



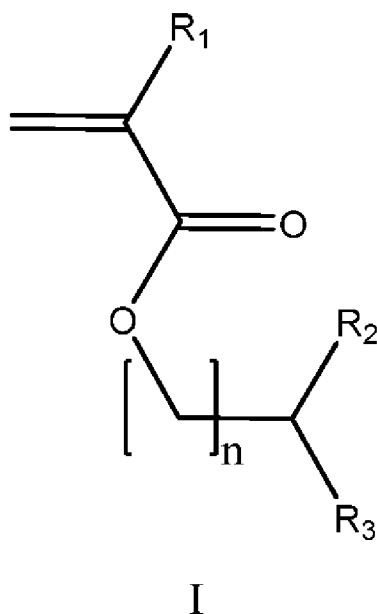
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(54) **Title:** HAIR COLORING COMPOSITION COMPRISING ONE OR MORE ACRYLATE MONOMERS

(57) **Abstract:** A hair coloring composition is provided and comprises, in a cosmetically acceptable carrier, one or more acrylate monomers. The one or more acrylate monomers have the general Formula I: wherein R₁ is selected from the group consisting of -H, -CH₃; n = 0, 1, 2, 3; R₂ is selected from the group consisting of -H, -CH₃, and -OH; R₃ is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH. The hair coloring composition has a pH from 8 to 12.

HAIR COLORING COMPOSITION COMPRISING ONE OR MORE ACRYLATE MONOMERS

FIELD OF THE INVENTION

A hair coloring composition comprising, in a cosmetically acceptable carrier, one or more acrylate monomers, and preferably with oxidative dye precursors, is provided for styling and coloring the hair simultaneously. Also, a kit for coloring hair is provided and comprises the hair coloring composition and an oxidizing formulation which are separately packaged. A method of coloring hair is also provided.

BACKGROUND OF THE INVENTION

Hair coloring or dyeing involves the application of a hair dye onto hair which results in the coloration of hair fibers. The total head of hair color may be changed subtly or dramatically, the root growth colored to match the remaining head of hair, effects introduced such as glitter, hair strand effects or other sectional effects, or the same color “freshened up” to combat fade and/or wash-out. In modern times, the consumer has a wide variety of options for coloring the hair (whether in the salon or at home) from direct dyes that wash out relatively quickly, hair make-up for applying glitter and/or hair strand effects, to conventional (semi-) permanent dyeing technology.

Hair style formation and retention traditionally has been accomplished by the use of styling products comprising polymers and other components that at least partially coat the hair and act on the surface of hair fibers. Several disadvantages are associated with this approach. Loss of hair style due to passage of time, elevated humidity, excessive motion, etc. may cause a consumer to feel the need to refresh a hair style throughout the day. This often requires application of additional styling product(s). The benefits of traditional styling products also may be diminished when applied to hair to which conditioning agents also have been applied. In addition, application of materials to the surface of hair may compromise the natural feel and appearance of the hair and result in a dull appearance and/or a stiff or otherwise unpleasant feel.

Methods for chemically modifying the internal region of the hair shaft have been developed. The methods typically use ethylenic monomers to chemically modify the internal region of the hair shaft. In particular, the ethylenic monomers may bond to the hair and/or to each other to form larger molecules, e.g. polymers inside the hair. The polymers formed inside the hair and formed from the ethylenic monomers can help to increase the rigidity of the hair, which provides styling advantages, e.g. allowing styling formation or increased hair volume and style

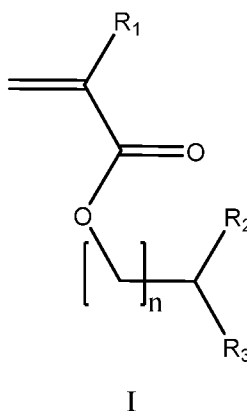
retention for longer periods of time than conventional styling methods. 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) is a known acrylate monomer which can be used for chemically modifying the internal region of the hair shaft, see for example International Patent Application WO 2009/088501.

Compositions comprising ethylenic monomers that are used for chemically modifying the internal region of the hair shaft can be applied prior to color the hair. Typically, in a first step, a hair shaft composition comprising an ethylenic monomer is applied on the hair, and in a second step, an adequate hair coloring composition is applied on the hair. The resulting color possesses a relatively increased vibrancy and shine. The polymers formed from the ethylenic monomers are located in the voids of the hair, which can enhance the light reflexion on the whole surface of the hair, thus increase the vibrancy of the resulting color.

There is a need for hairdressers and stylists to decrease the overall time needed to treat the hair with the hair shaft composition of the first step and then with the hair coloring composition of the second step. Hence, there is a need to provide a method that could combine the hair shaft composition with the hair coloring composition in order to reduce the overall time needed to treat the hair with these two compositions.

SUMMARY OF THE INVENTION

The present invention is related to a hair coloring composition comprising, in a cosmetically acceptable carrier, one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or a mixture thereof:



wherein

R_1 is selected from the group consisting of -H, -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH.

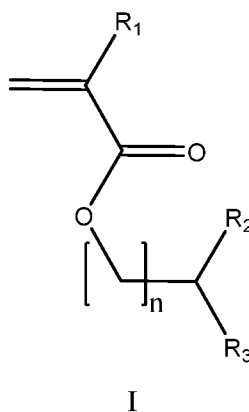
The hair coloring composition has a pH from 8 to 12. The hair coloring composition may preferably comprise oxidative dye precursors comprising one or more couplers and one or more primary intermediates.

The hair coloring composition may comprise from 0.5% to 50% preferably from 0.5% to 15% of the one or more acrylate monomers by total weight of the hair coloring composition.

The hair coloring composition may comprise a polymerisation inhibitor. The polymerisation inhibitor may be selected from the group consisting of 4-methoxyphenol, nitrobenzene, diphenyl picryl hydrazyl (DPPH) and mixtures thereof.

Alternatively, the polymerisation inhibitor may be selected from the group consisting of 2-tert-butyl-4-hydroxy-anisole, 3-tert-butyl-4-hydroxy-anisole, and mixtures thereof.

A use of one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or a mixture thereof, in a hair coloring composition:



wherein

R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH for improving the hair stiffness of hair without impacting the hair color.

A kit for coloring hair is provided and comprises:

(a) a hair coloring composition according to the present invention;

(b) an oxidizing formulation comprising one or more oxidizing agents; and

wherein the hair coloring composition (a) and the oxidizing formulation (b) are separately packaged.

A method of coloring hair is provided and comprises:

- (a) mixing the hair coloring composition according to the present invention with an oxidizing formulation comprising one or more oxidizing agents to form a mixture; and
- (b) applying the mixture onto hair.

BRIEF DESCRIPTION OF THE DRAWINGS

While the specification concludes with claims particularly pointing out and distinctly claiming the present invention, it is believed that the same will be better understood from the following description read in conjunction with the accompanying drawings in which:

Fig. 1 is a photography showing pairs of two hair strands treated by the respective hair coloring compositions A1-F3;

Fig. 2 is a schematic representation of a device suitable for the Hair Stiffness Test Method;

Fig. 3 is the device of Fig. 2 with a fibre-pulling means which is pulling the fibres of a hair strand;

Fig. 4 shows the hair stiffness of the fibres when treated with different compositions of 3-SPA;

Fig. 5 shows the hair stiffness of the fibres treated with different composition of hydroxypropyl methacrylate.

DETAILED DESCRIPTION OF THE INVENTION

General and definitions

In this document, including in all embodiments of all aspects of the present invention, the following definitions apply unless specifically stated otherwise.

All percentages are by total weight (w/w) of the hair coloring composition unless otherwise specified. All ratios are weight ratios. "wt%" means percentage by weight. References to 'parts' e.g. a mixture of 1 part X and 3 parts Y, is a ratio by weight. When more than one composition are used during a treatment, 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"), typically resulting from mixing an oxidative composition (also called developer and/or oxidizing composition/component) with a dye composition (also called tint, and/or dye composition/component), unless otherwise specified. All ratios or percentages are weight ratios or weight percentages unless specifically stated otherwise.

“QS” or “QSP” means sufficient quantity for 100% or for 100g. +/- indicates the standard deviation. All ranges are inclusive and combinable. The number of significant digits conveys neither a limitation on the indicated amounts nor on the accuracy of the measurements. All numerical amounts are understood to be modified by the word “about”.

