

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

30 December 2020 (30.12.2020)



(10) International Publication Number

WO 2020/260486 A1

(51) International Patent Classification:

A61K 8/49 (2006.01) A61K 8/89 (2006.01)

A61K 8/73 (2006.01) A61Q 5/06 (2006.01)

A61K 8/898 (2006.01)

(21) International Application Number:

PCT/EP2020/067883

(22) International Filing Date:

25 June 2020 (25.06.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

FR1906998 27 June 2019 (27.06.2019) FR

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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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR DYEING KERATIN FIBERS USING A PARTICULAR CYCLIC POLYCARBONATE, A COMPOUND COMPRISING AT LEAST ONE AMINE GROUP AND A COLORING AGENT, COMPOSITION AND DEVICE

(57) Abstract: The present invention relates to a process for dyeing keratin fibers, comprising the application to the keratin fibers of a) at least one particular carbonate ester, b) at least one compound comprising at least one amine group and c) at least one coloring agent chosen from pigments, direct dyes, and mixtures thereof.



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PROCESS FOR DYEING KERATIN FIBERS USING A PARTICULAR CYCLIC POLYCARBONATE, A COMPOUND COMPRISING AT LEAST ONE AMINE GROUP AND A COLORING AGENT, COMPOSITION AND DEVICE

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FIELD OF THE INVENTION

The present invention relates to a process for dyeing keratin fibers, comprising the application to the keratin fibers of a) at least one particular carbonate ester, b) at least one compound comprising at least one amine group and c) at least one coloring agent chosen from pigments, direct dyes, and mixtures thereof.

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BACKGROUND OF THE INVENTION

Many people have sought for a long time to modify the color of their hair in order, for example, to mask their gray hair.

Essentially two types of dyeing have been developed for dyeing keratin fibers.

15

The first type of dyeing is "permanent" or oxidation dyeing, which uses dye compositions containing oxidation dye precursors, generally known as oxidation bases. These oxidation bases are colorless or weakly colored compounds which, when combined with oxidizing products, can give rise to colored compounds via a process of oxidative condensation. The shades obtained with these oxidation bases can be varied by combining them with couplers or color modifiers. The variety of molecules used as oxidation bases and couplers allows a wide range of colors to be obtained.

20

The second type of dyeing is "semi-permanent" dyeing or direct dyeing, which consists in applying, to the keratin fibers, direct dyes, which are colored and coloring molecules that have affinity for said fibers, in leaving them on for a time, and then in rinsing them off.

25

This type of process does not require the use of an oxidizing agent to develop the coloring. However, it is possible to use such an agent in order to obtain, along with the coloring, a lightening effect. This is then referred to as direct dyeing or semi-permanent dyeing under lightening conditions.

30

Permanent or semi-permanent dyeing processes under lightening conditions therefore need to use, with the dye composition, an aqueous composition comprising at least one oxidizing agent, under alkaline pH conditions in the vast majority of cases.

35

These conventional dyeing processes may be insufficient to meet the demands of consumers who may desire special effects, and/or may damage the integrity of the keratin fibers. Milder solutions, which are also known as makeup solutions, make it possible to deposit coloring and/or nacreous agents at the surface without threatening the fiber integrity. Among the coloring agents that may be used in these makeup

compositions, pigments and in particular naces, such as naces of mica/iron oxide type, have advantageous dyeing properties.

It is currently possible to deposit these coloring agents onto fibers to obtain the desired effect. However, the colorings thus obtained are only short-lasting. Specifically, the
5 colorings have a tendency to fade out, or even to disappear, rapidly, with respect to external agents, such as light, sweat, mechanical actions (brushing, styling) and notably after a few shampoo washes.

Moreover, the dyeing power of these compositions may not be entirely satisfactory, or even may be poor, and lead to a restricted range of colors. The colorings may also be
10 too selective, i.e. the difference in coloring is too great along the same keratin fiber that is differently sensitized between its end and its root.

Finally, added to these drawbacks are the risks of leaching with water, leading to staining of fabrics in contact with the dyed fibers.

Thus, there is a real need to develop a process for dyeing keratin fibers, and in particular
15 human keratin fibers such as the hair, which makes it possible to obtain good dyeing properties, notably in terms of intensity, fastness and homogeneity, and also satisfactory cosmetic properties, while at the same time preserving the integrity of the keratin fibers. The dyeing properties, and notably the intensity, the fastness and the homogeneity, must also be persistent with respect to shampoo washing.

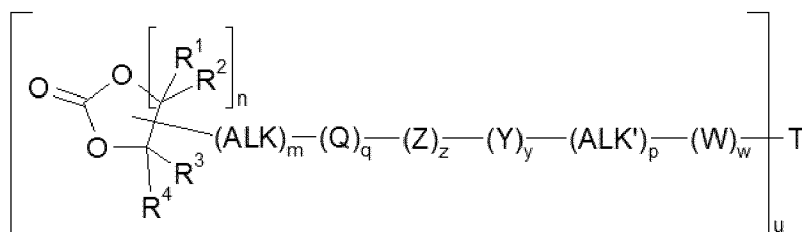
Moreover, there is a real need to propose a process that is easy to perform and that
20 makes it possible to reduce the risk of leaching with water leading to staining of fabrics in contact with the dyed fibers.

It has been discovered, surprisingly, that the application to keratin fibers a) of at least
25 one particular carbonate ester, b) of at least one compound comprising one or more amine groups and c) of at least one coloring agent chosen from pigments, direct dyes and mixtures thereof makes it possible to achieve these objectives; and notably to afford colorings that have good properties, in particular in terms of intensity, homogeneity and fastness with respect to external agents, while at the same time respecting the integrity of the keratin fibers and reducing the risk of leaching with water leading to staining of
30 fabrics in contact with the dyed fibers.

SUMMARY OF THE INVENTION

According to a first aspect, a subject of the present invention is a process for dyeing keratin fibers, comprising:

35 (i) a step consisting in applying to the keratin fibers at least a) one compound of formula (I) below:



in which formula (I):

- **R¹, R², R³ and R⁴**, which may be identical or different, represent a hydrogen atom or a (C₁-C₆)alkyl and particularly (C₁-C₄)alkyl group, it being understood that one of the groups **R¹, R², R³ or R⁴** denotes a chain -(ALK)_m-(Q)_q-(Z)_z-(Y)_y-(ALK')_p-(W)_w; preferentially, **R¹, R² and R³** denote a hydrogen atom, and **R⁴** denotes the chain: -(ALK)_m-(Q)_q-(Z)_z-(Y)_y-(ALK')_p-(W)_w;
- **ALK and ALK'**, which may be identical or different, represent a (C₁-C₁₂)alkylene group optionally substituted and/or interrupted with one or more heteroatoms such as oxygen, sulfur, or NR⁸ with R⁸ as defined below; in particular, ALK and ALK' represent (C₁-C₆)alkylene, preferably (C₁-C₄)alkylene, such as methylene;
- **Q, Y and W**, which may be identical or different, represent an oxygen or sulfur atom or NR⁸, with R⁸ representing a hydrogen atom or a (C₁-C₄)alkyl or benzyl group, preferably oxygen or NR⁸ such as NH;
- **Z** represents a carbonyl C=O, thiocarbonyl C=S or imino C=NR⁸ group with R⁸ as defined previously, preferably carbonyl,
- **m, p, q, z, y and w**, which may be identical or different, represent 0 or 1; preferably, m = 1 and **p, q, z, y and w**, which may be identical or different, represent 0 or 1;
- **n** represents an integer ranging from 1 to 4; in particular, n is equal to 1, 2 or 3, preferably 1 or 2; more preferentially, n = 1;
- **T** represents a polyvalent group, said polyvalent group being chosen, when u = 2, from:
 - i) (C₁-C₁₀₀)alkylene optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹)(R²)- with R¹ and R², which may be identical or different, representing a hydrogen atom, hydroxyl, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkylene radical denotes a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen atoms and/or with one or more -SiMe₂ radicals,
 - ii) (C₂-C₁₀₀)alkenylene optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹)(R²)- with R¹ and R², which may be identical or different, representing a hydrogen atom, hydroxyl, (C₁-

C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkenylene radical denotes a (C₂-C₁₀₀)alkenylene radical optionally interrupted with one or more oxygen atoms and/or with one or more -SiMe₂ radicals,

iii) (hetero)arylene such as phenylene, for instance 1,3-phenylene,

5 iv) (hetero)cycloalkylene,

said polyvalent group being chosen, when u = 3 or 4, from:

i) a multivalent (trivalent or tetravalent) saturated or unsaturated, linear or branched hydrocarbon-based radical containing from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms;

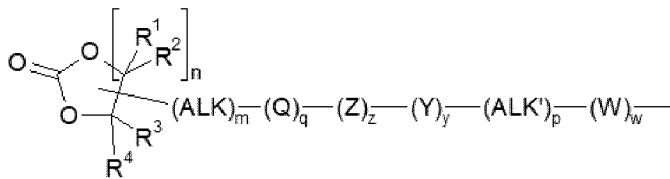
10 ii) a multivalent (trivalent or tetravalent) aromatic or nonaromatic (hetero)cyclic radical preferably containing 5 or 6 carbon atoms;

▪ u represents an integer ranging from 2 to 4, preferably 2 or 3,

it being understood that:

- T is divalent when u is 2, is trivalent when u is 3, and tetravalent when u is 4;

15 - the following units:



are identical or different; and

(ii) a step consisting in applying to the keratin fibers at least b) one compound comprising at least one amine group; and

20 (iii) a step consisting in applying to the keratin fibers at least c) one coloring agent chosen from pigments, direct dyes and mixtures thereof.

According to a second aspect, a subject of the present invention is a composition (C₁) comprising:

25 a) at least one compound of formula (I) as defined above; and

b) at least one compound comprising at least one amine group; and

c) at least one coloring agent chosen from pigments, direct dyes and mixtures thereof.

According to a third aspect, a subject of the present invention is a multi-compartment device comprising:

30 - a first compartment containing a composition (C₂) comprising a) at least one compound of formula (I) as defined above, and

- a second compartment containing a composition (C₃) different from composition (C₂), composition (C₃) comprising b) at least one compound comprising at least one amine

35 group,

it being understood that:

- composition (C₂) and/or composition (C₃) comprise c) at least one coloring agent chosen from pigments, direct dyes and mixtures thereof.

5 DETAILED DESCRIPTION OF THE INVENTION

In the following text, unless indicated otherwise:

- 10 ▪ the term "keratin fibers" means fibers of human or animal origin such as head hair, bodily hair, the eyelashes, the eyebrows, wool, angora, cashmere or fur. According to the present invention, the keratin fibers are preferably human keratin fibers, more preferentially the hair.
- 15 ▪ when compounds are mentioned in the present patent application, this also includes the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, the salts thereof or the solvates thereof, alone or as a mixture. In particular, the term "compound of formula (I)" also means the corresponding salts thereof.
- 20 ▪ the term "*compound comprising at least one amine group*" means a compound comprising at least one primary -NH₂, secondary >NH or tertiary -N< amino group and not comprising any carbonate functions -O-CO-O-; preferably, said compound comprises at least one primary or secondary amine group; more preferentially, said compound comprises at least one primary amine group;
- 25 ▪ the term "*alkyl*" means a linear or branched hydrocarbon-based radical containing from 1 to 8 carbon atoms, in particular from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, for example methyl, ethyl, *n*-propyl, isopropyl, butyl, *n*-pentyl or *n*-hexyl, preferably methyl;
- 30 ▪ the term "*alkenyl*" means a linear or branched hydrocarbon-based radical containing from 2 to 8 carbon atoms, in particular from 2 to 6 carbon atoms, preferably from 2 to 4 carbon atoms, and comprising at least one or more conjugated or non-conjugated ethylenic unsaturations, such as ethylenyl, *n*-propylenyl, isopropylenyl, butylenyl, *n*-pentylenyl or *n*-hexylenyl;
- 35 ▪ the term "*alkoxy*" means an alkyl-oxy group with "*alkyl*" as defined previously;
- 40 ▪ the term "*alkylene*" means a linear or branched divalent hydrocarbon-based radical containing from 1 to 8 carbon atoms, in particular from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methylene, ethylene, *n*-propylene, *n*-butylene, *n*-pentylene or *n*-hexylene;
- 45 ▪ the term "*alkenylene*" means a hydrocarbon-based radical as defined for "*alkenyl*";
- 50 ▪ the term "*(hetero)arylene*" means a divalent "aryl" or divalent "heteroaryl" group, said aryl or heteroaryl groups being as defined below;

- the term “(hetero)cycloalkylene” means a divalent "cycloalkyl" or divalent "heterocycloalkyl" group, said cycloalkyl or heterocycloalkyl groups being as defined below;
- the term “*optionally substituted*” preceded by the alkyl, alkenyl, alkylene, alkenylene or alkoxy groups means that said groups may be substituted on the hydrocarbon-based radical with one or more groups, which may be identical or different, chosen from i) hydroxyl, ii) thiol, iii) halogen, iv) (C₁-C₄)alkoxy, v) hydroxy(C₂-C₄)alkoxy; vi) (di)(hydroxy(C₁-C₄)(alkyl)amino, vii) cyano, viii) nitro(so), ix) R_a-Z_a-C(Z_b)-Z_c-, and x) R_a-Z_a-S(O)_t-Z_c- with Z_b representing an oxygen or sulfur atom or a group NR_a', Z_a and Z_c, which may be identical or different, representing a bond, an oxygen or sulfur atom, or a group NR_a; R_a representing a hydrogen atom or a (C₁-C₄)alkyl group and R_a' representing a hydrogen atom or an alkyl group and t is 1 or 2;
- an "aryl" radical represents a monocyclic or fused or nonfused polycyclic carbon-based group comprising from 6 to 22 carbon atoms, and in which at least one ring is aromatic; preferentially, the aryl radical is a phenyl, biphenyl, naphthyl, indenyl, anthracenyl or tetrahydronaphthyl; more preferentially, the aryl radical is a phenyl;
- a "*heteroaryl radical*" represents a 5- to 22-membered monocyclic or fused or nonfused polycyclic group, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen, sulfur and selenium, and at least one ring of which is aromatic; preferentially, a heteroaryl radical is chosen from acridinyl, benzimidazolyl, benzobistriazolyl, benzopyrazolyl, benzopyridazinyl, benzoquinolyl, benzothiazolyl, benzotriazolyl, benzoxazolyl, pyridyl, tetrazolyl, dihydrothiazolyl, imidazopyridyl, imidazolyl, indolyl, isoquinolyl, naphthoimidazolyl, naphthooxazolyl, naphthopyrazolyl, oxadiazolyl, oxazolyl, oxazolopyridyl, phenazinyl, phenoxazolyl, pyrazinyl, pyrazolyl, pyrilyl, pyrazoyltriazyl, pyridyl, pyridinoimidazolyl, pyrrolyl, quinolyl, tetrazolyl, thiadiazolyl, thiazolyl, thiazolopyridyl, thiazoylimidazolyl, thiopyrylyl, triazolyl and xanthyl;
- a "*heterocyclic radical*" is a 5- to 22-membered, monocyclic or fused or nonfused polycyclic radical which may contain one or two unsaturations but is not aromatic, including from 1 to 6 heteroatoms chosen from nitrogen, oxygen and sulfur;
- a "*heterocycloalkyl radical*" is a heterocyclic radical comprising at least one saturated ring and at least one heteroatom chosen from nitrogen, oxygen and sulfur;
- the "aryl" or "*heteroaryl*" radicals or the aryl or heteroaryl part of a radical may be substituted with at least one substituent borne by a carbon atom, chosen from:
 - a C₁-C₁₆ and preferably C₁-C₈ alkyl radical optionally substituted with one or more radicals chosen from hydroxyl, C₁-C₂ alkoxy, (poly)hydroxy(C₂-C₄)alkoxy, acylamino, amino substituted with two C₁-C₄ alkyl radicals, which may be identical or different, optionally bearing at least one hydroxyl group, or the two radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally

- substituted 5- to 7-membered and preferably 5- or 6-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
- a halogen atom;
 - a hydroxyl group;
 - 5 - a C₁-C₂ alkoxy radical;
 - a (poly)hydroxy(C₂-C₄)alkoxy radical;
 - an amino radical;
 - a 5- or 6-membered heterocycloalkyl radical;
 - an optionally cationic 5- or 6-membered heteroaryl radical, preferentially imidazolium,
 - 10 optionally substituted with a (C₁-C₄)alkyl radical, preferentially methyl;
 - an amino radical substituted with one or two identical or different C₁-C₆ alkyl radicals, optionally bearing at least:
 - i) a hydroxyl group,
 - ii) an amino group optionally substituted with one or two optionally substituted C₁-C₃
 - 15 alkyl radicals, said alkyl radicals possibly forming with the nitrogen atom to which they are attached a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom,
 - iii) a 5- or 6-membered heteroaryl radical, optionally substituted with a (C₁-C₄)alkyl
 - 20 radical, preferentially methyl;
 - an acylamino radical (-NR-C(O)-R') in which the radical R is a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group and the radical R' is a C₁-C₂ alkyl radical;
 - a carbamoyl radical ((R)₂N-C(O)-) in which the radicals R, which may be identical or
 - 25 different, represent a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group;
 - an alkylsulfonylamino radical (R'-S(O)₂-N(R)-) in which the radical R represents a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group and the radical R' represents a C₁-C₄ alkyl radical or a phenyl radical; an aminosulfonyl
 - 30 radical ((R)₂N-S(O)₂-) in which the radicals R, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group;
 - a carboxylic radical in acid or salified (preferably with an alkali metal or a substituted or unsubstituted ammonium) form;
 - 35 - a cyano group;
 - a polyhaloalkyl group, preferentially trifluoromethyl;
- preferably, the "aryl" or "heteroaryl" radicals or the aryl or heteroaryl part of a radical may be substituted with at least one substituent borne by a carbon atom, chosen from a

C₁-C₆ alkyl radical, a halogen atom; a C₁-C₂ alkoxy radical; a polyhaloalkyl group, preferentially trifluoromethyl, more preferentially from a C₁-C₆ alkyl radical; the cyclic or heterocyclic part of a nonaromatic radical may be substituted with at least one substituent chosen from the following groups:

- 5 - hydroxyl;
- C₁-C₄ alkoxy, (poly)hydroxy(C₂-C₄)alkoxy;
- C₁-C₄ alkyl;
- alkylcarbonylamino (R-C(O)-N(R')-) in which the radical R' is a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group, and the radical R is a C₁-C₂ alkyl radical or an amino radical optionally substituted with one or two C₁-C₄ alkyl groups, which may be identical or different, themselves optionally bearing at least one hydroxyl group, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
15 - alkylcarbonyloxy (R-C(O)-O-) in which the radical R is a C₁-C₄ alkyl radical or an amino group optionally substituted with one or two identical or different C₁-C₄ alkyl groups themselves optionally bearing at least one hydroxyl group, said alkyl radicals possibly forming with the nitrogen atom to which they are attached a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
20 - alkoxy carbonyl (R-G-C(O)-) in which the radical R is a C₁-C₄ alkyl radical, G is an oxygen atom or an amino group optionally substituted with a C₁-C₄ alkyl group itself optionally bearing at least one hydroxyl group, said alkyl radical possibly forming, with the nitrogen atom to which it is attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
25 preferably, the cyclic or heterocyclic part of a nonaromatic radical may be substituted with at least one substituent chosen from C₁-C₄ alkoxy, (poly)hydroxy(C₂-C₄)alkoxy or C₁-C₄ alkyl groups; more preferentially with at least one C₁-C₄ alkyl radical such as methyl;
30 ▪ a cyclic or heterocyclic radical, or a nonaromatic part of an aryl or heteroaryl radical, may also be substituted with one or more oxo groups;
▪ the expressions "at least one" and "one or more" are synonymous and may be used interchangeably.
35

Dyeing process

According to a first aspect, a subject of the present invention is a process for dyeing keratin fibers as defined above.

