silicone liquid fatty substance or substances described above, optionally one or more additional oxidation bases other than the compound of formula (I) or its salts and optionally one or more couplers and the other comprising one or more oxidizing agents as described above.

The composition of the invention is thus applied to the hair for the colouring of the keratinous fibres either as is or in the presence of one or more oxidizing agents for the colouring of the keratinous fibres.

The method for colouring the keratinous fibres:

The method of the present invention is a method in which the composition devoid of oxidizing agent according to the present invention as defined above is applied to the fibres, either alone or in the presence of one or more oxidizing agents, for a time sufficient to develop the desired colouring.

The colour can be developed at acidic, neutral or alkaline pH. Furthermore, the oxidizing agent, if it is present, can be added to the composition of the invention only at the time of use or it can be employed

starting from an oxidizing composition comprising it, applied simultaneously with or sequentially to the composition of the invention.

According to a specific embodiment, the composition devoid of oxidizing agent according to the present invention is mixed, preferably at the time of use, with a composition comprising, in a medium appropriate for dyeing, one or more oxidizing agents. The mixture obtained is subsequently applied to the keratinous fibres.

The oxidizing agents are those indicated above.

The temperature during the application of the composition is conventionally between ambient temperature (between 15 and 25°C) and 80°C, preferably between ambient temperature and 60°C.

Whether with or without oxidizing agent, after a leave-in time of 3 to 50 minutes approximately, preferably of 5 to 30 minutes approximately, the keratinous fibres are rinsed, washed with a shampoo, rinsed again and then dried.

The oxidizing composition can also include various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The pH of the oxidizing composition including the oxidizing agent is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to the keratinous fibres preferably varies between 3 and 12 approximately and more preferably still between 5 and 11. It can be adjusted to the desired value using acidifying or basifying agents commonly used in the dyeing of keratinous fibres and as defined above.

The ready-for-use composition, with or without oxidizing agent, which is finally applied to the keratinous fibres can be provided in various forms, such as in the form of liquids, creams or gels or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

The dyeing kit or multicompartment device:

Another subject-matter of the invention is a dyeing kit or multicompartment device in which a first compartment includes the dyeing composition devoid of oxidizing agent of the present invention as defined above and a second compartment includes one or more oxidizing agents as described above.

A second device is composed of a first compartment, comprising a composition comprising one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid as described above, optionally one or more additional oxidation bases other than the compound of formula (I) or its salts as described above and optionally one or more couplers as described above, and a second compartment, comprising a composition comprising a) the non-silicone liquid fatty substance or substances or b) the silicone or silicones as described above.

A third device can optionally comprise the two compartments of the second device plus a third compartment including a composition comprising one or more oxidizing agents.

These devices can be equipped with a means allowing the desired product to be deposited on the hair, such as the devices described in Patent FR-2 586 913 on behalf of the Applicant Company.

Starting from these devices, it is possible to dye keratinous fibres by a method which comprises mixing the compositions present in each of the compartments of the said devices and applying the mixture obtained to the keratinous fibres for a time sufficient to develop the desired colouring.

The examples which follow serve to illustrate the invention without, however, exhibiting a limiting nature.

EXAMPLES

DYEING EXAMPLES

The following Examples 1 and 2 are carried out:

Example 1

The amounts are expressed in g

Composition A1	
Oxyethylenated sorbitan monolaurate (4EO)	21.67
Pyrogenic silica having a hydrophobic nature	11
Liquid petrolatum	q.s. for 100

Composition C1	
2-[{2-[(4-Aminophenyl)amino]ethyl}(2-hydroxy-ethyl)amino]ethanol	1.55
2-Methyl-5-[(2-hydroxyethyl)amino]phenol	1.08
Sodium metabisulphite	0.455
Erythorbic acid	0.31
Pure monoethanolamine	40.07
Demineralized water	q.s. for 100

