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(54) Title: COMPOSITIONS FOR DYEING HAIR WITH CATIONIC DIRECT DYES

(57) Abstract: Described herein is a hair color composition for dyeing the hair. The hair color composition includes one or more direct dye compounds and one or more additional ingredients. The one or more direct dye compounds each include a chromophore, one or two permanent cations, and one to four incipient cations. The one to four incipient cations are pendant to the core structure and are neutral. The one or more direct dye compounds enter the hair shaft after the hair color composition is applied to the hair. The hair color composition has a pH of from about 7 to about 11.



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COMPOSITIONS FOR DYEING HAIR WITH CATIONIC DIRECT DYES

TECHNICAL FIELD OF THE INVENTION

5 Provided is a composition for dyeing hair with one or more washfast direct dye compounds. The direct dye compounds each have one to four incipient cations. A decrease in pH when rinsing the hair causes one or more of the incipient cations to change from neutral to positively charged inside of the hair shaft.

BACKGROUND OF THE INVENTION

10 In general, direct dye products last only 6 – 10 shampoos and are hence known as semi-permanent. However, many consumers want more permanent results, and therefore default to oxidative dye products that contain hydrogen peroxide or other oxidants. The direct dye compounds and the method described herein can be used in either direct dye or oxidation dye products.

15 The permanent alteration of the color of keratinous fibers, in particular human hair, by the application of hair dyes is well known. In order to provide the consumer with the shade, longevity, and the intensity of color desired, an oxidative coloring process involving complex chemical reactions is utilized. Permanent hair dyeing formulations typically comprise primary intermediates (also known as oxidative hair dye precursors or developers) and couplers (also
20 known as color modifiers or secondary intermediates). These dye precursors are sufficiently small, polar and soluble to diffuse into the hair shaft where, once activated by an oxidizing agent under basic conditions, such as hydrogen peroxide, the primary intermediates react with other dye precursors, *e.g.*, couplers, to form larger colored chromophores in the hair shaft. The chromophores formed in the hair shaft do not readily diffuse out of the hair during subsequent
25 washing with water and/or detergents because they are bigger, less polar and soluble than dye precursors that diffused in.

Hair colorant products are typically sold in the form of kits containing a dye component (e.g., a dye solution) and an oxidizing component (e.g., a hydrogen peroxide solution). In use, the dye component is mixed with the oxidizing component and the resultant mixture is applied to
30 hair. When the two components are mixed, oxidizing agents present in the oxidizing component begins to oxidize primary intermediates present in the dye component and the oxidized primary intermediates begin to react with couplers to form chromophores. Since coloring hair is one of the beauty routines, it is highly desirable that the dyeing process, excluding bleaching, be rather a

physical process, which would allow it to be aligned with many other beauty routines such as applying lip color and facial touchups. The challenge is to still meet all of the other requirements of hair color (e.g., washfastness, little or no bleeding of color from the hair when it is wet, evenness).

5 Many attempts have been made by the hair color industry to enhance the washfastness of direct dyes by either forming a covalent bond between chromophore and proteins inside hair or increasing the number of binding sites, typically cationic centers, on the chromophore. However, each attempt has its drawbacks. The approach through covalent bonding does not differentiate proteins in hair from skin. The approach through multiple binding sites on the dyes (*i.e.* multiple
10 positive charges to interact with negative sites on hair, either by bonding several monocationic dyes together or by installing multiple cationic centers on a single chromophore) runs into the obstacles of uneven color due to uneven damage (negative charges) along the length of the hair fibers and reduced dye penetration into hair fibers because the dyes are typically at least twice as large as common oxidative dye precursors. An increase in the number of binding sites minimizes
15 bleeding and color loss caused by rinsing by providing stronger hair-chromophore interactions. However, the same strong binding force to the cuticle also prevents the chromophores from penetrating deep into the cortex of hair, because it is difficult for dyes with multiple positive charges to diffuse through negatively charged networks of keratin proteins. Additionally, since polycationic dyes remain bound to the hair surface rather than penetrating into the fiber, it's
20 difficult to produce dark shades due to limited binding sites on the surface of hair.

Accordingly, there is a need for a direct dye compound with improved washfastness without the drawbacks previously described.

SUMMARY OF THE INVENTION

25 Described herein is a the hair a hair color composition comprising one or more direct dye compounds and one or more additional ingredients, the one or more direct dye compounds each comprising (i) a chromophore; (ii) one or two permanent cations, wherein the permanent cations are pendant to the chromophore or part of the chromophore, and wherein the chromophore and the permanent cations form a core structure; and (iii) one to four incipient cations, wherein the
30 one to four incipient cations are pendant to the core structure, and wherein the incipient cations are neutral; wherein the one or more direct dye compounds enter the hair shaft after the hair color composition is applied to the hair; and wherein the hair color composition has a pH of from about 7 to about 11.

DETAILED DESCRIPTION OF THE INVENTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified. When more than one composition is used during a treatment, as in mixing of the components of a typical oxidative dye product, the total weight to be considered is the total weight of all the compositions applied on the hair simultaneously (i.e. the weight found "on head") unless otherwise specified. The term "weight percent" may be denoted as "wt. %" herein.

As used herein, the term "hair" to be treated may be "living" i.e. on a living body or may be "non-living" i.e. in a wig, hairpiece or other aggregation of non-living keratinous fibers. Mammalian, particularly human, hair is preferred. However, wool, fur, and other keratin containing fibers are suitable substrates for the compositions according to the present invention.

As used herein, the term "pendant group" means a group of atoms attached to the core structure or chromophore. As described herein, the pendant group itself is not colored although it may influence the color of the chromophore. The pendant group may be further classified as an anchoring group or a hydrophobic group. A hydrophobic group is typically a carbon chain. An anchoring group is a group attached to either a permanent cation or incipient cation, occasionally it is attached to both a permanent cation and one or more incipient cations.

As used herein, the term "chromophore" means the part of the direct dye compound responsible for its color.

As used herein, the term "direct dye compound" means a dye used in a process in which dye molecules are attracted by physical forces at the molecular level to a textile or substrate such as the hair. As opposed to oxidative dyes, there is no chemical reaction required to form the chromophore. Additionally, there is no covalent bond formation between the direct dye and the substrate as opposed to reactive dyes. The direct dye compound does not undergo a chemical transformation before and after the dyeing process.

As used herein, the term "core structure" means the chromophore including one or two permanent cations that are pendant to the chromophore or part of the chromophore. In an

embodiment, the chromophore is charged. In an embodiment, the chromophore is not charged as the permanent cation is pendant to the chromophore.

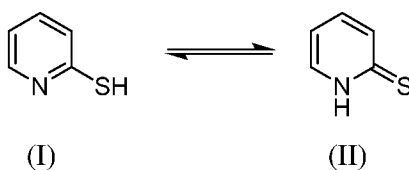
As used herein, the term “pendant” means when a functional group is linked to a core structure via covalent bond.

5 As used herein, the term “incipient cation” means a functional group that goes from neutral to positively charged due to protonation during a drop in pH.

As used herein, the term “non-anionic foaming agent” is a material that facilitates formation of foam. The term typically refers to a surfactant which, when present in small amounts, reduces the surface tension of a liquid or increases its colloidal stability by inhibiting
10 coalescence of bubbles.

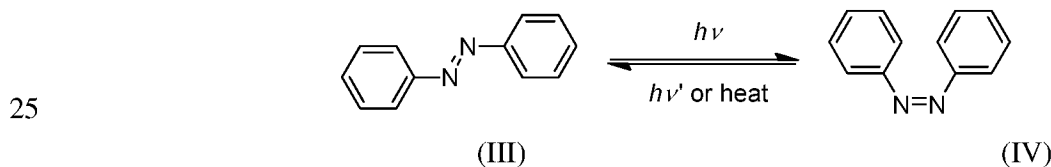
The hair colorant compositions of the present invention comprise one or more washfast direct dyes, optionally, oxidative dyes as well.

With regards to the direct dye compounds described herein, numerous tautomeric compounds may be involved. Thus, for example, 2-mercaptopyridine (I) may exist under known
15 conditions in the pyridine-2-thione tautomer form (II).



It is to be understood that when this development refers to a particular structure, all of the reasonable additional tautomeric structures are included. In the art, tautomeric structures are
20 frequently represented by one single structure and the method described herein follows this general practice.

It is also understood that within the scope of this invention, E, Z isomers may be involved. Thus, for example, (*E*)-diphenyldiazene (III) converts under known conditions to (*Z*)-diphenyldiazene (IV), which is also reversible.



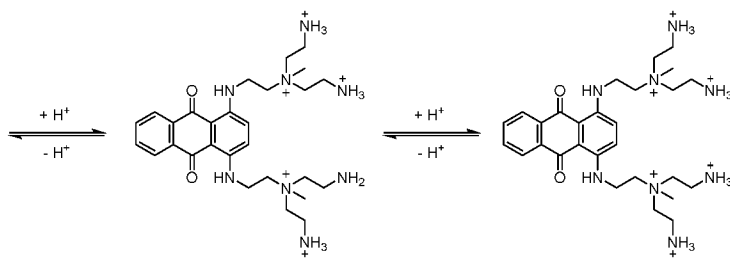
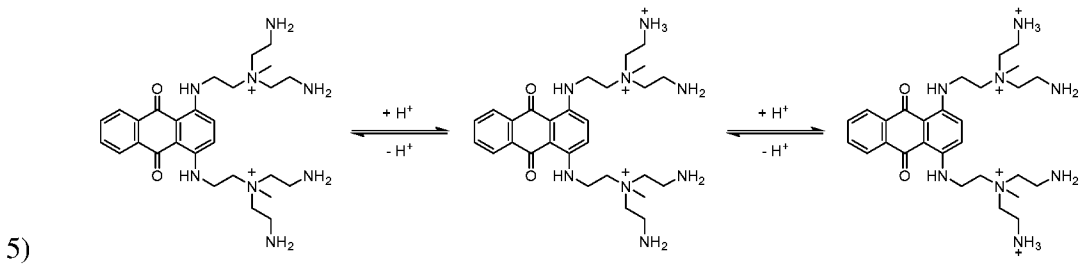
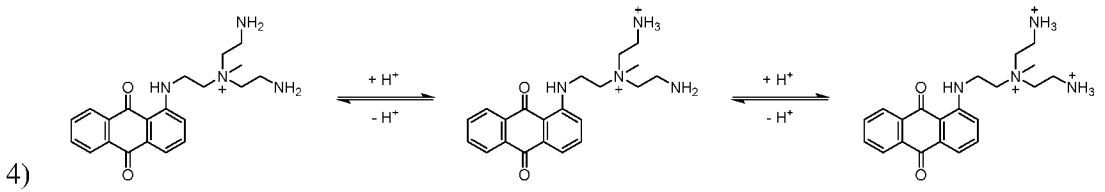
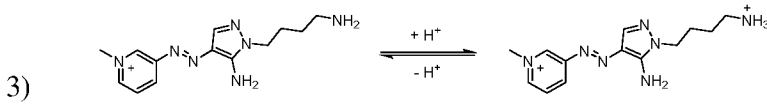
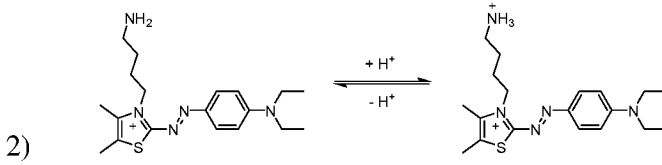
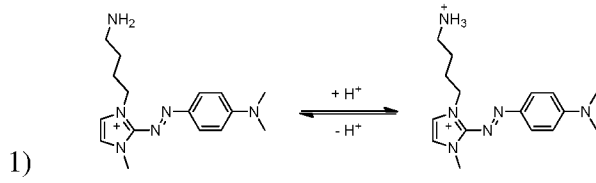
It is to be understood that when this development refers to a particular structure, all of the reasonable additional E, Z isomers are included.

I. Washfast Direct Dyes

Described herein is a hair color composition comprising one or more direct dye compounds; the one or more direct dye compounds each comprising (i) a chromophore; (ii) one or two permanent cations, wherein the permanent cations are pendant to the chromophore or part of the chromophore, and wherein the chromophore and the permanent cations form a core structure; and (iii) one to four incipient cations, wherein the one to four incipient cations are pendant to the core structure, and wherein the incipient cations are neutral; wherein the one or more direct dye compounds enter the hair shaft after the hair color composition is applied to the hair; and wherein the hair color composition has a pH of from about 7 to about 11.

The one to four incipient cations, typically an amino group or groups, are attached to the chromophore in addition to the existing permanent cation(s) to overcome the problems encountered in previous attempts to make cationic direct dyes more washfast. The chromophore would typically carry only one or two permanent positive charges such as quaternary ammonium salts, pyridinium, imidazolium, thiazolium, oxazolium, triazolium, pyrimidinium, triazinium, tetrazolium phenoxazinium, phenazinium or an analogous cation under basic conditions for typical hair color applications. The amino group(s) would remain mostly neutral under dyeing conditions (pH 10~11) because the typical pK_a of aliphatic amines falls between 9~10.5. The dye would carry only one or two cationic charges under dyeing conditions, which provides the needed affinity (Coulombic attraction) for optimized uptake without preventing penetration due to relatively low charge density compared to polycationic dyes. However, once the coloring application is done and hair is rinsed, pH inside hair drops back to its natural pH, which is acidic, the amino group(s) attached to the chromophore would be protonated to become an ammonium cation, which adds one or more binding sites to the chromophore. The pH change functions as a convenient switch to turn on additional binding group(s) to make the chromophores more washfast. Primary amines work the best when compared to secondary and tertiary amines for the following two reasons: 1. primary amines resist oxidation by hydrogen peroxide, while secondary and tertiary amines can be oxidized and lose their anchoring capability when used together with a bleaching agent; 2. the protonated primary ammonium cation is the smallest in size, which allows stronger interaction with anions on hair compared to secondary and tertiary amines with more steric hindrance. The following are examples of washfast dyes wherein one or more incipient cations change from neutral to positively charged due to the decrease of pH:

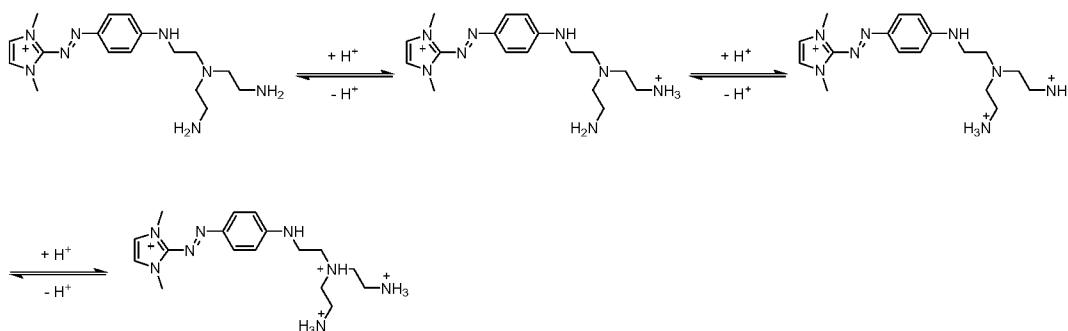
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6)

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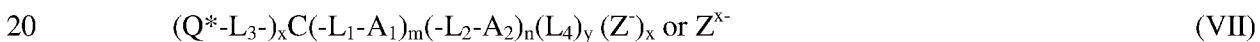
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The linker groups, typically linear alkyl groups, would also function as modulators for the overall hydrophobicity of the dye. One of the common drawbacks of using exclusively cationic direct dyes for shading is off-tone fading as different dyes would be washed off hair at different rates, causing undesirable gradual color shift over time. Our technical approach minimizes off-tone fading by designing dyes of different colors with identical charge patterns with similar overall hydrophobicity, at the mean time, the fact that these inventive dyes are far more washfast than typical cationic dyes also contributes to minimal color lost and on-tone fading.

