ABSTRACT

The invention relates to a dye composition for keratin fibers, in particular for human keratin fibers such as the hair, this composition having, in a medium suitable for dyeing, at least one cationic direct dye of given formula, and containing at least one specific cationic or amphoteric substantive polymer. The invention also relates to the dyeing processes and devices using it.
DYE COMPOSITION FOR KERATIN FIBERS, WITH A CATIONIC DIRECT DYE AND A SUBSTANTIVE POLYMER

[0001] The invention relates to a dye composition for keratin fibers, especially human keratin fibers, such as the hair, this composition comprising, in a medium suitable for dyeing; at least one cationic direct dye of the below given formulae and at least one specific cationic or amphoteric substantive polymer.

[0002] The invention also relates to the dyeing processes and devices using this composition.

[0003] Two types of dyeing can be distinguished in the hair sector. The first type of dyeing is semi-permanent or temporary dyeing, also known as direct dyeing, which uses dyes capable of giving the hair’s natural coloration a more or less pronounced color change that may be resistant to several shampoo-washes. These dyes are known as direct dyes; they can be used with or without an oxidizing agent. In the presence of an oxidizing agent, the aim is to effect a lightening dyeing. The lightening dyeing is carried out by applying the mixture, prepared at the time of use, of a direct dye and of an oxidizing agent to the hair, and obtains, by lightening the melanin in the hair, an advantageous effect, such as unifying the color in the case of grey hair, or bringing out the color in the case of naturally pigmented hair.

[0004] The second type of dyeing is permanent dyeing or oxidation dyeing. This type of dyeing is carried out with so-called “oxidation” dyes comprising oxidation dye precursors and couplers. Oxidation dye precursors, commonly referred to as “oxidation bases,” are compounds that are initially colorless or only weakly colored, and that develop their dyeing power on the hair in the presence of oxidizing agents added at the time of use, leading to the formation of colored compounds and dyes. The formation of these colored compounds and dyes results either from an oxidative condensation of the “oxidation bases” with themselves, or from an oxidative condensation of the “oxidation bases” with coloration modifier compounds, commonly known as “couplers,” which are generally present in the dye compositions used in oxidation dyeing.

[0005] To vary the shades obtained with oxidation dyes, or to enrich them with glints, it is known practice to add direct dyes thereto.

[0006] Among the cationic direct dyes available in the field of dyeing keratin fibers, especially human keratin fibers, the compounds whose structure is developed in the following text are already known; however, these dyes lead to insufficient colorations, both regarding the homogeneity of the color distributed along the fiber (“unisoni”), where the coloration is said to be too selective, and regarding the staying power, when the hair resists various attacking factors, including light, bad weather, and shampooing.

[0007] Now, after considerable research conducted in this area, the Inventor has discovered that it is possible to obtain novel compositions for dyeing keratin fibers capable of giving colorations that are less selective and that show good resistance to the various attacking factors to the hair, by combining at least one specific cationic or amphoteric substantive polymer with at least one cationic direct dye known in the art and of formulae respectively defined below.

[0008] This discovery forms the basis of the present invention.

[0009] Additional features and advantages of the invention are set forth in the description that follows, and, in part, will be apparent from the description or may be learned from practice of the invention. The advantages of the invention will be realized and attained by the dyeing compositions, processes, and kits particularly pointed out in the written description and claims.

[0010] Both the foregoing general description and the following detailed description of the invention are exemplary and explanatory only and are not restrictive of the claimed invention.

[0011] A first subject of the present invention is thus a composition for dyeing keratin fibers, and especially human keratin fibers, such as the hair, which composition comprises, in a medium suitable for dyeing, (i) at least one cationic direct dye whose structure corresponds to the following formulae, and (ii) at least one specific cationic or amphoteric substantive polymer.

[0012] (i) The cationic direct dye which can be used according to the present invention is a compound selected from those of formulae (I), (II), (III) and (III) below:

[0013] a) the compounds of formula (I) below:

\[
\begin{align*}
A & \equiv D \equiv D' \\
N & \equiv R_1 \equiv R_2 \equiv R_3 \equiv R_4
\end{align*}
\]

[0014] wherein:

[0015] D represents a nitrogen atom or a —CH group;

[0016] R₁ and R₂ are identical or different and represent a hydrogen atom, a C₁₋₄ alkyl radical which is unsubstituted or substituted with a —CN, —OH or —NH₂ radical, or R₁ and R₂ form, with a carbon atom of the benzene ring, an optionally oxygenated or nitrogenous heterocycle which is unsubstituted or substituted with one or more C₁₋₄ alkyl radicals, or R₁ and R₂ may each be a 4’-aminophenyl radical;

[0017] R₃ and R’₃ are identical or different and represent a hydrogen atom, a halogen atom selected from chlorine, bromine, iodine and fluorine, a cyano group, a C₁₋₄ alkyl radical, or a C₁₋₄ alkoxy or acetoxy radical;