The process of the invention in particular makes it possible to obtain colorings which have good properties, in particular in terms of intensity, homogeneity, fastness toward external agents and persistence with respect to shampoo washing, while at the same time respecting the integrity of the keratin fibers and reducing the risk of leaching with water leading to staining of fabrics in contact with the dyed fibers.

Steps (i), (ii) and (iii) may be performed in this order or in any order.

Steps (i), (ii) and (iii) may be performed sequentially in this order, i.e. (i) then (ii) and then (iii) or in any order.

Some or all of the steps (i), (ii) and (iii) may be performed simultaneously.

By way of example, steps (ii) and (iii) may be performed simultaneously, followed by step (i).

Alternatively, steps (i) and (iii) may be performed simultaneously, followed by step (ii).

Preferably, all of the steps (i), (ii) and (iii) are performed simultaneously.

All of the steps (i), (ii) and (iii) may be repeated several times, for example twice. In the case where all of the steps (i), (ii) and (iii) are repeated several times, the compound(s) (I), the compound(s) comprising at least one amine group and the coloring agent(s) applied, respectively, during steps (i), (ii) and (iii) may be identical or different.

The process according to the present invention comprises (i) a step consisting in applying to the keratin fibers at least a) one compound of formula (I) as defined above.

Compound(s) of formula (I)

According to one embodiment, u is equal to 2 or 3 and T represents a divalent or trivalent group chosen from ii) (C₁-C₆)alkylene, iv) (hetero)arylene and v) cycloalkylene.

According to another embodiment, u is equal to 2 and T represents a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹)(R²)- with R¹ and R², which may be identical or different, representing a hydrogen atom, hydroxyl, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkylene radical denotes a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen atoms and/or with one or more -SiMe₂ radicals. According to this embodiment, T preferably represents a radical T1 of formula -(CH₂)_{x1}-[O-(CH₂)_{x2}]_{x3} (O)_{x4}- with x₁ = 0 to 10, x₂ = 2 or 3, x₃ = 1 to 50, preferably 3 to 20, x₄ = 0 or 1 or a radical T2 of formula -(CH₂)_{y1}-[Si(R¹)(R²)-O]_{y2}- Si (R¹)(R²)- (CH₂)_{y3} - with y₁ = 0 to 10, y₂ = 1 to 50,

preferably 3 to 20, $y_3 = 0$ to 10, preferably 1 to 5 and R^{11} and R^{12} , which may be identical or different, representing a (C₁-C₄)alkyl radical such as methyl.

According to another embodiment, u is equal to 2 and T represents a divalent (hetero)arylene group, preferably arylene such as phenylene, more particularly 1,3-phenylene.

According to another embodiment, u is equal to 2 and T represents a divalent cycloalkylene group, preferably cyclohexylene, preferably substituted with one or more C₁-C₄ alkyl radicals such as methyl.

According to another embodiment, u is equal to 2 and T represents a divalent C₁-C₄ alkylene group such as methylene, ethylene or butylene.

According to another embodiment, u is equal to 3 and T represents i) a saturated or unsaturated, preferably saturated, linear or branched trivalent hydrocarbon-based radical containing from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, ii) an aromatic or nonaromatic, preferably aromatic, trivalent (hetero)cyclic radical containing 5 or 6 carbon atoms, preferably 6 carbon atoms, such as a trivalent 1,3,5-phenyl radical.

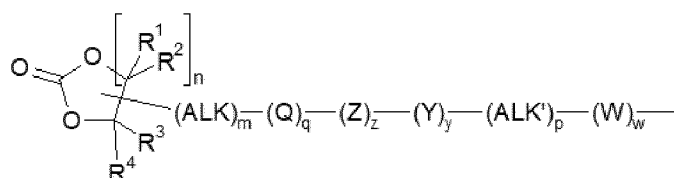
More preferentially, u is 2, Q represents an oxygen atom, and ALK and ALK' represent a (C₁-C₄)alkylene, such as methylene.

According to an advantageous embodiment, the compound of formula (I) is such that u is 2 and:

- m = 1;
- ALK represents a (C₁-C₄)alkylene, such as methylene;
- Q represents an oxygen atom;
- q = 0 or 1;
- Z represents a carbonyl;
- z = 0 or 1;
- Y represents NH;
- y = 0 or 1;
- ALK' represents a (C₁-C₄)alkylene, such as methylene;
- p = 0 or 1;
- w = 0.

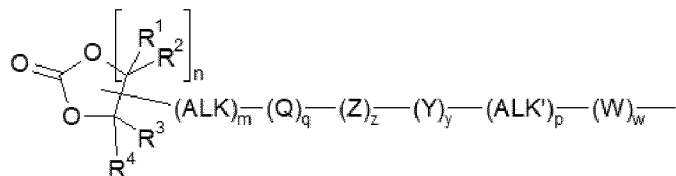
According to an advantageous embodiment, the compound of formula (I) is such that u is 2 and:

- one of the units:

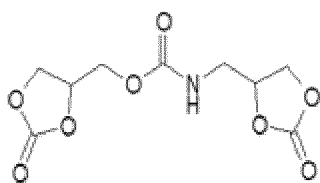


is such that $m + p$ is an integer greater than or equal to 1; preferably, m is 1 and p is 0, and preferentially $q = z = y = 1$; and

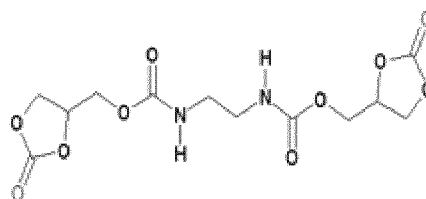
- the other unit:



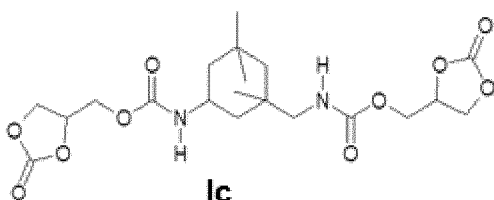
- 5 is such that $m + p$ is 0; preferably, the other unit is such that $m+p+q+z+y+w$ is 0. According to a preferred embodiment, the compound of formula (I) is chosen from the following compounds:



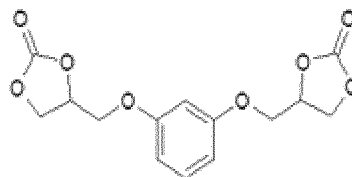
Ia



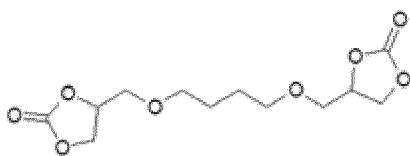
Ib



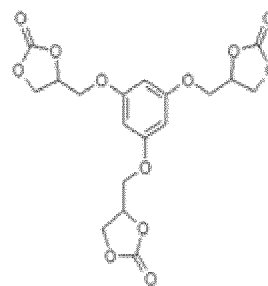
Ic



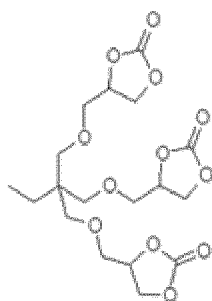
Id



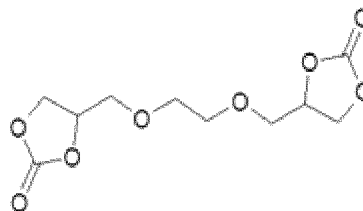
Ie



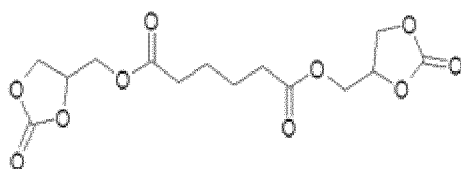
If



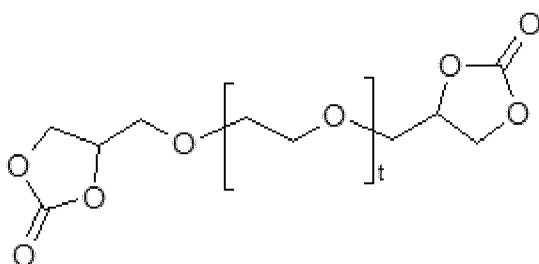
Ig



Ih

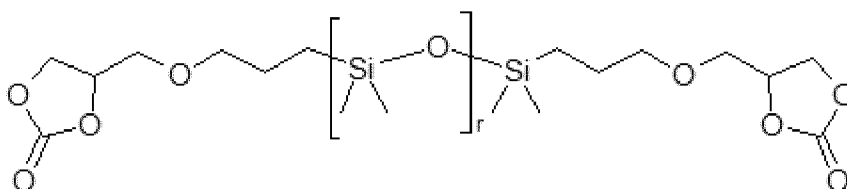


Ii



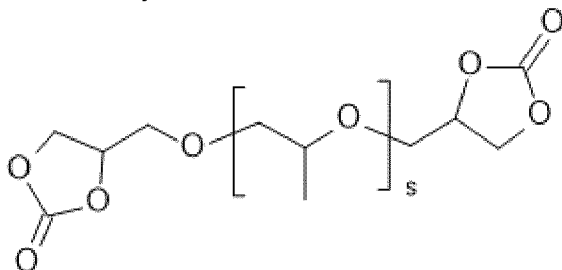
Ij

with t being an integer ranging from 1 to 50, preferably from 3 to 30 and more preferentially from 5 to 20;



Ik

5 with r being an integer ranging from 1 to 50, preferably from 3 to 30 and more preferentially from 5 to 20;



Im

with s being an integer ranging from 4 to 30, preferably from 5 to 10;
and mixtures thereof.

The process according to the present invention also comprises (ii) a step consisting in
5 applying to the keratin fibers at least b) one compound comprising at least one amine
group.

Compound(s) comprising at least one amine group

Preferably, the compound comprising at least one amine group is chosen from:

- 10 - amino silicones;
- amine derivatives of alkoxy silane;
- organic amines not comprising any silicon atoms;
- nonsilicone polymers comprising at least one amine group;
- and mixtures thereof.

15 More preferentially, the compound comprising at least one amine group may be chosen
from amino silicones, nonsilicone polymers comprising at least one amine group, and
mixtures thereof.

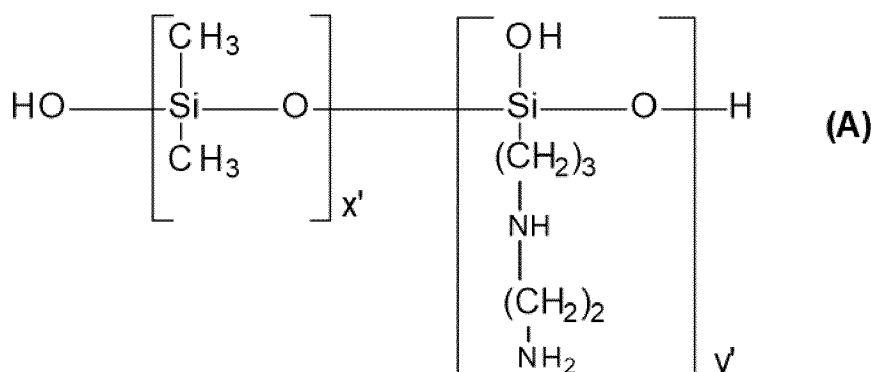
Amino silicone(s):

20 The term "amino silicone" means any silicone including at least one primary, secondary
or tertiary amine function.

The weight-average molecular masses of these amino silicones may be measured by
gel permeation chromatography (GPC) at room temperature (25°C), as polystyrene
equivalent. The columns used are μ styragel columns. The eluent is THF and the flow
25 rate is 1 ml/minute. 200 μ l of a 0.5% by weight solution of silicone in THF are injected.
Detection is performed by refractometry and UV-metry.

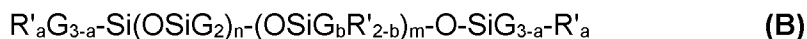
Preferably, the amino silicones that may be used in the context of the invention are
chosen from:

a) the polysiloxanes of formula (A) below:



in which x' and y' are integers such that the weight-average molecular weight (Mw) ranges from 5000 to 500 000;

b) the amino silicones of formula **(B)** below:



5 in which:

- G, which may be identical or different, denotes a hydrogen atom or a phenyl, OH, C₁-C₈ alkyl, for example methyl, or C₁-C₈ alkoxy, for example methoxy, group,

- a, which may be identical or different, denotes 0 or an integer from 1 to 3, in particular 0,

10 - b denotes 0 or 1, in particular 1,

- m and n are numbers such that the sum (n + m) varies from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;

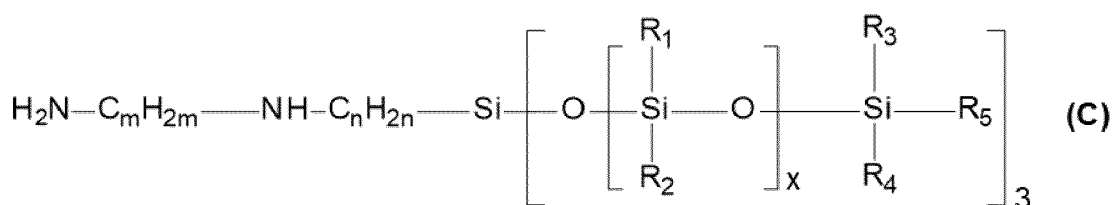
15 - R', which may be identical or different, denotes a monovalent radical of formula -C_qH_{2q}L in which q is a number ranging from 2 to 8 and L is an optionally quaternized amine group chosen from the following groups:

-N(R'')₂; -N⁺(R'')₃ A⁻; -NR''-Q-N(R'')₂ and -NR''-Q-N⁺(R'')₃ A⁻,

in which R'', which may be identical or different, denotes hydrogen, phenyl, benzyl, or a saturated monovalent hydrocarbon-based radical, for example a C₁-C₂₀ alkyl radical;

20 Q denotes a linear or branched group of formula C_rH_{2r}, r being an integer ranging from 2 to 6, preferably from 2 to 4; and A⁻ represents a cosmetically acceptable anion, notably a halide such as fluoride, chloride, bromide or iodide;

c) the amino silicones of formula **(C)** below:



25

in which:

- R₁, R₂, R₃ and R₄, which may be identical or different, denote a C₁-C₄ alkyl radical or a phenyl group,

- R₅ denotes a C₁-C₄ alkyl radical or a hydroxyl group,

30 - n is an integer ranging from 1 to 5,

- m is an integer ranging from 1 to 5, and

- x is chosen such that the amine number ranges from 0.01 to 1 meq/g;

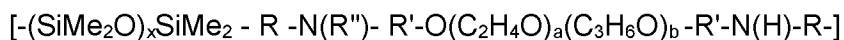
d) the multiblock polyoxyalkylenated amino silicones of the type (AB)_n, A being a polysiloxane block and B being a polyoxyalkylene block including at least one amine group,

e) and mixtures thereof.

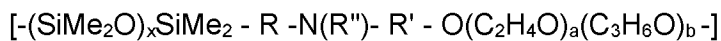
5

Multiblock polyoxyalkylenated amino silicones of the type (AB)_n

The multiblock polyoxyalkylenated amino silicones of the type (AB)_n are preferably formed from repeating units having the following general formulae:



10 or alternatively



in which:

- a is an integer greater than or equal to 1, preferably ranging from 5 to 200 and more particularly ranging from 10 to 100;

15 - b is an integer ranging from 0 to 200, preferably ranging from 4 to 100 and more particularly ranging from 5 to 30;

- x is an integer ranging from 1 to 10 000 and more particularly from 10 to 5000;

- R'' is a hydrogen atom or a methyl;

20 - R, which may be identical different, represent a linear or branched divalent C2-C12 hydrocarbon-based radical, optionally including one or more heteroatoms such as oxygen; preferably, R denotes an ethylene radical, a linear or branched propylene radical, a linear or branched butylene radical or a radical

-CH₂CH₂CH₂OCH₂CH(OH)CH₂-; preferentially, R denotes a radical

-CH₂CH₂CH₂OCH₂CH(OH)CH₂-;

25 - R', which may be identical or different, represent a linear or branched divalent C2-C12 hydrocarbon-based radical, optionally including one or more heteroatoms such as oxygen; preferably, R' denotes an ethylene radical, a linear or branched propylene radical, a linear or branched butylene radical or a radical

-CH₂CH₂CH₂OCH₂CH(OH)CH₂-; preferentially, R' denotes -CH(CH₃)-CH₂-.

30 The siloxane blocks preferably represent from 50 mol% to 95 mol% of the total weight of the silicone, more particularly from 70 mol% to 85 mol%.

The amine content preferably ranges from 0.02 to 0.5 meq/g of copolymer in a 30% solution in dipropylene glycol, more particularly from 0.05 to 0.2.

35 The weight-average molecular mass (M_w) of the silicone preferably ranges from 5000 to 1 000 000 and more particularly from 10 000 to 200 000.

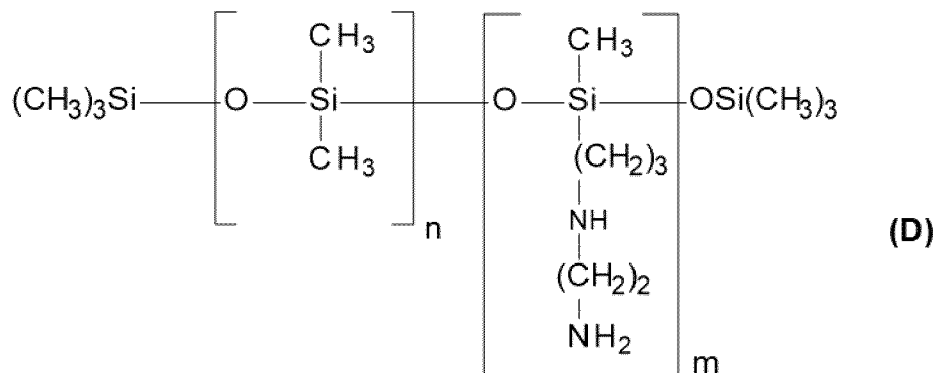
Mention may notably be made of the silicones sold under the name Silsoft A-843 or Silsoft A+ by Momentive.

Preferably, the amino silicones are chosen from the amino silicones of formula (B).

Amino silicone(s) of formula (B)

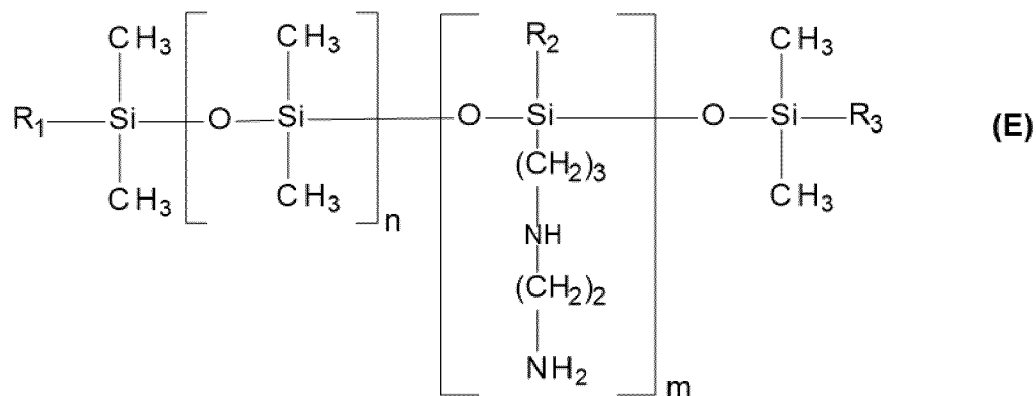
The amino silicones of formula (B) may be chosen from the amino silicones
5 corresponding to formulae (D), (E), (F), (G), (H), (J) and (K) below, and mixtures thereof.