Example 2

The amounts are expressed in g

Composition A2	
Oxyethylenated sorbitan monolaurate (4EO)	21.67
Pyrogenic silica having a hydrophobic nature	11
Avocado oil	q.s. for 100

Composition C2	
2-[{2-[(4-Aminophenyl)amino]ethyl}(2-hydroxy-ethyl)amino]ethanol as a 50% aqueous solution	1.90 (A.M)

2,4-Diaminophenoxyethanol dihydrochloride	1.93
Sodium metabisulphite	0.455
Erythorbic acid	0.31
Pure monoethanolamine	40.07
Demineralized water	q.s. for 100

A.M. = active materials

Method of application

The following are mixed at the time of use:
For Example 1:
- 9 parts by weight of the composition (A1) with
- 1 part by weight of the composition (C1) and
- 10 parts by weight of an aqueous oxidizing composition comprising 6% of hydrogen peroxide at a pH of 2.3 (B);

For Example 2:
- 9 parts by weight of the composition (A2) with
- 1 part by weight of the composition (C2) and
- 10 parts by weight of an aqueous oxidizing composition comprising 6% of hydrogen peroxide at a pH of 2.3 (B).

Each of these mixtures, the pH of which is approximately 10, was applied to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 minutes at ambient temperature.

The hair was subsequently rinsed, washed with a standard shampoo and dried.

Results

The hair colouring was evaluated (height of tone and highlight) visually:

Example	Height of tone	Highlight
1	Light Chestnut	Iridescent
2	Chestnut	Blue

Example 3

The following Composition 3 is prepared:

Composition 3	g
2-[{2-[(4-Aminophenyl)amino]ethyl}(2-hydroxyethyl)amino]ethanol as a 50% aqueous solution	2.15 g (A.M.) (0.009 mol)
6-Hydroxybenzomorpholine	1.36 g (A.M.) (0.009 mol)
Oxyethylenated lauryl alcohol comprising 12 mol of ethylene oxide	7.5 g
Oxyethylenated oleocetyl alcohol comprising 30 mol of ethylene oxide	6 g
Lauric acid	2.5 g
Cetearyl (50/50) alcohol	10 g
Crosslinked polyacrylic acid	0.4 g
Pyrogenic silica	1 g
Glycerol monostearate	1 g
Polyquaternium-6, sold under the name Merquat 100 by Ondeo	3 g
Propylene glycol	10 g
DC2-8299® from Dow Corning	**3 g % A.M.**
Anhydrous sodium metasilicate	2 g
Pure monoethanolamine	10 g
Reducing agent, sequestering agent, antioxidant, fragrance	q.s.
Water	q.s. for 100 g

Example 4

The following Composition 4 is prepared:

Composition 4	**g**
2-[{2-[(4-Aminophenyl)amino]ethyl}(2-hydroxyethyl)amino]ethanol	1.67 g (A.M.) (0.007 mol)
6-Chloro-2-methyl-5-aminophenol	1.10 g (A.M.) (0.007 mol)
Oxyethylenated lauryl alcohol comprising 12 mol of ethylene oxide	7.5 g
Oxyethylenated oleocetyl alcohol comprising 30 mol of ethylene oxide	6 g
Lauric acid	2.5 g
Cetearyl (50/50) alcohol	10 g
Crosslinked polyacrylic acid	0.4 g
Pyrogenic silica	1 g
Glycerol monostearate	1 g
Polyquaternium-6, sold under the name Merquat 100 by Ondeo	3 g
Propylene glycol	10 g
DC 200 Fluid 350 cSt® from Dow Corning	**3 g % A.M.**
Anhydrous sodium metasilicate	2 g
Pure monoethanolamine	10 g
Reducing agent, sequestering agent, antioxidant, fragrance	q.s.
Water	q.s. for 100 g

Method of application

Each of Composition 3 or Composition 4 is diluted at the time of use with 1.5 times its weight of 20 volume aqueous hydrogen peroxide solution.