[0018] X⁺ represents an anion preferably selected from chloride, methyl sulphate and acetate;
A represents a group selected from structures A1 to A19 below:

-continued

A9

A10

A11

A12

A13

A14

A15

A16

A17

A18

A19
[0020] wherein R₉ represents a C₁₋₄ alkyl radical which is unsubstituted or substituted with a hydroxyl radical and R₁₀ represents a C₁₋₄ alkoxyl radical, with the proviso that when D represents —CH₂ and A represents A₂ or A₃ and R₁ is other than an alkoxyl radical, then R₉ and R₁₀ do not simultaneously represent a hydrogen atom;

[0021] b) the compounds of formula (II) below:

[0022] wherein:

[0023] R₉ represents a hydrogen atom or a C₁₋₄ alkyl radical;

[0024] R₁₀ represents a hydrogen atom, an alkyl radical which is unsubstituted or substituted with a —CN radical or with an amino group, a 4-aminophenyl radical, or forms, with R₁₁, an optionally oxygenated and/or nitrogenous heterocycle which is unsubstituted or substituted with a C₁₋₄ alkyl radical;

[0025] R₉ and R₁₀ are identical or different and represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C₁₋₄ alkyl or C₁₋₄ alkoxyl radical or a —CN radical;

[0026] X' represents an anion, preferably selected from chloride, methyl sulphate and acetate;

[0027] B represents a group selected from structures B₁ to B₆ below:

[0028] wherein R₁₀ represents a C₁₋₄ alkyl radical; R₁₁ and R₁₂ are identical or different, represent a hydrogen atom or a C₁₋₄ alkyl radical;

[0029] c) the compounds of formulae (III) and (III') below:

[0030] wherein:

[0031] R₁₃ represents a hydrogen atom, a C₁₋₄ alkoxy radical, a halogen atom, such as bromine, chlorine, iodine or fluorine, or an amino radical;

[0032] R₁₄ represents a hydrogen atom, a C₁₋₄ alkyl radical, or forms, with a carbon atom of the benzene ring, a heterocycle which is optionally oxygenated and/or substituted with one or more C₁₋₄ alkyl groups;
[0033] $R_{14}$ represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine;

[0034] $R_{15}$ and $R_{17}$ are identical or different and represent a hydrogen atom or a C$_1$-C$_4$ alkyl radical;

[0035] $D_1$ and $D_2$ are identical or different and represent a nitrogen atom or a $\text{--CH}$ group;

[0036] $m=0$ or 1;

[0037] with the proviso that when $R_{13}$ represents an unsubstituted amino group, then $D_1$ and $D_2$ simultaneously represent a $\text{--CH}$ group and $m=0$;

[0038] $X^-$ represents an anion, preferably selected from chloride, methyl sulphate and acetate; and

[0039] $E$ represents a group selected from structures E1 to E8 below:

![E1](image1)
![E2](image2)

[0040] wherein $R'$ represents a C$_1$-C$_4$ alkyl radical;

[0041] with the proviso that when $m=0$ and $D_1$ represents a nitrogen atom, then $E$ can also represent a group of structure E9 below:

![E9](image3)

[0042] wherein $R'$ represents a C$_1$-C$_4$ alkyl radical.

[0043] The cationic direct dyes of formulae (I), (II), (III) and (III') that can be used in the dye compositions in accordance with the invention are known compounds and are described, for example, in patent applications WO 95/01772, WO 95/15144 and EP-A-0,714,954.

[0044] The preferred cationic direct dyes of formula (I) that can be used in the dye compositions in accordance with the invention include the compounds corresponding to structures (I1) to (I55) below:

![I1](image4)

![I2](image5)

![I3](image6)
-continued

14

15

16

17

18

19

20

-continued
Among the compounds of structures (I1) to (I55) described above, those most preferred compounds include those corresponding to structures (II1) to (II12) below:

[0045] The preferred cationic direct dyes of formula (II) that can be used in the dye compositions in accordance with the invention, include the compounds corresponding to structures (III) to (II12) below:
The preferred cationic direct dyes of formula (III) that can be used in the dye compositions in accordance with the invention, include the compounds corresponding to structures (III1) to (III18) below:
Among the preferred compounds of structures (III1) to (III18) described above, those most preferred are the compounds corresponding to structures (III4), (III5) and (III13).

The preferred cationic direct dyes of formula (III') that can be used in the dye compositions in accordance with the invention, include the compounds corresponding to structures (III'1) to (III'3) below:

The at least one cationic direct dye used according to the invention preferably is present in amount ranging from about 0.001 to about 10% by weight relative to the total weight of the dye composition, and even more preferably from about 0.005 to about 5% by weight relative to this weight.