According to a first embodiment, the amino silicones corresponding to formula (B) are
10 chosen from the silicones known as "trimethylsilyl amodimethicone" corresponding to formula (D):



in which m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in
particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably
15 from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1
to 10.

According to a second embodiment, the amino silicones corresponding to formula (B)
are chosen from the silicones of formula (E) below:



in which:

20 - m and n are numbers such that the sum (n + m) ranges from 1 to 1000, in particular
from 50 to 250 and more particularly from 100 to 200; n possibly denoting a number
from 0 to 999 and notably from 49 to 249 and more particularly from 125 to 175, and m

possibly denoting a number from 1 to 1000, notably from 1 to 10 and more particularly from 1 to 5;

- R1, R2 and R3, which may be identical or different, represent a hydroxyl or C1-C4 alkoxy radical, at least one of the radicals R1 to R3 denoting an alkoxy radical.

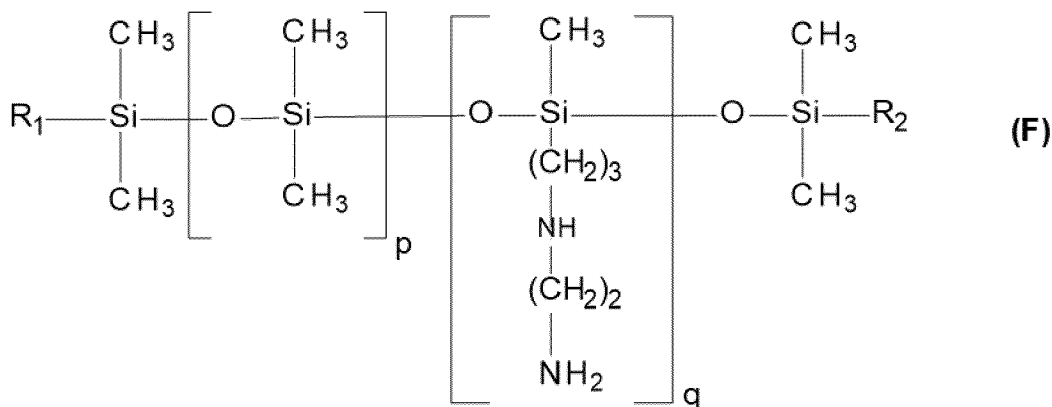
5 Preferably, the alkoxy radical is a methoxy radical.

The hydroxy/alkoxy mole ratio preferably ranges from 0.2:1 to 0.4:1 and preferably from 0.25:1 to 0.35:1 and more particularly is equal to 0.3:1.

The weight-average molecular mass (Mw) of these silicones preferably ranges from 2000 to 1 000 000 and more particularly from 3500 to 200 000.

10

According to a third embodiment, the amino silicones corresponding to formula (B) are chosen from the silicones of formula (F) below:



in which:

15 - p and q are numbers such that the sum (p + q) ranges from 1 to 1000, in particular from 50 to 350 and more particularly from 150 to 250; p possibly denoting a number from 0 to 999, notably from 49 to 349 and more particularly from 159 to 239, and q possibly denoting a number from 1 to 1000, notably from 1 to 10 and more particularly from 1 to 5;

20 - R1 and R2, which are different, represent a hydroxyl or C1-C4 alkoxy radical, at least one of the radicals R1 or R2 denoting an alkoxy radical.

Preferably, the alkoxy radical is a methoxy radical.

The hydroxy/alkoxy mole ratio generally ranges from 1:0.8 to 1:1.1 and preferably from 1:0.9 to 1:1 and more particularly is equal to 1:0.95.

25 The weight-average molecular mass (Mw) of the silicone preferably ranges from 2000 to 200 000, even more particularly from 5000 to 100 000 and more particularly from 10 000 to 50 000.

The commercial products comprising silicones of structure (E) or (F) may include in their composition one or more other amino silicones whose structure is different from

30 formula (E) or (F).

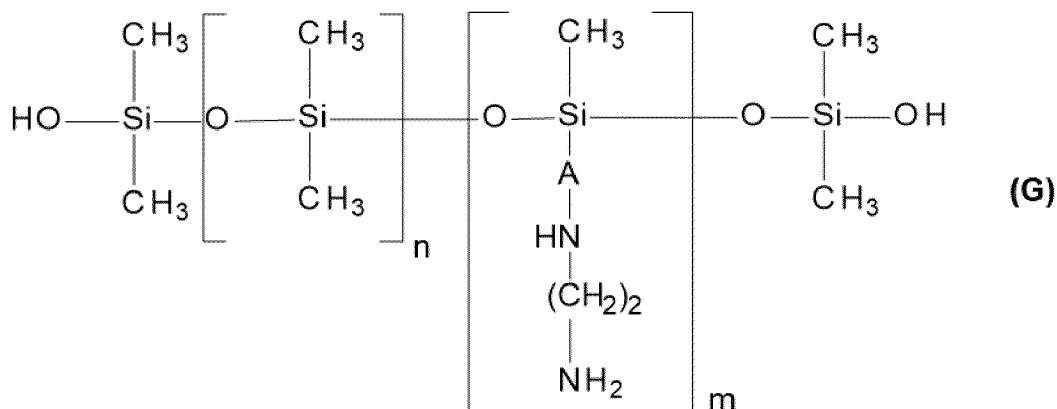
A product containing amino silicones of structure (E) is sold by the company Wacker under the name Belsil® ADM 652.

A product containing amino silicones of structure (F) is sold by the company Wacker under the name Fluid WR 1300®.

5 Among the amino silicones of formula (F), mention may also be made of the product Belsil ADM Log 1 from Wacker.

When these amino silicones are used, one particularly advantageous embodiment consists in using them in the form of an oil-in-water emulsion. The oil-in-water emulsion may comprise one or more surfactants. The surfactants may be of any nature but are preferably cationic and/or nonionic. The number-mean size of the silicone particles in the emulsion generally ranges from 3 nm to 500 nanometers. Preferably, notably as amino silicones of formula (E), use is made of microemulsions with a mean particle size ranging from 5 nm to 60 nanometers (limits included) and more particularly from 10 nm to 50 nanometers (limits included). Thus, use may be made according to the invention of the amino silicone microemulsions of formula (E) sold under the name Finish CT 96 E® or SLM 28020® by the company Wacker.

According to a fourth embodiment, the amino silicones corresponding to formula (B) are chosen from the silicones of formula (G) below:



20

in which:

- m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;

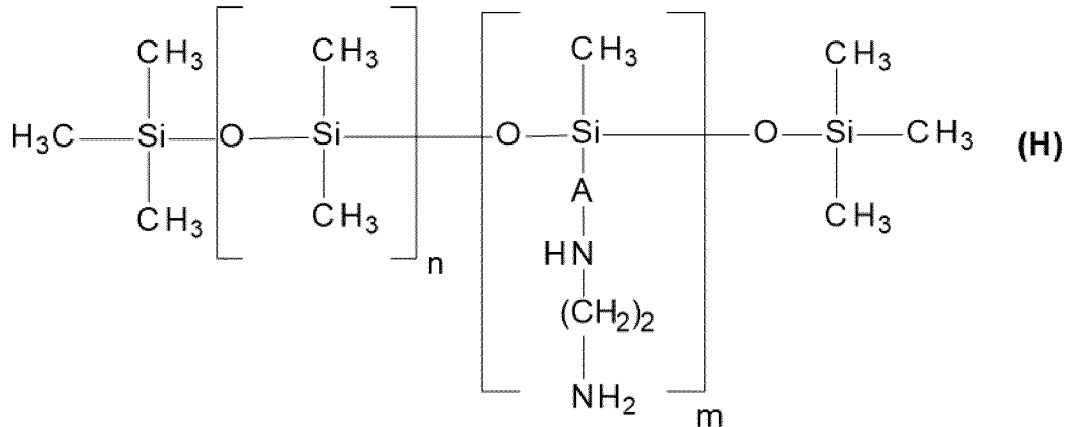
25

- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms. This radical is preferably linear.

The weight-average molecular mass (Mw) of these amino silicones preferably ranges from 2000 to 1 000 000 and even more particularly from 3500 to 200 000.

A silicone corresponding to this formula is, for example, the Xiameter MEM 8299 Emulsion from Dow Corning.

5 According to a fifth embodiment, the amino silicones corresponding to formula (B) are chosen from the silicones of formula (H) below:



in which:

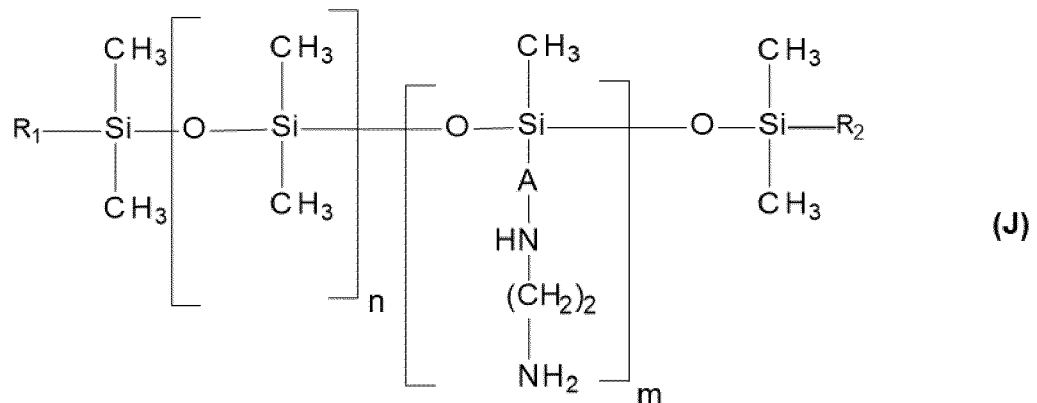
- m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;

- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms. This radical is preferably branched.

15 The weight-average molecular mass (Mw) of these amino silicones preferably ranges from 500 to 1 000 000 and even more particularly from 1000 to 200 000.

A silicone corresponding to this formula is, for example, DC2-8566 Amino Fluid from Dow Corning.

20 According to a sixth embodiment, the amino silicones corresponding to formula (B) are chosen from the silicones of formula (J) below:



in which:

- m and n are numbers ranging from 1 to 5000, and in particular n possibly denoting a number ranging from 10 to 2000 and notably from 100 to 1000, and in particular m possibly denoting a number from 1 to 100;

- 5 - R₁ and R₂, which may be identical or different, preferably identical, represent a linear or branched, saturated or unsaturated alkyl radical comprising from 6 to 30 carbon atoms, preferably from 8 to 24 carbon atoms, preferably from 12 to 20 carbon atoms;
- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms; this radical is preferably branched.

10 Preferably, A comprises from 3 to 6 carbon atoms, better still 4 carbon atoms; preferably, A is branched. In particular, A denotes the following divalent radicals:
-CH₂CH₂CH₂- or -CH₂CH(CH₃)CH₂-.

15 Preferably, R₁ and R₂, which may be identical or different, represent a saturated linear alkyl radical comprising 6 to 30 carbon atoms, preferably 8 to 24 carbon atoms, preferably 12 to 20 carbon atoms; in particular, R₁ and R₂ denote dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals;

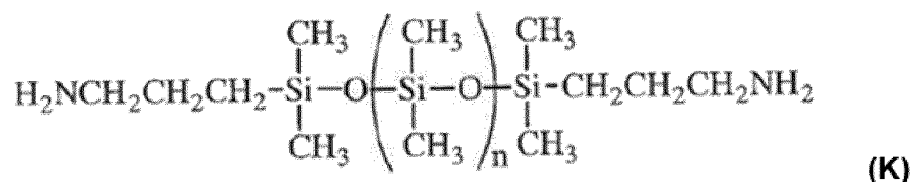
preferably, R₁ and R₂, which may be identical or different, are chosen from hexadecyl and octadecyl radicals.

Preferably, the amino silicone(s) of formula (J) are such that:

- 20 - n is a number ranging from 10 to 2000 and notably from 100 to 1000;
- m is a number ranging from 1 to 100;
- R₁ and R₂, which may be identical or different, represent a saturated linear alkyl radical comprising from 6 to 30 carbon atoms, preferably from 8 to 24 carbon atoms and preferably from 12 to 20 carbon atoms; chosen in particular from dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl
- 25 radicals; preferably, R₁ and R₂, which may be identical or different, are chosen from hexadecyl and octadecyl radicals; and
- A comprises from 3 to 6 carbon atoms and preferably 4 carbon atoms; preferably, A is branched; more preferentially, A is chosen from the following divalent radicals:
-CH₂CH₂CH₂- and -CH₂CH(CH₃)CH₂-.

30 The amino silicones of formula (J) that are particularly preferred are those corresponding to the INCI name *bis*-cetearylamodimethicone. In particular, the amino silicones of formula (J) correspond to the silicone sold by the company Momentive under the name Silsoft AX.

35 According to a seventh embodiment, the amino silicones corresponding to formula (B) are chosen from the silicones of formula (K) below:



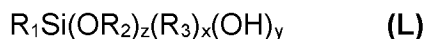
in which the value of n is such that the weight-average molecular weight (Mw) of the silicone ranges from 500 to 55 000.

- 5 As examples of amino silicone corresponding to formula **(K)**, mention may be made of those sold under the names DMS-A11, DMS-A12, DMS-A15, DMS-A21, DMS-A31, DMS-A32 and DMS-A35 by the company Gelest, and under the reference 481688 from Aldrich.
- 10 Preferably, the amino silicones of formula **(B)** are chosen from the amino silicones of formulae **(J)** and **(K)**, and mixtures thereof.

Amine derivatives of alkoxy silane

The amine derivatives of alkoxy silane may be chosen from the compounds of formula

- 15 **(L)** below, oligomers thereof, hydrolysis products thereof and/or mixtures thereof:



in which formula **(L)**:

- R₁ is a linear or branched, saturated or unsaturated, cyclic or acyclic C₁-C₆ hydrocarbon-based chain substituted with a group chosen from the following groups:
- 20 - amine NH₂ or NHR (R = C₁-C₂₀ and notably C₁-C₆ alkyl optionally substituted with a radical including a silicon atom, C₃-C₄₀ cycloalkyl or C₆-C₃₀ aromatic),
- an aryl or aryloxy group substituted and/or interrupted with at least one amino group or with at least one C₁-C₄ aminoalkyl group;
- R₁ possibly being interrupted with a heteroatom (O, S, NH) or a carbonyl (CO) group;
- 25 ▪ R₂ and R₃, which may be identical or different, represent a linear or branched alkyl group comprising from 1 to 6 carbon atoms;
 - y denotes an integer ranging from 0 to 3; and
 - z denotes an integer ranging from 0 to 3; and
 - x denotes an integer ranging from 0 to 2;
- 30 with z + x + y = 3.

The term "oligomer" refers to the polymerization products of the compounds of formula **(L)** including from 2 to 10 silicon atoms.

- Preferably, R₂ represents an alkyl group comprising from 1 to 4 carbon atoms, better still a linear alkyl group comprising from 1 to 4 carbon atoms, and preferably an ethyl
- 35 group.

Preferably, R₃ represents an alkyl group comprising from 1 to 4 carbon atoms, better still a linear alkyl group comprising from 1 to 4 carbon atoms, and preferably methyl or ethyl groups.

Preferably, R₁ is an acyclic chain.

- 5 Preferably, the compounds of formula (L) include only one silicon atom in their structure.

Preferably, R₁ represents an alkyl group and even more preferentially a linear alkyl group comprising from 1 to 6 carbon atoms or a C₁-C₆ aminoalkyl group.

Preferably, z ranges from 1 to 3. Even more preferentially, z is equal to 3.

- 10 Preferably, R₁ is a linear or branched, saturated or unsaturated C₁-C₆ hydrocarbon-based chain substituted with an amine group NH₂ or NHR (R = C₁-C₂₀ and notably C₁-C₆ alkyl, C₃-C₄₀ cycloalkyl or C₆-C₃₀ aromatic).

Preferably, the amine derivatives of alkoxy silane are chosen from

3-aminopropyltriethoxysilane (APTES), 3-aminoethyltriethoxysilane (AETES),

- 15 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-(m-aminophenoxy)propyltrimethoxysilane, p-aminophenyltrimethoxysilane and N-(2-aminoethylaminomethyl)phenethyltrimethoxysilane, and mixtures thereof, and more preferentially from 3-aminopropyltriethoxysilane (APTES), 3-aminoethyltriethoxysilane (AETES), 3-aminopropylmethyldiethoxysilane and N-(2-aminoethyl)-3-aminopropyltriethoxysilane, oligomers thereof, hydrolysis products thereof and mixtures thereof.

According to a particularly preferred embodiment, the amine derivatives of alkoxy silane are chosen from 3-aminopropyltriethoxysilane (APTES), oligomers thereof, hydrolysis products thereof and mixtures thereof.

25

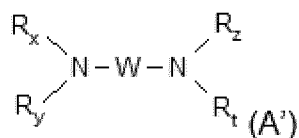
Organic amines not comprising any silicon atoms

The organic amines not comprising any silicon atoms may be chosen from:

- alkanolamines such as mono-, di- and triethanolamines, mono-, di- and tri-(hydroxymethyl)aminomethanes, and derivatives thereof,

- 30 - amino acids,

- the compounds of formula (A') below:



in which formula (A') W is a (C₁-C₆)alkylene group such as propylene optionally

substituted with a hydroxyl or amino group or a C₁-C₄ alkyl radical; R_x, R_y, R_z and R_t,

- 35 which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

Examples of amines of formula (A') that may be mentioned include 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

The term "alkanolamine" means an organic amine comprising a primary, secondary or tertiary amine function, and one or more linear or branched C₁-C₈ alkyl groups bearing one or more hydroxyl radicals.

Organic amines chosen from alkanolamines such as monoalkanolamines, dialkanolamines or trialkanolamines comprising one to three identical or different C₁-C₄ hydroxyalkyl radicals are in particular suitable for performing the invention.

Among the compounds of this type, mention may be made of monoethanolamine

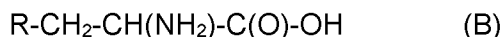
(MEA), diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, N,N-dimethylethanolamine, 2-amino-2-methyl-1-propanol, triisopropanolamine, 2-amino-2-methyl-1,3-propanediol, 3-amino-1,2-propanediol, 3-dimethylamino-1,2-propanediol and tris(hydroxymethylamino)methane.

More particularly, the amino acids that may be used are of natural or synthetic origin, in their L, D or racemic form, and include at least one acid function chosen more particularly from carboxylic acid, sulfonic acid, phosphonic acid and phosphoric acid functions. The amino acids may be in neutral or ionic form.

As amino acids that may be used in the present invention, mention may notably be made of aspartic acid, glutamic acid, alanine, arginine, ornithine, citrulline, asparagine, carnitine, cysteine, glutamine, glycine, histidine, lysine, isoleucine, leucine, methionine, N-phenylalanine, proline, serine, taurine, threonine, tryptophan, tyrosine and valine.

Advantageously, the amino acids are basic amino acids comprising an additional amine function optionally included in a ring or in a ureido function.

Such basic amino acids are preferably chosen from those corresponding to formula (B) below, and also salts thereof:



in which formula (B) R represents a group chosen from: imidazolyl, preferably imidazolyl-5-yl; -(CH₂)₃-NH₂; -(CH₂)₂-NH₂; -(CH₂)₂N(H)-C(O)-NH₂; and -(CH₂)₂-N(H)-C(NH)-NH₂.