The direct dye compounds may be substituted with one permanent cationic charge, alternatively two permanent cationic charges. The direct dye compounds may comprise and one to four terminal amino groups and derivatives thereof, alternatively two terminal amino groups and derivatives thereof, and alternatively one terminal amino group and derivatives thereof, according to the following formula:

The chemical formulas of the direct dye compounds can be represented in the following ways, but not limited to what is shown below:



wherein

C is a chromophore;

Q* is an organic cation;

* stands for a permanent cationic charge, it can also be part of a chromophore bearing a cationic charge;

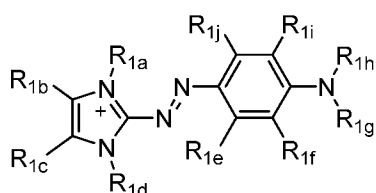
L is a linker or hydrophobic chain and;

A is the anchoring group, the fastness enhancer. It is typically a primary, secondary or tertiary amino group, preferably a primary amine. It is also a switch to allow the anchor to go between neutral and charged states when the pH in the surrounding environment changes.

Z is a counter anion. It is typically a halide, sulfate, methylsulfate, hydrogen sulfate, phosphate, hydrogen phosphate, dihydrogen phosphate, nitrate, perchlorate, tetrafluoroborate, hexafluorophosphate, triflate, acetate, formate or hydroxide.

$n = 1\sim 4$; $m = 1\sim 4$; $n+m \leq 4$; $x = 1\sim 2$; $y = 0\sim 2$.

In some embodiments, C is of formula Xa



(Xa)

10 wherein

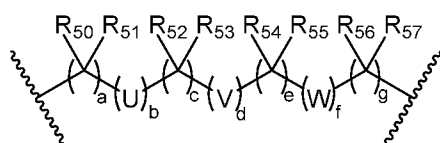
R_{1b}, R_{1c}, R_{1e}, R_{1f}, R_{1i}, R_{1j} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

15 R_{1h} and R_{1g} are each independently hydrogen, C₁-C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{1a} and R_{1d} are each independently C₁-C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached;

20 The total number of amino groups attached to R_{1a}, R_{1d}, R_{1g} and R_{1h} is 1-4; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In some embodiments, L is of formula (XI)



(XI)

wherein

L is covalently linked to the chromophore C of formula (Xa); L can be linked to C either by its left-hand or right-hand side.

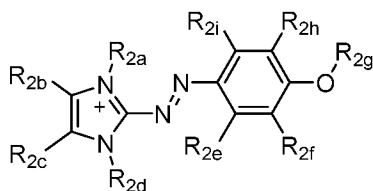
a, c, e and g are each independently an integer from 0 - 3, provided that the sum of a, c, e and g is greater than or equal to 2; b, d and f are each independently either 0 or 1; R₅₀, R₅₁, R₅₂, R₅₃, R₅₄, R₅₅, R₅₆ and R₅₇ are each independently hydrogen or C₁-C₂ alkyl group;

U is an aromatic ring, alkenyl or alkynyl moiety;

V is a hetero atom O, N or S;

W is a cyclic aliphatic ring.

5 In other embodiments, the chromophore C is of formula (Xb);



(Xb)

wherein

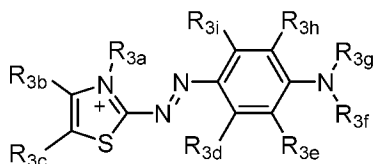
10 R_{2b}, R_{2c}, R_{2e}, R_{2f}, R_{2h}, R_{2i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{2g} is hydrogen, C₁-C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

15 R_{2a} and R_{2d} are each independently C₁-C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{2a}, R_{2d} and R_{2g} is 1-3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xc);



(Xc)

20 wherein

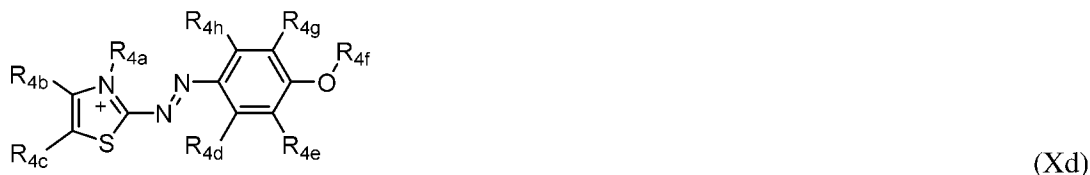
R_{3b}, R_{3c}, R_{3d}, R_{3e}, R_{3h}, R_{3i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

25 R_{3f} and R_{3g} are each independently hydrogen, C₁-C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{3a} is C_1 – C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{3a} , R_{3f} and R_{3g} is 1–3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

5 In other embodiments, the chromophore C is of formula (Xd);



wherein

R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4g} , R_{4h} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{4f} is hydrogen, C_1 – C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

15 R_{4a} is C_1 – C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{4a} and R_{4f} is 1 or 2; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xe);



20 wherein

R_{5c} , R_{5d} , R_{5e} , R_{5f} , R_{5g} , R_{5h} and R_{5i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

25 R_{5a} is linker group L with a cationic moiety attached, the cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; R_{5a} can also take on the

following form as $L_1-Q^*(-L_2A)_n$, where L_1 and L_2 can be the same or different, Q^* is the cationic moiety, A is an amino group and n is either 1 or 2; and

R_{5b} is a hydrogen, alkyl or linker group L with a primary, secondary or tertiary amino group attached;

- 5 The total number of amino groups attached to R_{5a} and R_{5b} is 1, 2 or 3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xf);



wherein

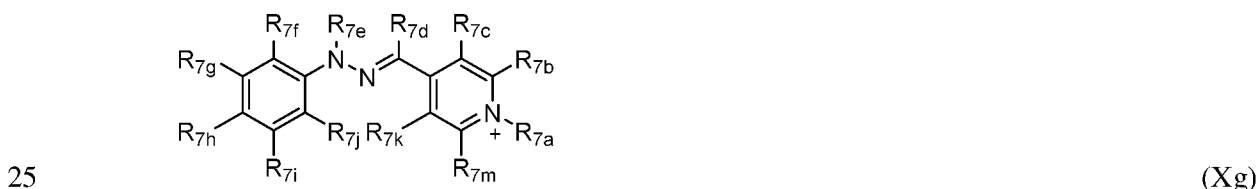
- 10 R_{6c} , R_{6d} , R_{6e} , R_{6g} , R_{6h} , R_{6i} and R_{6j} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

- R_{6a} and R_{6e} are each independently linker group L with a cationic moiety attached, the
15 cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; R_{6a} and R_{6e} can also each independently take on the following form as $L_1-Q^*(-L_2A)_n$, where L_1 and L_2 can be the same or different, Q^* is the cationic moiety, A is an amino group and n is either 1 or 2; and

- R_{6b} and R_{6f} are each independently a hydrogen, alkyl or linker group L with a primary,
20 secondary or tertiary amino group attached;

The total number of amino groups attached to R_{6a} , R_{6b} , R_{6e} and R_{6f} is 1, 2, 3 or 4; amino group can be primary, secondary or tertiary; the total number of cationic moiety attached to R_{6a} and R_{6e} is 1 or 2; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xg);



25

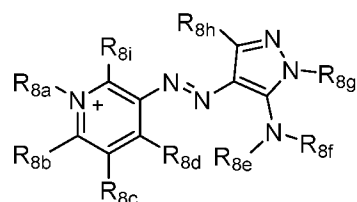
wherein

R_{7b} , R_{7c} , R_{7d} , R_{7f} , R_{7g} , R_{7h} , R_{7i} , R_{7j} , R_{7k} and R_{7m} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

5 R_{7a} and R_{7e} are each independently C_1 - C_8 alkyl or a linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{7a} and R_{7e} is 1 or 2; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xh);



10

(Xh)

wherein

R_{8b} , R_{8c} , R_{8d} , R_{8h} and R_{8i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

15

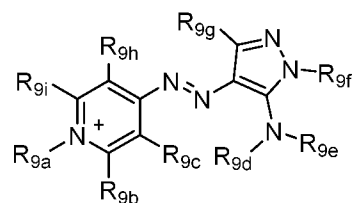
R_{8e} and R_{8f} are each independently hydrogen, C_1 - C_8 alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{8a} and R_{8g} are each independently C_1 - C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

20

The total number of amino groups attached to R_{8a} , R_{8g} , R_{8e} and R_{8f} is 1-4; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xi);



(Xi)

wherein

25

R_{9b} , R_{9c} , R_{9g} , R_{9h} and R_{9i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano,

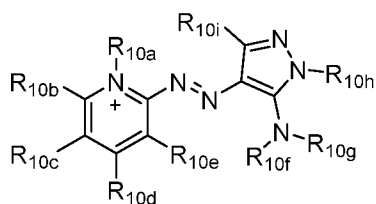
a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{9a} and R_{9f} are each independently C₁–C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

5 R_{9d} and R_{9e} are each independently hydrogen, C₁–C₈ alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{9a}, R_{9d}, R_{9e} and R_{9f} is 1–4; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xj);



10

(Xj)

wherein

R_{10b}, R_{10c}, R_{10d}, R_{10e} and R_{10i} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

15

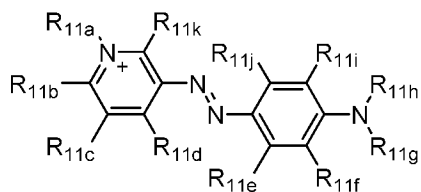
R_{10a} and R_{10h} are each independently C₁–C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{10f} and R_{10g} are each independently hydrogen, C₁–C₈ alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

20

The total number of amino groups attached to R_{10a}, R_{10f}, R_{10g} and R_{10h} is 1–4; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xk);



(Xk)

wherein

25

R_{11b}, R_{11c}, R_{11d}, R_{11e}, R_{11f}, R_{11g}, R_{11h}, R_{11j} and R_{11k} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen,

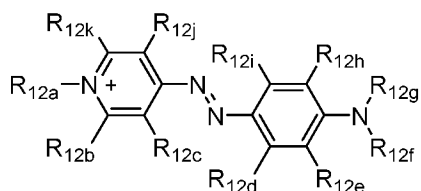
nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{11a} is C_1 - C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

5 R_{11g} and R_{11h} are each independently hydrogen, C_1 - C_8 alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{11a} , R_{11g} and R_{11h} is 1-3; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (XI);



(XI)

wherein

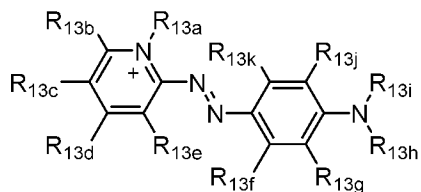
R_{12b} , R_{12c} , R_{12d} , R_{12e} , R_{12h} , R_{12i} , R_{12j} and R_{12k} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{12a} is C_1 - C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{12f} and R_{12g} are each independently hydrogen, C_1 - C_8 alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{12a} , R_{12f} and R_{12g} is 1-3; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xm);



(Xm)

wherein

R_{13b} , R_{13c} , R_{13d} , R_{13e} , R_{13f} , R_{13g} , R_{13j} and R_{13k} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen,

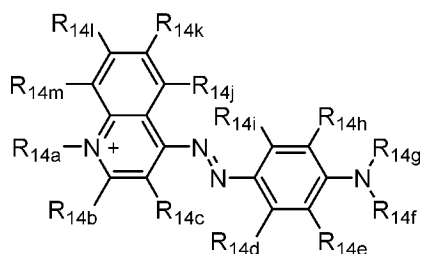
nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{13a} is C₁–C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

5 R_{13h} and R_{13i} are each independently hydrogen, C₁–C₈ alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{13a}, R_{13f} and R_{13g} is 1–3; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xn);



(Xn)

wherein

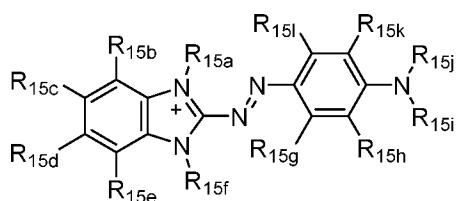
R_{14b}, R_{14c}, R_{14d}, R_{14e}, R_{14h}, R_{14i}, R_{14j}, R_{14k}, R_{14l} and R_{14m} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{14a} is C₁–C₈ alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

R_{14g} and R_{14h} are each independently hydrogen, C₁–C₈ alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{14a}, R_{14f} and R_{14g} is 1–3; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xo);



(Xo)

wherein

R_{15b}, R_{15c}, R_{15d}, R_{15e}, R_{15g}, R_{15h}, R_{15k} and R_{15l} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen,

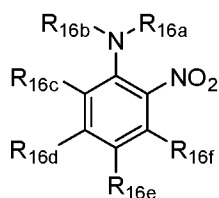
nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

R_{15a} and R_{15f} are each independently C_1-C_8 alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

5 R_{15i} and R_{15j} are each independently hydrogen, C_1-C_8 alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached; and

The total number of amino groups attached to R_{15a} , R_{15f} , R_{15i} and R_{15j} is 1–4; amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xp);



10 (Xp)

wherein

R_{16c} , R_{16d} , R_{16e} and R_{16f} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group;

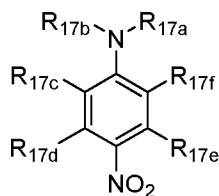
15 and

R_{16a} is linker group L with a cationic moiety attached, the cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; R_{16a} can also take on the following form as $L_1-Q^*(-L_2A)_n$, where L_1 and L_2 can be the same or different, Q^* is the cationic moiety, A is an amino group; and n is either 1 or 2; and