All measurements are understood to be made at 20°C and at ambient conditions, where “ambient conditions” means at 1 atmosphere (atm) of pressure and at 65% relative humidity, unless otherwise stated. “Relative humidity” refers to the ratio (stated as a percent) of the moisture content of air compared to the saturated moisture level at the same temperature and pressure. Relative humidity can be measured with a hygrometer, in particular with a probe hygrometer from VWR[®] International.

Herein “min” means “minute” or “minutes”. Herein “mol” means mole. Herein “g” following a number means “gram” or “grams”. “Ex.” means “example”. All amounts as they pertain to listed ingredients are based on the active level (‘solids’) and do not include carriers or by-products that may be included in commercially available materials.

Herein, “comprising” means that other steps and other ingredients can be in addition. “Comprising” encompasses the terms “consisting of” and “consisting essentially of”. The compositions, formulations, methods, uses, kits, and processes of the present invention can comprise, consist of, and consist essentially of the elements and limitations of the invention described herein, as well as any of the additional or optional ingredients, components, steps, or limitations described herein. Embodiments and aspects described herein may comprise or be combinable with elements, features or components of other embodiments and/or aspects despite not being expressly exemplified in combination, unless an incompatibility is stated.

Where amount ranges are given, these are to be understood as being the total amount of said ingredient in the composition, or where more than one species fall within the scope of the ingredient definition, the total amount of all ingredients fitting that definition, in the composition.

For example, if the composition comprises from 1% to 5% fatty alcohol, then a composition comprising 2% stearyl alcohol and 1% cetyl alcohol and no other fatty alcohol, would fall within this scope.

The amount of each particular ingredient (e.g. a primary intermediate, a coupler, an oxidizing agent, etc) or mixtures thereof described hereinafter can account for up to 100% (or 100%) of the total amount of the ingredient(s) in the hair coloring composition.

The term “molecular weight” or “M.Wt.” as used herein refers to the weight average molecular weight unless otherwise stated. The weight average molecular weight may be measured by gel permeation chromatography.

The term “substantially free from” or “substantially free of” as used herein means less than 1%, less than 0.8%, less than 0.5%, less than 0.3%, or less than an immaterial amount of by total weight of the composition or formulation.

The term “hair” as used herein means mammalian hair including scalp hair, facial hair and body hair, more preferably hair on the human head and scalp. Hair comprises hair fibers. “Hair shaft” means an individual hair strand and may be used interchangeably with the term “hair.” “Internal region of the hair shaft,” as used herein, means any non-surface portion of the hair shaft, including the inner portion of the cuticle, underneath the cuticle and the cortex. “Non-surface portion” may be understood to mean that portion of the hair that is not in direct contact with the outside environment. 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, preferably human hair is preferred. However wool, fur and other keratin containing fibers are suitable substrates for the hair coloring compositions according to the present invention.

By “hair coloring composition”, it is meant a composition suitable for changing the color of hair. The hair coloring composition is referred hereinafter as “the composition”, unless otherwise specified. The hair coloring composition can comprise oxidative dye precursors, direct dyes. The term “hair coloring composition” as used herein covers hair bleaching and hair oxidative dyeing products.

The term “cosmetically acceptable” as used herein means that the compositions, formulations or components described are suitable for use in contact with human keratinous tissue without undue toxicity, incompatibility, instability, allergic response, and the like. All compositions and formulations described herein which have the purpose of being directly applied to keratinous tissue are limited to those being cosmetically acceptable.

The term “derivatives” as used herein includes but is not limited to: ester, amide, carboxyl, amino, ether, acetyl, acid, salt and/or alcohol or hydroxy derivatives of a given compound.

The term “monomer” as used herein means a discrete, non-polymerised chemical moiety capable of undergoing polymerisation in the presence of an initiator. “Ethylenic monomer”, as used herein, means a monomer that contains an olefinic carbon-carbon double bond ($C=C$) and is

capable of undergoing polymerisation, preferably radical polymerisation, in the presence of an initiator.

The term “polymer” as used herein means a chemical formed from the polymerisation of two or more monomers. The term “polymer” as used herein shall include all materials made by the polymerisation of monomers as well as natural polymers. Polymers made from only one type of monomer are called homopolymers. A polymer comprises at least two monomers. Polymers made from two or more different types of monomers are called copolymers. The distribution of the different monomers can be calculated statistically or block-wise. Except if stated otherwise, the term “polymer” used herein includes any type of polymer including homopolymers and copolymers.

The term “molecular weight of a polymer” or “M.Wt. of a polymer” as used herein refers to the weight average molecular weight unless otherwise stated. The weight average molecular weight may be measured by gel permeation chromatography.

The term “cosmetically acceptable salt” as used herein refers to conventional base-addition salts that retain the properties of the one or more acrylate monomers of the present invention and are formed from suitable organic or inorganic bases. Sample base-addition salts include those derived from sodium, potassium, ammonium, calcium, magnesium, iron, zinc, zirconium and aluminum hydroxide. Chemical modification of a compound bearing a carboxylic acid function into the corresponding carboxylate salt is a technique well known in the art.

The term “viscosity” as used herein is measured at 25°C using a HAAKE Rotation Viscometer VT 550 with cooling/heating vessel and sensor systems according to DIN 53019 at a shear rate of 12.9 s⁻¹.

The term “water-soluble” as used herein refers to any material that is sufficiently soluble in water to form a clear solution to the naked eye at a concentration of 0.1% by weight of the material in water at 25°C. The term “water-insoluble” refers to any material that is not “water-soluble”.

The term “separately packaged” as used herein means any form of packaging that prevents a first composition or formulation from coming into physical contact, or admixing, with a second composition or formulation. “Separately packaged” may mean that the individual first and second compositions are packaged in separate containers, or alternatively in a single container partitioned such that the first and second compositions are not in physical contact.

The term “kit” as used herein means a packaging unit comprising a plurality of components i.e. a kit of parts. An example of a kit is, for example, a first composition and a separately packaged second composition. Another kit may comprise application instructions comprising a method and a composition/formulation.

When using a method of coloring hair which comprises (a) mixing an hair coloring composition comprising 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) and oxidative dye precursors with an oxidizing formulation comprising an oxidizing agent to form a mixture; and (b) applying the mixture onto hair, the obtained color looks like relatively paler than the color obtained by sequentially applying onto hair an adequate hair coloring composition onto hair as a first step, followed by applying a hair shaft composition comprising 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) onto hair.

While not wishing to be bound by theory, it is believed that 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) and the polymer formed from 3-SPA might be interacted with the oxidative dye precursors in situ. It is assumed that the sulfo moiety of the 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) can interfere with the oxidative dye precursors, which leads to a relatively lighter or paler color (See experimental part more below).

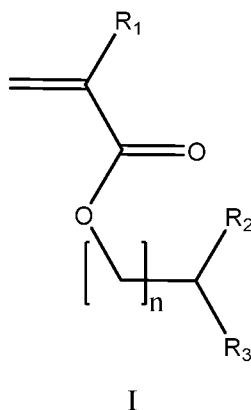
There is thus a need to substitute 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) with a new type of ethylenic monomer that will not provide any adverse color lightening when applied simultaneously with oxidative dye precursors onto hair.

Hair coloring composition

The present invention is related to a hair coloring composition as stated hereinbefore. The hair coloring composition comprises in a cosmetically acceptable carrier, one or more acrylate monomers as described more in detail below.

Acrylate monomer(s)

It has been surprisingly found that it is possible to improve the vibrancy of the color while providing hair strength improvement by replacing the 3-sulfopropyl(meth)acrylate potassium salt (3-SPA) by one or more acrylate monomers of Formula I:



wherein

R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH;

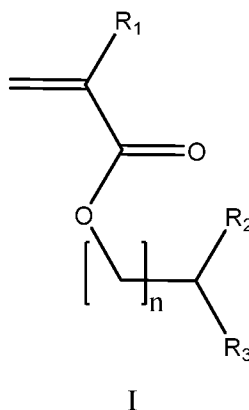
The sulfonic moiety has been replaced by R_2 and/or R_3 groups. The R_2 and/or R_3 groups are alleged to interact less or not with the oxidative dye precursors. Hence, the one or more acrylate monomers of Formula I do not affect the formation of oxidative dyes onto hair. At the same time, the one or more acrylate monomers of Formula I can polymerize in the hair and modify the internal region of the hair shaft. It has been observed that the hair coloring composition of the present invention applied onto hair can help to increase the rigidity of the hair, in terms of hair stiffness as shown in the experimental part more below.