The compounds corresponding to formula (B) are histidine, lysine, arginine, ornithine and citrulline.

The organic amines may also be chosen from organic amines of heterocyclic type.

Besides histidine that has already been mentioned in the amino acids, mention may be made in particular of pyridine, piperidine, imidazole, triazole, tetrazole and benzimidazole.

The organic amines may also be chosen from amino acid dipeptides. As amino acid dipeptides that may be used in the present invention, mention may notably be made of carnosine, anserine and balenine.

The organic amines may also be chosen from compounds including a guanidine function. As amines of this type that may be used in the present invention, besides arginine, which has already been mentioned as an amino acid, mention may be made notably of creatine, creatinine, 1,1-dimethylguanidine, 1,1-diethylguanidine, glycocyanine, metformin, agmatine, n-amidinoalanine, 3-guanidinopropionic acid, 4-guanidinobutyric acid and 2-([amino(imino)methyl]amino)ethane-1-sulfonic acid.

Nonsilicone polymers comprising at least one amine group

The nonsilicone polymers comprising at least one amine group may be chosen from polyamines, polyamino acids, polysaccharides comprising at least one amine group, and mixtures thereof.

The term "poly"amines or "poly"amino acids means alkaline agents comprising at least two amino or amino acid groups linked to the same molecule; they are in particular polymers whose backbone comprises or is substituted with one or more amine groups or amino acid groups.

Polyamines

The polyamines may be chosen from poly((C2-C5)alkyleneimines), poly(allylamines), polyvinylamines and mixtures thereof.

The poly((C2-C5)alkyleneimines) may be chosen from polyethyleneimines, polypropyleneimines and mixtures thereof, preferably polyethyleneimines. An example that may be mentioned of a polyethyleneimine that may be used according to the present invention is the product sold under the reference 46,852-3 by the company Aldrich Chemical.

As an example of a poly(allylamine) that may be used according to the present invention, mention may be made of the poly(allylamine) which may be sold under the reference 47,913-6 by the company Aldrich Chemical.

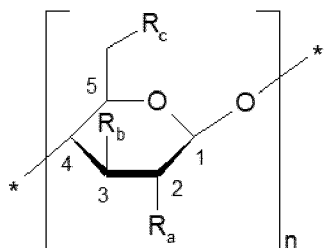
Polyamino acids

As polyamino acid that is suitable for use in the present invention, mention may be made of la poly-L-lysine, for instance the product sold by the company JNC Corporation (formerly Chisso).

Polysaccharides comprising at least one amine group

Preferably, the nonsilicone polymers comprising at least one amine group are chosen from polysaccharides comprising at least one amine group.

More preferentially, the polysaccharides comprising at least one amine group are chosen from the polysaccharides bearing monosaccharide units of formula (IIa) below:



(IIa)

5 in which formula (IIa):

- n is an integer greater than or equal to 2, preferably ranging from 3 to 3000, more preferentially ranging from 5 to 2500, and better still ranging from 10 to 2300;

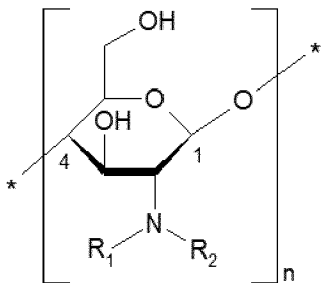
- R_a, R_b and R_c, which may be identical or different for each monosaccharide unit, represent (1) a hydroxyl group, (2) a (C₁-C₄)alkoxy group, the alkyl chain of which may

10 be optionally substituted notably with one or more hydroxyl and/or carboxyl groups, (3) a carboxyl group, or (4) a group NR₁R₂ with R₁ and R₂, which may be identical or different, representing i) a hydrogen atom, ii) a (C₁-C₆)alkyl group that is optionally substituted, preferably with one or more hydroxyl or NH₂ groups, iii) an aryl group such as phenyl, iv) an aryl(C₁-C₄)alkyl group such as benzyl, v) a (hetero)cyclo(C₅-C₇)alkyl

15 group such as cyclohexyl, morpholinyl, piperazinyl, piperidyl, vi) a (hetero)cyclo(C₅-C₇)alkyl(C₁-C₄)alkyl group such as cyclohexylmethyl, vii) a group -C(Y)-(Y')_p-R'₁ with Y and Y', which may be identical or different, representing an oxygen or sulfur atom or N(R'₂), p is equal to 0 or 1, and R'₁ and R'₂ representing i) to vi) of R₁ and R₂ defined previously,

20 it being understood that at least one of the radicals R_a, R_b or R_c of at least one monosaccharide unit represents an NH₂ group.

Even more preferentially, the polysaccharides comprising at least one amine group are chosen from the polysaccharides bearing monosaccharide units of formula (IIb) below:



(IIb)

in which formula (IIb):

- R₁ and R₂, which may be identical or different for each monosaccharide unit, are as defined above for formula (IIa),

- n is an integer greater than or equal to 2, preferably ranging from 3 to 3000, more preferentially from 5 to 2500 and more preferentially from 10 to 2300;
5 it being understood that at least one monosaccharide unit bears an amino group NH₂.

According to a particularly preferred embodiment, the polysaccharides comprising at least one amine group are chosen from chitin, chitosan, derivatives thereof and
10 mixtures thereof, more preferentially from chitin, chitosan and mixtures thereof, even more preferentially chitosan.

The process according to the present invention also comprises (iii) a step consisting in applying to the keratin fibers at least c) one coloring agent chosen from pigments,
15 direct dyes and mixtures thereof.

Coloring agent(s)

Preferably, the coloring agent(s) are chosen from pigments.

The term "pigment" is intended to denote a white or colored solid particle which is naturally insoluble in the hydrophilic and lipophilic liquid phases usually employed in
20 cosmetics or which is rendered insoluble by formulation in the form of a lake, where appropriate. More particularly, the pigment has little or no solubility in aqueous-alcoholic media.

Pigments that may be mentioned include organic and mineral pigments such as those defined and described in Ullmann's Encyclopedia of Industrial Chemistry
25 "Pigment organics", 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a20_371 and ibid, "Pigments, Inorganic, 1. General" 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a20_243.pub3.
Mention may be made notably of azo pigments which contain one or more azo groups A-N=N-B with A representing an optionally substituted (hetero)aryl, B
30 representing optionally substituted (hetero)aryl or -CH[C(O)-R]-C(O)-X1-A', A' representing an optionally substituted (hetero)aryl and R representing a hydrogen atom or a (C₁-C₆)alkyl group, with the (hetero)aryl groups A, A' and B not containing any solubilizing groups such as -SO₃H or -COOH.

They may in particular be monoazo pigments, including β-naphthols,
35 monoazopyrrolone pigments or benzimidazolone pigments; diazo pigments, such as diazodiarylide pigments and bis(N-acetoacetylide) pigments, or triazo or tetraazo pigments.

Mention may also be made of azo metal complex pigments.

Other pigments are also advantageous, namely isoindolinone and isoindoline pigments, phthalocyanine pigments; quinacridone pigments; perinone pigments; perylene pigments; anthraquinone pigments such as hydroxyanthraquinone pigments; aminoanthraquinone pigments including acylaminoanthraquinones and azo anthraquinone pigments; heterocyclic anthraquinones; polycarbocyclic anthraquinone pigments, pyranthrone pigments; anthranthrone pigments; diketopyrrolopyrrole (DPP) pigments; thioindigo pigments; dioxazine pigments; triphenylmethane pigments; quinophthalone pigments; and fluorescent pigments.

When the dyes comprise one or more solubilizing groups such as $-\text{SO}_3\text{H}$ or $-\text{COOH}$, these dyes are made insoluble and consequently pigments by formation of a lake, i.e. by salification (e.g. Na, Ca, St, Ba, etc.) and divided mainly into β -naphthol and 2-hydroxy-3-naphthoic acid pigments "(BON) pigment lakes".

In the context of the present invention, the pigment may be at least partly organic. According to one embodiment of the invention, the pigment is an organic pigment.

According to another embodiment of the invention, the pigment is a mineral pigment.

As illustrations of pigments that may be used in the present invention, mention may be made of carbon black, titanium oxide, chromium oxide, pigments of D&C or FD&C type and lakes thereof, and notably those known under the names D&C Blue No. 4, D&C Brown No. 1, FD&C Green No. 3, D&C Green No. 5, D&C Green No. 6, FD&C Green No. 8, 20, D&C Orange No. 4, D&C Orange No. 5, D&C Orange No. 10, D&C Orange No. 11, FD&C Red No. 4, D&C Red No. 6, D&C Red No. 7 (CI 15850), D&C Red No. 17, D&C Red No. 21, D&C Red No. 22, D&C Red No. 27, D&C Red No. 28, D&C Red No. 30, D&C Red No. 31, D&C Red No. 33, D&C Red No. 34, D&C Red No. 36, FD&C Red No. 40, FD&C Red 40 lake, D&C Violet No. 2, Ext. D&C Violet No. 2, FD & C Blue No. 1, D&C Yellow No. 6, FD&C Yellow No. 6, D&C Yellow No. 7, 25 Ext. D&C Yellow No. 7, D&C Yellow No. 8, D&C Yellow No. 10 or D&C Yellow No. 11, it being understood that when said pigment is not naturally insoluble in the hydrophilic and lipophilic phases usually used in cosmetics, it is used in the form of a corresponding lake, as explained previously.

Examples of lakes that may notably be mentioned include lakes based on barium, strontium, calcium or aluminum, or alternatively diketopyrrolopyrroles.

As further examples of pigments that may be used in the present invention, mention may be made notably of mineral pigments, optionally surface-treated and/or coated, and notably titanium dioxide, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, or alternatively metal powders, for instance aluminum powder, copper powder, gold powder and silver powder.

Mention may also be made of pigments with an optical effect such as particles including a natural or synthetic organic or mineral substrate, for example glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, said substrate being optionally covered with metal substances, for instance
5 aluminum, gold, silver, platinum, copper or bronze, or with metal oxides, for instance titanium dioxide, iron oxide or chromium oxide.

They may also be naces.

The term "naces" means iridescent pigments, which are notably produced by certain molluscs in their shell, or alternatively which are synthesized.

10 The nacreous pigments may be chosen from mica coated with titanium or with bismuth oxychloride, titanium mica coated with iron oxides, titanium mica coated notably with ferric blue or with chromium oxide, titanium mica coated with an organic pigment of the abovementioned type, and also nacreous pigments based on bismuth oxychloride. Use may also be made of interference pigments, notably liquid-crystal or
15 multilayer pigments.

They may also be pigments having a structure that may be, for example, of sericite/brown iron oxide/titanium dioxide/silica type.

They may also be pigments having a structure that may be, for example, of silica microsphere type containing iron oxide.

20 As examples of pigments that are most particularly suitable for use in the present invention, mention may be made notably of D&C Red No. 7, titanium oxide, chromium oxide, lakes of the pigments of D&C and FD&C type mentioned above, and notably D&C Red No. 22 lake, Yellow No. 6 lake and FD&C Blue No. 1 lake. The pigments in accordance with the invention may be in the form of pigment powder
25 or paste. They may be coated or uncoated.

The pigments in accordance with the invention may be chosen, for example, from white or colored pigments, lakes, pigments with special effects such as naces or glitter flakes, and mixtures thereof.

30 Examples of white or colored mineral pigments that may be mentioned include zirconium oxide or cerium oxide, chromium oxides, manganese violet, ultramarine blue, chromium hydrate and ferric blue.

Examples of white or colored organic pigments that may be mentioned include nitroso, nitro, azo, xanthene, quinoline, anthraquinone and phthalocyanine compounds, compounds of metallic complex type, and isoindolinone, isoindoline,
35 quinacridone, perinone, perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

In particular, the white or colored organic pigments may be chosen from carmine, carbon blacks such as Black 2, aniline black, azo yellow, quinacridone,

phthalocyanine blue, sorghum red, the blue pigments codified in the Color Index under the references CI 42090, 69800, 69825, 73000, 74100, 74160, the yellow pigments codified in the Color Index under the references CI 11680, 11710, 15985, 19140, 20040, 21100, 21108, 47000, 47005, the green pigments codified in the Color Index under the references CI 61565, 61570, 74260, the orange pigments codified in the Color Index under the references CI 11725, 15510, 45370, 71105, the red pigments codified in the Color Index under the references CI 12085, 12120, 12370, 12420, 12490, 14700, 15525, 15580, 15620, 15630, 15800, 15850, 15865, 15880, 17200, 26100, 45380, 45410, 58000, 73360, 73915, 75470, the pigments obtained by oxidative polymerization of indole or phenolic derivatives as described in patent FR 2 679 771.

Preferably, carbon blacks such as Black 2 or lakes such as D&C Red 7.

Use may be made of pigment pastes of organic pigments, such as the products sold by the company Hoechst under the names:

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

The pigments in accordance with the invention may also be in the form of composite pigments, as described in patent EP 1 184 426. These composite pigments may be composed notably of particles including:

- a mineral core,
- at least one binder for fixing the organic pigments to the core, and
- at least one organic pigment at least partially covering the core.

The term "lake" refers to dyes adsorbed onto insoluble particles, the assembly thus obtained remaining insoluble during use. The inorganic substrates onto which the dyes are adsorbed are, for example, alumina, silica, calcium sodium borosilicate, calcium aluminum borosilicate and aluminum. Among the organic dyes, mention may be made of cochineal carmine.

Examples of lakes that may be mentioned include the products known under the following names: D & C Red 21 (CI 45 380), D & C Orange 5 (CI 45 370), D & C Red 27 (CI 45 410), D & C Orange 10 (CI 45 425), D & C Red 3 (CI 45 430), D & C Red 7 (CI 15 850:1), D & C Red 4 (CI 15 510), D & C Red 33 (CI 17 200), D & C Yellow 5

(CI 19 140), D & C Yellow 6 (CI 15 985), D & C Green (CI 61 570), D & C Yellow 10 (CI 77 002), D & C Green 3 (CI 42 053) or D & C Blue 1 (CI 42 090).

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

Examples of pigments with special effects that may be mentioned include white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, colored nacreous pigments such as mica coated with titanium and with iron oxides, mica coated with titanium and notably with ferric blue or with chromium oxide, mica coated with titanium and with an organic pigment as defined previously, and also nacreous pigments based on bismuth oxychloride.

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 flakes (Geometric Pigments or Spectra f/x from Spectratek). Pigments with special effects also comprise fluorescent pigments, whether these are substances that are fluorescent in daylight or that produce an ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, sold, for example, by the company Quantum Dots Corporation.

Quantum dots are luminescent semiconductor nanoparticles that are capable of emitting, under light excitation, radiation with a wavelength of between 400 nm and 700 nm. These nanoparticles are known from the literature. In particular, they may be manufactured according to the processes described, for example, in US 6 225 198 or US 5 990 479, in the publications cited therein and also in the following publications: Dabboussi B.O. et al., "(CdSe)ZnS core-shell quantum dots: synthesis and characterisation of a size series of highly luminescent nanocrystallites", *Journal of Physical Chemistry B*, vol. 101, 1997, pages 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, pages 7019-7029.

The pigments in accordance with the invention are preferably colored pigments.

The variety of pigments used makes it possible to obtain a wide range of colors, and also particular optical effects such as metallic or interference effects.

The size of a pigment other than the nacles in solution generally ranges from 10 nm to 10 μ m, preferably from 50 nm to 5 μ m and even more preferentially from 100 nm

to 3 µm. The size of a nacre in solution is generally from 1 to 200 µm, preferably from 1 to 80 µm and even more preferentially from 1 to 50 µm.

Among the mineral pigments, examples that may be mentioned include titanium dioxide (rutile or anatase) optionally surface-treated and codified in the Color Index
5 under the reference CI 77891; black, yellow, red and brown iron oxides, codified under the references CI 77499, 77492 and 77491; manganese violet (CI 77742); ultramarine blue (CI 77007); hydrated chromium oxide (CI 77289); ferric blue (CI 77510).

Among the organic pigments that may be mentioned, for example, are the pigment
10 Yellow 3 sold notably under the trade name Jaune Covonor W 1603 by the company Wackherr (CI 17710), D & C Red No. 19 (CI 45170), D & C Red No. 9 (CI 15585), D & C Red No. 21 (CI 45380), D & C Orange No. 4 (CI 15510), D & C Orange No. 5 (CI 45370), D & C Red No. 27 (CI 45410), D & C Red No. 13 (CI 15630), D & C Red No. 7 (CI 15850-1), D & C Red No. 6 (CI 15850-2), D & C Yellow No. 5 (CI 19140), D & C
15 Red No. 36 (CI 12085), D & C Orange No. 10 (CI 45425), D & C Yellow No. 6 (CI 15985), D & C Red No. 30 (CI 73360), D & C Red No. 3 (CI 45430), carbon black (CI 77266) and lakes based on cochineal carmine (CI 75470).

It is also possible to use nacreous pigments, which may be chosen notably from
20 white nacreous pigments such as mica coated with titanium oxide or bismuth oxide; colored nacreous pigments such as titanium mica with iron oxides, titanium mica with ferric blue or with chromium oxide, titanium mica with an organic pigment of the abovementioned type, and also those based on bismuth oxychloride.

Pigment pastes of organic pigment are used more particularly, such as the products sold by the company Hoechst under the name:

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

The dyestuff(s) are advantageously chosen from pigments, preferably from white
35 organic pigments, colored organic pigments, and mixtures thereof, and more preferentially carbon blacks, such as Black 2, lakes, such as D&C Red 7, and mixtures thereof.

The coloring agents may be chosen from direct dyes.

The term "direct dye" means natural and/or synthetic dyes, other than oxidation dyes.

These are dyes that will spread superficially on the fiber.

They may be ionic or nonionic, preferably cationic or nonionic, i.e. as sole dyes.

- 5 These direct dyes are chosen, for example, from neutral, acidic or cationic nitrobenzene direct dyes, neutral, acidic or cationic azo direct dyes, tetraazapentamethine dyes, neutral, acidic or cationic quinone and in particular anthraquinone dyes, azine direct dyes, triarylmethane direct dyes, azomethine direct dyes and natural direct dyes.
- 10 Examples of suitable direct dyes that may be mentioned include azo direct dyes; (poly)methine dyes such as cyanines, hemicyanines and styryl dyes; carbonyl dyes; azine dyes; nitro(hetero)aryl dyes; tri(hetero)arylmethane dyes; porphyrin dyes; phthalocyanine dyes, and natural direct dyes, alone or as mixtures.
- 15 Preferentially, the direct dye(s) contain at least one quaternized cationic chromophore or at least one chromophore bearing a quaternized or quaternizable cationic group.
- According to a particular embodiment of the invention, the direct dyes comprise at least one quaternized cationic chromophore.
- As direct dyes according to the invention, mention may be made of the following
- 20 dyes: acridines; acridones; anthranthrones; anthrapyrimidines; anthraquinones; azines; (poly)azos, hydrazono or hydrazones, in particular arylhydrazones; azomethines; benzanthrones; benzimidazoles; benzimidazolones; benzindoles; benzoxazoles; benzopyrans; benzothiazoles; benzoquinones; bisazines; bis-isindolines; carboxanilides; coumarins; cyanines such as azacarbocyanines, diazacarbocyanines, diazahemicyanines, hemicyanines, or tetraazacarbocyanines;
- 25 diazines; diketopyrrolopyrroles; dioxazines; diphenylamines; diphenylmethanes; dithiazines; flavonoids such as flavanthrones and flavones; fluorindines; formazans; indamines; indantrones; indigoids and pseudo-indigoids; indophenols; indoanilines; isindolines; isindolinones; isoviolanthrones; lactones; (poly)methines such as
- 30 dimethines of stilbene or styryl type; naphthalimides; naphthanilides; naphtholactams; naphthoquinones; nitro, notably nitro(hetero)aromatics; oxadiazoles; oxazines; perilonones; perinones; perylenes; phenazines; phenoxazine; phenothiazines; phthalocyanine; polyenes/carotenoids; porphyrins; pyranthrones; pyrazolanthrones; pyrazolones; pyrimidinoanthrones; pyronines; quinacridones;
- 35 quinolines; quinophthalones; squaranes; tetrazoliums; thiazines, thioindigo; thiopyronines; triarylmethanes, or xanthenes.