The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 min for Composition 3 and 20 min for Composition 4.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

Results

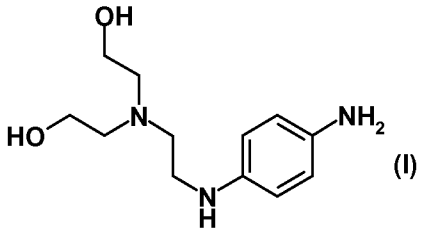
The hair colourings were evaluated visually.

	Height of tone	Highlight
Composition 3	Dark Blond	Green
Composition 4	Light Chestnut	Deep Purple

CLAIMS

1. Composition for dyeing keratinous fibres comprising, in a medium appropriate for dyeing keratinous fibres:

- one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid:



(I)

and

- one or more fatty substances chosen from a) non-silicone liquids and b) silicones.

2. Composition according to the preceding claim, characterized in that the content of compound of formula (I) is between 0.001 and 10% by weight approximately of the total weight of the dyeing composition.

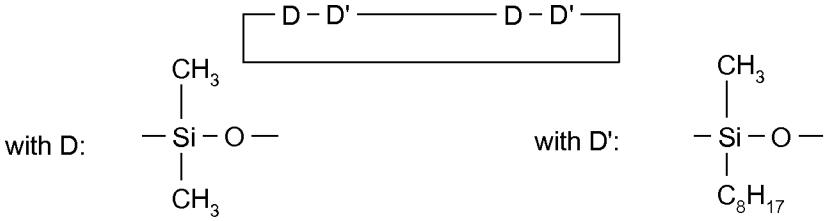
3. Composition according to either one of the preceding claims, characterized in that the fatty substance or substances are a) non-silicone liquids and are chosen in particular from:

- linear or branched C_6-C_{16} alkanes;
- hydrocarbon oils of animal origin;
- triglyceride oils of vegetable or synthetic origin;
- linear or branched hydrocarbons of mineral or synthetic origin and of more than 16 carbon atoms;
- fluorinated oils;
- liquid fatty alcohols;
- liquid fatty acids;
- liquid fatty alcohol and/or acid esters other than the triglycerides.

4. Composition according to the preceding claim, in which the liquid fatty substance or substances are chosen from linear or branched C_6-C_{16} alkanes, hydrocarbons of more than 16 carbon atoms, liquid triglycerides of fatty acids comprising from 6 to 30 carbon atoms, liquid fatty acids or liquid fatty alcohol and/or acid esters other than the triglycerides.

5. Composition according to Claim 1 or Claim 2, characterized in that the fatty substance or substances are b) silicones in particular which are volatile or nonvolatile and soluble or insoluble in the composition and which are present especially in the form of oils, waxes, resins or gums.

6. Composition according to any one of Claims 1, 2 and 5, in which the silicone or silicones b) are volatile and are chosen from:
(i) cyclic silicones comprising from 3 to 7 silicon atoms, such as the cyclic silicones octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and their mixtures, cyclocopolymers of the dimethylsiloxane/methylalkylsiloxane type, with the chemical structure of following formula:



mixtures of octamethylcyclotetrasiloxane and of tetratrimethylsilylpentaerythritol and the mixture of octamethylcyclotetrasiloxane and of 1,1'-oxy(hexa-2,2,2',2',3,3'-trimethylsilyloxy)bisneopentane; and
(ii) linear volatile silicones having from 2 to 9 silicon atoms and having a viscosity of less than or equal to 5×10^{-6} m^2/s at 25°C.