The different aspects of the present invention will now be discussed in more details.

A hair coloring composition is provided. The hair coloring composition is for coloring the hair fibers and also for increasing the rigidity of the hair, which provides styling advantages, e.g. allowing styling formation or increased hair volume and style retention for longer periods of time than conventional styling methods.

The hair coloring composition comprises, in a cosmetically acceptable carrier one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or a mixture thereof:

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wherein

R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH;

The hair coloring composition has a pH from 8 to 12, or from 9 to 10.

The hair coloring composition may comprise from 0.5% to 50%, or preferably from 0.5% to 15%, or more preferably from 1% to 15%, or even more preferably from 1% to 10%, or from 1% to 5% of one or more acrylate monomers of Formula I by total weight of the hair coloring composition.

The hair coloring composition may comprise a polymerisation inhibitor. The hair coloring composition may comprise a polymerisation inhibitor in an amount of from 1 milligram to 1000 milligram per kilogram of the one or more acrylate monomers of Formula I.

The polymerisation inhibitor may be selected from the group consisting of 4-methoxyphenol, nitrobenzene, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and mixtures thereof. For instance, Irganox[®] from BASF may be used. Irganox[®] 1330 is a Tris-BHT Mesitylene compound. Ethanox from SI Group is a non-coloring, odorless antioxidant. For example, ETHANOX 330 or 330G may also be used.

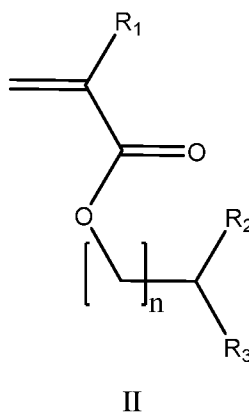
Alternatively, the polymerisation inhibitor may be selected from the group consisting of 2-tert-butyl-4-hydroxy-anisole, 3-tert-butyl-4-hydroxy-anisole, and mixtures thereof. Regarding the hydroxyl anisole compound as a polymerisation inhibitor, it is believed that upon any formation of a carbon radical from the double bond of the one or more acrylate monomers of Formula I, the radical of the one or more acrylate monomers can be trapped by the proton

provided from the hydroxyl group of the anisole compound. Then, the resulting one or more acrylate monomers are unable to polymerize since a radical is no longer present.

The hair coloring composition may be substantially free of any initiator of free-radical polymerisation. Indeed, the hair coloring composition being substantially free of any initiator of free-radical polymerisation has the advantage that the risk of the one or more acrylate monomers polymerizing with themselves in the hair coloring composition is reduced.

The hair coloring composition may be substantially free of poly(meth)acrylate polymer derivative(s) obtained from the one or more acrylate monomers of the present invention. This may be with the exception of any poly(meth)acrylate polymer derivative(s) employed in any particles, such as capsules that could be used for encapsulating the hair coloring composition of the present invention.

The one or more acrylate monomers of the hair coloring composition may preferably conform to the general Formula II:



wherein

R_1 is selected from the group consisting of -H, and -CH₃;

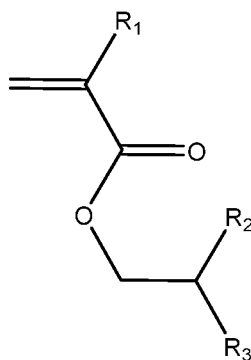
$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, and -COOH.

The one or more acrylate monomers of the hair coloring composition may more preferably conform to the general Formula III:

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III

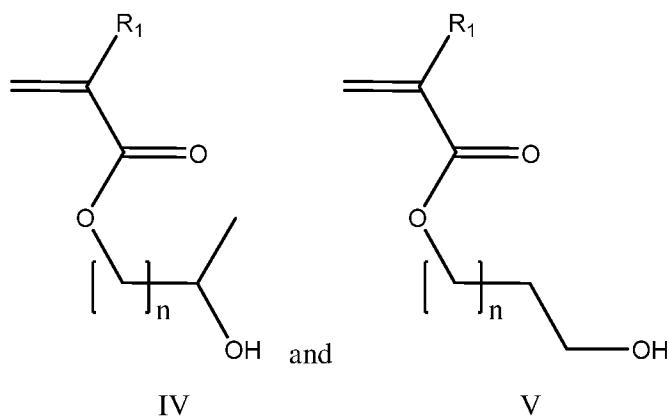
wherein

R_1 is selected from the group consisting of -H, and -CH₃;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, and -COOH.

The one or more acrylate monomers of the hair coloring composition may even more preferably comprise a mixture of a first acrylate monomer of Formula IV and a second acrylate monomer of Formula V:



wherein

R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$; more preferably $n = 1$;

Oxidative dye precursors

The hair coloring composition may preferably comprise oxidative dyes precursors comprising one or more couplers (also known as secondary intermediate) and one or more primary intermediates (also known as developer). Various couplers may be used with primary intermediates in order to obtain different shades.

The oxidative dye precursors suitable for use herein, in so far as they are bases, may be used as free bases or in the form of any acceptable salts obtained with the corresponding organic or inorganic acids, such as hydrochloric, hydrobromic, citric, acetic, lactic, succinic, tartaric, or sulfuric acids, or, in so far as they have aromatic hydroxyl groups, in the form of any acceptable salts obtained with the corresponding bases, such as alkali phenolates.

Oxidative dye precursors are known in the art, and include aromatic diamines, aminophenols, aromatic diols and their derivatives (a representative but not exhaustive list of oxidation dye precursors can be found in Sagarin, "Cosmetic Science and Technology, Interscience, Special Edn. Vol. 2 pages 308 to 310). Suitable oxidative dye precursors are also disclosed in the Canadian Patent Application No. CA2576189A1 – in particular, from Table 1 dye combinations No. 1 to 2394, which span pages 49 to 238, are incorporated herein by reference. It is to be understood that the primary intermediates and couplers (collectively known as oxidative dye precursors) detailed below are only by way of example and are not intended to limit the hair coloring compositions and other aspects herein described. The primary intermediates and couplers may be used in the form of any acceptable salts, for example sulphate salts.

The one or more primary intermediates of the hair coloring composition may be selected from the group consisting of 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)ethylazanediyl)diethanol, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol, 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 sulphate, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-ethylpyrazole, 4,5-diamino-1-isopropylpyrazole, 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, 2,3-diamino-6,7-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one dimethosulfonate, 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.

The one or more primary intermediates of the hair coloring composition may be particularly 1,4-diamino-2-(methoxymethyl)-benzene. 1,4-diamino-2-(methoxymethyl)-benzene has the advantage of an improved sensitisation profile (i.e. reduced risks of scalp skin reaction).

The one or more primary intermediates may be 4,5-diamino-1-hexylpyrazole. 4,5-diamino-1-hexylpyrazole may be used as a sulphate salt.

The one or more primary intermediates may be selected from the group consisting of 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, 2,3-diamino-6,7-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one dimethosulfonate, 4,5-diamino-1-hexylpyrazole, 4,5-diamino-1-heptylpyrazole, methoxymethyl-1,4-diaminobenzene, and mixtures thereof; and the acceptable salts thereof such as chlorides, sulphates and hemi-sulphates in particular.

The one or more couplers may be a compound comprising at least one phenyl ring substituted with at least one hydroxyl group. The coupler may be selected from the group consisting of 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(azanediyl)diethanol, 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, 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-methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, pyridine-2,6-diol, 5,6-dihydroxyindole, 6-hydroxyindole, 5,6-dihydroxyindoline, 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one, 1,2,4-trihydroxybenzene, 2-(benzo[d][1,3]dioxol-5-ylamino)ethanol (also known as hydroxyethyl-3,4-methylenedioxyaniline), and mixtures thereof.