(ii) The cationic or amphoteric substantive polymer that can be used according to the present invention is selected from:

(a) cellulose cationic derivatives, with the exception of Polyquaternium 10;
(b) copolymers of dimethyldiallylammonium halide and of (meth)acrylic acid;
(c) methacryloyloxyethyltrimethylammonium halide homopolymers and copolymers;
(d) polyquaternary ammonium polymers selected from:

polymers comprising repeating units corresponding to formula (IV) below:

polymers comprising repeating units corresponding to formula (V) below:
and polymers comprising repeating units corresponding to formula (VI) below:

\[
\begin{array}{c}
\text{CH}_3 \ \text{C} \ \text{H} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \\
\text{CH}_3 \ \text{C} \ \text{H} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \ \text{D} \ \text{N} \ \text{O} \\
\end{array}
\]

[0059] in which \( p \) represents an integer ranging from 1 to 6 approximately, \( D \) can be zero or can represent a group \( -(\text{CH}_2)_n-\) in which \( r \) represents a number equal to 4 or 7;

[0060] (e) vinylpyrrolidone copolymers containing cationic units; and

[0061] (f) mixtures thereof.

[0062] The substantive nature, i.e., the ability to be deposited on the hair, of the polymers used in the present invention is conventionally determined using the test described by Richard J. Crawford, Journal of the Society of Cosmetic Chemists, 1980, 31-(5)-pages 273 to 278 (development with Red 80 acidic dye).

[0063] These substantive polymers can be selected from those previously described in the literature, especially in European patent application EP-A-0,557,203, from page 4, line 19 to page 12, line 14.

[0064] Preferred cationic cellulosic derivatives include quaternized cellulose ether derivatives such as those described in European patent application EP-A-0,189,935, 1 and in particular the polymer sold under the name “Quatsol 4” by the company Union Carbide. These polymers are also defined in the CITA dictionary (5th edition, 1993) as quaternary ammoniums of hydroxyethylcellulose that have reacted with an epoxide substituted with a lauryldimethylammonium group, and are listed therein under the name “Polyquaternium 24”.

[0065] Preferred substantive polymers of the methacryloyloxyethyltrimethylammonium chloride homopolymer and copolymer type that can be used according to the invention, include the products that are referred to in the CITA dictionary (5th edition, 1993) as (1) “Polyquaternium 37”, (2) “Polyquaternium 32” and (3) “Polyquaternium 35”, and which correspond (1) to crosslinked poly(methacryloyloxyethyltrimethylammonium chloride) homopolymer, as a 50% dispersion in mineral oil, sold under the name Suncare SC95 by the company Allied Colloids, (2) to the crosslinked copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium chloride (20:80 by weight), as a 50% dispersion in mineral oil, sold under the name Suncare SC92 by the company Allied Colloids, and (3) to the methosulfate of the copolymer of methacryloyloxyethyltrimethylammonium and of methacryloyloxyethyltrimethylacrylammonium, sold under the name Plex 7525L by the company Rohm GmbH.

[0066] The preferred substantive polymers of the copolymer of dimethylallylammonium halide and of (meth)acrylic acid type that can be used according to the invention, include the copolymers of diallyldimethylammonium chloride and of acrylic acid, such as the one in proportions (80:20 by weight) sold under the name Merquat 280 by the company Calgon.

[0067] The preferred substantive polymers of the polyquaternary ammonium type which can be used according to the invention, include:

[0068] the polymers prepared and described in French Patent No. 2,270,846, comprising repeating units corresponding to formula (IV) below:
and especially those in which the molecular weight, determined by gel permeation chromatography, ranges from 9500 to 9900;

[0070] the polymers prepared and described in French Patent No. 2,270,846, comprising repeating units corresponding to formula (V) below:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{N}^+ & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{C}_2 & \quad \text{H}_5 \\
\text{N}^+ & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{Br}
\end{align*}
\]

[0071] and especially those in which the molecular weight, determined by gel permeation chromatography, is about 1200;

[0072] the polymers described and prepared in U.S. Pat. Nos. 4,157,388, 4,390,689, 4,702,906 and 4,719,282, comprising repeating units corresponding to formula (VI) below:

\[
\begin{align*}
\text{CH}_3 & \quad \text{N}^+ \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{NH} \quad \text{CO} \quad \text{D} \quad \text{NH} \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

[0073] wherein \( p \) represents an integer ranging from 1 to 6 approximately, \( D \) can be zero or can represent a group \(-(\text{CH}_2)-\text{CO}\) further wherein \( r \) represents a number equal to 4 or 7, and wherein the molecular mass of said polymers is preferably less than 100,000, and even more preferably less than or equal to 50,000. Such polymers are sold, for example, by the company Miranol under the names “Mirapal A15”, “Mirapal AD1”, “Mirapal AZ1” and “Mirapal 175”.