For the cationic azo dyes, mention may be made particularly of those resulting from the cationic dyes described in Kirk-Othmer's Encyclopedia of Chemical Technology, "Dyes, Azo", J. Wiley & Sons, updated on April 19, 2010.

Among the azo dyes that may be used according to the invention, mention may be
5 made of the cationic azo dyes described in patent applications WO 95/15144, WO 95/01772 and EP-714954.

According to a preferred embodiment of the invention, the direct dye(s) are chosen from cationic dyes known as "basic dyes".

Among the azo dyes described in the Colour Index International 3rd edition, mention
10 may be made notably of the following compounds:

- Basic Red 22
- Basic Red 76
- Basic Yellow 57
- Basic Brown 16
- 15 - Basic Brown 17.

Among the cationic quinone dyes, those mentioned in the abovementioned Colour Index International are suitable for use and, among these, mention may be made, inter alia, of the following dyes:

- Basic Blue 22
- 20 - Basic Blue 99.

Among the azine dyes that are suitable for use, mention may be made of those listed in the Colour Index International, for example the following dyes:

- Basic Blue 17
- Basic Red 2.

25 Among the cationic triarylmethane dyes that may be used according to the invention, mention may be made, in addition to those listed in the Colour Index, of the following dyes:

- Basic Green 1
- Basic Violet 3
- 30 - Basic Violet 14
- Basic Blue 7
- Basic Blue 26.

Mention may also be made of the cationic dyes described in US 5 888 252, EP 1 133 975, WO 03/029 359, EP 860 636, WO 95/01772, WO 95/15144 and EP 714 954.

35 Mention may also be made of those listed in the encyclopedia "The Chemistry of Synthetic Dyes" by K. Venkataraman, 1952, Academic Press, vol. 1 to 7, in the "Kirk-Othmer Encyclopedia of Chemical Technology", in the chapter "Dyes and Dye

Intermediates", 1993, Wiley and Sons, and in various chapters of "Ullmann's Encyclopedia of Industrial Chemistry", 7th edition, Wiley and Sons.

Preferably, the cationic direct dyes are chosen from those resulting from dyes of azo and hydrazono type.

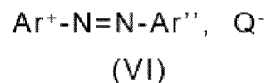
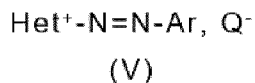
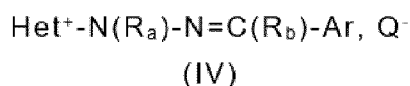
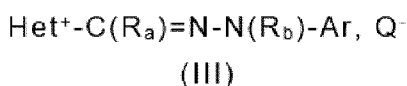
- 5 According to a particular embodiment, the direct dyes are cationic azo dyes, described in EP 850 636, FR 2 788 433, EP 920 856, WO 99/48465, FR 2 757 385, EP 850 637, EP 918 053, WO 97/44004, FR 2 570 946, FR 2 285 851, DE 2 538 363, FR 2 189 006, FR 1 560 664, FR 1 540 423, FR 1 567 219, FR 1 516 943, FR 1 221 122, DE 4 220 388, DE 4 137 005, WO 01/66646, US 5 708 151, WO 95/01772, 10 WO 515 144, GB 1 195 386, US 3 524 842, US 5 879 413, EP 1 062 940, EP 1 133 976, GB 738 585, DE 2 527 638, FR 2 275 462, GB 1974-27645, Acta Histochem. (1978), 61(1), 48-52; Tsitologiya (1968), 10(3), 403-5; Zh. Obshch. Khim. (1970), 40(1), 195-202; Ann. Chim. (Rome) (1975), 65(5-6), 305-14; Journal of the Chinese Chemical Society (Taipei) (1998), 45(1), 209-211; Rev. Roum. Chim. (1988), 33(4), 15 377-83; Text. Res. J. (1984), 54(2), 105-7; Chim. Ind. (Milan) (1974), 56(9), 600-3; Khim. Tekhnol. (1979), 22(5), 548-53; Ger. Monatsh. Chem. (1975), 106(3), 643-8; MRL Bull. Res. Dev. (1992), 6(2), 21-7; Lihua Jianyan, Huaxue Fence (1993), 29(4), 233-4; Dyes Pigm. (1992), 19(1), 69-79; Dyes Pigm. (1989), 11(3), 163-72.

- Preferably, the cationic direct dye(s) comprise(s) a quaternary ammonium group; 20 more preferentially, the cationic charge is endocyclic.

These cationic radicals are, for example, a cationic radical:

- bearing an exocyclic (di/tri)(C1-C8)alkylammonium charge, or
- bearing an endocyclic charge, such as comprising a cationic heteroaryl group chosen from: acridinium, benzimidazolium, benzobistriazolium, benzopyrazolium, 25 benzopyridinium, benzoquinolium, benzothiazolium, benzotriazolium, benzoxazolium, bipyridinium, bis-tetrazolium, dihydrothiazolium, imidazopyridinium, imidazolium, indolium, isoquinolium, naphthoimidazolium, naphthoxazolium, naphthopyrazolium, oxadiazolium, oxazolium, oxazolopyridinium, oxonium, phenazinium, phenoaxazolium, pyrazinium, pyrazolium, pyrazoyltriazolium, 30 pyridinium, pyridinoimidazolium, pyrrolium, pyrylium, quinolium, tetrazolium, thiadiazolium, thiazolium, thiazolopyridinium, thiazoylimidazolium, thiopyrylium, triazolium or xanthylium.

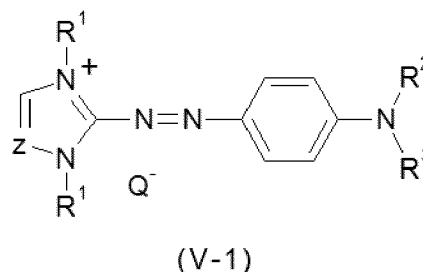
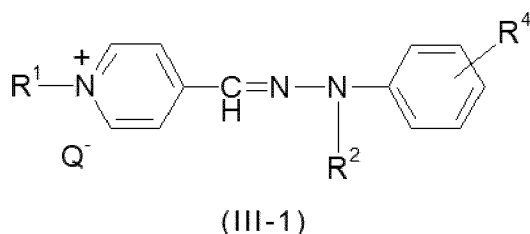
Mention may be made of the hydrazono cationic dyes of formulae (III) and (IV) and the azo cationic dyes of formulae (V) and (VI) below:



in which formulae (III) to (VI):

- Het⁺ represents a cationic heteroaryl radical, preferentially bearing an endocyclic cationic charge, such as imidazolium, indolium or pyridinium, which is optionally substituted, preferentially with at least one (C₁-C₈) alkyl group such as methyl;
- Ar⁺ represents an aryl radical, such as phenyl or naphthyl, bearing an exocyclic cationic charge, preferentially ammonium, particularly tri(C₁-C₈)alkylammonium, such as trimethylammonium;
- Ar represents an aryl group, notably phenyl, which is optionally substituted, preferentially with one or more electron-donating groups such as i) optionally substituted (C₁-C₈)alkyl, ii) optionally substituted (C₁-C₈)alkoxy, iii) (di)(C₁-C₈)(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group, iv) aryl(C₁-C₈)alkylamino, v) optionally substituted N-(C₁-C₈)alkyl-N-aryl(C₁-C₈)alkylamino or alternatively Ar represents a julolidine group;
- Ar'' represents an optionally substituted (hetero)aryl group, such as phenyl or pyrazolyl, which are optionally substituted, preferentially with one or more (C₁-C₈)alkyl, hydroxyl, (di)(C₁-C₈)(alkyl)amino, (C₁-C₈)alkoxy or phenyl groups;
- R_a and R_b, which may be identical or different, represent a hydrogen atom or a (C₁-C₈)alkyl group, which is optionally substituted, preferentially with a hydroxyl group;
- or else the substituent R_a with a substituent of Het⁺ and/or R_b with a substituent of Ar form, together with the atoms that bear them, a (hetero)cycloalkyl; in particular, R_a and R_b represent a hydrogen atom or a (C₁-C₄)alkyl group optionally substituted with a hydroxyl group;
- Q⁻ represents an organic or mineral anionic counterion, such as a halide or an alkyl sulfate.

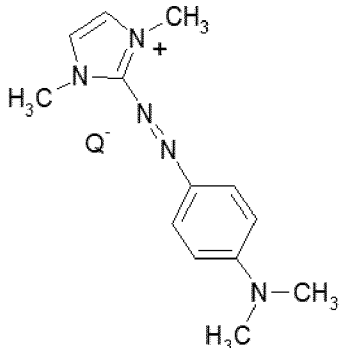
In particular, mention may be made of the azo and hydrazono direct dyes bearing an endocyclic cationic charge of formulae (III) to (VI) as defined previously. More particularly, the cationic direct dyes of formulae (III) to (VI) bearing an endocyclic cationic charge described in patent applications WO 95/15144, WO 95/01772 and EP 714 954. Preferentially the following direct dyes:



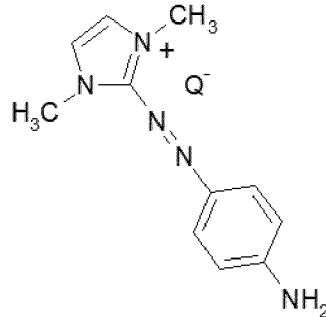
in which formulae (III-1) and (V-1):

- R¹ represents a (C₁-C₄)alkyl group such as methyl;
- R² and R³, which may be identical or different, represent a hydrogen atom or a (C₁-C₄)alkyl group, such as methyl; and
- R⁴ represents a hydrogen atom or an electron-donating group such as optionally substituted (C₁-C₈)alkyl, optionally substituted (C₁-C₈)alkoxy, or (di)(C₁-C₈)(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group; particularly, R⁴ is a hydrogen atom,
- Z represents a CH group or a nitrogen atom, preferentially CH,
- Q⁻ is an anionic counterion as defined previously, in particular a halide, such as chloride, or an alkyl sulfate, such as methyl sulfate or mesyl.

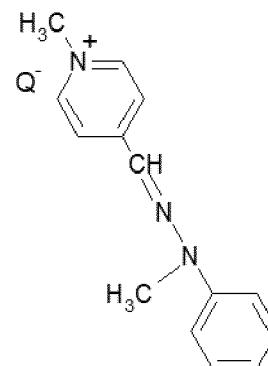
In particular, the dyes of formulae (III-1) and (V-1) are chosen from Basic Red 51, Basic Yellow 87 and Basic Orange 31 or derivatives thereof:



Basic Red 51



Basic Orange 31



Basic Yellow
87

with Q⁻ being an anionic counterion as defined previously, in particular a halide, such as chloride, or an alkyl sulfate, such as methyl sulfate or mesityl.

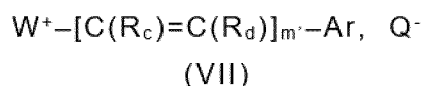
According to a particular embodiment of the invention, the direct dyes are fluorescent, that is to say that they contain at least one fluorescent chromophore as defined previously.

Fluorescent dyes that may be mentioned include the radicals resulting from the following dyes: acridines, acridones, benzanthrones, benzimidazoles, benzimidazolones, benzindoles, benzoxazoles, benzopyrans, benzothiazoles, coumarins, difluoro{2-[(2H-pyrrol-2-ylidene-kN)methyl]-1H-pyrrolato-kN}borons

(BODIPY®), diketopyrrolopyrroles, fluorindines, (poly)methines (notably cyanines and styryls/hemicyanines), naphthalimides, naphthanilides, naphthylamines (such as dansyls), oxadiazoles, oxazines, perilones, perinones, perylenes, polyenes/carotenoids, squaranes, stilbenes and xanthenes.

5 Mention may also be made of the fluorescent dyes described in EP 1 133 975, WO 03/029 359, EP 860 636, WO 95/01772, WO 95/15144 and EP 714 954 and those listed in the encyclopedia "The Chemistry of Synthetic Dyes" by K. Venkataraman, 1952, Academic Press, vol. 1 to 7, in the "Kirk-Othmer Encyclopedia of Chemical Technology", in the chapter "Dyes and Dye Intermediates", 1993, Wiley and Sons, 10 and in various chapters of "Ullmann's Encyclopedia of Industrial Chemistry", 7th edition, Wiley and Sons, and in the handbook — "A Guide to Fluorescent Probes and Labeling Technologies", 10th Ed., Molecular Probes/Invitrogen – Oregon 2005, circulated on the Internet or in the preceding printed editions.

According to a preferred variant of the invention, the fluorescent dye(s) are cationic and comprise at least one quaternary ammonium radical, such as those of formula (VII) below:



in which formula (VII):

- W⁺ represents a cationic heterocyclic or heteroaryl group, particularly comprising a quaternary ammonium optionally substituted with one or more (C₁-C₈)alkyl groups, optionally substituted notably with one or more hydroxyl groups;
- Ar representing an aryl group such as phenyl or naphthyl, optionally substituted preferentially with i) one or more halogen atoms such as chlorine or fluorine; ii) one or more (C₁-C₈)alkyl groups, preferably of C₁-C₄ such as methyl; iii) one or more hydroxyl groups; iv) one or more (C₁-C₈)alkoxy groups such as methoxy; v) one or more hydroxy(C₁-C₈)alkyl groups such as hydroxyethyl, vi) one or more amino or (di)(C₁-C₈)alkylamino groups, preferably with the C₁-C₄ alkyl part optionally substituted with one or more hydroxyl groups, such as (di)hydroxyethylamino, vii) with one or more acylamino groups; viii) one or more heterocycloalkyl groups such as piperazinyl, piperidyl or 5- or 6-membered heteroaryl such as pyrrolidinyl, pyridyl and imidazoliny;
- m' represents an integer ranging from 1 to 4; in particular, m is 1 or 2; more preferentially 1;
- R_c and R_d, which may be identical or different, represent a hydrogen atom or an optionally substituted (C₁-C₈)alkyl group, preferentially of C₁-C₄, or

alternatively R_c contiguous with W^+ and/or R_d contiguous with Ar form, with the atoms that bear them, a (hetero)cycloalkyl; particularly, R_c is contiguous with W^+ and they form a (hetero)cycloalkyl such as cyclohexyl;

▪ Q^- is an organic or mineral anionic counterion as defined previously.

- 5 Among the natural direct dyes that may be used according to the invention, mention may be made of lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, isatin, curcumin, spinulosin, apigenidin and orceins. Use may also be made of extracts or decoctions comprising these natural dyes and notably henna-based poultices or extracts.

10

Particular embodiments of the invention

According to a particular embodiment of the invention, the process may comprise:

- (i) a step consisting in applying to the keratin fibers at least a) one compound of formula (I) as defined above;
- 15 (ii) a step consisting in applying to the keratin fibers at least b) one compound comprising at least one amine group, the compound comprising at least one amine group being chosen from amino silicones, nonsilicone polymers comprising at least one amine group, and mixtures thereof; and
- (iii) a step consisting in applying to the keratin fibers at least c) one coloring agent
- 20 chosen from pigments.

According to another particular embodiment of the invention, the process may comprise:

- (i) a step consisting in applying to the keratin fibers at least a) one compound of
- 25 formula (I) as defined above; and
- (ii) a step consisting in applying to the keratin fibers at least b) one compound comprising at least one amine group, the compound comprising at least one amine group being chosen from amino silicones; and
- (iii) a step consisting in applying to the keratin fibers at least c) one coloring agent
- 30 chosen from pigments.

According to another particular embodiment of the invention, the process may comprise:

- (i) a step consisting in applying to the keratin fibers at least a) one compound of
- 35 formula (I) as defined above; and
- (ii) a step consisting in applying to the keratin fibers at least b) one compound comprising at least one amine group, the compound comprising at least one amine

group being chosen from nonsilicone polymers comprising at least one amine group, preferably from polysaccharides comprising at least one amine group; and
(iii) a step consisting in applying to the keratin fibers at least c) one coloring agent chosen from pigments.

5

The technical features described in the context of the process according to the present invention also apply to these particular embodiments of the process of the invention.

10 **Additional features of the process**

Preferably, steps (i), (ii) and (iii) of the process are performed simultaneously by applying to the keratin fibers a composition (**C₁**) comprising:

- a) the compound(s) of formula (**I**) as defined above; and
- b) the compound(s) comprising at least one amine group as defined above; and
- 15 c) the coloring agent(s) as defined above.

Composition (**C₁**) may optionally comprise at least one organic solvent, preferably chosen from:

- isododecane;
- monoalcohols comprising a hydroxyl group and a C₁-C₆(alkyl) and preferably C₁-
20 C₄(alkyl) group such as methyl, ethyl or (iso)propyl;
- polyols comprising from 2 to 30 hydroxyl groups and a (C₂-C₈)alkyl group, preferably a (C₂-C₄)alkyl group; and mixtures thereof.

More preferentially, the organic solvent is chosen from monoalcohols and polyols comprising two hydroxyl groups, even more preferentially from ethanol and polyols
25 comprising two hydroxyl groups and at least three carbon atoms, most preferentially from ethanol, propylene glycol (1,2-propanediol); 1,3-propanediol; 1,3-butylene glycol; 1,2-pentanediol; dipropylene glycol; hexylene glycol; pentylene glycol; butylene glycol; glycerol; ethylene glycol, and mixtures thereof.

Composition (**C₁**) may comprise a total content of compounds of formula (**I**) ranging
30 from 0.01% to 20%, preferably from 0.05% to 15%, more preferentially from 0.1% to 10%, even more preferentially from 0.5% to 5%, most preferentially from 1% to 5% by weight relative to the total weight of composition (**C₁**).

Composition (**C₁**) may comprise a total content of compounds comprising at least one amine group ranging from 0.01% to 25%, preferably from 0.05% to 15%, more
35 preferentially from 1% to 10% by weight relative to the total weight of composition (**C₁**).

Composition (**C₁**) may comprise a total content of coloring agents ranging from 0.05% to 10% and preferably from 0.5% to 5% by weight relative to the total weight of composition (**C₁**).

Composition (**C**₁) may comprise a total content of organic solvents ranging from 45% to 99.7%, preferably from 50% to 99%, more preferentially from 60% to 80% by weight relative to the total weight of composition (**C**₁).

The pH of composition (**C**₁) may be less than or equal to 10; preferably, the pH of composition (**C**₁) may range from 3 to 9; more preferentially, the pH of composition (**C**₁) may range from 4 to 8. The pH of the composition may be adjusted with a compound known to those skilled in the art.

Alternatively, steps (i), (ii) and (iii) may be performed by applying to the keratin fibers:

- a composition (**C**₂) comprising a) the compound(s) of formula (**I**) as defined above;
 - and
 - a composition (**C**₃) comprising b) the compound(s) comprising at least one amine group as defined above;
- it being understood that:
- composition (**C**₂) and/or composition (**C**₃) comprise c) the coloring agent(s) as defined above; and
 - composition (**C**₂) is applied before composition (**C**₃) or composition (**C**₃) is applied before composition (**C**₂).

Preferably, composition (**C**₂) does not comprise any compound comprising at least one amine group and composition (**C**₃) does not comprise any compound of formula (**I**).