The oxidative dye precursors may be particularly selected from the group consisting of 1-naphthol, 2,4-diaminophenoxyethanol, toluene-2,5-diamine sulphate, resorcinol, 4-amino-m-cresol, 2-amino-6-chloro-4-nitrophenol, 2-amino-4-hydroxyethylaminoanisole

sulphate, hydroxyethyl-3,4-methylenedioxyaniline HCl, 1-hydroxyethyl 4,5-diamino pyrazole sulphate, 4-amino-2-hydroxytoluene, 2-methylresorcinol, m-aminophenol, 2-methyl-5-hydroxyethylaminophenol, and mixtures thereof.

The oxidative dye precursors may comprise preferably 5-amino-4-chloro-o-cresol and 1,4-diamino-2-(methoxymethyl)-benzene. The oxidative dye precursors may comprise more preferably 2,6-diaminopyridine and 1,4-diamino-2-(methoxymethyl)-benzene. The oxidative dye precursors may comprise even more preferably 2,6-dihydroxyethylaminotoluene and 2-methoxymethyl-1,4-diaminobenzene. The oxidative dye precursors may comprise even more preferably 2-methoxymethyl-1,4-diaminobenzene and p-phenylenediamine and/or toluene-2,5-diamine.

Typically, the hair coloring composition may comprise a total amount of oxidative dye precursors, namely the one or more couplers and the one or more primary intermediates, up to 12%, or from 0.001% to 12%, or from 0.01% to 10%, or from 0.3% to 8%, or from 0.05% to 9%, or from 0.5% to 6% of oxidative dye precursors by total weight of the hair coloring composition.

The hair coloring composition may be substantially free of oxidizing agent.

Direct dye

The hair coloring composition may further comprise one or more direct dyes, advantageously one or more oxidatively stable direct dyes.

The hair coloring composition may comprise a total amount from 0.001% to 4%, or from 0.005% to 3%, or from 0.01% to 2% of the one or more direct dyes by total weight of the hair coloring composition.

The presence of one or more direct dyes and the proportion thereof can help to provide or enhance coloring/dyeing, particularly with regard to the vibrancy of the color that is desired.

The hair coloring composition may be substantially free of direct dye. Indeed, sometimes consumers prefer direct dye-free compositions.

The one or more direct dyes may be selected from the group consisting of nitro dyes to provide a blue color, nitro dyes to provide wither a red color or a yellow color, quinone dyes, basic dyes, neutral azo dyes, acid dyes, and mixtures thereof. The one or more direct dyes may be a basic dye. The one or more direct dyes may be a neutral azo dye. The one or more direct dyes may be an acid dye.

The one or more direct dyes may be selected from the group consisting of 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 9, Acid Violet 43, Acid 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-methylsulphate, (E)-1-(2-(4-(4,5-dimethylthiazol-2-yl)diazenyl)phenyl)(ethylamino)ethyl-3-methyl-1H-imidazol-3-ium chloride, (E)-4-(2-(4-(dimethylamino)phenyl)diazenyl)-1-methyl-1H-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(azanediy)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, and Natural dyes such as Annato, Anthocyanin, Beetroot, Carotene, Capsanthin, Lycopene, Chlorophyll, Henna, Indigo, Cochineal, and mixtures thereof.

Other ingredients

The hair coloring composition according to the present invention may comprise, in addition to the ingredients indicated above, further ingredients in order to further enhance the properties of the hair coloring composition, as long as these are not excluded by the claims.

Suitable further ingredients may include, but not limited to: pigments, colored material, solvents, radical scavengers, peroxymonocarbonate ions, surfactants, thickening agents, conditioning agents (such as silicones and cationic polymers), cosmetically acceptable carrier, preservatives, perfume and mixtures thereof.

Suitable further ingredients referred to above, but not specifically described below, are listed in 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.

Pigments

The hair coloring composition may comprise one or more pigments. The one or more pigments of the hair coloring composition may be a colored pigment which imparts color effects to the hair coloring composition or to the hair.

Alternatively, the one or more pigments of the hair coloring composition may be a lustre effect pigment which imparts desirable and aesthetically pleasing lustre effects to the hair coloring composition or to the keratin fibers of the hair. The color or lustre effects on the keratin fibers of the hair are preferably temporary. Indeed, the color or lustre effects on the keratin fibers of the hair last until the next hair wash and can be removed again by washing the hair with customary shampoos.

The hair coloring composition may be substantially free of pigment. Indeed, having a hair coloring composition substantially free of pigment can help to prevent the formation of residues, precipitation and/or rough hair feel.

The hair coloring composition may comprise one or more pigments having a D_{50} particle diameter of from 5 μm to 60 μm measured according to the following test method. Particle diameter is represented by D_{50} , which is the median diameter by volume. D_{50} is measured with a Malvern Mastersizer 2000, which is a laser diffraction particle size and it is measured according to ISO 13320:2009(en) with Hydro 2000G or Hydro 2000S where the dispersant is water or ethanol. Detection range is from 0.02 μm to 2000 μm . D_{50} is expressed as x_{50} in ISO 13320:2009(en). Laser diffraction measures particle size distributions by measuring an angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample analyser and the particle size is reported as a volume equivalent sphere diameter. A

discussion of calculating D_{50} is provided in Barber *et al*, Pharmaceutical Development and Technology, 3(2), 153-161 (1998), which is incorporated herein by reference.

The hair coloring composition may comprise one or more pigments having a D_{50} particle diameter from 10 μm to 40 μm . The one or more pigments of the hair coloring composition may be present in the hair coloring composition in an undissolved form. The hair coloring composition may comprise from 0.01% to 25%, or from 0.1% to 20%, or from 1% to 15%, or from 4% to 10% of the one or more pigments by total weight of the hair coloring composition.

The one or more pigments of the hair coloring composition may be a colorant which is virtually insoluble in the hair coloring composition, and may be inorganic or organic. Inorganic-organic mixed pigments may be also possible. The hair coloring composition may comprise one or more inorganic pigments. The advantage of an inorganic pigment is its excellent resistance to light, weather and temperature. The one or more inorganic pigments of the hair coloring composition may be of natural origin, and may be, for example, derived from a material selected from the group consisting of chalk, ochre, umber, green earth, burnt sienna, and graphite.

The one or more pigments of the hair coloring composition may be a white pigment, such as, for example, titanium dioxide or zinc oxide. Alternatively, the one or more pigments of the hair coloring composition may be a black pigment, such as, for example, iron oxide black. Alternatively, the one or more pigments of the hair coloring composition may be a colored pigment, such as, for example, ultra-marine or iron oxide red, or a lustre pigment, or a metal effect pigment, or a pearlescent pigment, and/or a fluorescent or phosphorescent pigment.

The one or more pigments of the hair coloring composition may be colored or a non-white pigment. The one or more pigments of the hair coloring composition may be selected from the group consisting of metal oxides, hydroxides and oxide hydrates, mixed phase pigments, sulfur-containing silicates, metal sulfides, complex metal cyanides, metal sulphates, chromates and molybdates, the metals themselves (bronze pigments), and combinations thereof. The one or more pigments of the hair coloring composition may be selected from the group consisting of are titanium dioxide (CI 77891), black iron oxide (CI 77499), yellow iron oxide (CI 77492), red and brown iron oxide (CI 77491), manganese violet (CI 77742), ultramarine (sodium aluminium silfosilicates, CI 77007, Pigment Blue 29), chromium oxide hydrate (CI 77289), Prussian blue (ferric ferrocyanide, CI 77510), carmine (cochineal), and combinations thereof.

The one or more pigments of the hair coloring composition may be a pearlescent and colored pigment based on mica which is coated with a metal oxide or a metal oxychloride, such as titanium dioxide or bismuth oxychloride, and optionally further color-imparting substances,

such as iron oxides, Prussian blue, ultramarine, and carmine. The color exhibited by the pigment may be adjusted by varying the layer thickness. Such pigments are sold, for example, under the trade names Rona[®], Colorona[®], Dichrona[®], RonaFlair[®], Ronastar[®], Xirona[®] and Timiron[®] all of which are available from Merck, Darmstadt, Germany. For example, Xirona[®] is a brand for color travel pigments that display color shifting effects depending on the viewing angle and are based on either natural mica, silica or calcium aluminium borosilicate flakes, coated with varying layers of titanium dioxide.