20 R_{16b} is a hydrogen, alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{16a} and R_{16b} is 1, 2 or 3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xq);



25 (Xq)

wherein

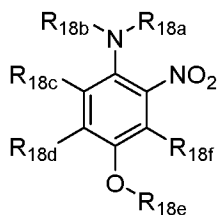
R_{17c} , R_{17d} , R_{17e} and R_{17f} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

5 R_{17a} is linker group L with a cationic moiety attached, the cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; R_{17a} can also take on the following form as $L_1-Q^*(-L_2A)_n$, where L_1 and L_2 can be the same or different, Q^* is the cationic moiety, A is an amino group; and n is either 1 or 2; and

10 R_{17b} is a hydrogen, alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{17a} and R_{17b} is 1, 2 or 3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xr);



(Xr)

15 wherein

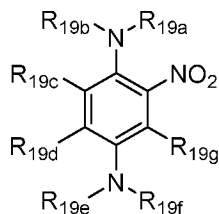
R_{18c} , R_{18d} and R_{18f} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

20 R_{18a} is linker group L with a cationic moiety attached, the cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; R_{18a} can also take on the following form as $L_1-Q^*(-L_2A)_n$, where L_1 and L_2 can be the same or different, Q^* is the cationic moiety, A is an amino group; and n is either 1 or 2; and

25 R_{18b} and R_{18e} are each independently a hydrogen, alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{18a} , R_{18b} and R_{18e} is 1, 2 or 3; the amino group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

In other embodiments, the chromophore C is of formula (Xs);



(Xs)

wherein

R_{19c}, R_{19d} and R_{19g} are each independently hydrogen, alkyl, halogen substituted alkyl, alkenyl, alkynyl, aryl, hydroxyl alkyl, alkoxy, aryloxy, acyl, halogen, nitro, nitroso, cyano, a
 5 heterocyclic moiety, thioether or are attached to linker L with or without a terminal amino group; and

One of R_{19a} and R_{19e} is linker group L with a cationic moiety attached, the cationic group is quaternary ammonium, imidazolium, pyridinium, oxazolium or thiazolium; it can also take on the following form as L₁-Q*(-L₂A)_n, where L₁ and L₂ can be the same or different, Q* is the
 10 cationic moiety, A is an amino group; and n is either 1 or 2; and the other one is a hydrogen, alkyl, hydroxyl alkyl or attached to an amino group through linker L; and

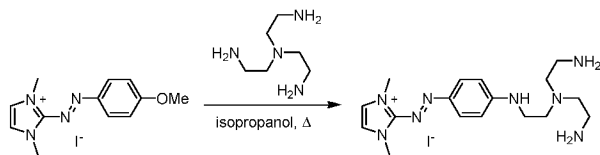
R_{19b} and R_{19e} are each independently a hydrogen, alkyl, hydroxyl alkyl or linker group L with a primary, secondary or tertiary amino group attached;

The total number of amino groups attached to R_{19a}, R_{19b}, R_{19e} and R_{19f} is 1–4; the amino
 15 group can be primary, secondary or tertiary; and cosmetically acceptable salt thereof.

The following are examples of the synthesis of various washfast direct dye compounds as described herein:

20 Example 1

In example 1, the permanent cation is part of the chromophore and resides on the imidazolium moiety. The incipient cations are linked to the chromophore via ethylene groups.



(XII)

Method

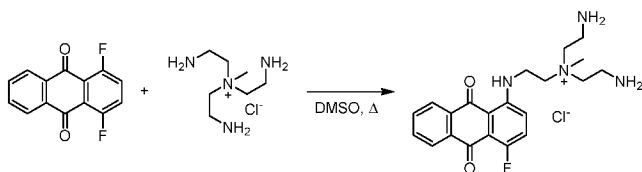
2-((4-methoxyphenyl)diazenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (500 mg) was suspended in isopropanol (20 mL), then added dropwise to 10 eq. of tris(2-aminoethyl)amine in refluxing isopropanol (100 mL) to produce the red dye 2-((4-((2-(bis(2-aminoethyl)amino)ethyl)amino)phenyl)diazenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide in near quantitative yield. The desired red dye was purified on preparative HPLC with C18 reverse phase column and water/acetonitrile (with 0.1% TFA) as mobile phase. The final product (XII) was collected as a trifluoroacetate salt.

¹H NMR: (600.1 MHz, D₂O) δ = 2.84 (2 H, t, J = 6.4 Hz), 2.86 (4 H, t, J = 6.4 Hz), 3.05 (4 H, t, J = 6.4 Hz), 3.41 (2 H, t, J = 6.4 Hz), 3.88 (6 H, s), 6.74 (2 H, d, J = 9.1 Hz), 7.28 (2 H, s), 7.85 (2 H, d, J = 8.9 Hz).

¹³C NMR: (150.9 MHz, D₂O) δ = 35.82, 36.79, 39.58, 50.30, 51.00, 112.83, 116.37 (q, J_{C-F} = 292.7 Hz), 122.30, 144.69, 145.21, 155.73, 162.93 (q, J_{C-F} = 35.2 Hz).

15 Example 2

In example 2, the permanent cation is not part of the chromophore. It is linked to the chromophore via an ethylene group. Incipient cations are connected to the chromophore via the permanent cation.



20

(XIII)

Method

1,4-Difluoroanthraquinone (240 mg) was mixed with *N,N,N*-tris(2-aminoethyl)-*N*-methylammonium chloride (1.1 eq.) in DMSO (20 mL). The mixture was heated at 85 °C for 12 hours until all the difluoroanthraquinone had been consumed. The resulting red dye 2-amino-*N*-(2-aminoethyl)-*N*-(2-((4-fluoro-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)ethyl)-*N*-methylethan-1-aminium salt was purified on C18 reverse phase column with water/acetonitrile (with 0.1% TFA) as mobile phase. The final product (XIII) was collected as its corresponding trifluoroacetate salt.

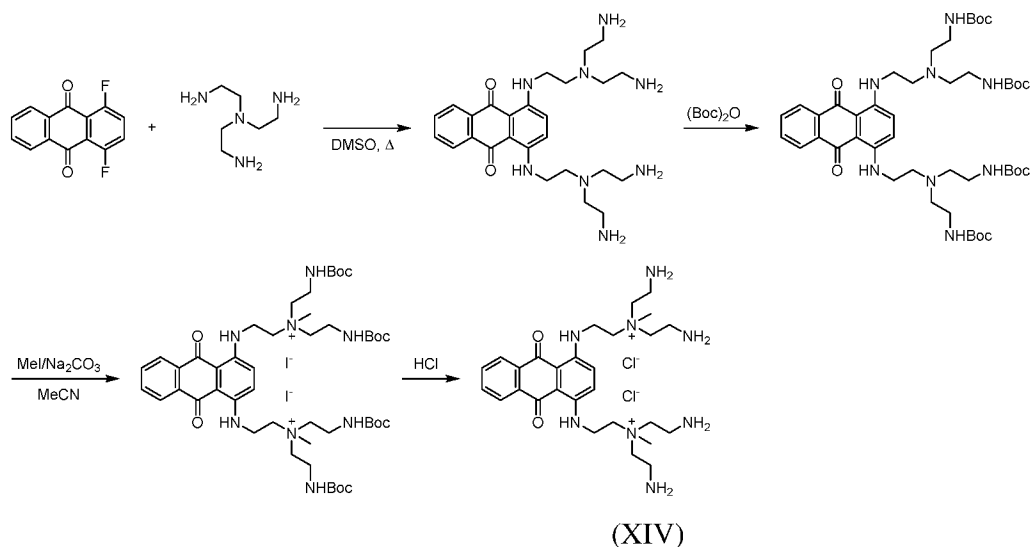
25

^1H NMR: (600.1 MHz, D_2O) δ = 3.38 (3 H, s), 3.59 (4 H, t, J = 8.2 Hz), 3.77 (4 H, dd, J_1 = 9.4 Hz, J_2 = 4.6 Hz), 3.85~3.93 (4 H, m), 6.85 (1 H, dd, J_1 = 9.5 Hz, J_2 = 3.8 Hz), (1 H, dd, J_1 = 11.3 Hz, J_2 = 9.8 Hz), 7.50~7.56 (3 H, m), 7.65~7.66 (1 H, m).

^{13}C NMR: (150.9 MHz, D_2O) δ = 32.42, 35.97, 49.51, 58.24, 61.86, 111.34, 116.31 (q, $J_{\text{C-F}}$ = 291.6 Hz) 118.65, 121.05 (d, $J_{\text{C-F}}$ = 8.81 Hz), 126.20 (d, $J_{\text{C-F}}$ = 17.6 Hz), 126.79 (d, $J_{\text{C-F}}$ = 26.4 Hz), 131.93, 132.64, 134.07, 134.83, 147.18, 152.85, 154.57, 162.79 (q, $J_{\text{C-F}}$ = 35.6 Hz), 182.69, 184.30 (d, $J_{\text{C-F}}$ = 4.41 Hz).

Example 3

10 The dye in example 3 is constructed in a similar fashion as in example 2, but with twice the anchoring power. The color is blue instead of red.



Method

15 1,4-Difluoroanthraquinone was treated with 4 eq. of tris(2-aminoethyl)amine in DMSO, the mixture was heated until all anthraquinone starting material was consumed. The resulting blue dye, 1,4-bis((2-(bis(2-aminoethyl)amino)ethyl)amino)anthraquinone, was treated with $(\text{Boc})_2\text{O}$ to yield tetra Boc protected intermediate, which was then quaternized with MeI in acetonitrile. The Boc group was removed by HCl to yield the final product, 2,2'-((anthraquinone-1,4-
20 diyl)bis(azanediyl))bis(N,N-bis(2-aminoethyl)-N-methylethan-1-ammonium) chloride.

^1H NMR: (600.1 MHz, D_2O) δ = 3.39 (6 H, s), 3.57 (8 H, t, J = 8.3 Hz), 3.86~3.93 (12 H, m), 3.96 (4 H, t, J = 6.2 Hz), 7.01 (2 H, s), 7.64 (2 H, dd, J_1 = 5.9 Hz, J_2 = 3.3 Hz), 7.81 (2 H, dd, J_1 = 5.8 Hz, J_2 = 3.4 Hz).

^{13}C NMR: (150.9 MHz, D_2O) δ = 32.62, 36.08, 49.77, 58.19, 62.42, 110.42, 124.23, 125.82, 133.15, 133.34, 144.97, 182.93.

Exemplary Formulations

	% by weight
Composition A	
Washfast Direct Dye ¹	0.50
Ammonium Hydroxide (aq. 28% active)	4.50
Water	95.00
Composition B	
Washfast Direct Dye ¹	0.50
Ammonium carbonate	10.00
Water	89.50
Composition C	
Washfast Direct Dye ¹	0.50
FlexiThix™ ³	5.00
Phenoxyethanol	0.30
Sodium Benzoate	0.30
Disodium EDTA	0.10
Ammonium Hydroxide (aq. 28% active)	4.00
Water	89.80
Composition D	
Washfast Direct Dye ¹	0.50
Aculyn™ 46 ⁴	15.80
Phenoxyethanol	0.30
Sodium Benzoate	0.30
Disodium EDTA	0.10
Ammonium Hydroxide (aq. 28% active)	4.00
Water	79.00
Composition E	
Washfast Direct Dye ¹	0.50
Plantaren® 2000 N UP ²	20.00
Phenoxyethanol	0.30

Sodium Benzoate	0.30
Disodium EDTA	0.10
Ammonium Hydroxide (aq. 28% active)	4.00
Water	74.80
Composition F	
Washfast Direct Dye ¹	0.50
Non-anionic foaming agent	5.00
Phenoxyethanol	0.30
Sodium Benzoate	0.30
Disodium EDTA	0.10
Ammonium Hydroxide (aq. 28% active)	4.00
Water	89.80

¹: The washfast direct dye may be any washfast direct dye described herein

²: (chemical makeup supplied by BASF)

³: PVP polymer supplied by Ashland

⁴: PEG-150/Stearyl/SMDI copolymer supplied by Rhom and Haas

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The hair color compositions described herein may be formed as thick liquid, cream, gel, emulsion, foam, aerosol mousse or as a solid form to which water is added to generate the oxidant and form a thickened vehicle suitable for hair coloring. They may comprise in addition to the ingredients indicated above further ingredients in order to further enhance the properties of the composition, including but not limited to: solvents; oxidative dyes, direct dyes; oxidizing agents; radical scavengers; thickeners and or rheology modifiers; chelants; pH modifiers and buffering agents; carbonate ion sources; peroxymonocarbonate ion sources; anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, or mixtures thereof; anionic, cationic, nonionic, amphoteric or zwitterionic polymers, or mixtures thereof; fragrances; enzymes; dispersing agents; peroxide stabilizing agents; antioxidants; natural ingredients, e.g. proteins and protein compounds, and plant extracts; conditioning agents including silicones and cationic polymers, ceramides, preserving agents; and opacifiers and pearling agents (such as titanium dioxide and mica). Some adjuvants referred to above, but not specifically described below, which are suitable are listed in the International Cosmetics Ingredient Dictionary and Handbook, (8th ed.; The Cosmetics, Toiletry, and Fragrance Association). Particularly, vol. 2, sections 3 (Chemical

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15

20

Classes) and 4 (Functions) are useful in identifying specific adjuvants to achieve a particular purpose or multipurpose. A few of these ingredients are discussed hereinbelow, whose disclosure is of course non-exhaustive.

5 **Optional Ingredients**

The hair color compositions described herein may comprise, in addition to the ingredients indicated above, optional ingredients in order to further enhance the properties of the composition.

Suitable optional ingredients include, but are not limited to: solvents; oxidizing agents; 10 alkalizing agents; oxidative dye precursors, direct dyes; chelants; radical scavengers; pH modifiers and buffering agents; thickeners and/or rheology modifiers; carbonate ion sources; peroxy monocarbonate ion sources; anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, and mixtures thereof; anionic, cationic, nonionic, amphoteric or zwitterionic 15 polymers, and mixtures thereof; fragrances; enzymes; dispersing agents; peroxide stabilizing agents; antioxidants; natural ingredients (such as proteins, protein compounds, and plant extracts); conditioning agents (such as silicones and cationic polymers); ceramides; preserving agents; opacifiers and pearling agents (such as titanium dioxide and mica); and mixtures thereof. Suitable further ingredients referred to above, but not specifically described below, are listed in 20 the International Cosmetics Ingredient Dictionary and Handbook, (8th ed.; The Cosmetics, Toiletry, and Fragrance Association). Particularly, vol. 2, sections 3 (Chemical Classes) and 4 (Functions), which are useful in identifying specific adjuvants to achieve a particular purpose or multipurpose. A few of these ingredients are discussed hereinbelow, whose disclosure is of course non-exhaustive.