[0074] The preferred vinylpyrrolidone polymers (PVP) containing cationic units that can be used in accordance with the invention, include:

[0075] a) vinylpyrrolidone polymers containing dimethylaminoethyl methacrylate units; for example:

[0076] the vinylpyrrolidone/dimethylaminoethyl methacrylate (20/80 by weight) copolymer sold under the trade name Copolymer 845 by the company ISP;

[0077] the vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers quaternized with diethyl sulphate, sold under the names Gafquat 734, 755, 755 S and 755 L by the company ISP,

[0078] the PVP/dimethylaminoethyl methacrylate/ hydrophilic polyurethane copolymers sold under the trade name Pecogel GC-310 by the company UCIB or alternatively under the names Aquamere C 1031 and C 1511 by the company Blagden Chemicals,

[0079] the quaternized or non-quaternized PVP/ dimethylaminoethyl methacrylate/C8 to C16 olefin copolymers sold under the names Ganex ACP 1050 to 1057, 1062 to 1069 and 1079 to 1086 by the company ISP,

[0080] the PVP/dimethylaminoethyl methacrylate/ vinylecaprolactam copolymer sold under the name Gallux VC 713 by the company ISP;

[0081] b) vinylpyrrolidone polymers containing methacrylamido-propyltrimethylammonium (MAP-TAC) units, for example:

[0082] the vinylpyrrolidone/MAPTAC copolymers sold under the trade names Gafquat ACP 1011 and Gafquat HS 100 by the company ISP,

[0083] c) vinylpyrrolidone, polymers containing methylvinylimidazolium units, for example:

[0084] the PVP/methylvinylimidazolium chloride copolymers sold under the names Luviquat FC 370, FC 550, FC 905 and HM 552 by the company BASF,

[0085] the PVP/methylvinylimidazolium chloride/ vinylimidazole copolymer sold under the name Luviquat 8155 by the company BASF,

[0086] the PVP/methylvinylimidazolium methosulphate copolymer sold under the name Luviquat MS 370 by the company BASF.

[0087] The concentration of substantive polymer (ii) in the dye composition according to i) the invention can range from about 0.01 to about 10% relative to the total weight of the dye composition, and preferably from 0.1 to 5%.

[0088] The medium suitable for dyeing (or support) generally comprises water or a mixture of water and at least one organic solvent, which can dissolve the compounds that would not be sufficiently soluble in the water. Preferred organic solvents include, for example, C1-C4 lower alkanols, such as ethanol and isopropanol; aromatic alcohols such as benzyl alcohol or phenoxyethanol, as well as similar products and mixtures thereof.

[0089] The solvents can be present in preferred proportions ranging from about 1 to about 40% by weight relative
to the total weight of the dye composition, and even more preferably from about 5 to about 30% by weight.

[0090] The pH of the dye composition in accordance with the invention generally ranges from about 2 to about 11 and preferably from about 5 to about 10. The pH can be adjusted to the desired value using acidifying or basifying agents typically used in the dyeing of keratin fibers.

[0091] Examples of acidifying agents include inorganic or organic acids, such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, and sulfonic acids.

[0092] Examples of basifying agents include aqueous ammonia, alkaline carbonates, alkanoamines, such as mono- di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VII) below:

\[
\begin{align*}
W &\begin{array}{c}
\text{N} \\
\text{R}_{16} &\text{N} \\
\text{R}_{19} &\text{N} \\
\text{R}_{20} &\text{N} \\
\text{R}_{21}
\end{array}
\end{align*}
\]

wherein W is a propylene residue optionally substituted with a hydroxyl group or a \( \text{C}_3\text{C}_6 \) alkyl radical; \( \text{R}_{16}, \text{R}_{19}, \text{R}_{20} \) and \( \text{R}_{21} \) are identical or different and represent a hydrogen atom or a \( \text{C}_3\text{C}_6 \) alkyl or \( \text{C}_1\text{C}_6 \) hydroxyalkyl radical.

[0094] In addition to the at least one cationic direct dye (i) defined above, the dye composition in accordance with the invention can contain at least one additional direct dye that can be selected, for example, from nitrobenzene dyes, anthraquinone dyes, naphthoquinone dyes, triarylmethane dyes, xanthine dyes and azo dyes which are non-cationic.

[0095] When it is intended for oxidation dyeing, the dye composition in accordance with the invention contains, in addition to the at least one cationic direct dye (i), at least one oxidation base selected from the oxidation bases conventionally used for oxidation dyeing, for example, para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases.

[0096] When they are used, the at least one oxidation base is preferably present in an amount ranging from about 0.0005 to about 12% by weight relative to the total weight of the dye composition, and even more preferably from about 0.005 to about 6% by weight relative to the total weight of the dye composition.

[0097] When it is intended for oxidation dyeing, the dye composition in accordance with the invention can contain, in addition to the at least one cationic direct dye (i), the at least one substantive polymer (ii), and the at least one oxidation base, at least one coupler so as to modify the shades obtained or to enrich them with glints, by using the at least one cationic direct dye (i) and the at least one oxidation base.