Pigments from the line KTZ[®] from Kobo Products, Inc., 3474 So. Clinton Ave., So. Plainfield, USA, may be also useful herein, in particular the Surface Treated KTZ[®] Pearlescent Pigments from Kobo. Particularly useful are KTZ[®] FINE WHITE (mica and TiO₂) having a D₅₀ particle diameter from 5 µm to 25 µm and also KTZ[®] CELESTIAL LUSTER (mica and TiO₂, from 10 µm to 60 µm) as well as KTZ[®] CLASSIC WHITE (mica and TiO₂, from 10 µm to 60 µm). Another useful pigment may be SynCrystal Sapphire from Eckart Effect Pigments, which is a blue powder comprising platelets of synthetic fluorphlogopite coated with titanium dioxide, ferric ferrocyanide and small amounts of tin oxide. Another useful pigment may also be SYNCRYSTAL Almond also from Eckart, which is a beige powder with a copper reflection color and is composed of platelets of synthetic fluorphlogopite and coated with titanium dioxide and iron oxides. Another useful pigment may be Duocrome[®] RV 524C from BASF, which provides a two color look via a lustrous red powder with a violet reflection powder due to its composition of mica, titanium dioxide and carmine.

The one or more pigments of the hair coloring composition may be an organic pigment. The organic pigment of the hair coloring composition may be selected from the group consisting of natural pigments sepia, gamboge, bone charcoal, Cassel brown, indigo, chlorophyll and other plant pigments.

The one or more pigments of the hair coloring composition may be a synthetic organic pigment. The synthetic organic pigment of the hair coloring composition may be selected from the group consisting of azo pigments, anthraquinoids, indigoids, dioxazine, quinacridone, phthalocyanine, isoindolinone, perylene and perinone, metal complex, alkali blue, diketopyrrolopyrrole pigments, and combinations thereof.

The one or more pigments of the hair coloring composition may be selected from the group consisting of iron oxide, titanium dioxide, mica, borosilicate, and combinations thereof. The one or more pigments of the hair coloring composition may comprise an iron oxide (Fe₂O₃)

pigment. The one or more pigments of the hair coloring composition may comprise a combination of mica and titanium dioxide.

Colored material

The hair coloring composition may comprise one or more colored materials. The one or more colored materials of the hair coloring composition may be particulate in form. The one or more colored materials of the hair coloring composition may be selected from the group consisting of colored fibers, colored beads, colored particles such as nano-particles, colored polymers comprising covalently attached dyes, liquid crystals, particles having diffraction properties, UV absorber and photoprotective substances, pressure- or light-sensitive pigments, and combinations thereof.

The hair coloring composition may be substantially free of colored material. Indeed, having a hair coloring composition substantially free of colored material can help to prevent the formation residues and precipitation.

The one or more colored materials of the hair coloring composition may be capable of changing color via a mechanism selected from the group consisting of thermochromism, photochromism, hydrochromism, magnetochromism, electrochromism, piezochromism, chemichromism, mechano-optics. Suitable colored material of the hair coloring composition may include 3D Magnetic Pigments, Glow Dust, Fluorescent Pigments, Thermo Dust, Chameleon Pigments and other color changing materials from Solar Color Dust (<http://solarcolordust.com/>).

The hair coloring composition may comprise one or more photoprotective substances. The hair coloring composition may comprise from 0.01% to 10%, or from 0.1% to 5%, or from 0.2% to 2% of the one or more photoprotective substances by total weight of the hair coloring composition. Useful photoprotective substances of the hair coloring composition are specified in European Patent Application 1084696A1 from §0036 to §0053, which is incorporated herein by reference. The one or more photoprotective substances of the hair coloring composition may be selected from the group consisting of 2-ethylhexyl 4-methoxycinnamate, methyl methoxycinnamate, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, polyethoxylated p-aminobenzoates, di-butyl-hydroxytoluene (BHT), and mixtures thereof.

The hair coloring composition may comprise from 0.01% to 10%, or from 0.05% to 5% of one or more particulate substances by total weight of the hair coloring composition. The one or more particulate substances of the hair coloring composition may be a substance which is solid at room temperature (23°C) and in the form of a particle. The one or more particulate substances

of the hair coloring composition may be selected from the group consisting of silica, silicates, aluminates, clay earths, mica, and insoluble salts. The one or more particulate substances of the hair coloring composition may be selected from the group consisting of insoluble inorganic metal salts, metal oxides, minerals and insoluble polymer particles. The one or more particulate substances of the hair coloring composition may be titanium dioxide.

The one or more particulate substances of the hair coloring composition may be present in the hair coloring composition in an undissolved, or a stably dispersed form, and, following application to the hair and evaporation of the solvent, can deposit on the hair in a solid form.

The one or more particulate substances of the hair coloring composition may be selected from the group consisting of silica (silica gel, silicon dioxide) and metal salts, in particular inorganic metal salts. The one or more particulate substances of the hair coloring composition may be silica. The one or more particulate substances of the hair coloring composition may be selected from the group consisting of metal salts such as alkali metal or alkaline earth metal halides, e.g. sodium chloride or potassium chloride; alkali metal or alkaline earth metal sulphates, such as sodium sulphate or magnesium sulphate.

Solvents

The hair coloring composition according to the present invention may further comprise one or more solvents. The one or more solvents 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 for the hair coloring composition may include, but are not limited to: from C₂ to C₄ lower alkanols (such as 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.

The one or more solvents of the hair coloring composition may be selected from the group consisting of water, ethanol, propanol, isopropanol, glycerol, 1,2-propylene glycol, hexylene glycol, ethoxy diglycol, and mixtures thereof.

Typically, the hair coloring composition may comprise water as a main ingredient, particularly in a total amount ranging from at least 50%, alternatively from at least 60%,

alternatively from at least 70%, by total weight of the hair coloring composition. Typically, when present, the hair coloring composition may comprise a total amount of organic solvents ranging from 1% to 30%, by total weight of the hair coloring composition.

Radical scavenger

The hair coloring composition may comprise one or more radical scavengers. The one or more radical scavengers of the hair coloring composition may be present in a sufficient amount to reduce damage to the hair during an oxidative bleaching or coloring process.

The one or more radical scavengers may be a species that can react with a radical species, preferably a carbonate radical to convert the radical species by a series of fast reactions to a less reactive species. The one or more radical scavengers may be advantageously selected such that the radical scavenger is different from an alkalisng agent and/or is present in an amount sufficient to reduce the damage to the hair during the coloring /bleaching process.

The one or more radical scavengers may be selected from the classes of: alkanolamines, amino sugars, amino acids, esters of amino acids, and mixtures thereof. Alternatively, the one or more radical scavengers may be selected from the group consisting of: monoethanolamine, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 1-amino-2-propanol, 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, and potassium, sodium and ammonium salts of the above, and mixtures thereof. The radical scavenger of the hair coloring composition may be selected from the group consisting of: benzylamine, glutamic acid, imidazole, di-tert-butylhydroxytoluene, hydroquinone, catechol, and mixtures thereof.

Peroxymonocarbonate ions

The hair coloring composition according to the present invention 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.

The hair coloring composition may preferably comprise at least one source of peroxymonocarbonate ions. Peroxymonocarbonate ions may be formed in situ from a source of hydrogen peroxide and a carbonate ion source. the hair coloring composition may comprise a source of carbonate ions or carbamate ions or hydrocarbonate ions or any mixture thereof. The

source of peroxymonocarbonate ions may be selected from the group consisting of sodium, potassium, guanidine, arginine, lithium, calcium, magnesium, barium, ammonium salts of carbonate, carbamate and hydrocarbonate ions, and mixtures thereof.

The carbonate ion source for peroxymonocarbonate ions may be selected from the group consisting of 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 also be utilized to provide both the source of carbonate ions and oxidizing agent. The source of carbonate ions, carbamate and hydrocarbonate ions may be selected from the group consisting of: sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium carbamate, and mixtures thereof.

Surfactant

The hair coloring composition may comprise one or more surfactants. A surfactant can help to provide an emulsion. The hair coloring composition may be in the form of an emulsion.