25 **Solvents**

The hair color compositions described herein may further comprise a solvent. The solvent may be selected from water or a mixture of water and at least one organic solvent to dissolve the compounds that would not typically be sufficiently soluble in water.

Suitable organic solvents include, but are not limited to: C1 to C4 lower alkanols (such as 30 ethanol, propanol, isopropanol); aromatic alcohols (such as benzyl alcohol and phenoxyethanol); polyols and polyol ethers (such as carbitols, 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether, monomethyl ether, hexylene glycol,

glycerol, ethoxy glycol, butoxydiglycol, ethoxydiglycerol, dipropyleneglycol, polyglycerol); propylene carbonate; and mixtures thereof.

In an embodiment, the solvent may be selected from the group consisting of water, ethanol, propanol, isopropanol, glycerol, 1,2-propylene glycol, hexylene glycol, ethoxy diglycol,
5 and mixtures thereof.

The composition may comprise water as a main ingredient, particularly in a total amount ranging from at least about 50%, alternatively from at least about 60%, alternatively from at least about 70%, by weight of the total composition. In an embodiment, the composition may comprise a total amount of organic solvents ranging from about 1% to about 30%, by weight of the total
10 hair color composition.

Oxidizing Agent

The hair color composition described herein may comprise at least one source of an oxidizing agent. Preferred oxidizing agents for use herein are water soluble peroxygen oxidizing
15 agents. Water-soluble peroxygen oxidizing agents are well known in the art and include, but are not limited to, hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate and sodium peroxide and organic peroxides such as urea peroxide, melamine peroxide, and inorganic perhydrate salt bleaching compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulfates and the like. These inorganic perhydrate salts may be
20 incorporated as monohydrates, tetrahydrates etc. Alkyl and aryl peroxides, and or peroxidases, oxidases, and uricases and their substrates may also be used. Mixtures of two or more such oxidizing agents can also be used if desired. The oxidizing agents may be provided in aqueous solution or as a powder which is dissolved prior to use. In an embodiment, the oxidizing agents may be selected from the group consisting of hydrogen peroxide, percarbonate, persulfates and
25 combinations thereof.

In an embodiment, the hair color composition may comprise from 0.1% to 20% by weight, or from 1% to 15% by weight, or from 2% to 10% by weight of the oxidizing agent.

A potential oxidizing agent for use herein is a source of peroxymonocarbonate ions formed in situ from a source of hydrogen peroxide and a hydrogen carbonate ion source.
30 Moreover, this system is also particularly effective in combination with a source of ammonia or ammonium ions. Accordingly, any source of these peroxymonocarbonate ions may be used. Suitable sources for use herein include sodium, potassium, guanidine, arginine, lithium, calcium, magnesium, barium, ammonium salts of carbonate, carbamate and hydrocarbonate ions and

mixtures thereof such as sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, guanidine carbonate, guanidine hydrogen carbonate, lithium carbonate, calcium carbonate, magnesium carbonate, barium carbonate, ammonium carbonate, ammonium hydrogen carbonate and mixtures thereof. Percarbonate salts may be used both as an oxidizing agent and as a source of carbonate ions. Preferred sources of carbonate ions, carbamate and hydrocarbonate ions are sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium carbamate, and mixtures thereof.

The oxidizing agent may comprise from 0.1% to 15% by weight, or from 1% to 10% by weight, or from 1% to 8% by weight of a hydrogen carbonate ion; and from 0.1% to 10% by weight, or from 1% to 7% by weight, or from 2% to 5% by weight of the oxidizing agent of a source of hydrogen peroxide.

Alkalizing agent

The hair color composition described herein may further comprise an alkalizing agent as known in the art. Any alkalizing agent known in the art may be used such as ammonia, alkanolamines for example monoethanolamine, diethanolamine, triethanolamine, monopropylamine, dipropylamine, tripropylamine, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-1,3-propanediol, guanidinium salts, alkali metal and ammonium hydroxides such as sodium hydroxide, alkali metal and ammonium carbonates, and mixtures thereof. In an embodiment, the alkalizing agent may be ammonia and/or monoethanolamine.

The hair color compositions described herein may comprise from about 0.1% to about 10%, preferably from about 0.5% to about 6%, more preferably from about 1% to about 4% by weight of the alkalizing agent relative to the total weight of the composition.

The hair colorant compositions described above may have a pH of from 7 to 12, alternatively from 8 to 11. For embodiments comprising a peroxydicarbonate ion, the pH may be up to and including pH 9.5, alternatively from 7.5 to 9.5, alternatively from 8.4 to 9.5, alternatively from 8.5 to 9.4, alternatively 9.0, and alternatively 9.3.

Any sub-components of the hair color compositions, such as a tint composition or an oxidizing composition, may have a different pH from the hair colorant composition. For example, if the tint composition comprises an alkalizing agent, the tint composition will have an alkaline pH, such as higher than 7. In an embodiment, the oxidizing composition may comprise an acidic pH of less than 7.

When the hair color composition described herein is obtained by mixing a developer and a tint composition prior to use, the alkalizing agent is generally present in the tint composition.

Oxidative dye precursors

5 In addition to the direct dye compounds described herein, the hair color composition may further comprise one or more oxidative dye precursors, which are usually classified either as primary intermediates (also known as developers) or couplers (also known as secondary intermediates). Various couplers may be used with primary intermediates in order to obtain different shades. Oxidative dye precursors may be free bases or the cosmetically acceptable salts
10 thereof.

In an embodiment, the hair color composition may comprise a total amount of oxidative dye precursors ranging up to about 12%, alternatively from about 0.1% to about 10%, alternatively from about 0.3% to about 8%, alternatively from about 0.5% to about 6%, by weight of the total composition.

15 Suitable primary intermediates include, but are not limited to: toluene-2,5-diamine, p-phenylenediamine, *N*-phenyl-p-phenylenediamine, *N,N*-bis(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, hydroxypropyl-bis-(*N*-hydroxyethyl-p-phenylenediamine), 2-methoxymethyl-p-phenylenediamine, 2-(1,2-dihydroxyethyl)-p-phenylenediamine, 2,2'-(2-(4-aminophenylamino)ethylazanediyloxy)ethane, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol,
20 2-(7-amino-2H-benzo[*b*][1,4]oxazin-4(3H)-yl)ethanol, 2-chloro-p-phenylenediamine, p-aminophenol, p-(methylamino)phenol, 4-amino-*m*-cresol, 6-amino-*m*-cresol, 5-ethyl-*o*-aminophenol, 2-methoxy-p-phenylenediamine, 2,2'-methylenebis-4-aminophenol, 2,4,5,6-tetraminopyrimidine, 2,5,6-triamino-4-pyrimidinol, 1-hydroxyethyl-4,5-diaminopyrazole sulfate, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-ethylpyrazole, 4,5-diamino-1-isopropylpyrazole,
25 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, (2,3-diamino-6,7-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazol-1-one dimethanesulfonate), 4,5-diamino-1-hexylpyrazole, 4,5-diamino-1-heptylpyrazole, methoxymethyl-1,4-diaminobenzene, *N,N*-bis(2-hydroxyethyl)-*N*-(4-aminophenyl)-1,2-diaminoethane, 2-[(3-aminopyrazolo[1,5-*a*]pyridin-2-yl)oxy]ethanol hydrochloride, salts thereof and mixtures thereof.

30 Suitable couplers include, but are not limited to: resorcinol, 4-chlororesorcinol, 2-chlororesorcinol, 2-methylresorcinol, 4,6-dichlorobenzene-1,3-diol, 2,4-dimethylbenzene-1,3-diol, *m*-aminophenol, 4-amino-2-hydroxytoluene, 2-methyl-5-hydroxyethylaminophenol, 3-amino-2,6-dimethylphenol, 3-amino-2,4-dichlorophenol, 5-amino-6-chloro-*o*-cresol, 5-amino-4-

chloro-*o*-cresol, 6-hydroxybenzomorpholine, 2-amino-5-ethylphenol, 2-amino-5-phenylphenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol, 5-methyl-2-(methylamino)phenol, 2,4-diaminophenoxyethanol, 2-amino-4-hydroxyethylaminoanisole, 1,3-bis-(2,4-diaminophenoxy)-propane, 2,2'-(2-methyl-1,3-phenylene)bis(azanediy)diethanol, 5 benzene-1,3-diamine, 2,2'-(4,6-diamino-1,3-phenylene)bis(oxy)diethanol, 3-(pyrrolidin-1-yl)aniline, 1-(3-(dimethylamino)phenyl)urea, 1-(3-aminophenyl)urea, 1-naphthol, 2-methyl-1-naphthol, 1,5-naphthalenediol, 2,7-naphthalenediol or 1-acetoxy-2-methylnaphthalene, 4-chloro-2-methylnaphthalen-1-ol, 4-methoxy-2-methylnaphthalen-1-ol, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-pyridinediamine, 3-amino-2-methylamino-6-10 methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, pyridine-2,6-diol, 5,6-dihydroxyindole, 6-hydroxyindole, 5,6-dihydroxyindoline, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,2,4-trihydroxybenzene, 2-(benzo[d][1,3]dioxol-5-ylamino)ethanol (also known as hydroxyethyl-3,4-methylenedioxyaniline), and mixtures thereof.

When the hair color composition described herein is obtained by mixing a tint 15 composition and a developer composition, the primary intermediates and couplers may be incorporated into the tint composition.

Additional Direct Dyes

The hair color composition may further comprise additional compatible direct dyes, in an 20 amount sufficient to provide additional coloring, particularly with regard to intensity. In an embodiment, the composition may comprise a total amount of direct dyes ranging from about 0.05% to about 4%, by weight of the total composition.

Suitable direct dyes include but are not limited to: Acid dyes such as Acid Yellow 1, Acid Orange 3, Acid Black 1, Acid Black 52, Acid Orange 7, Acid Red 33, Acid Yellow 23, Acid Blue 25 9, Acid Violet 43, HC Blue 16, Acid Blue 62, Acid Blue 25, Acid Red 4; Basic Dyes such as Basic Brown 17, Basic Red 118, Basic Orange 69, Basic Red 76, Basic Brown 16, Basic Yellow 57, Basic Violet 14, Basic Blue 7, Basic Blue 26, Basic Red 2, Basic Blue 99, Basic Yellow 29, Basic Red 51, Basic Orange 31, Basic Yellow 87, Basic Blue 124, 4-(3-(4-amino-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)propyl)-4-methylmorpholin-4-ium-methylsulfate, (*E*)-1-(2-(4-30 (4,5-dimethylthiazol-2-yl)diazenyl)phenyl)(ethylamino)ethyl)-3-methyl-1*H*-imidazol-3-ium chloride, (*E*)-4-(2-(4-(dimethylamino)phenyl)diazenyl)-1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate, (*E*)-4-(4-(2-methyl-2-phenylhydrazono)methyl)pyridinium-1-yl)butane-1-sulfonate, N,N-dimethyl-3-(4-(methylamino)-9,10-dioxo-4a,9,9a,10-tetrahydroanthracen-1-

ylamino)-N-propylpropan-1-aminium bromide; Disperse Dyes such as Disperse Red 17, Disperse Violet 1, Disperse Red 15, Disperse Black 9, Disperse Blue 3, Disperse Blue 23, Disperse Blue 377; Nitro Dyes such as 1-(2-(4-nitrophenylamino)ethyl)urea, 2-(4-methyl-2-nitrophenylamino)ethanol, 4-nitrobenzene-1,2-diamine, 2-nitrobenzene-1,4-diamine, Picramic acid, HC Red No. 13, 2,2'-(2-nitro-1,4-phenylene)bis(azanediyl)diethanol, HC Yellow No. 5, HC Red No. 7, HC Blue No.2, HC Yellow No. 4, HC Yellow No. 2, HC Orange No. 1, HC Red No. 1, 2-(4-amino-2-chloro-5-nitrophenylamino)ethanol, HC Red No. 3, 4-amino-3-nitrophenol, 4-(2-hydroxyethylamino)-3-nitrophenol, 2-amino-3-nitrophenol, 2-(3-(methylamino)-4-nitrophenoxy)ethanol, 3-(3-amino-4-nitrophenyl)propane-1,2-diol, HC Yellow No. 11, HC Violet No. 1, HC Orange No. 2, HC Orange No. 3, HC Yellow No. 9, HC Red No. 10, HC Red No. 11, 2-(2-hydroxyethylamino)-4,6-dinitrophenol, HC Blue No. 12, HC Yellow No. 6, HC Yellow No. 12, HC Blue No. 10, HC Yellow No. 7, HC Yellow No. 10, HC Blue No. 9, 2-chloro-6-(ethylamino)-4-nitrophenol, 6-nitropyridine-2,5-diamine, HC Violet No. 2, 2-amino-6-chloro-4-nitrophenol, 4-(3-hydroxypropylamino)-3-nitrophenol, HC Yellow No. 13, 6-nitro-1,2,3,4-tetrahydroquinoxaline, HC Red No. 14, HC Yellow No. 15, HC Yellow No. 14, N2-methyl-6-nitropyridine-2,5-diamine, N1-allyl-2-nitrobenzene-1,4-diamine, HC Red No. 8, HC Green No.1, HC Blue No. 14; Natural dyes such as Annato, Anthocyanin, Beetroot, Carotene, Capsanthin, Lycopene, Chlorophyll, Henna, Indigo, Cochineal; and mixtures thereof.

When the hair color composition is obtained by mixing a tint composition and a developer composition, the additional direct dyes may be incorporated into the tint composition.

Chelants

The hair color composition described herein may further comprise chelants (also known as “chelating agent”, “sequestering agent”, or “sequestrant”) in an amount sufficient to reduce the amount of metals available to interact with formulation components, particularly oxidizing agents, more particularly peroxides. Chelants are well known in the art and a non-exhaustive list thereof can be found in AE Martell & RM Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and AE Martell & RD Hancock, Metal Complexes in Aqueous Solution, Plenum Press, New York & London (1996), both incorporated herein by reference.

In an embodiment, the hair color composition may comprise a total amount of chelants ranging from at least about 0.01%, alternatively from about 0.01% to about 5%, alternatively

from about 0.25% to about 3%, alternatively from about 0.5% to about 1%, by weight of the total composition.