[0098] The at least one coupler that can be used in the dye composition in accordance with the invention can be selected from the couplers conventionally used in oxidation dyeing, for example, meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

[0099] When they are present, the at least one coupler is preferably present in an amount ranging from about 0.0001 to about 10% by weight relative to the total weight of the dye composition, and even more preferably from about 0.005 to about 5% by weight relative to the total weight of the dye composition.

[0100] The dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, surfactants, film-forming agents, ceramides, preserving agents, screening agents and opacifiers.

[0101] Needless to say, a person skilled in the art will take care to select this or these optionally complementary compounds such that the advantageous properties intrinsically associated with the dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

[0102] The dye composition according to the invention can be in various forms, such as in the form of liquids, shampoos, creams or gels or in any other form which is suitable for dyeing keratin fibers, and, especially, human hair. The presentation in shampoo form is particularly preferred.

[0103] When the combination of the at least one cationic direct dye (i) and of the at least one substantive polymer (ii) according to the invention is used in a composition intended for oxidation dyeing (at least one oxidation base is then used, optionally in the presence of at least one coupler), or when it is used in a composition intended for lightening direct dyeing, then the dye composition in accordance with the invention also contains at least one oxidizing agent selected, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, such as perborates and persulphates, and enzymes, such as peroxidases, lactases and two-electron oxidoreductases. The use of hydrogen peroxide or of enzymes is particularly preferred.

[0104] Another subject of the invention is a method for dyeing keratin fibers, especially human keratin fibers, such as the hair, using the dye composition as defined above.

[0105] According to a first variant of this dyeing process in accordance with the invention, at least one dye composition as defined above is applied to the keratin fibers, for a period of time sufficient to develop the desired coloration, after which the fibers are rinsed, optionally washed with shampoo, rinsed again and dried.

[0106] The time required to develop the coloration on the keratin fibers generally ranges from 3 to 60 minutes, and more preferably ranges from 5 to 40 minutes.

[0107] According to a second variant of this dyeing process in accordance with the invention, at least one dye composition as defined above is applied to the keratin fibers, for a period which is sufficient to develop the desired coloration, without final rinsing.

[0108] According to a specific embodiment of this dyeing process, when the dye composition in accordance with the invention contains at least one oxidation base and at least
one oxidizing agent, the dyeing process includes a first step which comprises separately storing, on the one hand, a composition (A1) comprising, in a medium suitable for dyeing, at least one cationic direct dye (i) as defined above and at least one oxidation base, and, on the other hand, a composition (B1) containing, in a medium suitable for dyeing, at least one oxidizing agent, followed by mixing them together at the time of use, before applying this mixture to the keratin fibers, the composition (A1) or the ordinary skill in the art how to practice the invention. The following examples are intended to illustrate the invention without limiting its scope.

EXAMPLES

Example 1

Cationic direct dye of formula I(2) 0.125 g
para-Aminophenol 0.120 g
5-N-β-Hydroxyethylamino-2-methylphenol 0.125 g
Substantive polymer: copolymer of diallyldimethylammonium chloride and of acrylic acid (80/20 by weight), sold under the name Mesquat 280 by the company Calgon 1.0 g A.M.*
Oleic acid 3.0 g
Oleylamine containing 2 mol of ethylene oxide, sold under the trade name Ethomox O12 by the company Akzo 7.0 g
Diethylaminoethyl laurylamine succinamic, sodium salt, containing 55% A.M. 3.0 g A.M.*
Oleyl alcohol 5.0 g
Oleic acid diethanolamide 12.0 g
Propylene glycol 3.5 g
Dipropylene glycol 0.5 g
Propylene glycol monomethylether 9.0 g
Ethanol 7.0 g
Sodium metaphosphite as an aqueous solution containing 35% 0.455 g A.M.*
A.M.
Ammonium acetate 0.8 g
Antioxidant, sequestering agent qs
Fragrance, preserving agent qs
Aqueous ammonia containing 20% NH₃ 10.0 g
A.M.*: Active material

At the time of use, this composition was mixed with an equal amount of an aqueous 20-volume hydrogen peroxide solution (6% by weight).

The resulting mixture was applied for 30 minutes to locks of natural grey hair II containing 90% white hairs. The locks of hair were then rinsed, washed with standard shampoo, and then dried.

The locks of hair were dyed a light blonde shade with an intense red glint.

Example 2

The dye composition below was prepared:

Cationic direct dye of formula I(14) 0.09 g
Substantive polymer of polyquaternary ammonium formula of type (IV) 1.0 g A.M.*
Nonylephnol containing 9 mol of ethylene oxide 8.0 g
2-Amino-2-methylpropanol . . . qs . . . pH 9
Demineralized water . . . qs
100 g
A.M.*: Active material

The above composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A1) or (A2) as defined above and a second compartment of which contains composition (B1) or (B2) as defined above. These devices can be equipped with a means for applying the desired mixture to the hair, such as the devices described in French Patent No. FR-2,586,913 in the name of L’Oréal.