The hair coloring composition may be in the form of a cream or gel. The hair coloring composition may have a lamellar structure and/or may have a gel network. The hair coloring composition may comprise micelles comprising a hydrophobic phase (see the description of the hydrophobic phase more below).

The hair coloring composition may comprise from 0.001% to 10%, or from 0.1% to 8%, or from 0.5% to 5%, or from 0.4% to 2%, or from 0.8% to 1.5% of the one or more surfactants by total weight of the hair coloring composition.

The hair coloring composition may comprise one or more surfactants which are selected from the group consisting of anionic surfactants, non-ionic surfactants, amphoteric surfactants, zwitterionic surfactants, cationic surfactants, and mixtures thereof. The one or more surfactants of the hair coloring composition can be useful for stabilising a hydrophobic phase in the hair coloring composition, e.g. for stabilising the gel network and/or lamellar structure.

The hair coloring composition may comprise an anionic surfactant. The anionic surfactant of the hair coloring composition may be sodium lauryl sulphate or sodium laureth sulphate.

The surfactant of the hair coloring composition may be a non-ionic surfactant. The non-ionic surfactant may be selected from the group consisting of lanolin alcohol, and polyoxyethylene ethers of fatty alcohols, and mixtures thereof. The non-ionic surfactant may be preferably cetareth-n, wherein n is from 2 to 100, or from 10 to 30. When the one or more

surfactants of the hair coloring composition are non-ionic, precipitation of others ingredients of the hair coloring composition can be prevented.

The hair coloring composition may comprise from 0.001% to 5%, or from 0.01% to 3%, or from 0.01% to 1%, or from 0.05% to 1%, or from 0.1% to 0.5%, or from 0.1% to 0.3% of a non-ionic surfactant by total weight of the hair coloring composition. The non-ionic surfactant of the hair coloring composition may be selected from the group consisting of lanolin alcohol, and polyoxyethylene ethers of fatty alcohols, and mixtures thereof.

The non-ionic surfactant of the hair coloring composition may be a castor oil having polyethylene glycol ether groups or polypropylene glycol ether groups. The polyethylene glycol ether groups of the non-ionic surfactant may be ethers of PEG-n groups, wherein n is an integer of from 2 to 12, or from 2 to 10, or from 3 to 8. When the total M.Wt. of polyethylene glycol ether groups is below 400 Da, the mixing of the hair coloring composition can be eased.

The polypropylene glycol ether groups may be ethers of PPG-n groups, wherein n is an integer of from 2 to 60, or from 10 to 50, or from 20 to 40. The polyethylene glycol ether groups or polypropylene glycol ether groups may be selected from the group consisting of: PPG-4, PPG-6, PEG-5, PEG-6, PEG-8, and mixtures thereof. The hair coloring composition may comprise PEG-40 Hydrogenated Castor Oil and/or PEG-60 Castor Oil and/or PEG-35 Castor Oil as non-ionic surfactant.

Thickening agent

The hair coloring composition may comprise one or more thickening agents. Thickening agents can help to provide the desired rheology for the hair coloring composition, which is useful in terms of mixing and anti-drip. The hair coloring composition may comprise from 0.01% to 5% of the one or more thickening agents by total weight of the hair coloring composition. The one or more thickening agents of the hair coloring composition may be a thickening polymer.

The hair coloring composition may comprise from 0.1% to 2% of the one or more thickening polymers by total weight of the hair coloring composition. The one or more thickening polymers of the hair coloring composition may be selected from the group consisting of associative polymers, crosslinked acrylic acid homopolymers, crosslinked copolymers of (meth)acrylic acid and of (C₁-C₆)alkyl acrylate, polysaccharides and mixtures thereof. The thickening polymer of the hair coloring composition may also serve as conditioning agents, as described below.

Conditioning agent

The hair coloring composition may comprise one or more conditioning agents. The one or more conditioning agents of the hair coloring composition may be selected from the group consisting of silicone materials, amino silicones, fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, cationic surfactants, insoluble oils and oil derived materials and mixtures thereof. The one or more conditioning agents of the hair coloring composition may be selected from the group consisting of mineral oils, glycerine, sorbitol and mixtures thereof.

The hair coloring composition may comprise from 0.05% to 20%, or from 0.1% to 15%, or from 0.2% to 10%, or from 0.2% to 2%, or from 0.5% to 2% of the one or more conditioning agents by total weight of the hair coloring composition. The one or more conditioning agents may be included in a separate pre- and/or post-treatment composition.

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

Particularly useful conditioning agents for the hair coloring composition may be cationic polymers and/or silicones. Cationic polymers may 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 of the main polymer chain, or be borne by a side substituent that is directly attached to the main polymer chain.

The one or more conditioning agents of the hair coloring composition may be a silicone. The silicone of the hair coloring composition may be selected from the group consisting of polyalkylsiloxane oils, linear polydimethylsiloxane oils containing trimethylsilyl or hydroxydimethylsiloxane endgroups, polymethylphenylsiloxane polydimethylphenylsiloxane, 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 polypropyleneoxy groups, (per)fluorinated groups, thiol groups, substituted or unsubstituted amino groups, carboxylate groups, hydroxylated groups, alkoxyated groups, quaternium ammonium groups, amphoteric, betain groups and mixtures thereof. The silicone of the hair coloring composition may be either used as a neat fluid or in the form of a pre-formed emulsion.

Cosmetically acceptable carrier

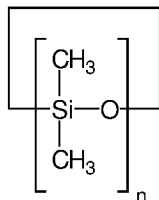
The hair coloring composition comprises a cosmetically acceptable carrier. The cosmetically acceptable carrier of the hair coloring composition may be an aqueous carrier. The hair coloring composition may comprise water. Water can provide a hydrophilic phase, which the hydrophilic portions of any other ingredients comprised in the hair coloring composition can interact with water. Water can also provide a fluid phase meaning that the hair coloring composition can be in liquid form and therefore easily mixed with other fluid formulations such as the oxidizing formulation. The hair coloring composition may comprise from 50% to 85% water, or from 65% to 75% of water by total weight of the hair coloring composition.

The cosmetically acceptable carrier is any carrier suitable for formulating the one or more acrylate monomers into a hair coloring composition being suitable for application onto hair. The cosmetically acceptable carrier may be selected from either an aqueous medium or an aqueous-alcoholic medium. When the cosmetically acceptable carrier is an aqueous-alcoholic carrier, the cosmetically acceptable carrier may comprise water and an alcohol. An alcohol can advantageously influence the viscosity of a relatively wide spectrum of ingredients of the hair coloring composition. The alcohol of the hair coloring composition may be selected from the group consisting of: ethanol, isopropanol, propanol, and mixtures thereof.

When the cosmetically acceptable carrier is an aqueous carrier, the aqueous carrier may consist essentially of water and may be substantially free of alcohol. The hair coloring composition may comprise a safe and effective amount of cosmetically acceptable carrier which is water. The hair coloring composition may comprise from 0.1% to 99%, or from 1% to 98%, or from 10% to 97%, or from 30% to 95% of water by total weight of the hair coloring composition.

The hair coloring composition may be substantially free of alcohol, such as volatile alcohols (e.g. ethanol, isopropanol, propanol). When the hair coloring composition is substantially free of alcohol, the hair coloring composition can have advantageously a reduced odour. Flammability issues can also be prevented.

The cosmetically acceptable carrier of the hair coloring composition may be an oily compound. The oily compound may be selected from the group consisting of cyclic silicones and volatile hydrocarbons. Cyclic silicones can be available from Dow Corning. The cyclic silicone may have from at least 3 silicone atoms or from at least 5 silicone atoms but no more than 7 silicone atoms or no more than 6 silicone atoms. The cyclic silicone may conform to the formula:



wherein n is from 3 or from 5 but no more than 7 or no more than 6. The cyclic silicone may have a kinematic viscosity of less than 10 cSt at 23°C. A Suitable cyclic silicone for use herein may include Cyclomethicone D5 (commercially available from G.E. Silicones). Alternatively, the hair coloring composition may be silicone-free.