Compositions (**C**₂) and/or (**C**₃) may optionally comprise at least one organic solvent. The organic solvents as defined above may also be used in compositions (**C**₂) and/or (**C**₃).

Compositions (**C**₁), (**C**₂) and (**C**₃) used in the process according to the invention may also comprise at least one common cosmetic ingredient other than the compounds described previously, notably chosen from surfactants, notably nonionic or cationic surfactants, solid or liquid fatty substances, thickeners, in particular polysaccharide-based thickeners, nonsilicone cationic polymers, silicones, sunscreens; moisturizers; antidandruff agents; antioxidants; chelating agents; nacreous agents and opacifiers; plasticizers or coalescers; fillers; fragrances; silanes other than the amine derivatives of alkoxysilane; crosslinking agents. Needless to say, the compositions may comprise several cosmetic ingredients featured in the above list.

Depending on their nature and the intended use of the composition, the usual cosmetic ingredients may be present in usual amounts, which may be readily determined by a person skilled in the art and which may be, for each ingredient, between 0.01% and 80% by weight. A person skilled in the art will take care to select the ingredients included in the composition, and also the amounts thereof, so that they do not harm the properties of the compositions of the present invention.

Compositions (C₁), (C₂) and (C₃) used in the process according to the invention may be in any presentation form conventionally used, and notably in the form of an aqueous, alcoholic or aqueous-alcoholic or oily solution or suspension; a solution or a dispersion of the lotion or serum type; an emulsion, notably of liquid or semiliquid consistency of the O/W, W/O or multiple type; a suspension or emulsion of soft consistency of the (O/W) or (W/O) cream type; an aqueous or anhydrous gel, or any other cosmetic form. These compositions may be packaged in pump-action bottles or in aerosol containers, so as to apply the composition in vaporized (lacquer) form or in the form of a mousse. Such packaging forms are indicated, for example, when it is desired to obtain a spray or a mousse, for treating the hair. In these cases, the composition preferably comprises at least one propellant.

Compositions (C₁), (C₂) and (C₃) which have just been described may be applied to keratin fibers. The bath ratio of the applied compositions, i.e. the weight amount of applied composition relative to the weight of treated keratin fibers, may range from 0.1 to 10, preferably from 0.2 to 5, more preferentially from 0.5 to 3. The term "bath ratio" means the ratio between the total weight of the applied composition and the total weight of keratin fibers to be treated.

Compositions (C₁), (C₂) and (C₃) of the invention may be applied to wet or dry keratin fibers, preferably wet or dry hair, preferably to dry hair. In particular, the step of application of each of the compositions (C₁), (C₂) and (C₃) may be followed by a leave-on time. The leave-on time, namely the time of contact of the composition on the hair, is preferably at least 5 minutes, preferably ranging from 10 to 60 minutes. Rinsing of the hair may optionally be envisaged after applying the last composition and optionally the leave-on time. The hair may then optionally be wrung dry, preferably wrung dry.

Heat treatment step

Preferably, the process according to the present invention also comprises, following the set of steps (i) to (iii), a step (iv) of heat treatment of the keratin fibers at a temperature ranging from 40°C to 230°C, preferably from 60°C to 190°C, more preferably from 60°C to 180°C.

Preferably, the heat treatment step has a duration ranging from 5 seconds to 1 hour, preferably ranging from 5 seconds to 1 minute, per lock of hair.

This heat treatment step is generally performed using a heating tool such as a straightening iron, a curling iron, a crimping iron, a waving iron, a steam iron, a hood, a hairdryer, an infrared heating system or a heating roller, preferably using a straightening iron. In the case where the heat treatment step is performed using a heating tool such

as a straightening iron, a curling iron, a crimping iron, a waving iron or a steam iron, the keratin fibers may be dried beforehand, naturally or using a hairdryer.

Composition (C₁)

5 According to a second aspect, a subject of the present invention is a composition (C₁) comprising:

- a) the compound(s) of formula (I) as defined above; and
- b) the compound(s) comprising at least one amine group as defined above; and
- c) the coloring agent(s) as defined above.

10

The technical features concerning composition (C₁) described in the context of the process according to the present invention also apply to composition (C₁) per se.

Device

15 According to a third aspect, a subject of the present invention is a multi-compartment device comprising:

- a first compartment containing a composition (C₂) comprising a) the compound(s) of formula (I) as defined above, and
- a second compartment containing a composition (C₃) different from composition (C₂), composition (C₃) comprising b) the compound(s) comprising at least one amine group as defined above;

20

it being understood that:

- composition (C₂) and/or composition (C₃) comprise c) the coloring agent(s) as defined above.

25

Preferably, composition (C₂) does not comprise any compound comprising at least one amine group and composition (C₃) does not comprise any compound of formula (I).

The technical features concerning compositions (C₂) and (C₃) described in the context of the process according to the present invention also apply to compositions (C₂) and

30

(C₃) included in the multi-compartment device.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

35

Examples

Example 1

The following compositions were prepared.

[Table 1]

Composition	Ingredient	Nature	Preparation
P1	Aqueous dispersion of D&C Black No. 2 Reference Distinctive Ink Black from the company Vantage Specialty Chemicals (comprising 20% AM)	Pigment	2 g in 8 g of water (i.e. 4% AM)
P2	Aqueous dispersion of Red 7 pigment Reference WD-R7-15(BP) from the company Daito Kasei Kogyo (comprising 15% AM)	Pigment	2 g in 8 g of water (i.e. 3% AM)
P3	Dispersion of D&C Black No. 2 in isododecane Reference Distinctive Ink Black DC2206 from the company Vantage Specialty Chemicals (comprising 20% AM)	Pigment	2 g in 8 g of isododecane (i.e. 4% AM)
PA1	Chitosan Reference Kionutrime CSG from the company Kitozyme	polymer containing amine groups	5% AM in water adjusted to pH 6.0 with acetic acid
PA2	Amodimethicone Reference Silsoft AX from the company Momentive	polymer containing amine groups	1 g in 4 g of isododecane (i.e. 20% AM)
PA3	Poly(dimethylsiloxane)bis(3-aminopropyl) terminated (PDMS = 25 kDa) Reference DMS-A31 from the company Gelest	polymer containing amine groups	1 g in 4 g of isododecane (i.e. 20% AM)
EoC1	Poly(Propylene Oxide) biscyclocarbonate from the company Specific Polymers (MW 500-800 g/mol)	Carbonate ester of formula Im	1 g in 4 g of water (i.e. 20% AM)

EoC2	Phloroglucinol tricyclocarbonate CAS No. 1980062-58-5 from the company Specific Polymers	Carbonate ester of formula If	1 g in 4 g of isododecane (i.e. 20% AM)
EoC3 (comparative)	Poly(Propylene Oxide) from the company Sigma reference 202312 (MW ~725 g/mol)	Comparative compound	1 g in 4 g of water (i.e. 20% AM)

“AM” means “active material”

Dyeing study

5 Preparation of the locks

A lock of hair (hair of natural type, 90% gray - 1 g, 20 cm long) is placed in a trough.

The compositions mentioned in step 1 of the table below are mixed and then applied to the lock. The lock is combed, left to stand for 10 minutes and then dried with a hairdryer. The lock is placed in a new trough. Next, the compositions mentioned in step

10 2 of the table below are mixed and then applied to the lock. The lock is combed, left to stand for 10 minutes and then dried with a hairdryer. If the lock is subjected to a heat treatment, it is suspended vertically and then subjected to a heat treatment which consists of three successive passes with a straightening iron at 190°C (Babyliss PRO, EP technology 5.0 sold by the company Babyliss). Spectrophotometric measurements

15 of the L*a*b* values are then taken.

The locks are then shampooed five times. The shampoo washing consists of five cycles. A cycle consists of soaking the lock in an aqueous 3% solution of sodium laureth sulfate adjusted to pH 8 with sodium hydroxide, for 15 seconds, followed by soaking the lock in a bath of clean water for 15 seconds, and drying with a hairdryer.

20 Spectrophotometric measurements of the L*a*b* values are then taken.

Summary of the studies

[Table 2]

Study	Step 1	Step 2	Step 3 (Treatment with a straightening iron)	Lock No.
1	P1 (2 mL) PA1 (3 mL)	EoC2 (0.5 mL) Isododecane (4 mL)	Yes	1-A (Invention)
			No	1-B (Invention)

	P1 (2 mL) PA1 (3 mL)	Isododecane (4.5 mL)	Yes	1-C (Comparative)
			No	1-D (Comparative)
2	P2 (2 mL) PA1 (3 mL) EoC1 (0.5 mL)	n/a	Yes	2-A (Invention)
			No	2-B (Invention)
	P2 (2 mL) PA1 (3 mL) EoC3 (0.5 mL)	n/a	Yes	2-C (Comparative)
			No	2-D (Comparative)
3	P3 (4 mL) EoC2 (1 mL) Isododecane (5 mL)	PA1 (5 mL)	Yes	3-A (Invention)
	P3 (4 mL) Isododecane (6 mL)	PA1 (5 mL)	Yes	3-B (Comparative)
4	P1 (4 mL) EoC2 (1 mL)	PA1 (1 mL) Ethanol (2 mL)	Yes	4-A (Invention)
	P1 (4 mL) EoC3 (1 mL)	PA1 (1 mL) Ethanol (2 mL)	Yes	4-B (Comparative)
5	P3 (3 mL) PA2 (6 mL) EoC2 (1 mL)	n/a	Yes	5-A (Invention)
	P3 (3 mL) PA2 (7 mL)	n/a	Yes	5-B (Comparative)
6	P2 (3 mL) PA1 (6 mL) EoC1 (1 mL)	EoC2 (1 mL) PA2 (4 mL) P2 (1 mL)	Yes	6-A (Invention)
	P2 (3 mL) PA1 (6 mL) EoC3 (1 mL)	PA2 (4 mL) P2 (1 mL)	Yes	6-B (Comparative)

NB: The volumes mentioned are the volumes applied per gram of hair

Spectrophotometric measurements

The color of the locks is evaluated by colorimetry in the CIE L* a* b* system, using a Minolta CM 3600 spectrophotometer (illuminant D65, angle 10°, specular component included).

In this L*a*b* system, L* represents the intensity of the color, a* indicates the green/red color axis and b* the blue/yellow color axis. The smaller the value of L*, the darker and more powerful the coloring.

The smaller the value of a*, the greener the color and the higher the value of a*, the redder the color.

The smaller the value of b*, the bluer the color and the higher the value of b*, the yellower the color.

The color buildup, corresponding to the variation in coloring between the locks of hair before and after dyeing, is defined by (ΔE^*) according to the following equation:

$$\Delta E^* = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

In this equation, L*, a* and b* represent the values measured on locks of hair after dyeing and L₀*, a₀* and b₀* represent the values measured on the locks of hair before dyeing. These last values are mean values of five untreated locks. The following values are obtained: L₀* = 61.33, a₀* = 1.16 and b₀* = 16.64

The resistance of the color to repeat shampooing corresponds to the variation in coloring between the locks of hair before and after repeated shampooing. It is defined by (ΔE^{**}) according to the following equation:

$$\Delta E^{**} = \sqrt{(L1^* - L^*)^2 + (a1^* - a^*)^2 + (b1^* - b^*)^2}$$

In this equation, L*, a* and b* represent the values measured on locks of hair after dyeing and L1*, a1* and b1* represent the values measured on respective locks of hair washed with the shampoo.

The lower the value of ΔE^{**} , the greater the resistance of the colorings with respect to shampoo washing.

Measurement results

[Table 3]

Study	Lock No.	After dyeing and before shampooing				After five shampoo washes			
		L*	a*	b*	ΔE^*	L1*	a1*	b1*	ΔE^{**}
1	1-A (Invention)	21.54	-0.21	0.94	42.80	26.54	-0.26	2.93	5.38
	1-B	19.32	-0.08	0.84	44.90	30.44	-0.1	3.95	11.55

	(Invention)								
	1-C (Comparative)	23.51	-0.06	1.18	40.88	44.03	0.11	8.2	21.69
	1-D (Comparative)	22.68	-0.14	1.38	41.57	50.14	-0.39	8.8	28.45
2	2-A (Invention)	34.09	26.82	11.43	37.78	36.65	31.13	12.04	5.05
	2-B (Invention)	31.47	33.39	21.15	44.17	38.55	28.63	11.98	12.52
	2-C (Comparative)	36.2	28.51	12.12	37.42	48	18.76	10.73	15.37
	2-D (Comparative)	36.26	33.62	17.91	41.03	51.34	12.6	12.01	26.53
3	3-A (Invention)	28.53	-0.33	1.78	36.04	39.63	-0.3	8.38	12.91
	3-B (Comparative)	28.52	-0.09	1.89	35.99	47.39	-0.09	9.22	20.24
4	4-A (Invention)	17.23	0.14	0.53	46.96	17.11	0.27	1.81	1.29
	4-B (Comparative)	17.1	0	1.3	46.83	32.95	-0.08	5.21	16.33
5	5-A (Invention)	17.11	-0.02	0.39	47.13	19.4	-0.04	1.16	2.42
	5-B (Comparative)	17.21	-0.07	0.26	47.08	29.37	0.28	3.96	12.72
6	6-A (Invention)	30.58	35.78	15.65	46.32	29.24	30.78	13.9	5.46
	6-B (comparative)	31.37	33.9	12.62	44.56	37.59	26.16	8.05	10.93

The results show that the process according to the present invention makes it possible to obtain a coloring with a good color buildup and good resistance to shampooing, in the presence (locks 1-A, 2-A, 3-A, 4-A, 5-A, 6-A) or in the absence (locks 1-B, 2-B, 3-B, 4-B, 5-B, 6-B) of a step of heat treatment of the hair. The resistance of the coloring to shampooing is better in the presence of a step of heat treatment of the hair.

When the hair is not treated with a process according to the invention, i.e. when the process does not comprise the application of a carbonate ester according to the

invention (locks 1-C, 1-D, 2-C, 2-D, 3-B, 4-B, 5-B, 6-B), the performance in terms of resistance of the coloring to shampooing is unsatisfactory.

Measurement of the color transfer onto a fabric

- 5 The color transfer onto a manufactured cotton fabric from the company Testfabrics Inc. (reference CrockSquares) is evaluated visually. The fabric (5 cm * 5 cm) is moistened with water (2 mL) and the fabric is then held in contact with the lock which has been dyed beforehand and after five shampoo washes, at a constant pressure using a finger. The color transfer onto the fabric is then evaluated. The results are
- 10 given in the table below.

[Table 4]

Study	Lock No.	Lock after five shampoo washes
1	1-A (Invention)	No transfer onto the fabric
	1-B (Invention)	Slight transfer onto the fabric
	1-C (Comparative)	N/A - Virtually total loss of color
	1-D (Comparative)	N/A - Virtually total loss of color
2	2-A (Invention)	No transfer onto the fabric
	2-B (Invention)	Slight transfer onto the fabric
	2-C (Comparative)	N/A - Virtually total loss of color
	2-D (Comparative)	N/A - Virtually total loss of color
3	3-A (Invention)	No transfer onto the fabric
	3-B (Comparative)	N/A - Virtually total loss of color
4	4-A (Invention)	No transfer onto the fabric
	4-B (Comparative)	N/A - Virtually total loss of color
5	5-A (Invention)	No transfer onto the fabric
	5-B (Comparative)	N/A - Virtually total loss of color
6	6-A (Invention)	No transfer onto the fabric
	6-B (Comparative)	N/A - Virtually total loss of color

The results show that the process according to the present invention makes it possible to obtain coloring characterized by a reduced risk (locks 1-B, 2-B, 3-B, 4-B, 5-B, 6-B) or even no risk (locks 1-A, 2-A, 3-A, 4-A, 5-A, 6-A) of leaching with water leading to staining of fabrics in contact with the hair which has been dyed beforehand and after five shampoo washes. When the hair is not dyed with a process according to the invention, i.e. when the process does not comprise the application of a carbonate ester according to the invention, the performance cannot be evaluated since the coloring virtually totally leached following the repeated shampooing (locks 1-C, 1-D, 2-C, 2-D, 3-B, 4-B, 5-B, 6-B).

Example 2

The following intermediate compositions were prepared

[Table 5]

Intermediate Composition	Ingredient	Nature	Preparation
A1	Dispersion of D&C BLACK NO. 2 in isododecane Référence Distinctive Ink Black DC2206 from Vantage Specialty Chemicals (contains 20% pigment)	Pigment	2g in 8g of isododecane
A2	Amodimethicone Reference Silsoft AX from the company Momentive	Polymer containing amine groups	4g in 20g of isododecane
A3	Phloroglucinol tricyclocarbonate CAS No. 1980062-58-5 from the company Specific Polymers	Carbonate ester of formula If	1g (2.35 mmol) in 4g of methanol
A4	Propylene carbonate CAS 108-32-7 from Sigma Aldrich reference :310328	Comparative compound	0.24g (2.35mmol) in 4g methanol

Using the above compositions A1 to A4, the following compositions B1 and B2 were prepared by mixing the intermediate compositions together and stirring for 5 minutes.

[Table 6]

Composition	Intermediate Compositions			
	A1	A2	A3	A4
B1	5g	10g	2g	-
B2	5g	10g	-	2g

5

Dyeing study

Swatches preparation

Four 90% grey natural hair swatches (1g, 20cm length) were placed horizontally in individual application trays and two swatches were treated with Formula B1 and two swatches were treated with Formula B2. The treatments consisted of applying 5g of the Formula B1 or B2 to each swatch, leaving for 15 minutes and then drying the swatch with a hairdryer.

Swatches 1 and 3 were suspended and subjected to heat treatment using a flat iron (Babyliss PRO, EP technology 5.0) set at 190°C. Three successive passes of the flat iron were made on each swatch. The swatches were suspended for one hour then the color of all four swatches was assessed by spectrophotometry. After color assessment, all four swatches were shampooed. The shampoo protocol consisted of 5 shampoo cycles. One cycle consisted of moistening the swatch under running tap water set at 37°C, applying 0.5g DOP shampoo, massaging the swatch for 15 seconds with the fingers and then rinsing the swatch for 15 seconds under running tap water set at 37°C. After the final shampoo, the hair was dried using a hairdryer, left suspended for 1 hour and then the color of all the swatches assessed by spectrophotometry.

25

Summary of the studies

[Table 7]

Swatch number	Formula applied	Treatment with a straightening iron
1	B1	Yes
2	B1	No
3	B2	Yes
4	B2	No

Spectrophotometric measurements

The color of the locks is evaluated by colorimetry in the CIE L* a* b* system, using a Minolta CM 3600 spectrophotometer (illuminant D65, angle 10°, specular component included).

5

The color buildup (ΔE^*) is calculated as in example 1 with $L_0^* = 61.73$, $a_0^* = 0.35$ and $b_0^* = 14.8$ measured on an untreated hair swatch. The resistance of the color to repeat shampooing (ΔE^{**}) is calculated as in example 1.

10 [Table 8]

No. swatch	After coloration and before shampooing				After 5 shampoos			
	L*	a*	b*	ΔE^*	L1*	a1*	b1*	ΔE^{**}
1 (Invention)	18.88	-0.16	0,1	45.30	20.37	0.56	2.97	3.31
2 (Invention)	14.5	-0.1	-0.29	49.58	29.31	0.47	4.86	15.69
3 (Comparative)	18.86	0.11	1.04	45.02	38.09	0.61	7.55	20.31
4 (Comparative)	17.89	-0.21	0.32	46.17	44.62	0.36	7.67	27.73

The results demonstrate that the process according to the invention gives good coloration and an excellent resistance to repeat shampooing. Swatch 1 colored using Formula B1 containing a triscarbonate ingredient and treated with the flat iron gives the best results. In comparison, Swatch 3 colored using Formula B2 containing a monocarbonate (propylene carbonate) ingredient and treated with the flat iron gives poor results – the shampoo resistance is unsatisfactory.