The present invention is further illustrated by the following examples which are designed to teach those of ordinary skill in the art how to practice the invention without limiting its scope.

Example 1

The dye composition below was prepared:

Cationic direct dye of formula I(2) 0.125 g
para-Aminophenol 0.120 g
5-N-β-Hydroxyethylamino-2-methylphenol 0.125 g
Substantive polymer: copolymer of diallyldimethylammonium chloride and of acrylic acid (80/20 by weight), sold under the name Mesquat 280 by the company Calgon 1.0 g A.M.*
Oleic acid 3.0 g
Oleylamine containing 2 mol of ethylene oxide, sold under the trade name Ethomox O12 by the company Akzo 7.0 g
Diethylaminoethyl laurylamine succinamic, sodium salt, containing 55% A.M. 3.0 g A.M.*
Oleyl alcohol 5.0 g
Oleic acid diethanolamide 12.0 g
Propylene glycol 3.5 g
Dipropylene glycol 0.5 g
Propylene glycol monomethylether 9.0 g
Ethanol 7.0 g
Sodium metaphosphite as an aqueous solution containing 35% 0.455 g A.M.*
A.M.
Ammonium acetate 0.8 g
Antioxidant, sequestering agent qs
Fragrance, preserving agent qs
Aqueous ammonia containing 20% NH₃ 10.0 g
A.M.*: Active material

At the time of use, this composition was mixed with an equal amount of an aqueous 20-volume hydrogen peroxide solution (6% by weight).

The resulting mixture was applied for 30 minutes to locks of natural grey hair II containing 90% white hairs. The locks of hair were then rinsed, washed with standard shampoo, and then dried.

The locks of hair were dyed a light blonde shade with an intense red glint.

Example 2

The dye composition below was prepared:

Cationic direct dye of formula I(14) 0.09 g
Substantive polymer of polyquaternary ammonium formula of type (IV) 1.0 g A.M.*
Nonylephnol containing 9 mol of ethylene oxide 8.0 g
2-Amino-2-methylpropanol . . . qs . . . pH 9
Demineralized water . . . qs
100 g
A.M.*: Active material

The above composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.
[0118] The locks of hair were dyed an intense coppery shade.

[0119] The foregoing written description relates to various embodiments of the present invention. Numerous changes and modifications may be made therein without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

I. A composition for dyeing keratin fibers, said composition comprising, in a medium suitable for dyeing,

(i) at least one cationic direct dye of formula (I), (II), (III) or (IV) below:

![Formula (I)]

wherein, in said formula (I):

D represents a nitrogen atom or a —CH group,

R₁ and R₂ are identical or different and represent a hydrogen atom, a C₁-C₄ alkyl radical which is unsubstituted or substituted with a —CN, —OH or —NH₂ radical, or R₁ and R₂ form, with a carbon atom of the benzene ring, an optionally oxygenated or nitrogenous heterocycle which is unsubstituted or substituted with one or more C₁-C₄ alkyl radicals, or a 4'-aminophenyl radical;

R₃ and R₁₃ are identical or different and represent a hydrogen atom, a halogen atom selected from chlorine, bromine, iodine and fluorine, a cyano group, a C₁-C₄ alkyl Al radical, or a C₁-C₄ alkoxy or acetyloxy radical;

X⁻ represents an anion;

A represents a group selected from structures A₁ to A₁₉ below:

![Structure A₁]

![Structure A₁₀]

![Structure A₁₁]
wherein

R₄ represents a C₁₋₄ alkoxy radical;

with the proviso that when D represents —CH₂, A represents A₈ or A₁₅, and R₃ is other than an alkoxy radical, then R₁ and R₂ do not simultaneously represent a hydrogen atom;

wherein, in said formula (II):

R₄ represents a hydrogen atom or a C₁₋₄ alkyl radical;

R₅ represents a hydrogen atom, an alkyl radical which is unsubstituted or substituted with a —CN radical or with an amino group, a 4'-aminophenyl radical, or R₅ forms, with R₆, an optionally oxygenated and/or nitrogenous heterocycle which is unsubstituted or substituted with a C₁₋₄ alkyl radical;

R₈ and R₉ are identical or different and represent a hydrogen atom, a halogen atom, a C₁₋₄ alkyl or C₁₋₄ alkoxy radical, or a —CN radical;

X⁻ represents an anion;

B represents a group selected from structures B₁ to B₆ below:

wherein

R₄ represents a C₁₋₄ alkyl radical which is unsubstituted or substituted with a hydroxyl radical; and
wherein

$R_{10}$ represents a $C_1$-$C_4$ alkyl radical;

$R_1$ and $R_2$, which are identical or different, represent a hydrogen atom or a $C_1$-$C_4$ alkyl radical;

wherein, in said formulae (III) and (III):

$R_{13}$ represents a hydrogen atom, a $C_1$-$C_4$ alkoxy radical, a halogen atom, or an amino radical;