Suitable chelants include, but are not limited to: carboxylic acids (such as aminocarboxylic acids), phosphonic acids (such as aminophosphonic acids), polyphosphoric acids (such as linear polyphosphoric acids), their salts thereof, and mixtures thereof. By “salts thereof”, it is meant – in the context of chelants – all salts comprising the same functional structure as the chelant they are referring to and including alkali metal salts, alkaline earth salts, ammonium salts, substituted ammonium salts, and mixtures thereof; alternatively sodium salts, potassium salts, ammonium salts, and mixtures thereof; alternatively monoethanolammonium salts, diethanolammonium salts, triethanolammonium salts, and mixtures thereof.

Suitable aminocarboxylic acid chelants comprise at least one carboxylic acid moiety (-COOH) and at least one nitrogen atom. Suitable aminocarboxylic acid chelants include, but are not limited to: diethylenetriamine pentaacetic acid (DTPA), ethylenediamine disuccinic acid (EDDS), ethylenediamine diglutamic acid (EDGA), 2-hydroxypropylenediamine disuccinic acid (HPDS), glycylamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), ethylenediaminetetraacetic acid (EDTA), ethylenedicysteic acid (EDC), ethylenediamine-N,N'-bis(ortho-hydroxyphenyl acetic acid) (EDDHA), diaminoalkyldi(sulfosuccinic acids) (DDS), N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED), their salts thereof, and mixtures thereof. Other suitable aminocarboxylic type chelants include, but are not limited to: iminodiacetic acid derivatives such as N-2-hydroxyethyl N,N diacetic acid or glyceryl imino diacetic acid, iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid, β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid chelants, ethanoldiglycine acid, their salts thereof, their derivatives thereof, and mixtures thereof. Further suitable aminocarboxylic type chelants include, but are not limited to: dipicolinic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, their salts thereof, their derivatives thereof, and mixtures thereof.

Suitable aminophosphonic acid chelants comprise an aminophosphonic acid moiety (-PO₃H₂) or its derivative - PO₃R₂, wherein R₂ is a C₁ to C₆ alkyl or aryl radical and salts thereof. Suitable aminophosphonic acid chelants include, but are not limited to: aminotri-(1-ethylphosphonic acid), ethylene-diaminetetra-(1-ethylphosphonic acid), aminotri-(1-propylphosphonic acid), aminotri-(isopropylphosphonic acid), their salts thereof, and mixtures

thereof; alternatively aminotri-(methylenephosphonic acid), ethylene-diamine-tetra-(methylenephosphonic acid) (EDTMP) and diethylene-triamine-penta-(methylenephosphonic acid) (DTPMP), their salts thereof, their derivatives thereof, and mixtures thereof.

Suitable alternative chelants include, but are not limited to: polyethyleneimines, polyphosphoric acid chelants, etidronic acid, methylglycine diacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, minodisuccinic acid, N,N-Dicarboxymethyl-L-glutamic acid, N-lauroyl-N,N',N''-ethylenediamine diacetic acid, their salts thereof, their derivatives thereof, and mixtures thereof.

In a specific embodiment, the composition comprises a chelant selected from the group consisting of diethylenetriamine-N,N',N''-polyacids, diethylenetriaminepentaacetic acid (DTPA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), diamine-N,N'-dipolyacid, monoamine monoamide-N,N'-dipolyacid, ethylenediaminedisuccinic acid (EDDS), their salts thereof, their derivatives thereof, and mixtures thereof; alternatively ethylenediaminedisuccinic acid (EDDS).

When the hair color composition is obtained by mixing a tint composition and a developer composition, the chelants may be incorporated in the tint composition and/or in the developer composition. A chelant may be present in the developer composition for stability.

Radical Scavengers

The hair color compositions described herein may comprise a radical scavenger. As used herein the term radical scavenger refers to a species that can react with a radical, to convert the radical species by a series of fast reactions to an unreactive or less reactive species. The radical scavenger is also preferably selected such that it is not an identical species as the alkalisng agent and is present in an amount sufficient to reduce the damage to the hair during the colouring /bleaching process. The compositions of the present invention comprise a radical scavenger from about 0.1% to about 10%, preferably from about 1% to about 7% by weight of the radical scavenger relative to the total weight of the composition.

Suitable radical scavengers for use herein may be selected from the classes of alkanolamines, amino sugars, amino acids, esters of amino acids and mixtures thereof. Suitable compounds include 3-substituted-pyrazol-5-ones, 3-carboxy-1H-pyrazol-5-one, 3-methyl-1-phenyl-pyrazol-5-one, 3-methyl-1-p-tolyl-pyrazol-5-one, 3-methyl-1-(4-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(4-sulfoamidophenyl)-pyrazol-5-one, 3-methyl-1-(3-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(3-sulfoamidophenyl)-pyrazol-5-one, 3-methyl-1-(2-chloro-5-sulfophenyl)-pyrazol-5-

one, 3-methyl-1-(2,5-dichloro-4-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(4-chlorophenyl)-pyrazol-5-one, 3-methyl-1-(4-carboxyphenyl)-pyrazol-5-one, 3-carboxy-1-phenyl-pyrazol-5-one, 3-carboxy-1-(4-sulfophenyl)-pyrazol-5-one, 1,3-diphenyl-pyrazol-5-one, methyl pyrazol-5-one-3-carboxylate, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 1-amino-2-propanol, 5 1-amino-2-butanol, 1-amino-2-pentanol, 1-amino-3-pentanol, 1-amino-4-pentanol, 3-amino-2-methylpropan-1-ol, 1-amino-2-methylpropan-2-ol, 3-aminopropane-1,2-diol, glucosamine, N-acetylglucosamine, glycine, arginine, lysine, proline, glutamine, histidine, sarcosine, serine, glutamic acid, tryptophan, or mixtures thereof, or the salts, such as the potassium, sodium, or ammonium salts thereof, or mixtures thereof. In some embodiments, the inventive compositions 10 may comprise glycine, sarcosine, lysine, serine, 2-methoxyethylamine, glucosamine, glutamic acid, morpholine, piperidine, ethylamine, 3-amino-1-propanol, or mixtures thereof.

pH Modifiers and buffering agents

The hair color compositions described herein may further comprise, in addition to the 15 alkalizing agent discussed above, a pH modifier and/or buffering agent in an amount that is sufficiently effective to adjust the pH of the composition to fall within a range from about 3 to about 13, alternatively from about 8 to about 12, alternatively from about 9 to about 11.

Suitable pH modifiers and/or buffering agents include, but are not limited to: ammonia; alkanolamides (such as monoethanolamine, diethanolamine, triethanolamine, 20 monopropylamine, dipropylamine, tripropylamine, tripropylamine, 2-amino-2-methyl-1-propanol, 2-amino-2-hydroxymethyl-1,3-propanediol); guanidium salts; alkali metal and ammonium hydroxides and carbonates; and mixtures thereof.

Further pH modifiers and/or buffering agents include, but are not limited to: sodium 25 hydroxide; ammonium carbonate; acidulents (such as inorganic and inorganic acids including for example phosphoric acid, acetic acid, ascorbic acid, citric acid or tartaric acid, hydrochloric acid); and mixtures thereof.

Thickeners and/or rheology modifiers

The hair color compositions described herein may further comprise a thickener in an 30 amount sufficient to provide the composition with a viscosity so that it can be readily applied to the hair without unduly dripping off the hair and causing mess.

In an embodiment, the hair color compositions may comprise a total amount of thickeners ranging from at least about 0.1%, alternatively at least about 1%, alternatively at least about 10%, alternatively at least about 20%, by weight of the total composition.

Suitable thickeners include, but are not limited to: associative polymers, polysaccharides, 5 non-associative polycarboxylic polymers, and mixtures thereof.

As used herein, the expression “associative polymers” means amphiphilic polymers comprising both hydrophilic units and hydrophobic units, for example, at least one C8 to C30 fatty chain and at least one hydrophilic unit. Associative polymers are capable of reversibly combining with each other or with other molecules. Suitable associative thickeners include, but 10 are not limited to: nonionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit; anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit; cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit; and amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit, and mixtures thereof.

Suitable nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit include, but are not limited to: celluloses modified with groups comprising at least one fatty chain (such as hydroxyethylcelluloses modified with groups comprising at least one fatty chain chosen from alkyl, alkenyl and alkylaryl groups); hydroxypropyl guar modified with groups comprising at least one fatty chain; polyether urethanes comprising at least one fatty 20 chain (such as C8-C30 alkyl or alkenyl groups); copolymers of vinylpyrrolidone and of fatty-chain hydrophobic monomers; copolymers of C1-C6 alkyl acrylates or methacrylates and of amphiphilic monomers comprising at least one fatty chain; copolymers of hydrophilic acrylates or methacrylates and of hydrophobic monomers comprising at least one fatty chain, and mixtures thereof. Commercially available anionic materials include those sold as Sepigel 305 by Seppic.

Suitable nonionic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit include, but are not limited to: those polymers comprising at least one fatty-chain allyl ether unit and at least one hydrophilic unit comprising an ethylenic unsaturated anionic monomeric unit (such as a vinylcarboxylic acid unit, particularly a unit chosen from units derived from acrylic acids, methacrylic acids, and mixtures thereof), wherein the fatty-chain allyl 30 ether unit corresponds to the monomer of formula (XV) below



in which R1 is chosen from H and CH3, B is an ethyleneoxy radical, n is chosen from zero and integers ranging from 1 to 100, R is chosen from hydrocarbon-based radicals chosen from alkyl,

alkenyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals, comprising from 8 to 30 carbon atoms, and, further, for example, from 10 to 24 carbon atoms and even further, for example, from 12 to 18 carbon atoms.

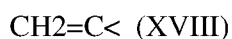
Suitable anionic amphiphilic polymers include, but are not limited to: those polymers comprising at least one hydrophilic unit of unsaturated olefinic carboxylic acid type, and at least one hydrophobic unit of the type such as a (C8-C30) alkyl ester or (C8-C30) oxyethylenated alkyl ester of an unsaturated carboxylic acid, wherein the hydrophilic unit of unsaturated olefinic carboxylic acid type corresponds to, for example, the monomer of formula (XVI) below



in which R1 is chosen from H, CH₃, C₂H₅ and CH₂COOH (i.e. acrylic acid, methacrylic, ethacrylic and itaconic acid units); and wherein the hydrophobic unit of the type such as a (C8-C30) alkyl ester or (C8-C30) oxyethylenated alkyl ester of an unsaturated carboxylic acid corresponds to, for example, the monomer of formula (XVII) below



in which R1 is chosen from H, CH₃, C₂H₅ and CH₂COOH (i.e. acrylate, methacrylate, ethacrylate and itaconate units), B is an ethyleneoxy radical, n is chosen from zero and integers ranging from 1 to 100, R2 is chosen from C8-C30 alkyl radicals, for example, C₁₂-C₂₂ alkyl radical. Anionic amphiphilic polymers may further be cross-linked. The crosslinking agent can be a monomer comprising a group (XVIII) below



with at least one other polymerizable group whose unsaturated bonds are not conjugated with respect to one another. Mention may be made, for example, of polyallyl ethers such as polyallylsucrose and polyallyl pentaerythritol.

Suitable cationic amphiphilic polymers include, but are not limited to: quaternized cellulose derivatives and polyacrylates comprising amino side groups. The quaternized cellulose derivatives are, for example, chosen from quaternized celluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, and mixtures thereof, quaternized hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, and mixtures thereof. The alkyl radicals borne by the above quaternized celluloses and hydroxyethylcelluloses, for example, contain from 8 to 30 carbon atoms. The aryl radicals, for example, are chosen from phenyl, benzyl, naphthyl and anthryl groups.

Suitable amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit, may be made, for example, of methacrylamidopropyltrimethylammonium chloride/acrylic acid/C8-C30 alkyl methacrylate copolymers, wherein the alkyl radical is, for example, a stearyl radical.

5 In an embodiment, the associative polymers may comprise at least one hydrophilic unit which is unsaturated carboxylic acid or its derivatives, and at least one hydrophobic unit which is a C8 to C30 alkyl ester or oxyethylenated C8-C30 alkyl ester of unsaturated carboxylic acid. The unsaturated carboxylic acid is preferably acrylic acid, methacrylic acid or itaconic acid. Commercially available materials include those sold as Aculyn-22 by Rohm & Haas; Permulen
10 TR1, Carbopol 2020, Carbopol Ultrez-21/-30 by Noveon, Structure 2001/3001 by National Starch. Other preferred associative polymers include polyether polyurethane, commercially available as Aculyn-44/-46 by Rohm and Haas. Further preferred associative polymers include cellulose modified with groups comprising at least one C8 – C30 fatty chain, commercially available under the trade name Natrosol Plus Grade 330 CS by Aqualon.

15 Suitable non-associative cross-linked polycarboxylic polymers include, but are not limited to: cross-linked acrylic acid homopolymers, copolymers of acrylic or (meth)acrylic acid and of C1-C6 alkyl acrylate or (meth)acrylate, and mixtures thereof. Commercially available materials include those sold as Carbopol 980/981/954/1382/2984/5984 by Noveon, Synthalen M/Synthalen L/Synthalen K/Synthalen CR by 3V, Aculyn-33 by Rohm and Haas.

20 Suitable polysaccharides include, but are not limited to: glucans, modified and unmodified starches (such as those derived, for example, from cereals, for instance wheat, corn or rice, from vegetables, for instance yellow pea, and tubers, for instance potato or cassava), amylose, amylopectin, glycogen, dextrans, celluloses and derivatives thereof (methylcelluloses, hydroxyalkylcelluloses, ethyl hydroxyethylcelluloses, and carboxymethylcelluloses), mannans,
25 xylans, lignins, arabans, galactans, galacturonans, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, alginic acid and alginates, arabinogalactans, carrageenans, agars, glycosaminoglucans, gum arabics, gum tragacanth, ghatti gums, karaya gums, carob gums, galactomannans, such as guar gums, and nonionic derivatives thereof (hydroxypropyl guar) and bio-polysaccharides, such as xanthan gums, gellan gums, welan
30 gums, scleroglucans, succinoglycans, and mixtures thereof. Suitable polysaccharides are described in “Encyclopedia of Chemical Technology”, Kirk-Othmer, Third Edition, 1982, volume 3, pp. 896-900, and volume 15, pp. 439-458, in “Polymers in Nature” by E. A. MacGregor and C. T. Greenwood, published by John Wiley & Sons, Chapter 6, pp. 240-

328,1980, and in “Industrial Gums—Polysaccharides and their Derivatives”, edited by Roy L. Whistler, Second Edition, published by Academic Press Inc., all three being incorporated herein by reference. A preferred polysaccharide is a bio-polysaccharide, particularly bio-polysaccharides selected from xanthan gum, gellan gum, welan gum, scleroglucan or succinoglycan; 5 commercially available as Keltrol® T by Kelco and Rheozan® by Rhodia Chimie. Another preferred polysaccharide is hydroxypropyl starch derivative, particularly hydroxypropyl starch phosphate, commercially available as Structure XL® by National Starch, a hydrophobically modified cellulose derivative, commercially available as Structure® Cel 500 HM by AkzoNobel.