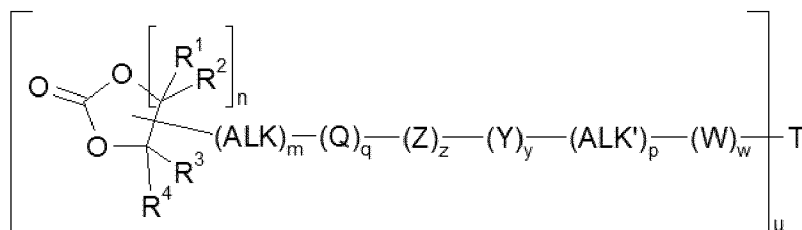
Swatch 2 colored using Formula B1 containing a triscarbonate ingredient and not treated with the flat iron gives slightly lower shampoo fastness results than Swatch 1 showing that the heat treatment used in swatch 1 improves shampoo resistance.

Swatch 4 colored using Formula B2 containing a monocarbonate (propylene carbonate) ingredient and not treated with the flat iron gives the poorest shampoo resistance and is unsatisfactory.

CLAIMS

1. A process for dyeing keratin fibers, comprising:

(i) a step consisting in applying to the keratin fibers at least a) one compound of formula (I) below:



5

(I)

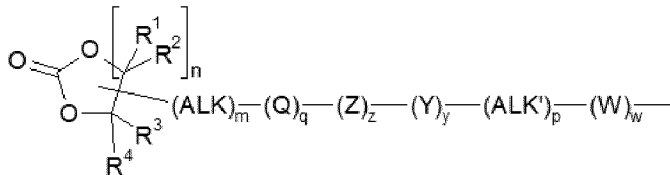
in which formula (I):

- **R¹, R², R³ and R⁴**, which may be identical or different, represent a hydrogen atom or a (C₁-C₆)alkyl and particularly (C₁-C₄)alkyl group, it being understood that one of the groups **R¹, R², R³ or R⁴** denotes a chain -(ALK)_m-(Q)_q-(Z)_z-(Y)_y-(ALK')_p-(W)_w;
- 10 preferentially, **R¹, R² and R³** denote a hydrogen atom, and **R⁴** denotes the chain: -(ALK)_m-(Q)_q-(Z)_z-(Y)_y-(ALK')_p-(W)_w;
- **ALK and ALK'**, which may be identical or different, represent a (C₁-C₁₂)alkylene group optionally substituted and/or interrupted with one or more heteroatoms such as oxygen, sulfur, or NR⁸ with R⁸ as defined below; in particular, ALK and ALK' represent
- 15 (C₁-C₆)alkylene, preferably (C₁-C₄)alkylene, such as methylene;
- **Q, Y and W**, which may be identical or different, represent an oxygen or sulfur atom or NR⁸, with R⁸ representing a hydrogen atom or a (C₁-C₄)alkyl or benzyl group, preferably oxygen or NR⁸ such as NH;
- **Z** represents a carbonyl C=O, thiocarbonyl C=S or imino C=NR⁸ group with R⁸ as
- 20 defined previously, preferably carbonyl,
- **m, p, q, z, y and w**, which may be identical or different, represent 0 or 1; preferably, m = 1 and **p, q, z, y and w**, which may be identical or different, represent 0 or 1;
- **n** represents an integer ranging from 1 to 4; in particular, n is equal to 1, 2 or 3, preferably 1 or 2; more preferentially, n = 1;
- 25 ▪ **T** represents a polyvalent group, said polyvalent group being chosen, when u = 2, from:
 - i) (C₁-C₁₀₀)alkylene optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹¹)(R¹²)- with R¹¹ and R¹²,
 - 30 which may be identical or different, representing a hydrogen atom, hydroxyl, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkylene radical denotes a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen atoms and/or with one or more -SiMe₂ radicals,

- ii) (C₂-C₁₀₀)alkenylene optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹)(R²)- with R¹ and R², which may be identical or different, representing a hydrogen atom, hydroxyl, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkenylene radical denotes a (C₂-C₁₀₀)alkenylene radical optionally interrupted with one or more oxygen atoms and/or with one or more -SiMe₂ radicals,
- iii) (hetero)arylene such as phenylene, for instance 1,3-phenylene,
- iv) (hetero)cycloalkylene,
- 10 said polyvalent group being chosen, when u = 3 or 4, from:
- i) a multivalent (trivalent or tetravalent) saturated or unsaturated, linear or branched hydrocarbon-based radical containing from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms;
- ii) a multivalent (trivalent or tetravalent) aromatic or nonaromatic (hetero)cyclic radical
- 15 preferably containing 5 or 6 carbon atoms;
- u represents an integer ranging from 2 to 4, preferably 2 or 3, it being understood that:

- T is divalent when u is 2, is trivalent when u is 3, and tetravalent when u is 4;

- the following units:



are identical or different; and

- (ii) a step consisting in applying to the keratin fibers at least b) one compound comprising at least one amine group; and
- (iii) a step consisting in applying to the keratin fibers at least c) one coloring agent
- 25 chosen from pigments, direct dyes and mixtures thereof.

2. The process as claimed in claim 1, in which the compound of formula (I) is such that u is equal to 2 or 3 and T represents a divalent or trivalent group chosen from ii) (C₁-C₆)alkylene, iv) (hetero)arylene and v) cycloalkylene.

30

3. The process as claimed in claim 1, in which the compound of formula (I) is such that u is equal to 2 and T represents a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen or sulfur atoms and/or with one or more radicals NR with R representing a hydrogen atom or a C₁-C₄ alkyl radical such as NH and/or with one or more radicals -Si(R¹)(R²)- with R¹ and R², which may be identical or different,

35

representing a hydrogen atom, hydroxyl, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, preferably a C₁-C₄ alkyl such as methyl; preferably, said alkylene radical denotes a (C₁-C₁₀₀)alkylene radical optionally interrupted with one or more oxygen atoms and/or with one or more –SiMe₂ radicals.

5

4. The process as claimed in the preceding claim, in which T represents a radical T1 of formula $-(\text{CH}_2)_{x1}-[\text{O}-(\text{CH}_2)_{x2}-]_{x3}(\text{O})_{x4}-$ with $x1 = 0$ to 10, $x2 = 2$ or 3, $x3 = 1$ to 50, preferably 3 to 20, $x4 = 0$ or 1 or a radical T2 of formula $-(\text{CH}_2)_{y1}-[\text{Si}(\text{R}^1)(\text{R}^2)-\text{O}-]_{y2}-\text{Si}(\text{R}^1)(\text{R}^2)-(\text{CH}_2)_{y3}-$ with $y1 = 0$ to 10, $y2 = 1$ to 50, preferably 3 to 20, $y3 = 0$ to 10, preferably 1 to 5 and R¹ and R², which may be identical or different, representing a (C₁-C₄)alkyl radical such as methyl.

10

5. The process as claimed in claim 1, in which the compound of formula (I) is such that u is equal to 2 and T represents:

15

- a divalent (hetero)arylene group, preferably arylene such as phenylene, more particularly 1,3-phenylene,
- a divalent cycloalkylene group, preferably cyclohexylene, preferably substituted with one or more C₁-C₄ alkyl radicals such as methyl, or
- a divalent C₁-C₄ alkylene group such as methylene, ethylene or butylene.

20

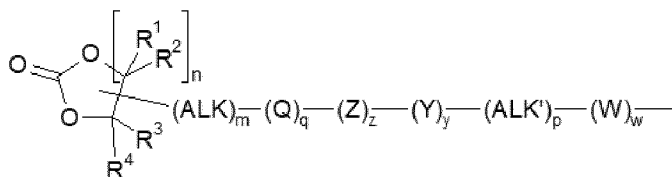
6. The process as claimed in claim 1, in which the compound of formula (I) is such that u is equal to 3 and T represents i) a saturated or unsaturated, preferably saturated, linear or branched trivalent hydrocarbon-based radical containing from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, ii) an aromatic or nonaromatic, preferably aromatic, trivalent (hetero)cyclic radical containing 5 or 6 carbon atoms, preferably 6 carbon atoms, such as a trivalent 1,3,5-phenyl radical.

25

7. The process as claimed in any one of the preceding claims, in which the compound of formula (I) is such that u is 2 and:

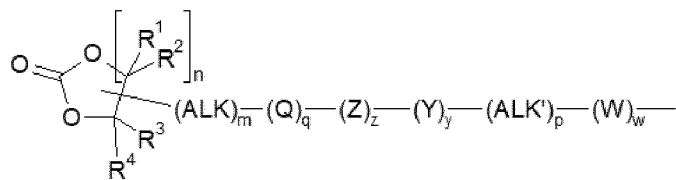
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- one of the units:



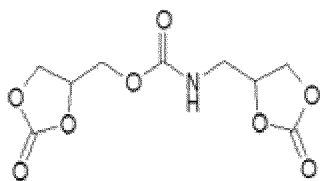
is such that $m + p$ is an integer greater than or equal to 1; preferably, m is 1 and p is 0, and preferentially $q = z = y = 1$; and

- the other unit:

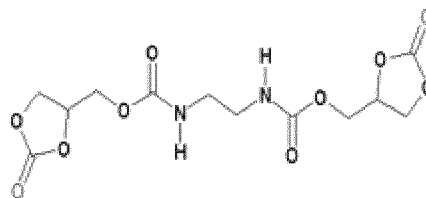


is such that $m + p$ is 0; preferably, the other unit is such that $m+p+q+z+y+w$ is 0.

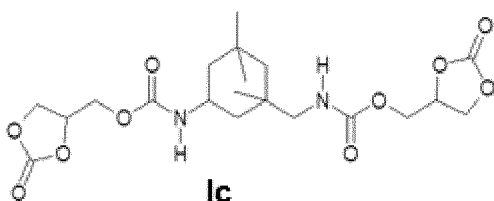
8. The process as claimed in any one of the preceding claims, in which the compound
5 of formula (I) is chosen from the following compounds:



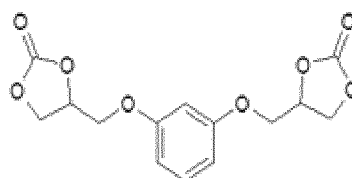
Ia



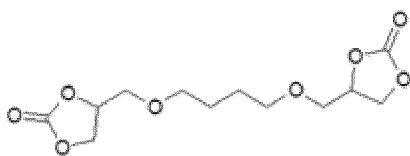
Ib



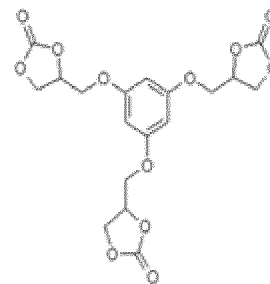
Ic



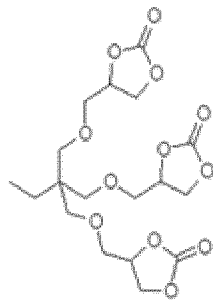
Id



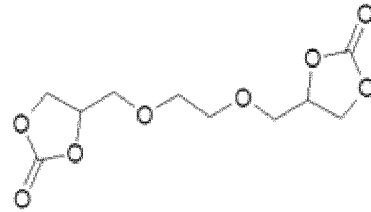
Ie



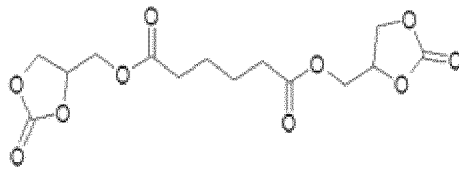
If



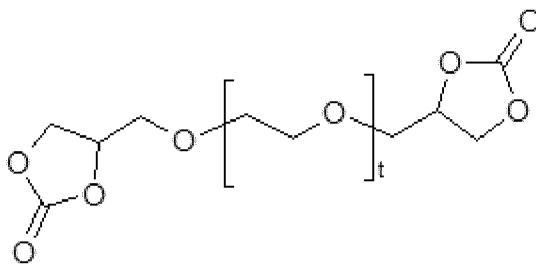
Ig



Ih

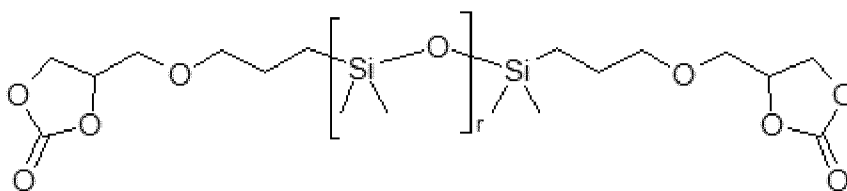


Ii



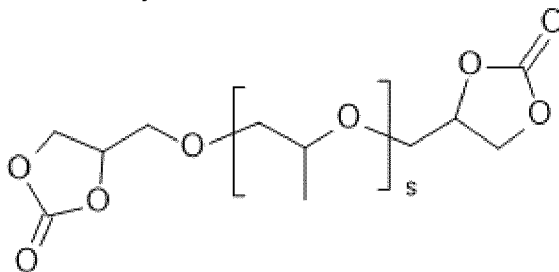
Ij

with t being an integer ranging from 1 to 50, preferably from 3 to 30 and more preferentially from 5 to 20;



Ik

5 with r being an integer ranging from 1 to 50, preferably from 3 to 30 and more preferentially from 5 to 20;



Im

with s being an integer ranging from 4 to 30, preferably from 5 to 10;
and mixtures thereof.

9. The process as claimed in any one of the preceding claims, also comprising,
5 following the set of steps (i) to (iii), a step (iv) of heat treatment of the keratin fibers at a temperature ranging from 40°C to 230°C, preferably from 60°C to 190°C, more preferably from 60°C to 180°C.

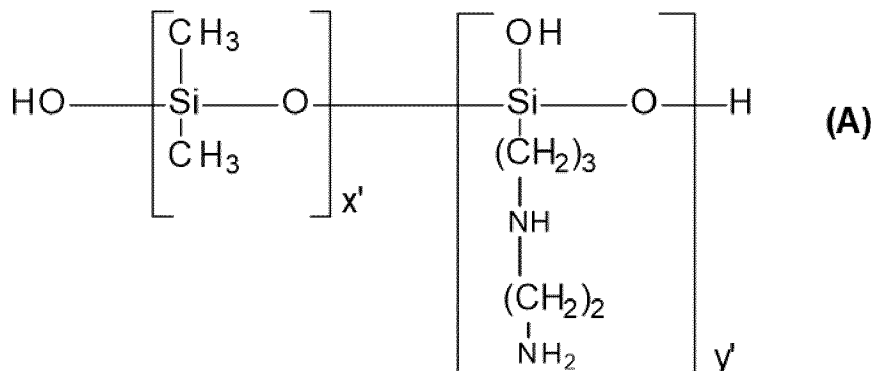
10. The process as claimed in any one of the preceding claims, in which the compound
10 comprising at least one amine group is chosen from:

- amino silicones;
- amine derivatives of alkoxysilane;
- organic amines not comprising any silicon atoms;
- nonsilicone polymers comprising at least one amine group;
- 15 - and mixtures thereof,

preferably from amino silicones, nonsilicone polymers comprising at least one amine group, and mixtures thereof.

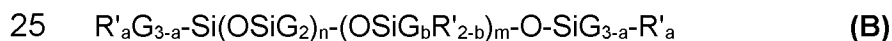
11. The process as claimed in claim 10, in which the amino silicones are chosen from:

20 a) the polysiloxanes of formula (A) below:



in which x' and y' are integers such that the weight-average molecular weight (Mw) ranges from 5000 to 500 000;

b) the amino silicones of formula (B) below:



in which:

- G, which may be identical or different, denotes a hydrogen atom or a phenyl, OH, C₁-C₈ alkyl, for example methyl, or C₁-C₈ alkoxy, for example methoxy, group,
- a, which may be identical or different, denotes 0 or an integer from 1 to 3, in particular
30 0,
- b denotes 0 or 1, in particular 1,

- m and n are numbers such that the sum (n + m) varies from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;

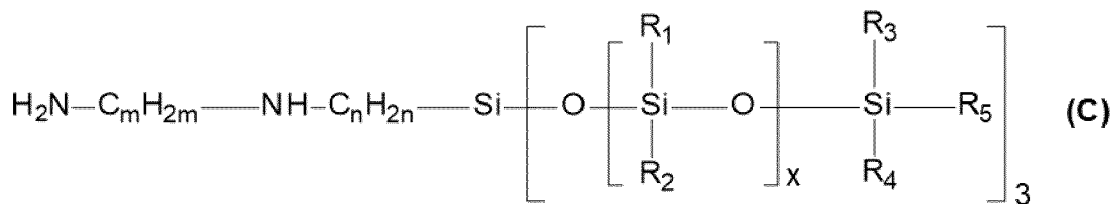
5 - R', which may be identical or different, denotes a monovalent radical of formula -C_qH_{2q}L in which q is a number ranging from 2 to 8 and L is an optionally quaternized amine group chosen from the following groups:

-N(R'')₂; -N⁺(R'')₃ A⁻; -NR''-Q-N(R'')₂ and -NR''-Q-N⁺(R'')₃ A⁻,

in which R'', which may be identical or different, denotes hydrogen, phenyl, benzyl, or a saturated monovalent hydrocarbon-based radical, for example a C₁-C₂₀ alkyl radical; Q denotes a linear or branched group of formula C_rH_{2r}, r being an integer ranging from 2 to 6, preferably from 2 to 4; and A⁻ represents a cosmetically acceptable anion, notably a halide such as fluoride, chloride, bromide or iodide;

10

c) the amino silicones of formula (C) below:



15

in which:

- R₁, R₂, R₃ and R₄, which may be identical or different, denote a C₁-C₄ alkyl radical or a phenyl group,

- R₅ denotes a C₁-C₄ alkyl radical or a hydroxyl group,

20

- n is an integer ranging from 1 to 5,

- m is an integer ranging from 1 to 5, and

- x is chosen such that the amine number ranges from 0.01 to 1 meq/g,

d) the multiblock polyoxyalkylenated amino silicones of the type (AB)_n, A being a polysiloxane block and B being a polyoxyalkylene block including at least one amine group,

25

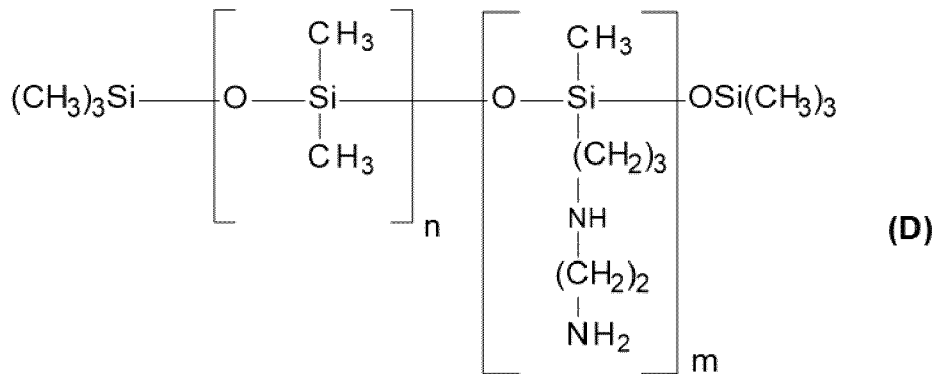
e) and mixtures thereof,

preferably from the amino silicones of formula (B).