$R_{14}$ represents a hydrogen atom, a $C_1$-$C_4$ alkyl radical, or $R_{13}$ forms, with a carbon atom of the benzene ring, a heterocycle which is optionally oxygenated and/or substituted with one or more $C_1$-$C_4$ alkyl groups;

$R_{15}$ represents a hydrogen atom or a halogen atom;

$R_{16}$ and $R_{17}$, which are identical or different, represent a hydrogen atom or a $C_1$-$C_4$ alkyl radical;

$D_1$ and $D_2$, which are identical or different, represent a nitrogen atom or a $-CH$ group;

$m=0$ or $1$;

with the proviso that when $R_{13}$ represents an unsubstituted amino group, then $D_1$ and $D_2$ simultaneously represent a $-CH$ group and $m=0$;

$X^{-}$ represents an anion; and
wherein R' represents a C₃-C₄ alkyl radical;  
with the proviso that when m=0 and D₁ represents a  
nitrogen atom, then E can also represent a group of  
structure E₉ below:

![Diagram](image-url)

wherein R' represents a C₃-C₄ alkyl radical; and

(ii) at least one cationic or amphoteric substantive poly- 
mer selected from the group formed by:

(a) cellulose cationic derivatives with the exception of  
Polyquaternium 10;

(b) copolymers of dimethyl diallylammonium halide  
and of (meth)acrylic acid;

(c) methacryloxyethyltrimethylammonium halide  
homopolymers and copolymers;

(d) polyquaternary ammonium polymers selected from:  
polymers of repeating units having formula (IV)  
below:

![Diagram](image-url)

polymers of repeating units having formula (V)  
below:

![Diagram](image-url)

and polymers of repeating units having formula (VI)  
below:

![Diagram](image-url)

wherein p represents an integer ranging from 1 to 6  
approximately, D is zero or represents a group  
-(CH₂)ₙ-CO- wherein r represents a number  
equal to 4 or 7; and

(c) vinylpyrrolidone copolymers containing cationic  
units.

2. A composition according to claim 1, wherein in said  
formula (I), (II), (III), or (IV), X⁻ represents an anion of  
chloride, methyl sulfate, or acetate.

3. A composition according to claim 1, wherein said  
keraatin fibers are human keratin fibers.

4. A composition according to claim 3, wherein said  
human keratin II fibers are human hair.

5. A composition according to claim 1, wherein said at  
least one cationic direct dye of formula (I) is selected from  
the compounds having structures (II) to (I51) and (I53) to  
(I55) below:

![Diagram](image-url)
6. A composition according to claim 5, wherein said at least one cationic direct dye has structure (I), (I2), (I14) or (I31).

7. A composition according to claim 1, wherein said at least one cationic direct dye of formula (II) is selected from the compounds having structures (II1) to (II3), (II5), (II6), (I8), and (II10) to (II12) below:
8. A composition according to claim 1, wherein said at least one cationic direct dye of formula (III) is selected from the compounds having structures (III1) to (III18) below:
Continued...

9. A composition according to claim 8, wherein said at least one cationic direct dye of formula (III) has structure (III4), (III5) or (III13).

10. A composition according to claim 1, wherein said at least one cationic direct dye of formula (III') is selected from the compounds having structures (III1') to (III3') below:

11. A composition according to claim 1, wherein said at least one cationic or amphoteric substantive polymer is Polyquaternium 24.

12. A composition according to claim 11, wherein said at least one cationic direct dye of formula (I), (II), (III) or (III') is present in an amount ranging from about 0.001 to about 10% by weight relative to the total weight of the composition.

13. A composition according to claim 1, wherein said at least one cationic or amphoteric substantive polymer is a copolymer of dimethyliallylammonium chloride and of acryric acid (80/20 by weight).

14. A composition according to claim 1, wherein said at least one cationic or amphoteric substantive polymer is a crosslinked poly(methacryloyloxyethyltrimethylammonium chloride) homopolymer, as a 50% dispersion in mineral oil; the crosslinked copolymer of acrylamide and of methacr-
loyloxyethyltrimethylammonium chloride (20/80 by weight), as a 50% dispersion in mineral oil; or the metho-
sulphate of the copolymer of methacroyloxyethyl-trim-
ethylammonium and of methacryloyloxyethyldimethyl-
acrylammonium.

16. A composition according to claim 1, wherein said at
least one cationic or amphoteric substantive polymer is:
a) a vinylpyrrolidone polymer containing dimethylami-
noprotoethyl methylacrylate units;
b) a vinylpyrrolidone polymer containing methacryla-
dopropyltrimethylammonium units; or
c) a vinylpyrrolidone polymer containing methylvinylimi-
dazolium units.

17. A composition according to claim 1, wherein said at
least one cationic or amphoteric substantive polymer is
present in an amount ranging from about 0.01 to about 10%
by weight relative to the total weight of the composition.