7. Composition according to any one of Claims 1, 2

and 5, in which the silicone or silicones b) are not volatile and are chosen from:

- poly(di)alkylsiloxanes,
- poly(di)arylsiloxanes,
- poly(di)alkyl(di)arylsiloxanes,
- silicone gums and resins,
- polyorganosiloxanes modified by organofunctional groups,
- polysiloxane(A)-polyoxyalkylene(B) linear block copolymers of $(A\text{-}B)_n$ type with $n>3$;
- grafted silicone polymers having a non-silicone organic backbone, composed of an organic main chain formed from organic monomers not comprising silicone, to which is grafted, inside the said chain and optionally at one at least of its ends, at least one polysiloxane macromonomer;
- grafted silicone polymers having a polysiloxane backbone grafted with non-silicone organic monomers, comprising a polysiloxane main chain to which is grafted, inside the said chain and optionally at one at least of its ends, at least one organic macromonomer not comprising silicone; and their mixtures.

8. Composition according to any one of Claims 1, 2 and 5 to 7, in which the silicone or silicones are chosen from aminated silicones; in particular are chosen from:

(**a**) the compounds corresponding to the following formula (**II**):

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

in which formula (**II**):

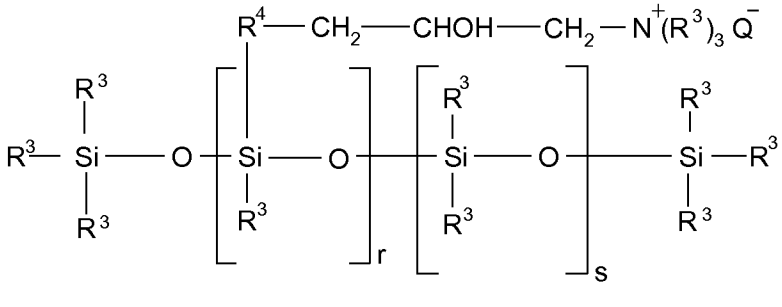
- **T**, which are identical or different, are a hydrogen atom, a phenyl radical, a hydroxyl (-OH) radical or a linear or branched C_1-C_8 alkyl radical,
- **a** denotes the number 0 or an integer from 1 to 3,
- **b** denotes 0 or 1,
- **m** and **n**, which are identical or different, are

integers such that the sum (n + m) can vary from 1 to 2000 inclusive, it being possible for n to denote an integer ranging from 0 to 1999 inclusive and it being possible for m to denote an integer ranging from 1 to 2000 inclusive;

- **R^1**, which are identical or different, are a monovalent radical of formula **$-C_qH_{2q}-L$**
  in which q is an integer from 2 to 8 inclusive and L is an aminated group, optionally quaternized, chosen from the groups:
  $-N(R^2)-CH_2-CH_2-N(R^2)_2$;
  $-N(R^2)_2$;
  $-N^+(R^2)_3\ Q^-$;
  $-N^+(R^2)H_2\ Q^-$;
  $-N^+(R^2)_2H\ Q^-$; and
  $-N(R^2)-CH_2-CH_2-N^+(R^2)H_2\ Q^-$,

in which R^2, which are identical or different, denote a hydrogen atom, a phenyl, a benzyl or a saturated monovalent hydrocarbon radical and Q^- represents an anionic counterion;

(**b**) the compounds corresponding to the following formula (**V**):



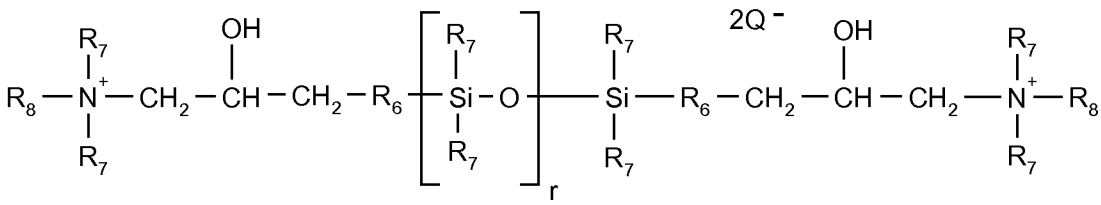
(V)

in which formula (**V**):