Commercially available salt-tolerant thickeners include, but not limited to: xanthan, guar, 10 hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (commercially available as Aquacote), hydroxyethyl cellulose (Natrosol), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (Klucel), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (Natrosol Plus 330), polyvinylpyrrolidone (Povidone, FlexiThix™), Acrylates/Ceteth-20 Itaconate Copolymer 15 (Structure 3001), hydroxypropyl starch phosphate (Structure ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester such as PEG-150/Decyl/SMDI copolymer (Aculyn 44), PEG-150/Stearyl/SMDI copolymer (Aculyn 46), trihydroxystearin (Thixcin), acrylates copolymer (Aculyn 33) or hydrophobically modified acrylate copolymers (such as Acrylates / Steareth-20 Methacrylate Copolymer as Aculyn 22), acrylates/steareth-20 methacrylate crosspolymer (Aculyn 20 88), acrylates/vinyl neodecanoate crosspolymer (Aculyn 38), acrylates/behene-25 methacrylate copolymer (Aculyn 28), acrylates/C10-30 alkyl acrylate crosspolymer (Carbopol ETD 2020), non-ionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit selected from polyether urethanes comprising at least one fatty chain, blends of Ceteth – 10 phosphate, Dicetyl phosphate and Cetearyl alcohol (available as Crodafos CES), and mixtures 25 thereof.

Salt

In an embodiment, cosmetically acceptable salt, such as ammonium, sodium or potassium salts with appropriate counter ions, may be added to the hair color compositions described herein 30 to act as leveling agents to minimize patchy coloring results.

Carbonate ion sources

The hair color compositions described herein may further comprise a source of carbonate ions, carbamate ions, hydrogen carbonate ions, and mixtures thereof in a sufficient amount to reduce damage to the hair during the coloring process.

5 In an embodiment, the hair color compositions may comprise a total amount of a carbonate ion source ranging from about 0.1% to about 15%, alternatively from about 0.1% to about 10%, alternatively from about 1% to about 7%, by weight of the total composition.

Suitable carbonate ion sources include, but are not limited to: sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, guanidine carbonate, 10 guanidine hydrogen carbonate, lithium carbonate, calcium carbonate, magnesium carbonate, barium carbonate, ammonium carbonate, ammonium hydrogen carbonate and mixtures thereof; alternatively sodium hydrogen carbonate, potassium hydrogen carbonate, and mixtures thereof; alternatively ammonium carbonate, ammonium hydrogen carbonate, and mixtures thereof.

15 Conditioning agents

The hair color compositions described herein may further comprise a conditioning agent, and/or be used in combination with a composition comprising a conditioning agent.

In an embodiment, the hair color compositions may comprise a total amount of conditioning agents ranging from about 0.05% to about 20%, alternatively from about 0.1% to 20 about 15%, alternatively from about 0.2% to about 10%, alternatively from about 0.2% to about 2% 25, alternatively from about 0.5% to 2%, by weight of the total composition. The conditioning agent may be included in a separate pre- and/or post-treatment composition.

Suitable conditioning agents include, but are not limited to: silicones, aminosilicones, fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, cationic 25 surfactants, insoluble oils and oil derived materials and mixtures thereof. Additional conditioning agents include mineral oils and other oils such as glycerin and sorbitol.

Particularly useful conditioning materials may be cationic polymers. Conditioners of cationic polymer type can be chosen from those comprising units of at least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part 30 of the main polymer chain, or be borne by a side substituent that is directly attached to the main polymer chain, described hereinafter.

Suitable silicones include, but are not limited to: polyalkylsiloxane oils, linear polydimethylsiloxane oils containing trimethylsilyl or hydroxydimethylsiloxane endgroups,

polymethylphenylsiloxane, polydimethylphenylsiloxane or polydimethyldiphenylsiloxane oils, silicone resins, organofunctional siloxanes having in their general structure one or a number of organofunctional group(s), the same or different, attached directly to the siloxane chain and mixtures thereof. Said organofunctional group(s) may be selected from: polyethyleneoxy and/or
5 polypropyleneoxy groups, (per)fluorinated groups, thiol groups, substituted or unsubstituted amino groups, carboxylate groups, hydroxylated groups, alkoxyated groups, quaternium ammonium groups, amphoteric and betaine groups. The silicone can either be used as a neat fluid or in the form of a pre-formed emulsion. Suitable silicones also include: silicones containing groups that may be ionized into cationic groups, for example aminosilicones containing at least
10 10 repeating siloxane (Si(CH₃)₂-O) units within the polymer chain, with either terminal, graft, or a mixture of terminal and graft aminofunctional groups. Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutyl, aminopropyl. In the case of graft polymers, the terminal siloxane units can be (CH₃)₃Si-O, R₁₂(CH₃)₂Si-O, where R₁₂ can be either OH or OR₁₃, where R₁₃ is a C1-C8 alkyl group, or a mixture of both terminal groups. These
15 silicones are also available as preformed emulsions. Commercially available aminosilicones include those sold as DC-2-8566, DC 7224, DC-2-8220 by Dow Corning; SF1708, SM2125 by GE Silicones; Wacker Belsil ADM 653/ADM 1100/ADM 1600/ADM 652/ADM 6057E/ADM 8020 by Wacker Silicones; DC929, DC939, DC949 by Dow Corning; SM2059 by GE Silicones. Suitable aminosilicones may also contain additional functional groups, particularly additional
20 functional groups including polyoxyalkylene, the reaction product of amines and carbinols, and alky chains. Commercially available materials are known as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone (e.g. Abil Soft AF100, by Degussa), or as Bis(C13-15 Alkoxy)PG Amodimethicone (e.g. DC 8500, by Dow Corning).

Suitable cationic polymers include, but are not limited to: polymers comprising units of at
25 least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part of the main polymer chain or be borne by a side substituent that is directly attached to the main polymer chain. Such cationic polymers generally have a number average molecular mass ranging from about 500 to about 5 x 10⁶, alternatively from about 1000 to about 3 x 10⁶. Preferably the cationic polymers are selected from polymers of the polyamine, polyamino
30 amide and polyquaternary ammonium type.

Suitable polymers of the polyamine, polyamino amide and polyquaternary ammonium type include, but are not limited to:

1) Homopolymers and copolymers derived from acrylic or methacrylic esters or amides. Copolymers of these polymers may also comprise at least one unit derived from comonomers which may be chosen from the family of acrylamides, methacrylamides, diacetone acylamides, acrylamides and methacrylicamides substituted on the nitrogen with at least one group chosen
5 from lower (C1-C4) alkyls, acrylic and methacrylic acids and esters thereof, vinylactams such as vinylpyrrolidone and vinylcaprolactam, and vinyl esters. Suitable examples include copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium methosulfate, including polymers known as Polyquaternium-5 (e.g. commercially available under the trade name Reten 210/220/230/240/1104/1105/1006 by Hercules; Merquat 5/5 SF by Nalco); copolymers of
10 vinylpyrrolidone and dimethylaminopropyl methacrylamide, including polymers known as Polyquaternium-28 (e.g. Gafquat HS-100 by ISP); copolymers of vinyl pyrrolidone and dialkylaminoalkyl acrylates or methactylates, including polymers known as Polquaternium-11 (see Gafquat 440/734/755/755N by ISP; Luviquat PQ11 PM by BASF; Polyquat-11 SL by Sino Lion); copolymers vinylpyrrolidone, dimethylaminopropyl methacrylamide and
15 methacryloylaminopropyl lauryldimonium chloride, including polymers known as polyquaternium-55 (e.g. Styleze W-20 by ISP); copolymers of acrylic acid, acrylamide and methacrylamidopropyltrimonium chloride, including polymers known as Polyquaternium-53 (e.g. Merquat 2003 by Nalco); copolymers of dimethyaminopropylacrylate (DMAPA), acrylic acid and acrylonitrogens and diethyl sulphate, including polymers known as Polyquaternium-31 (e.g.
20 Hypan QT100 by Lipo); copolymers of acrylamide, acrylamidopropyltrimonium chloride, 2-amidopropylacrylamide sulfonate, and dimethyaminopropylacrylate (DMAPA), including polymers known as polyquaternium-43 (e.g. Bozequat 4000 by Clairant); copolymers of acrylic acid, methylacrylate and methacrylamidopropyltrimonium chloride, including polymers known as Polyquaternium-47 (e.g. Merquat 2001/2001N by Nalco); copolymers of methacryloyl ethyl
25 betaine, 2-hydroxyethyl methacrylate and methacryloyl ethyl trimethyl ammonium chloride, including polymers known as Polyquaternium-48 (e.g. Plascize L-450 by Goo Chemical); copolymers of acrylic acid diallyl dimethyl ammonium chloride and acrylamide, including polymers known as polyquaternium-39 (e.g. Merquat 3330/3331 by Nalco). Further suitable examples include copolymers of methacrylamide methacrylamido-propyltrimonium and
30 methacryloylethyltrimethyl ammonium chloride and their derivatives, either homo or copolymerised with other monomers, including polymers known as Polyquaternium-8, Polyquaternium-9, Polyquaternium-12, Polyquaternium-13 Polyquaternium-14, Polyquaternium-15 (e.g. Rohagit KF 720 F by Rohm), Polyquaternium-30 (e.g. Mexomere PX by Chimex),

Polyquaternium-33, Polyquaternium-35, Polyquaternium-36 (e.g. Plex 3074 L by Rhon), Polyquaternium 45 (e.g. Plex 3073L by Rohn), Polyquaternium 49 (e.g. Plascize L-440 by Goo Chemicals), Polyquaternium 50 (e.g. Plascize L-441 by Goo Chemicals), Polyquaternium-52.

2) Cationic polysaccharides, such as cationic celluloses and cationic galactomannan gums.

5 Among the cationic polysaccharides that maybe mentioned, for example, are cellulose ether derivatives comprising quaternary ammonium groups and cationic cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer and cationic galactomannan gums. Suitable examples include copolymers of hydroxyethylcelluloses and diallyldimethyl ammonium chlorides, including polymers known as Polyquaternium-4 (e.g. 10 Celquat L 200 and Celquat H 100 by National Starch); copolymers of hydroxyethylcelluloses and a trimethyl ammonium substituted epoxide, including polymers known as Polyquaternium-10 (e.g. AEC Polyquaternium-10 by A&E Connock; Catinal C-100/HC-35/HC-100/HC-200/LC-100/LC-200 by Toho; Celquat SC-240C/SC-230M by National Starch; Dekaquat 400/3000 by Dekker; Leogard GP by Akzo Nobel; RITA Polyquat 400/3000 by RITA; UCARE Polymer JR-15 125/JR-400/JR-30M/LK/LR 400/LR 30M by Amerchol); copolymers of hydroxyethylcelluloses and lauryl dimethyl ammonium substituted epoxides, including polymers known as Polyquaternium-24 (e.g. Quatrisoft polymer LM-200 by Amerchol); derivatives of hydroxypropyl guar, including polymers as guar hydroxypropyltrimonium chloride (e.g. Catinal CG-100, Catinal CG-200 by Toho; Cosmedia Guar C-261N, Cosmedia Guar C-261N, Cosmedia 20 Guar C-261N by Cognis; DiaGum P 5070 by Freedom Chemical Diamalt; N-Hance Cationic Guar by Hercules/Aqualon; Hi-Care 1000, Jaguar C-17, Jaguar C-2000, Jaguar C-13S, Jaguar C-14S, Jaguar Excel by Rhodia; Kipro gum CW, Kipro gum NGK by Nippon Starch); hydroxypropyl derivatives of guar hydroxypropyltrimonium chloride, including polymers known as hydroxypropyl guar hydroxypropyltrimonium chloride (e.g. Jaguar C-162 by Rhodia).

25 3) Polyamino amide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids followed by alkylation with difunctional agents. Among the derivative, mention may be made for example to adipic acid / dimethylaminohydroxypropyl / diethylenetriamine.

4) Polymers obtained by reaction of a polyalkylene polyamine comprising two primary 30 amines groups and at last one secondary amine group with a decarboxylic acid chosen from diglycolic acids and saturated aliphatic dicarboxylic acids comprising from 3 to 8 carbon atoms. Suitable examples include the polymer adipic acid / epoxypropyl / diethylenetriamine.

5) Cyclopolymers of dialkldiallylamine or of dialkyldiallylammonium, including: Dimethyldiallylammonium chloride polymers, including polymers known as Polyquaternium-6 (e.g. Merquat 100 by Nalco; Mirapol 100 by Rhodia; Rheocare CC6 by Cosmetic Rheologies; AEC polyquaternium-6 by A&E Connock; Agequat 400 by CPS; Conditioner P6 by 3V Inc.;
5 Flocare C106 by SNF; Genamin PDAC by Clariant; Mackernium 006 by McIntyre); copolymers of acrylamides and dimethyldiallylammonium chlorides monomers, including polymers known as Polyquaternium-7 (e.g. AEC Polyquaternium-7 by A&E Connock; Agequat-5008/C-505 by CPS; Conditioner P7 by 3V Inc.; Flocare C 107 by SNF; Mackernium 007/007S by McIntyre; ME
10 Polymer 09W by Toho; Merquat 550/2200/S by Nalco; Mirapol 550 by Rhodia; Rheocare CC7/CCP7 by Cosmetic Rheologies; Salcare HSP-7/SC10/ Super 7 by Ciba); copolymers of dimethyldiallylammoniumchlorides and acrylic acids, including polymers known as polyquaternary-22 (e.g. Merquat 280/Merquat 295 by Nalco).

6) Quaternary diammonium polymers comprising repeat units corresponding to $[-N+(R1)(R2) - A1 - N+(R3)(R4) - B1 -] [2X-]$, in which R1, R2, R3 and R4, which may be
15 identical or different, are chosen from aliphatic, alicyclic and arylaliphatic radicals comprising from 1 to 20 carbon atoms and from lower hydroxyalkylaliphatic radicals, or R1, R2, R3 and R4, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other than nitrogen, or R1, R2, R3 and
20 R4, are chosen from linear or branched C1-C6 alkyl radicals substituted with at least one group chosen from nitrile, ester, acyl and amide groups and groups of $-CO-O-R5-D$ and $-CO-NH-R5-D$ wherein R5 is chosen from alkylene groups and D is chosen from quaternary ammonium groups. A1 and B1, which may be identical or different, are chosen from linear and branched, saturated or unsaturated polymethylene groups comprising 2 to 20 carbon atoms. The
25 polymethylene groups may comprise, linked to or intercalated in the main ring, at least one entity chosen from aromatic rings, oxygen and sulphur atoms and sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary, ammonium, ureido, amide and ester groups, and X- is an anion derived from inorganic and organic acids. D is chosen from a glycol residue, a bis-secondary diamine residue, a bis-primary diamine residue or a ureylene group. Suitable examples
30 include polymers known as Hexadimethrine chloride, where R1, R2, R3 and R4 are each methyl radicals, A1 is $(CH_2)_3$ and B1 is $(CH_2)_6$ and X = Cl; as polyquaternium-34 where R1 and R2 are ethyl radicals and R3 and R4 are methyl radicals and A1 is $(CH_2)_3$ and B1 is $(CH_2)_3$ and X = Br (e.g. Mexomere PAX by Chimax).