Volatile hydrocarbons e.g. Isopar can be obtained from ExxonMobil Petroleum and Chemical. The oily compound may be a mineral oil. Trade names for suitable mineral oils include Benol, Blandol, Hydrobrite, Kaydol (Sonneborn LLC Refined Products), Chevron Superla White Oil (Chevron Products Company), Drakeol, Parol (Calumet Penreco LLC), Penetack (Calumet Penreco LLC), Marcol, and Primol 352 (ExxonMobil Petroleum and Chemical).

Hydrophobic phase

The hair coloring composition may comprise a hydrophobic phase. The hydrophobic phase of the hair coloring composition may be selected from the group consisting of fatty alcohols, fatty acids, and mixtures thereof. The fatty alcohols and/or fatty acids may comprise from 10 to 30, or from 12 to 20, or from 16 to 18 carbon atoms. The hydrophobic phase of the hair coloring composition may comprise two different fatty alcohols. The hydrophobic phase of the hair coloring composition may comprise two different fatty alcohols, both comprising from 10 to 14 carbons.

Preservative

The hair coloring composition may comprise at least one preservative and/or a mixture of preservatives. The hair coloring composition may comprise from 0.01% to 1% preservative, or from 0.1% to 0.5% preservative. The preservative of the hair coloring composition may be selected from the group consisting of benzyl alcohol, phenoxyethanol, 1,3-bis(hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione, and mixtures thereof. The hair coloring composition may comprise at least one preservative; and wherein the preservative may be selected from the group consisting of benzyl alcohol, phenoxyethanol, and mixtures thereof; or wherein the preservative may be a mixture of benzyl alcohol and phenoxyethanol. The hair coloring composition may be

substantially free of benzoate compounds. Indeed, having benzoate compounds can help to prevent instability and/or precipitation of the hair coloring composition. The hair coloring composition may be substantially free of parabens.

Perfume

The hair coloring composition may comprise one or more perfumes. The hair coloring composition may comprise from 0.001% to 2% of the one or more perfumes by total weight of the hair coloring composition. Perfume can provide an enhanced user experience by making the composition smell pleasant and/or invoke emotions tailored to the visual effects on the fibers, such as relaxing or exciting smells.

Alternatively, the hair coloring composition may be substantially free of perfume and/or fragrance. Some consumers prefer perfume-free compositions.

The one or more perfumes of the hair coloring composition may be an animal fragrance or a plant fragrance. The animal fragrance may be selected from the group consisting of musk oil, civet, castoreum, ambergris, and mixtures thereof.

The plant fragrance may be selected from the group consisting of nutmeg extract, cardamon extract, ginger extract, cinnamon extract, patchouli oil, geranium oil, orange oil, mandarin oil, orange flower extract, cedarwood, vetiver, lavender, ylang extract, tuberose extract, sandalwood oil, bergamot oil, rosemary oil, spearmint oil, peppermint oil, lemon oil, lavender oil, citronella oil, chamomille oil, clove oil, sage oil, neroli oil, labdanum oil, eucalyptus oil, verbena oil, mimosa extract, narcissus extract, carrot seed extract, jasmine extract, olibanum extract, rose extract, and mixtures thereof.

The one or more perfumes of the hair coloring composition may be selected from the group consisting of acetophenone, adoxal, aldehyde C-12, aldehyde C-14, aldehyde C-18, allyl caprylate, ambroxan, amyl acetate, dimethylindane derivatives, α -amylcinnamic aldehyde, anethole, anisaldehyde, benzaldehyde, benzyl acetate, benzyl alcohol and ester derivatives, benzyl propionate, benzyl salicylate, borneol, butyl acetate, camphor, carbitol, cinnamaldehyde, cinnamyl acetate, cinnamyl alcohol, cis-3-hexanol and ester derivatives, cis-3-hexenyl methyl carbonate, citral, citronellol and ester derivatives, cumin aldehyde, cyclamen aldehyde, cyclo galbanate, damascones, decalactone, decanol, estragole, dihydromyrcenol, dimethyl benzyl carbinol, 6,8-dimethyl-2-nonanol, dimethyl benzyl carbonyl butyrate, ethyl acetate, ethyl isobutyrate, ethyl butyrate, ethyl propionate, ethyl caprylate, ethyl cinnamate, ethyl hexanoate, ethyl valerate, ethyl vanillin, eugenol, exaltolide, fenchone, fruity esters such as ethyl 2-methyl

butyrate, galaxolide, geraniol and ester derivatives, helional, 2-heptonone, hexenol, α -hexylcinnamic aldehyde, hydroxycitronellal, indole, isoamyl acetate, isoeugenol acetate, ionones, isoeugenol, isoamyl iso-valerate, iso E super, limonene, linalool, lilial, linalyl acetate, lyral, majantol, mayol, melonal, menthol, p-methylacetophenone, methyl anthranilate, methyl cedrylone, methyl dihydrojasmonate, methyl eugenol, methyl ionone, methyl- α -naphthyl ketone, methylphenylcarbonyl acetate, mugetanol, γ -nonalactone, octanal, phenyl ethyl acetate, phenyl-acetaldehyde dimethyl acetate, phenoxyethyl isobutyrate, phenyl ethyl alcohol, pinenes, sandalore, santalol, stemone, thymol, terpenes, triplal, triethyl citrate, 3,3,5-trimethylcyclohexanol, γ -undecalactone, undecenal, vanillin, veloutone, verdox, and mixtures thereof.

Viscosity

The hair coloring composition may have a kinematic viscosity of from 0.5 cSt to 1500 cSt, measured at 23°C according to the following method. “Viscosity” can mean dynamic viscosity (measured in mPa·s) or kinematic viscosity (measured in centistokes, cSt) of a liquid at 23°C and ambient conditions. Dynamic viscosity may be measured using a rotational viscometer, such as a Brookfield Dial Reading Viscometer Model 1-2 RVT available from Brookfield Engineering Laboratories (USA) or other substitutable model as known in the art. Typical Brookfield spindles which may be used include, without limitation, RV-7 at a spindle speed of 20 rpm, recognizing that the exact spindle may be selected as needed by one skilled in the art. Kinematic viscosity may be determined by dividing dynamic viscosity by the density of the liquid (at 23°C and ambient conditions), as known in the art.

The viscosity of the hair coloring composition may be useful in view of enabling the hair coloring composition to be readily applied to the hair fibers – e.g. spread evenly onto the hair. Viscosity can be influenced by the level of cosmetically acceptable carrier in the hair coloring composition and the level of the thickening agent.

The hair coloring composition may have a kinematic viscosity of from 1 cSt to 1000 cSt. The hair coloring composition may have a kinematic viscosity of from 1.5 cSt to 500 cSt, or from 2 cSt to 350 cSt, or from 2.5 cSt to 200 cSt, or from 3 cSt to 150 cSt, measured at 23°C. 1 centistoke (cSt) is equal to $1 \times 10^{-6} \text{ m}^2/\text{s}$.

The hair coloring composition may have a dynamic viscosity of from 1 mPa·s to 5000 mPa·s. The hair coloring composition may have a viscosity of from 2 mPa·s to 400 mPa·s, or

from 3 mPa·s to 100 mPa·s. Alternatively, the hair coloring composition may have a dynamic viscosity of from 30 mPa·s to 250 mPa·s, or from 100 mPa·s to 200 mPa·s.

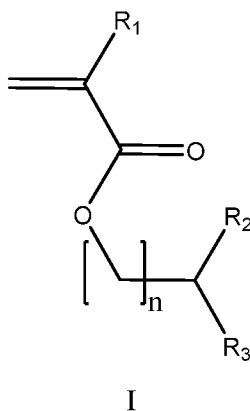
This viscosity range of the hair coloring composition may be useful in view of helping to prevent the hair coloring composition from dripping. When the viscosity is too high, the hair coloring composition may not be readily mixed, e.g. with the cosmetically acceptable carrier, where present.

Volatility

The hair coloring composition may be substantially free of compounds having a vapor pressure below 0.01 mmHg, or below 0.001 mm Hg, measured at 23°C and 1 atm. Having a hair coloring composition having a relatively low volatility can help to reduce the odour of the hair coloring composition and also can help to provide a relatively safer safety profile.

Use

A second aspect of the present invention relates to a use of the one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or a mixture thereof, in an hair coloring composition. The one or more acrylate monomers have the general Formula I:



wherein

R_1 is -H, -CH₃;

$n = 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is -H, -CH₃, -OH; and

R_3 is -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, -COOH.