30

12. The process as claimed in either of claims 10 and 11, in which the amino silicones are chosen from:

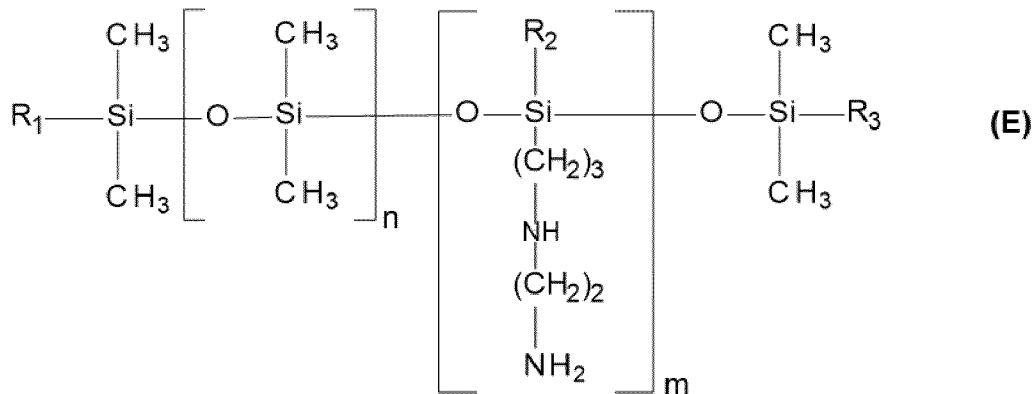
- the silicones known as "trimethylsilylamodimethicone" corresponding to formula (D):



in which m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1

5 to 10;

- the silicones of formula (E) below:

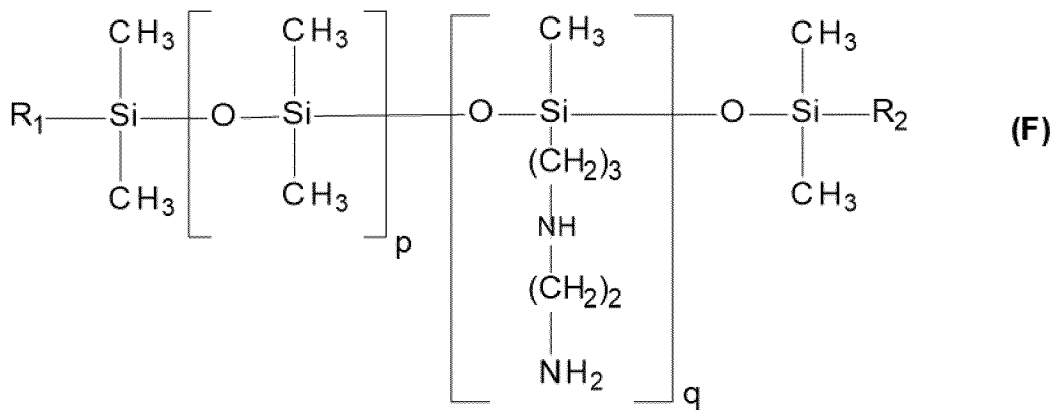


in which:

10 - m and n are numbers such that the sum (n + m) ranges from 1 to 1000, in particular from 50 to 250 and more particularly from 100 to 200; n possibly denoting a number from 0 to 999 and notably from 49 to 249 and more particularly from 125 to 175, and m possibly denoting a number from 1 to 1000, notably from 1 to 10 and more particularly from 1 to 5;

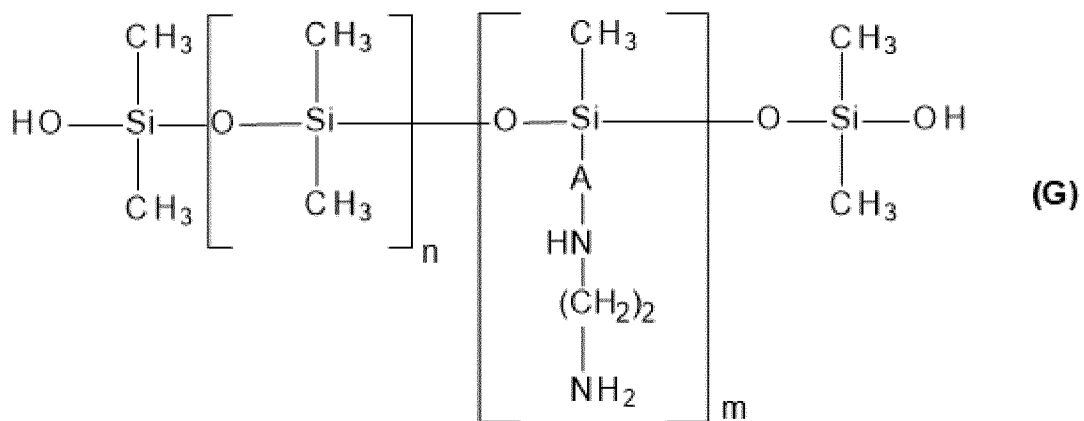
15 - R1, R2 and R3, which may be identical or different, represent a hydroxyl or C₁-C₄ alkoxy radical, at least one of the radicals R1 to R3 denoting an alkoxy radical;

- the silicones of formula (F) below:



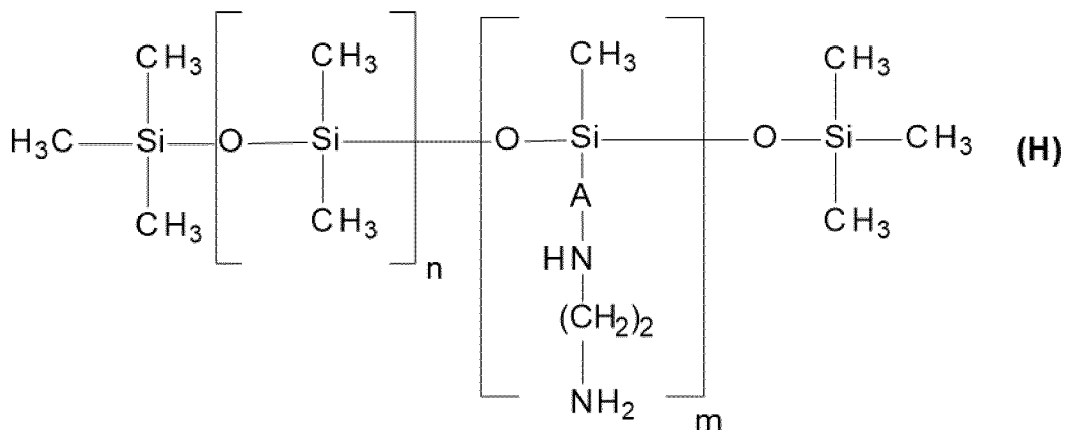
in which:

- p and q are numbers such that the sum (p + q) ranges from 1 to 1000, in particular from 50 to 350 and more particularly from 150 to 250; p possibly denoting a number from 0 to 999, notably from 49 to 349 and more particularly from 159 to 239, and q possibly denoting a number from 1 to 1000, notably from 1 to 10 and more particularly from 1 to 5;
- R1 and R2, which are different, represent a hydroxyl or C₁-C₄ alkoxy radical, at least one of the radicals R1 or R2 denoting an alkoxy radical;
- the silicones of formula (G) below:



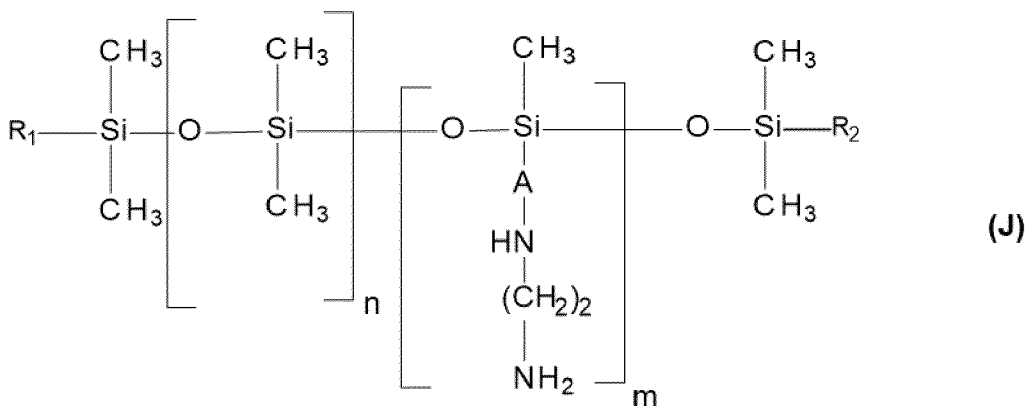
in which:

- m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;
- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms;
- the silicones of formula (H) below:



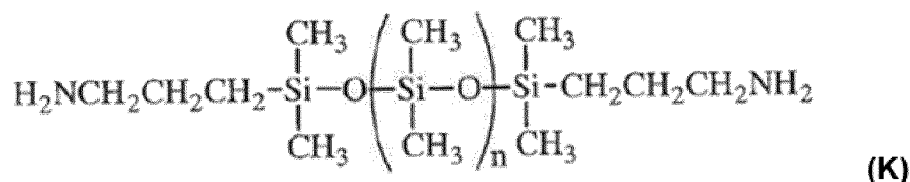
in which:

- m and n are numbers such that the sum (n + m) ranges from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and notably from 49 to 149, and m possibly denoting a number from 1 to 2000 and notably from 1 to 10;
- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms;
- the silicones of formula (J) below:



in which:

- m and n are numbers ranging from 1 to 5000, and in particular n possibly denoting a number ranging from 10 to 2000 and notably from 100 to 1000, and in particular m possibly denoting a number from 1 to 100;
- R₁ and R₂, which may be identical or different, preferably identical, represent a linear or branched, saturated or unsaturated alkyl radical comprising from 6 to 30 carbon atoms, preferably from 8 to 24 carbon atoms, preferably from 12 to 20 carbon atoms;
- A denotes a linear or branched alkylene radical containing from 4 to 8 carbon atoms and preferably 4 carbon atoms; this radical is preferably branched;
- the silicones of formula (K) below:



in which the value of n is such that the weight-average molecular weight (Mw) of the silicone ranges from 500 to 55 000;

- and mixtures thereof, preferably from the silicones of formulae **(J)** and **(K)** and mixtures thereof.

13. The process as claimed in claim 10, in which the amine derivatives of alkoxy silane are chosen from the compounds of formula **(L)** below, oligomers thereof, hydrolysis products thereof and mixtures thereof:



in which formula **(L)**:

- R₁ is a linear or branched, saturated or unsaturated, cyclic or acyclic C₁-C₆ hydrocarbon-based chain substituted with a group chosen from the following groups:
 - amine NH₂ or NHR (R = C₁-C₂₀ and notably C₁-C₆ alkyl optionally substituted with a radical including a silicon atom, C₃-C₄₀ cycloalkyl or C₆-C₃₀ aromatic),
 - an aryl or aryloxy group substituted and/or interrupted with at least one amino group or with at least one C₁-C₄ aminoalkyl group;

R₁ possibly being interrupted with a heteroatom (O, S, NH) or a carbonyl (CO) group;

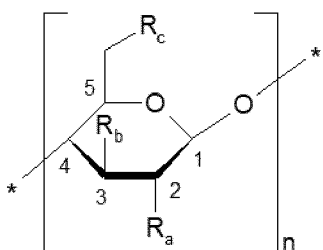
- R₂ and R₃, which may be identical or different, represent a linear or branched alkyl group comprising from 1 to 6 carbon atoms;
- y denotes an integer ranging from 0 to 3; and
- z denotes an integer ranging from 0 to 3; and
- x denotes an integer ranging from 0 to 2;

with z + x + y = 3.

14. The process as claimed in the preceding claim, in which the amine derivatives of alkoxy silane are chosen from 3-aminopropyltriethoxysilane (APTES), 3-aminoethyltriethoxysilane (AETES), 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-(m-aminophenoxy)propyltrimethoxysilane, p-aminophenyltrimethoxysilane and N-(2-aminoethylaminomethyl)phenethyltrimethoxysilane, and mixtures thereof, preferably from 3-aminopropyltriethoxysilane (APTES), 3-aminoethyltriethoxysilane (AETES), 3-aminopropylmethyldiethoxysilane and N-(2-aminoethyl)-3-aminopropyltriethoxysilane, oligomers thereof, hydrolysis products thereof and mixtures thereof, more preferentially

from 3-aminopropyltriethoxysilane, oligomers thereof, hydrolysis products thereof and mixtures thereof.

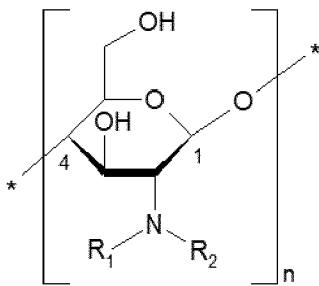
15. The process as claimed in claim 10, in which the nonsilicone polymers comprising
 5 at least one amine group are chosen from polyamines, polyamino acids, polysaccharides comprising at least one amine group, and mixtures thereof, preferably from polysaccharides comprising at least one amine group, more preferentially from polysaccharides comprising monosaccharide units of formula **(IIa)** below:



(IIa)

- 10 in which formula **(IIa)**:
- n is an integer greater than or equal to 2, preferably ranging from 3 to 3000, more preferentially ranging from 5 to 2500, and better still ranging from 10 to 2300;
 - R_a, R_b and R_c, which may be identical or different for each monosaccharide unit, represent (1) a hydroxyl group, (2) a (C₁-C₄)alkoxy group, the alkyl chain of which may
 15 be optionally substituted notably with one or more hydroxyl and/or carboxyl groups, (3) a carboxyl group, or (4) a group NR₁R₂ with R₁ and R₂, which may be identical or different, representing i) a hydrogen atom, ii) a (C₁-C₆)alkyl group that is optionally substituted, preferably with one or more hydroxyl or NH₂ groups, iii) an aryl group such as phenyl, iv) an aryl(C₁-C₄)alkyl group such as benzyl, v) a (hetero)cyclo(C₅-
 20 C₇)alkyl(C₁-C₄)alkyl group such as cyclohexylmethyl, vi) a (hetero)cyclo(C₅-C₇)alkyl(C₁-C₄)alkyl group such as cyclohexylmethyl, vii) a group -C(Y)-(Y')_p-R'₁ with Y and Y', which may be identical or different, representing an oxygen or sulfur atom or N(R'₂), p is equal to 0 or 1, and R'₁ and R'₂ representing i) to vi) of R₁ and R₂ defined previously,
- 25 it being understood that at least one of the radicals R_a, R_b or R_c of at least one monosaccharide unit represents an NH₂ group.

16. The process as claimed in claim 10 or 15, in which the polysaccharides comprising at least one amine group are chosen from the polysaccharides bearing
 30 monosaccharide units of formula **(IIb)** below:



(IIb)

in which formula (IIb):

- R₁ and R₂, which may be identical or different for each monosaccharide unit, are as defined in claim 15;

5 - n is an integer greater than or equal to 2, preferably ranging from 3 to 3000, more preferentially from 5 to 2500 and more preferentially from 10 to 2300;

it being understood that at least one monosaccharide unit bears an amino group NH₂,

preferably, the polysaccharides comprising at least one amine group are chosen from

10 chitin, chitosan, derivatives thereof and mixtures thereof, more preferentially from chitin, chitosan and mixtures thereof, even more preferentially chitosan.

17. The process as claimed in any one of the preceding claims, in which the coloring agents are chosen from pigments, preferably from white organic pigments, colored

15 organic pigments, and mixtures thereof, more preferentially carbon blacks, such as Black 2, lakes, such as D&C Red 7, and mixtures thereof.

18. The process as claimed in any one of the preceding claims, in which steps (i), (ii) and (iii) are performed simultaneously by applying to the keratin fibers a composition

20 (C₁) comprising:

a) the compound(s) of formula (I); and

b) the compound(s) comprising at least one amine group; and

c) the coloring agent(s); and

d) optionally at least one organic solvent, preferably chosen from:

25 - isododecane;

- monoalcohols comprising a hydroxyl group and a C₁-C₆(alkyl) and preferably C₁-C₄(alkyl) group such as methyl, ethyl or (iso)propyl;

- polyols comprising from 2 to 30 hydroxyl groups and a (C₂-C₈)alkyl group, preferably a (C₂-C₄)alkyl group; and mixtures thereof,

30 more preferentially from monoalcohols and polyols comprising two hydroxyl groups,

even more preferentially from ethanol and polyols comprising two hydroxyl groups and

at least three carbon atoms, most preferentially from ethanol, propylene glycol (1,2-propanediol); 1,3-propanediol; 1,3-butylene glycol; 1,2-pentanediol; dipropylene glycol; hexylene glycol; pentylene glycol; butylene glycol; glycerol; ethylene glycol, and mixtures thereof.

5

19. The process as claimed in claim 18, in which composition (**C**₁) comprises a total content of compounds of formula (**I**) ranging from 0.01% to 20%, preferably from 0.05% to 15%, more preferentially from 0.1% to 10%, even more preferentially from 0.5% to 5%, most preferentially from 1% to 5% by weight relative to the total weight of composition (**C**₁).

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20. The process as claimed in claim 18 or 19, in which composition (**C**₁) comprises a total content of compounds comprising at least one amine group ranging from 0.01% to 25%, preferably from 0.05% to 15%, more preferentially from 1% to 10% by weight relative to the total weight of composition (**C**₁).

15

21. The process as claimed in any one of claims 18 to 20, in which composition (**C**₁) comprises a total content of coloring agents ranging from 0.05% to 10% and preferably from 0.5% to 5% by weight relative to the total weight of composition (**C**₁).

20

22. The process as claimed in any one of claims 18 to 21, in which composition (**C**₁) comprises a total content of organic solvents ranging from 45% to 99.7% by weight, preferably ranging from 50% to 99% by weight, more preferentially ranging from 60% to 80% by weight, relative to the total weight of composition (**C**₁).

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23. The process as claimed in any one of claims 18 to 22, in which the pH of composition (**C**₁) is less than or equal to 10, preferably ranges from 3 to 9 and more preferentially from 4 to 8.

30

24. The process as claimed in any one of the preceding claims, in which steps (i), (ii) and (iii) are performed by applying to the keratin fibers:

- a composition (**C**₂) comprising a) the compound(s) of formula (**I**); and
- a composition (**C**₃) comprising b) the compound(s) comprising at least one amine group;

35

it being understood that:

- composition (**C**₂) and/or composition (**C**₃) comprise c) the coloring agent(s); and
- composition (**C**₂) is applied before composition (**C**₃) or composition (**C**₃) is applied before composition (**C**₂).

25. A composition (**C**₁) as defined in any one of claims 18 to 23.

26. A multi-compartment device comprising:

- 5 - a first compartment containing a composition (**C**₂) comprising a) the compound(s) of formula (**I**) as defined in any one of claims 1 to 17; and
 - a second compartment containing a composition (**C**₃) different from composition (**C**₂), composition (**C**₃) comprising b) the compound(s) comprising at least one amine group as defined in any one of claims 1 to 17;
- it being understood that:
- 10 - composition (**C**₂) and/or composition (**C**₃) comprise c) the coloring agent(s) as defined as defined in any one of claims 1 to 17.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/067883

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A61K8/49 A61K8/73 A61K8/898 A61K8/89 A61Q5/06
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 A61K A61Q
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/286486 A1 (HERLIHY SHAUN L [GB] ET AL) 20 November 2008 (2008-11-20) examples 4, 40, 44, 49 -----	25
X	US 2017/260418 A1 (WU BO [US] ET AL) 14 September 2017 (2017-09-14) paragraphs [0029] - [0039], [0064] - [0065] compounds 1-13, 17, 18 claims 1-6 ----- -/--	25

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search 11 August 2020	Date of mailing of the international search report 21/08/2020
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 Olausson Boulois, J

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/067883

C(Continuation). 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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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/067883

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