7) Polyquaternary ammonium polymers comprising repeating units of formula $[-N+(R_6)(R_7)-(CH_2)_r-NH-CO-(CH_2)_q-(CO)_t-NH-(CH_2)_s-N+(R_8)(R_9)-A-]_n[X^-]$, in which R₆, R₇, R₈ and R₉ which may be identical or different, are chosen from a hydrogen atom and a methyl, ethyl, propyl, hydroxyethyl, hydroxypropyl, and $-CH_2CH_2(OCH_2CH_2)_pOH$ radicals, wherein p is equal to 0 or an integer ranging from 1 to 6, wherein R₆, R₇, R₈ and R₉ do not all simultaneously represent a hydrogen atom. R and s which may be identical or different are each an integer ranging from 1 to 6, q is equal to 0 or an integer ranging from 1 to 34 and X⁻ is anion such as a halide. T is an integer chosen to be equal to 0 or 1. A is chosen from divalent radicals such as $-CH_2-CH_2-O-CH_2-CH_2-$. Suitable examples include: polymers known as polyquaternium-2, where r=s=3, q=0, t=0, R₆, R₇, R₈ and R₉ are methyl groups, and A is $-CH_2-CH_2-O-CH_2-CH_2-$ (e.g. Ethpol PQ-2 from Ethox; Mirapol A-15 by Rhodia); as polyquaternium-17 where r=s=3, q=4, t=1 R₆, R₇, R₈ and R₉ are methyl groups, and A is $-CH_2-CH_2-O-CH_2-CH_2-$; as Polyquaternium 18, where r=s=3, q=7, t=1 R₆, R₇, R₈ and R₉ are methyl groups, and A is $-CH_2-CH_2-O-CH_2-CH_2-$; as the block copolymer formed by the reaction of Polyquaternium-2 with Polyquaternium-17, which are known as Polyquaternium 27 (e.g. Mirapol 175 by Rhodia).

8) Copolymers of vinylpyrrolidones and of vinylimidazoles and optionally vinylcaprolactams, including polymers known as Polyquaternary-16 formed from methylvinylimidazolium chlorides and vinylpyrrolidones (e.g. Luviquat FC370//FC550/FC905/HM-552 by BASF); copolymers of vinylcaprolactams and vinylpyrrolidones with methylvinylimidazolium methosulfates, including polymers known as Polyquaternium-46 (e.g. Luviquat Hold by BASF); copolymers of vinylpyrrolidones and quaternized imidazolines, including polymers known as polyquaternary 44 (e.g. Luviquat Care by BASF).

9) Polyamines such as Polyquart H sold by Cognis under the reference name polyethylene glycol (15) tallow polyamine.

10) Cross linked methacryloyloxy(C1-C4)alkyltri(C1-C4)alkylammonium salt polymers such as the polymers obtained by homopolymerisation of dimethylaminoethyl methacrylates quaternized with methyl chloride, or by copolymerisation of acrylamides with dimethylaminoethyl methacrylates quaternized with methyl chloride, the homo or copolymerisation being followed by crosslinking with a compound comprising olefinic unsaturation, such as methylenebisacrylamides, including polymers known as Polyquaternium-37 (e.g. Synthalen CN/CR/CU sold by 3V sigma; or as a dispersion in another media such as Salcare

SC95/SC96 by Ciba; Rheocare CTH(E) by Cosmetic Rheologies) and polymers known as Polyquaternium-32 (e.g. sold as a dispersion in mineral oil such as Salcare SC92 by Ciba).

11) Further examples of cationic polymers include polymers known as Polyquaternium 51 (e.g. Lipidure-PMB by NOF), as Polyquaternium 54 (e.g. Quality-Hy by Mitsui), as
5 Polyquaternium 56 (e.g. Hairrol UC-4 by Sanyo chemicals), as Polyquaternium 87 (e.g. Luviquat sensation by BASF).

12) Silicone polymers comprising cationic groups and/or groups which may be ionised into cationic groups. Suitable examples include cationic silicones of the general formula $(R_{10}-N+(CH_3)_2)-R_{11}-(Si(CH_3)_2-O)_x-R_{11}-(N+(CH_3)_2)-R_{10}$, where R10 is an alkyl derived from
10 coconut oil, and R11 is $(CH_2CHOCH_2O(CH_2)_3)$ and x is a number between 20 and 2000, including polymers known as Quaternium 80 (e.g. Abil Quat 3272/3474 sold by Goldschmidt); silicones containing groups which may be ionised into cationic groups, for example aminosilicones containing at least 10 repeating siloxane $-(Si(CH_3)_2-O)$ units within the polymer chain, with either terminal, graft or a mixture of terminal and graft aminofunctional groups.
15 Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutyl, aminopropyl. In the case of graft polymers, the terminal siloxane units can either be $(CH_3)_3Si-O$ or $R_{12}(CH_3)_2Si-O$, where R12 can be either OH or OR13, where R13 is a C1-C8 alkyl group, or a mixture of both functional terminal groups. These silicones are also available as preformed emulsions. Polymer with terminal siloxane units of $(CH_3)_3Si-O$ examples includes polymers
20 known as trimethylsilylamodimethicone (e.g. DC-2-8566, DC 7224, DC-2-8220 by Dow Corning; SF1708, SM 2125 GE Silicones; Wacker Belsil ADM 653 by Wacker silicones). Further examples include polymers with terminal siloxane units of $(R_{12O})(CH_3)_2Si-O$ where R12 can be either OH or OR13, where R13 is a C1-C8 alkyl group, or a mixture of both functional terminal groups, known as amodimethicone (e.g. Wacker Belsil ADM 1100/ADM 1600/ADM
25 652/ADM 6057E/ADM 8020 by Wacker Silicones; DC929, DC939, DC949 by Dow Corning; SM2059 by GE silicones). Silicones containing groups which may be ionised into cationic groups – for example silicones containing at least 10 repeating siloxane $-(Si(CH_3)_2-O)$ units within the polymer chain, with either terminal, graft or a mixture of terminal and graft aminofunctional groups, together with additional functional groups. Additional functional groups can include
30 polyoxyalkylene, the reaction product of amines and carbinols, alkyl chains. For example products known as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone (e.g. Abil Soft AF100 by Degussa). For example products known as Bis (C13-15 Alkoxy) PG Amodimethicone (e.g. DC 8500 by Dow Corning).

In an embodiment, the cationic polymer is selected from the group consisting of polyquaternium 37, polyquaternium 7, polyquaternium 22, polyquaternium 87, and mixtures thereof; alternatively from the group consisting of polyquaternium 37, polyquaternium 22, and mixtures thereof.

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Surfactants

The hair color compositions described herein may further comprise a surfactant. Suitable surfactants generally have a lipophilic chain length of from about 8 to about 30 carbon atoms and can be selected from anionic surfactants, nonionic surfactants, amphoteric surfactants, cationic surfactants, and mixtures thereof.

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In an embodiment, the hair color compositions may comprise a total amount of surfactants ranging from about 0.01% to about 60%, alternatively from about 0.05% to about 30%, alternatively from about 0.1% to about 25%, alternatively from about 0.1% to about 20%, by weight of the total composition.

15

The compositions may comprise a mixture of an anionic surfactant and an amphoteric surfactant with one or more nonionic surfactants. The composition may comprise a total amount of anionic surfactant ranging from about 0.01% to about 20%, alternatively from about 0.05% to about 15%, alternatively from about 0.1% to about 15%, by weight of the total composition; and a total amount of amphoteric and/or nonionic components, which may range independently from each other from about 0.01% to about 15%, alternatively from about 0.05% to about 10%, alternatively from about 0.1% to about 8%, by weight of the total composition.

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Suitable anionic surfactants include, but are not limited to: salts (such as alkaline salts, for example, sodium salts, ammonium salts, amine salts, amino alcohol salts and magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylaryl polyether sulphates, monoglyceride sulphates; alkyl sulphonates, alkyl phosphates, alkylamide sulphonates, alkylaryl sulphonates, α -olefin sulphonates, paraffin sulphonates; alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamide sulphosuccinates; alkyl sulphosuccinamates; alkyl sulphoacetates; alkyl ether phosphates; acyl sarcosinates; acyl isethionates; N-acyltaurates; and mixtures thereof. The alkyl or acyl radical of all of these various compounds, for example, comprises from 8 to 24 carbon atoms, and the aryl radical, for example, is chosen from phenyl and benzyl groups. Among the anionic surfactants, which can also be used, mention may also be made of fatty acid salts such as the salts of oleic, ricinoleic, palmitic and stearic acids, coconut oil acid or hydrogenated coconut oil acid; acyl lactylates in which the acyl

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radical comprises from 8 to 20 carbon atoms. Weakly anionic surfactants can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated (C₆-C₂₄) alkyl ether carboxylic acids, polyoxyalkylenated (C₆-C₂₄) alkylaryl ether carboxylic acids, polyoxyalkylenated (C₆-C₂₄) alkylamido ether carboxylic acids and their salts, for example, those comprising from 2 to 50 ethylene oxide groups, and mixtures thereof. Anionic derivatives of polysaccharides, for example carboxyalkyl ether of alkyl polyglucosides, can be also used.

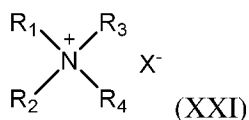
Nonionic surfactants are compounds that are well known (see, for example, in this respect "Handbook of Surfactants" by M. R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178). Suitable non-ionic surfactants include, but are not limited to: polyethoxylated, polypropoxylated and polyglycerolated fatty acids, alkyl phenols, α -diols and alcohols comprising a fatty chain comprising, for example, from 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene oxide groups to range, for example, from 2 to 200 and for the number of glycerol groups to range, for example, from 2 to 30. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide and their monoethanolamine and diethanolamine derivatives, polyglycerolated fatty amides, for example, comprising on average from 1 to 5, and such as from 1.5 to 4, glycerol groups; polyethoxylated fatty amines such as those containing from 2 to 30 mol of ethylene oxide; oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as (C₁₀-C₁₄)alkylamine oxides or N-acylaminopropylmorpholine oxides.

Suitable amphoteric surfactants include, but are not limited to: aliphatic secondary and tertiary amine derivatives in which the aliphatic radical is chosen from linear and branched chains comprising from 8 to 22 carbon atoms and comprising at least one water-soluble anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); mention may also be made of (C₈-C₂₀)alkylbetaines, sulphobetaines, (C₈-C₂₀)alkylamido(C₁-C₆)alkylbetaines or (C₈-C₂₀)alkylamido(C₁-C₆)alkylsulphobetaines. Among the amine derivatives, mention may be made of the products sold as Miranol, as described, for example, in U.S. Pat. Nos. 2,528,378 and 2,781,354 and having the structures of: R₂-CONHCH₂CH₂-N⁺(R₃)(R₄)(CH₂COO⁻), (XIX) in which: R₂ is chosen from alkyl radicals derived from an acid R₂-COOH present in hydrolysed coconut oil, and heptyl, nonyl and undecyl radicals, R₃ is a β -hydroxyethyl group and R₄ is a carboxymethyl group; and of R₅-CONHCH₂CH₂-N(B)(C) (XX) wherein B represents —

CH₂CH₂OX', C represents —(CH₂)_z—Y', with z=1 or 2, X' is chosen from the —CH₂CH₂—COOH group and a hydrogen atom, Y' is chosen from —COOH and —CH₂—CHOH—SO₃H radicals, R₅ is chosen from alkyl radicals of an acid R₅-COOH present in coconut oil or in hydrolysed linseed oil, alkyl radicals, such as C₇, C₉, C₁₁ and C₁₃ alkyl radicals, a C₁₇ alkyl radical and its iso form, and unsaturated C₁₇ radical. These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid, and cocoamphodipropionic acid. Salts of diethyl aminopropyl cocoaspartamid can be also used.

Suitable cationic surfactants include, but are not limited to, the quaternary ammonium salts A) to D) as defined hereinafter:

A) Quaternary ammonium salts of general formula (XXI) below:



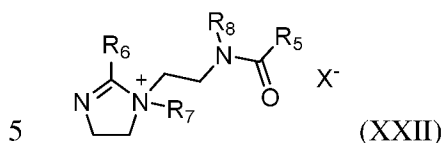
wherein X⁻ is an anion chosen from halides (chloride, bromide and iodide), (C₂-C₆)alkyl sulphates, such as methyl sulphate, phosphates, alkyl and alkylaryl sulphonates, and anions derived from organic acids, such as acetate and lactate, and wherein R₁ to R₄ are as below in i) or ii).

i) Radicals R₁ to R₃, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals may comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals may be chosen from: alkyl, alkoxy and alkylamide radicals. R₄ is chosen from linear and branched alkyl radicals comprising from 16 to 30 carbon atoms. A suitable cationic surfactant is, for example, a behenyltrimethylammonium salt (for example chloride).

ii) Radicals R₁ and R₂, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals may comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals may be chosen from alkyl, alkoxy, alkylamide and hydroxyalkyl radicals comprising from about 1 to 4 carbon atoms. Radicals R₃ and R₄, which may be identical or different, are chosen from linear and branched alkyl radicals comprising from 12 to 30 carbon atoms, the said alkyl radicals comprise at least one function

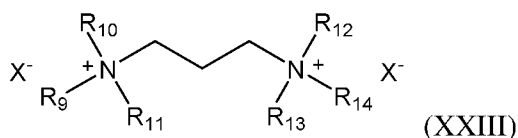
chosen from ester and amide functions. R_3 and R_4 may be chosen from $(C_{12}-C_{22})$ alkylamido(C_2-C_6)alkyl and $(C_{12}-C_{22})$ alkylacetate radicals. A suitable cationic surfactant is, for example, a dicetyldimethyl ammonium salt (for example chloride);

B) Quaternary ammonium salts of imidazolinium of formula (XXII) below:



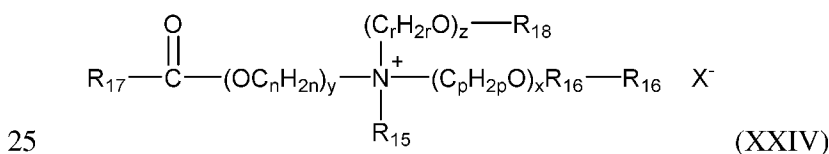
in which R_5 is chosen from alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms, for example fatty acid derivatives of tallow, R_6 is chosen from a hydrogen atom, C_1-C_4 alkyl radicals and alkenyl and alkyl radicals comprising from 8 to 30 carbon atoms, R_7 is chosen from C_1-C_4 alkyl radicals, R_8 is chosen from a hydrogen atom and C_1-C_4 alkyl radicals, and X^- is an anion
 10 chosen from halides, phosphates, acetates, lactates, alkyl sulphates, alkyl sulphonates and alkylaryl sulphonates. In one embodiment, R_5 and R_6 are, for example, a mixture of radicals chosen from alkenyl and alkyl radicals comprising from 12 to 21 carbon atoms, such as fatty acid derivatives of tallow, R_7 is methyl and R_8 is hydrogen. Such a product is, for example, Quaternium-27 (CTFA 1997) or Quaternium-83 (CTFA 1997), commercially available as
 15 “Rewoquat®” W75/W90/W75PG/W75HPG by Witco.