- **R^3** represents a monovalent C_1-C_{18} hydrocarbon radical or a linear or branched C_2-C_{18} alkenyl radical;
- **R^4** represents a divalent C_1-C_{18} hydrocarbon radical or a linear or branched divalent C_1-C_{18} alkyleneoxy radical;
- **Q^-** is an anionic counterion;
- **r** represents a mean statistical value between 2 and 20 inclusive;

- **s** represents a mean statistical value between 20 and 200 inclusive;

(c) the quaternary ammonium silicones of formula (**VI**):



(VI)

in which formula (**VI**):

- $\mathbf{R_7}$, which are identical or different, represent a monovalent hydrocarbon radical having from 1 to 18 carbon atoms;
- $\mathbf{R_6}$ represents a divalent C_1-C_{18} hydrocarbon radical or a linear or branched divalent C_1-C_{18} alkyleneoxy radical;
- $\mathbf{R_8}$, which are identical or different, represent a hydrogen atom, a C_1-C_{18} monovalent hydrocarbon radical having from 1 to 18 carbon atoms, a linear or branched C_2-C_{18} alkenyl radical or an $-R_6-NHCOR_7$ radical with R_6 and R_7 as defined above;
- $\mathbf{Q^-}$, which are identical or different, represent an anionic counterion;
- **r** represents a mean statistical value between 2 and 200 inclusive.

9. Composition according to any one of Claims 1 to 4, characterized in that the non-silicone fatty substance or substances a) are used in the composition of the invention in proportions of between 0.01 and 80% by weight, with respect to the total weight of the composition, preferably between 1 and 70% by weight.

10. Composition according to any one of Claims 1, 2 and 5 to 7, in which the silicone fatty substance or substances b) are present in an amount varying from 0.01 to 20% by weight, preferably in an amount varying from 0.1 to 15% by weight and more preferably still in an amount varying from 0.1 to 10% by weight, with

respect to the total weight of the composition.

11. Composition according to any one of the preceding claims, characterized in that it comprises one or more couplers chosen in particular from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene couplers, heterocyclic couplers and their addition salts.

12. Composition according to the preceding claim, characterized in that the coupler or couplers represent an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

13. Composition according to any one of the preceding claims, characterized in that it comprises one or more additional oxidation bases other than the compound of formula (I) or its salts chosen in particular from ortho- or para-phenylenediamines, double bases, ortho- or para-aminophenols and heterocyclic bases and also the addition salts of these compounds with an acid.

14. Composition according to any one of the preceding claims, characterized in that it comprises one or more oxidizing agents chosen in particular from hydrogen peroxide, urea hydrogen peroxide, persalts, peracids, alkali metal bromates and oxidase enzymes and preferably hydrogen peroxide.

15. Method for dyeing keratinous fibres, characterized in that a composition as defined in any one of Claims 1 to 13 is applied to the keratinous fibres without an oxidizing agent.

16. Method for dyeing keratinous fibres, characterized in that a composition as defined in any one of Claims 1 to 13 is applied to the keratinous fibres in the

presence of one or more oxidizing agents as defined in Claim 14.

17. Multicompartment device, in which:

- a first compartment comprises a dyeing composition as defined in any one of Claims 1 to 13 and
- a second compartment comprises a composition comprising one or more oxidizing agents as defined in Claim 14;

or alternatively

- a first compartment comprises one or more oxidation bases chosen from the compound of formula (I) or its salts with an acid according to Claim 1 or Claim 2, optionally one or more oxidation bases other than the compound of formula (I) or its salts as defined in Claim 13 and optionally one or more couplers as defined in Claim 11;
- a second compartment includes a composition comprising one or more non-silicone liquid fatty substances a) as described in any one of Claims 1, 3, 4 and 9 or comprising one or more silicone fatty substances b) as described in any one of Claims 1, 5, 8 and 10; and optionally
- a third compartment includes a composition comprising one or more oxidizing agents as described in Claim 14.

18. Use for dyeing keratinous fibres of a composition according to any one of Claims 1 to 14.