18. A composition according to claim 17, wherein said at
least one cationic or amphoteric substantive polymer is
present in an amount ranging from about 0.1 to about 5% by
weight relative to the total weight of the composition.

19. A composition according to claim 1, wherein said
medium suitable for dyeing comprises water or a mixture of
Water and at least one organic solvent.

20. A composition according to claim 1, wherein said
composition has a pH ranging from about 2 to about 11.

21. A composition according to claim 20, wherein said
composition has a pH ranging from about 5 to about 10.

22. A composition according to claim 1, further comprising
at least one additional direct dye.

23. A composition according to claim 22, wherein said at
least one additional direct dye is a nitrobenzene dye,
anthraquinone dye, naphthaquinone dye, triarylmethane
dye, xanthine dye, or an azo dye that is non-cationic.

24. A composition according to claim 1, further comprising
at least one oxidation base selected from para-phen-
ylenediarnines, bis(phenylalkylenediarnines, para-am
ophenols, ortho-aminophenols and heterocyclic bases.

25. A composition according to claim 24, wherein said
at least one oxidation base is present in an amount ranging
from about 0.0005 to about 12% by weight relative to the
total weight of the dye composition.

26. A composition according to claim 25, wherein said at
least one oxidation base is present in an amount ranging
from about 0.0005 to about 6% by weight relative to the total
weight of the dye composition.

27. A composition according to claim 24, further comprising
at least one coupler selected from meta-phenylenedi-
arnines, meta-aminophenols, meta-diphenols and hetero-
cyclic couplers.

28. A composition according to claim 27, wherein said at
least one coupler is present in an amount ranging from about
0.0001 to about 10% by weight relative to the total weight
of the dye composition.

29. A composition according to claim 28, wherein said at
least one coupler is present in an amount ranging from about
0.0005 to about 5% by weight relative to the total weight
of the dye composition.

30. A composition according to claim 1, further comprising
at least one oxidizing agent.

31. A composition according to claim 30, wherein said at
least one oxidizing agent is hydrogen peroxide, urea perox-
ide, alkali metal bromate, a persalt, or an enzyme.

32. A method for dyeing keratin fibers, said method
comprising applying at least one dyeing composition
according to claim 1 to said keratin fibers, and allowing said
at least one dyeing composition to remain on said keratin
fibers for a period of time sufficient to develop the desired
coloration.

33. A method for dyeing keratin fibers according to claim
32, further comprising rinsing said keratin fibers after said
period of time sufficient to develop the desired coloration.

34. A method for dyeing keratin fibers according to claim
33, further comprising, after said rinsing, washing said
keratin fibers with shampoo, rinsing said keratin fibers
again, and drying said keratin fibers.

35. The method according to claim 33, wherein said
period of time ranges from 3 to 60 minutes.

36. The method according to claim 35, wherein said
period of time ranges from 5 to 40 minutes.

37. A method for dyeing keratin fibers, said method
comprising

(1) mixing a composition (A1), said composition (A1)
comprising at least one cationic direct dye of formula
(I), (II), (III) or (IV) as defined in claim 1, and at least
one oxidation base with a composition (B1), said
composition (B1) comprising, in a medium suitable for
dyeing, at least one oxidizing agent, wherein said
composition (A1) or said composition (B1) contains at
least one cationic or amphoteric substantive polymer as
defined in claim 1, and

(2) applying said mixture of said composition (A1) and
said composition (B1) to said keratin fibers for a period
of time sufficient to dye said keratin fibers, wherein said
mixing occurs before the time of application to said
keratin fibers.

38. A method for dyeing keratin fibers, said method
comprising

(1) mixing a composition (A2), said composition (A2)
comprising at least one cationic direct dye of formula
(I), (II), (III) or (IV) as defined in claim 1, with a
composition (B2), said composition (B2) comprising,
in a medium suitable for dyeing, at least one oxidizing
agent, wherein said composition (A2) or said composi-
tion (B2) contains at least one cationic or amphoteric
substantive polymer as defined in claim 1, and

(2) applying said mixture of said composition (A2) and
said composition (B2) to said keratin fibers for a period
of time sufficient to dye said keratin fibers, wherein said
mixing occurs before the time of application to said
keratin fibers.

39. A multi-compartment dyeing device or multi-compartment
dyeing kit for dyeing keratin fibers comprising at
least two compartments, wherein

a first compartment comprises a composition (A1) as
defined in claim 37, and

a second compartment comprises a composition (B1) as
defined in claim 37.

40. A multi-compartment dyeing device or multi-compartment
dyeing kit for dyeing keratin fibers comprising at
least two compartments, wherein

a first compartment comprises a composition (A2) as
defined in claim 38, and
a second compartment comprises a composition (B2) as defined in claim 38.

41. A composition according to claim 1 in the form of a liquid, a shampoo, a cream, or a gel.

42. A composition according to claim 41 in the form of a shampoo.