C) Diquaternary ammonium salts of formula (XXIII):



in which R_9 is chosen from aliphatic radicals comprising from about 16 to 30 carbon atoms, R_{10} , R_{11} , R_{12} , R_{13} and R_{14} , which may be identical or different, are chosen from hydrogen and alkyl
 20 radicals comprising from 1 to 4 carbon atoms, and X^- is an anion chosen from halides, acetates, phosphates, nitrates and methyl sulphates. Such diquaternary ammonium salts, for example, include propanetallowdiammonium dichloride.

D) Quaternary ammonium salts comprising at least one ester function, of formula (XXIV) below:



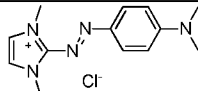
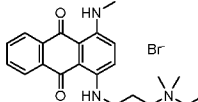
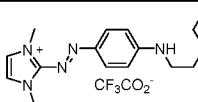
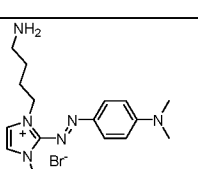
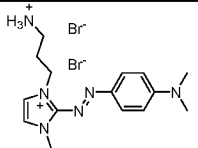
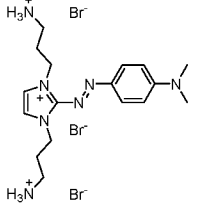
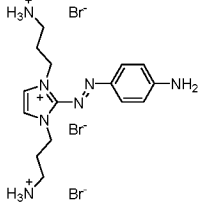
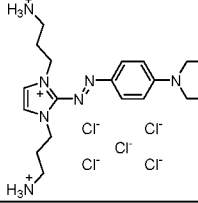
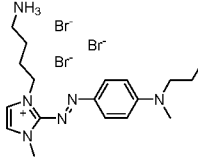
in which: R_{15} is chosen from C_1-C_6 alkyl radicals and C_1-C_6 hydroxyalkyl and dihydroxyalkyl radicals; R_{16} is chosen from: a radical $R_{19}C(O)-$, linear and branched, saturated and unsaturated

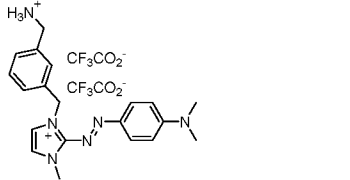
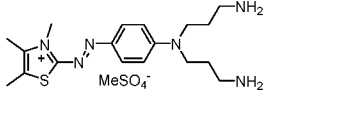
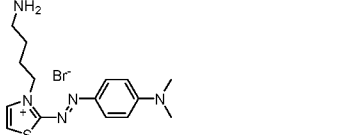
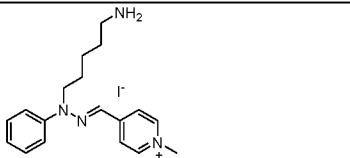
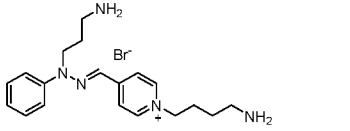
C1-C22 hydrocarbon-based radicals R20, and a hydrogen atom, R18 is chosen from: a radical R21C(O)-, linear and branched, saturated and unsaturated C1-C6 hydrocarbon-based radicals R22, and a hydrogen atom, R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21 hydrocarbon-based radicals; n, p and r, which may be identical or different, are chosen from integers ranging from 2 to 6; y is chosen from integers ranging from 1 to 10; x and z, which may be identical or different, are chosen from integers ranging from 0 to 10; X⁻ is an anion chosen from simple and complex, organic and inorganic anions; with the proviso that the sum x+y+z is from 1 to 15, that when x is 0, then R16 is R20 and that when z is 0, then R18 is R22. In one embodiment, the ammonium salts of formula (XXXXI) can be used, in which: R15 is chosen from methyl and ethyl radicals, x and y are equal to 1; z is equal to 0 or 1; n, p and r are equal to 2; R16 is chosen from: a radical R19C(O)-, methyl, ethyl and C14-C22 hydrocarbon-based radicals, and a hydrogen atom; R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21, hydrocarbon-based radicals; R18 is chosen from: a radical R21C(O)- and a hydrogen atom. Such compounds are commercially available as Dehyquat by Cognis, Stepanquat by Stepan, Noxamium by Ceca, and Rewoquat WE 18 by Rewo-Witco.

DATA

Uptake and washfastness: The uptake total color change (ΔE^1) describes how much the hair color has changed after white Piedmont hair strands supplied by International Hair Importers & Products has been dyed. ΔE is calculated as the square root of sum of squares of ΔL^* , Δa^* and Δb^* . The total color change for washfastness (ΔE^2) is measured after the dyed hair switches are processed through a 12-cycle rinse study. One cycle is defined as two shampoo treatments followed by a conditioning treatment. The hair switches are blow dried between each shampoo treatment. Color data is collected after the hair is properly dried on a Minolta spectrophotometer CM-3700d. Examples A and B are commercially available direct dye compounds known in the art. Examples C through N are embodiments of the washfast direct dye compounds described herein.

Table 1. Washfastness data

	Name	Structure	ΔE^1	ΔE^2
A	Vibracolor [®] Ruby Red		60	15
B	HC Blue 16		76	17
C	(E)-2-((4-((2-(bis(2-aminoethyl)amino)ethyl)amino)phenyl)diazenyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoroacetate		61	5
D	(E)-3-(4-aminobutyl)-2-((4-(dimethylamino)phenyl)diazenyl)-1-methyl-1H-imidazol-3-ium bromide		61	7
E	(E)-3-(3-ammoniopropyl)-2-((4-(dimethylamino)phenyl)diazenyl)-1-methyl-1H-imidazol-3-ium bromide		61	7
F	(E)-1,3-bis(3-ammoniopropyl)-2-((4-(dimethylamino)phenyl)diazenyl)-1H-imidazol-3-ium bromide		60	5
G	(E)-2-((4-aminophenyl)diazenyl)-1,3-bis(3-ammoniopropyl)-1H-imidazol-3-ium bromide		59	4
H	(E)-1,3-bis(3-ammoniopropyl)-2-((4-(bis(3-ammoniopropyl)amino)phenyl)diazenyl)-1H-imidazol-3-ium chloride		61	5
I	(E)-3-(4-ammoniobutyl)-2-((4-(3-ammoniopropyl)(methyl)amino)phenyl)diazenyl)-1-methyl-1H-imidazol-3-ium bromide		60	5

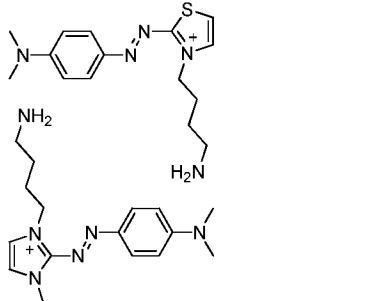
J	(E)-3-(3-(ammoniomethyl)benzyl)-2-((4-(dimethylamino)phenyl)diazenyl)-1-methyl-1H-imidazol-3-ium trifluoroacetate		61	7
K	(E)-2-((4-(bis(3-aminopropyl)amino)phenyl)diazenyl)-3,4,5-trimethylthiazol-3-ium methylsulfate		67	6
L	(E)-3-(4-aminobutyl)-2-((4-(dimethylamino)phenyl)diazenyl)thiazol-3-ium bromide		62	7
M	(E)-4-((2-(5-aminopentyl)-2-phenylhydrazono)methyl)-1-methylpyridin-1-ium iodide		57	6
N	(E)-1-(4-aminobutyl)-4-((2-(3-aminopropyl)-2-phenylhydrazono)methyl)pyridin-1-ium bromide		54	6

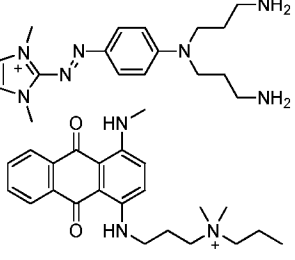
¹: uptake on blonde virgin hair

²: washfastness on blonde virgin hair

The smaller the total color change (ΔE^2) for washfastness after 24 shampoos, the more washfast the dye is. Notably, examples C through N, embodiments of the washfast direct dyes described herein, exhibited superior washfastness to examples A and B, commercially available direct dye compounds known in the art.

Table 2. On-tone fading data on hue angle change for mixed dye systems

Structures	Structural Analysis	Δh after a 12-cycle rinse – blonde virgin hair
	<p>Matching structural construction</p> <p>Both the blue dye and red dye carry one permanent cation plus one incipient cation.</p>	3.6

	<p>Mismatching structural construction.</p> <p>The blue dye carries one permanent cation without additional anchoring group.</p> <p>The red dye carries one permanent charge plus two incipient cations.</p>	12.0
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The smaller the hue angle change (Δh), the better the on-tone fading.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

What is claimed is:

- 1) A hair color composition comprising:
 - a. one or more direct dye compounds, the one or more direct dye compounds each comprising:
 - i. a chromophore;
 - ii. one or two permanent cations, wherein the permanent cations are pendant to the chromophore or part of the chromophore, wherein the chromophore and the permanent cations form a core structure; and
 - iii. one to four incipient cations, wherein each of the incipient cations is pendant via a linker group to the core structure, and wherein the incipient cations are neutral; and
 - b. an additional ingredient selected from the group consisting of organic solvents, oxidizing agents, alkalizing agents, oxidative dye precursors, direct dyes, chelants, radical scavengers, pH modifiers, buffering agents, thickeners, rheology modifiers, carbonate ion sources, peroxy monocarbonate ion sources, surfactants, polymers, natural ingredients, fragrances, enzymes, dispersing agents, peroxides, peroxide stabilizing agents, antioxidants, protein compounds, plant extracts, conditioning agents, ceramides, phospholipids, UV blockers, preserving agents, emollients, moisturizing agents, pigments, opacifiers, pearling agents, and mixtures thereof; wherein the hair color composition has a pH of from 7 to 11.
- 2) The hair color composition of claim 1, wherein the one or more direct dye compounds each comprise two incipient cations.
- 3) The hair color composition of claim 1 or claim 2, wherein the one or more direct dye compounds each has a molecular weight of less than 1,000 g/mol.
- 4) The hair color composition of any preceding claim, wherein the hair color composition has a pH of from 9 to 11.

- 5) The hair color composition of any preceding claim, wherein the hair color composition has a pH of from 7 to 9.
- 6) The hair color composition of any preceding claim, wherein an oxidizing agent is applied before or during the application of the hair color composition.
- 7) The hair color composition of claim 6, wherein the oxidizing agent is selected from the group consisting of peroxides, perborates, percarbonates, persulfates, oxidant generating enzymes, oxidant generating substrates, and combinations thereof.
- 8) The hair color composition of any preceding claim, wherein the hair color composition further comprises one or more oxidation dyes.
- 9) A hair color kit comprising the hair color composition of any preceding claim.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/022728

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A61Q5/06 A61Q5/10 A61K8/35 A61K8/49
 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)
 A61Q A61K
 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 855 967 A1 (OREAL [FR]) 17 December 2004 (2004-12-17) pages 22-27; claims 11-27; compounds C1-C5 -----	1-9
X	WO 2005/095522 A2 (CIBA SC HOLDING AG [CH]; ELIU VICTOR PAUL [DE]; SAUDER THOMAS [CH]; KA) 13 October 2005 (2005-10-13) pages 24-61; claims 1-22; compounds 101-115 page 1, paragraph 3 -----	1-9
X	WO 03/032937 A1 (CIBA SC HOLDING AG [CH]; MOECKLI PETER [CH]) 24 April 2003 (2003-04-24) page 14, last line - page 16; claims 1-5 page 1, paragraph 2-3 pages 13-14, last paragraph page 5, last paragraph -----	1-9
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 30 May 2016	Date of mailing of the international search report 10/06/2016
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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 Nopper, Agathe
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/022728

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 619 221 A1 (OREAL [FR]) 25 January 2006 (2006-01-25) paragraphs [0103] - [0107], [0115]; claims 21,25-31; example 2 -----	1,3-6,8, 9
X	EP 1 574 205 A2 (OREAL [FR]) 14 September 2005 (2005-09-14) claim 32; examples 1-2,14-15,21,23 paragraphs [0011], [0136], [0172] - [0183] -----	1-9
X	EP 1 757 660 A1 (OREAL [FR]) 28 February 2007 (2007-02-28) paragraphs [0138] - [0145]; examples 4-5; compounds 4-5 paragraphs [0001], [0006] - [0007], [0015]; claim 63 -----	1-9
A	WO 95/01772 A1 (CIBA GEIGY AG [CH]; MOECKLI PETER [CH]) 19 January 1995 (1995-01-19) examples 3,18,30-31,46-50,52-55,61,69,74-75,80-83 -----	1-9
A	US 5 708 151 A (MOECKLI PETER [CH]) 13 January 1998 (1998-01-13) the whole document -----	1-9
A	EP 2 359 909 A2 (JOHNSON & JOHNSON CONSUMER [US]) 24 August 2011 (2011-08-24) the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/022728

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: **1-9(partially)**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-9(partially)

Present claims 1-9 relate to an extremely large number of possible direct dye compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds, see page 5 line 31 - page 7 line 10, page 18 line 20-page page 22 line 4, page 47 line 18 - page 50 line 3.

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-9 (PCT Guidelines 9.19 and 9.23).

The search of claims 1-9 was restricted to those claimed compounds which appear to be supported and a generalisation of their structural formulae, namely the compounds of formula 1) - 6) disclosed on pages 6-7, compounds of formula (V) to (IX) with C of formula (Xa-o) and the compounds disclosed in examples 1-3.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/022728

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/022728

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