The use of the one or more acrylate monomers of Formula I can help to improve the color result intensity in an hair coloring composition. The use of the one or more acrylate monomers of Formula I can improve the vibrancy of the color while providing hair strength.

Kit

A third aspect of the present invention is related to a kit for coloring hair comprising:

- (a) a hair coloring composition according to the first aspect;
- (b) an oxidizing formulation comprising one or more oxidizing agents; wherein the hair coloring composition (a) and the oxidizing formulation (b) are separately packaged.

The kit may further comprise (c) a conditioning formulation comprising one or more conditioning agents. Conditioning agents have already been described above.

The kit may further comprise (d) a thickening formulation. Such thickening formulations are currently on the market as under the brand “Color.id” from Wella™ Professionals. The thickening formulation of the kit may comprise one or more thickening polymers capable of interacting with the hydrophobic phase and the hydrophilic phase.

The thickening formulation of the kit may comprise from 0.001% to 10.0%, or from 0.01%, or 0.05%, or 0.1%, or 0.15%, or 0.25%, or 0.6%, or 1%, or 2%, or 2.5% to 8%, or 7%, or 6%, or 5%, or 4%, or 3%, or 2%, or 1% of the one or more thickening polymers by total weight of the thickening formulation. The one or more thickening polymers of the thickening formulation may be an associative thickening polymer.

The kit may further comprise a mixing receptacle and/or a mixing means. The mixing receptacle of the kit may be a bowl. The mixing means of the kit may be a spatula.

The oxidizing formulation of the kit may comprise one or more oxidizing agents. Preferred oxidizing agents are water-soluble peroxygen oxidizing agents. As used herein, “water-soluble” means that in standard conditions at least 0.1 g, preferably 1 g, more preferably 10 g of the oxidizing agent can be dissolved in 1 liter of deionized water at 25°C. The one or more oxidizing agents can be valuable for the initial solubilisation and decolorisation of the melanin (bleaching) and accelerate the oxidation of the oxidative dye precursors (oxidative dyeing) in the hair shaft.

The one or more oxidizing agents may be present in an amount sufficient to bleach melanin pigment in hair and/or cause formation of dye chromophores from oxidative dye precursors. Typically, the oxidizing formulation of the kit may comprise a total amount of the one or more oxidizing agents ranging from 0.1% to 20%, or from 0.5% to 12%, or from 1% to 10%, or from 2% to 5%, by total weight of the oxidizing formulation of the kit.

Suitable water-soluble oxidizing agents may include, but are not limited to: inorganic peroxygen materials capable of yielding hydrogen peroxide in an aqueous solution.

Suitable water-soluble peroxygen oxidizing agents may include, but are not limited to: hydrogen peroxide; inorganic alkali metal peroxides (such as sodium periodate and sodium peroxide); organic peroxides (such as urea peroxide and melamine peroxide); inorganic perhydrate salt bleaching compounds (such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like); and mixtures thereof. Inorganic perhydrate salts may be incorporated for example as monohydrates, tetrahydrates. Alkyl/aryl peroxides and/or peroxidases may also be used. Mixtures of two or more such oxidizing agents can be used if desired. The oxidizing agents may be provided in aqueous solution or as a powder which is dissolved prior to use.

The oxidizing formulation of the kit may preferably comprise a water-soluble oxidizing agent which is selected from the group consisting of hydrogen peroxide, percarbonates (which may be used to provide a source of both oxidizing agent and carbonate ions), persulphates, and mixtures thereof. The one or more oxidizing agents of the oxidizing formulation of the kit may be sodium percarbonate. The oxidizing formulation of the kit may be substantially free of persulphate.

The hair coloring composition (a) and the oxidizing formulation (b) may be packaged in separate sealed containers. The hair coloring composition (a) may be packaged in a flexible tube packaging composed of metal, plastics or a combination thereof. The oxidizing formulation (b) may be packaged in a squeezable container. The squeezable container may have at least 50% headspace. The squeezable container may have a headspace being at least the volume of the hair coloring composition (a). The oxidizing formulation may be packaged in a plastic container according to claim 1 of European Patent Application EP 2 801 281 A1, wherein the plastic container has two symmetrical collapsible side panels and a non-collapsible squeezable back panel; wherein the ratio of the average thicknesses between front and/or back panels and the side panels is at least 2:1 (EP 2 801 281 A1 paragraphs [0025] to [0044] as well as the Figures are incorporated herein by reference). The plastic container has the advantage that it is resistant to random, uncontrolled deformation under a substantial pressure differential between the environment and inside the container, yet having an affordable cost of manufacture and/or being appealing to the consumer.

Method

A fourth aspect of the present invention is related to a method of coloring hair comprising:

(a) mixing the hair coloring composition according to the first aspect with an oxidizing formulation comprising one or more oxidizing agent to form a mixture; and

(b) applying the mixture onto hair.

Steps (a) and (b) are carried out in the order (a) and then (b).

The mixture in the method may be obtained from mixing the hair coloring composition according to the first aspect and the oxidizing formulation at a 1:1 ratio by weight.

The hair coloring composition may comprise a redox partner, preferably sodium thiosulphate. A redox partner can help to increase the hair stiffness as shown more below.

Rheology

The hair coloring formulation may further comprise a hydrophobic phase, a hydrophilic phase, a surfactant, and a thickening polymer capable of interacting with the hydrophobic phase and the hydrophilic phase, wherein the composition has a storage modulus of at least 3000 Pa, or at least 3300 Pa, or at least 3500 Pa, or at least 4000 Pa, or at least 4500 Pa, or at least 5000 Pa, measured by frequency sweep at an angular frequency of 0.6 rad/s at 23°C, and wherein the thickening polymer is an associative thickening polymer and comprises hydrophobic moieties and hydrophilic moieties. The storage modulus may be not more than 10 kPa, or 9 kPa, or 8 kPa, or 7 kPa, or 6kPa, measured by frequency sweep at an angular frequency of 0.6 rad/s at 23°C. The hydrophilic moieties of the associative thickening polymer may comprise urethane units.

All details vis-à-vis the other aspects are compatible and combinable with the fifth aspect.

EXAMPLES

The following examples are non-limiting examples of the hair coloring compositions of the present invention. The examples are given solely for the purpose of illustration, and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from the spirit and scope of the invention, which would be recognized by one of ordinary skill in the art. All concentrations are listed as weight percent (% wt.), unless otherwise specified.

Hair coloring composition examples 1 to 7

Ingredients	Ex.1 (% wt.)	Ex.2 (% wt.)	Ex.3 (% wt.)	Ex.4 (% wt.)	Ex.5 (% wt.)	Ex.6 (% wt.)	Ex.7 (% wt.)
Hydroxybutyl methacrylate	11.0	10.0	-	-	9.0	5.0	-

Hydroxypropyl methacrylate	-	-	9.0	12.0	-	6.0	-
4-hydroxybutyl acrylate	-	-	-	-	-	-	12.0
Cetyl alcohol	7.0	14.0	-	7.0	-	6.0	6.5
Stearyl alcohol	7.0	-	12.0	7.0	-	6.0	6.5
Sodium laureth-6 carboxylate	-	-	-	-	-	2.0	-
Coconut alcohol	-	-	0.2	-	-	0.5	-
Propylene glycol	-	-	-	-	25.0	-	10.0
Sodium myreth sulphate	-	-	-	-	-	2.0	-
Glyceryl stearate	4.0	3.5	5.0	4.0	-	-	-
Glyceryl oleate	4.0	3.5	-	4.0	-	-	-
PEG-7 Glyceryl Cocoate	5.0	5.5	-	5.0	-	-	2.0
2,5-diaminotoluene sulphate	2.1	1.8	-	2.1	-	1.5	1.5
2,4-diamino phenoxyethanol HCl	-	0.01	2.0	-	-	-	-
1-methyl-2,5-diamino benzene	-	-	-	-	1.7	-	-
N,N-bis(2-hydroxyethyl)-p-phenylenediamine sulphate	-	-	2.5	-	-	-	-
2-amino-4-hydroxyethylamino anisole sulphate monohydrate	-	-	1.5	-	-	-	-
2-methyl-5-hydroxyethyl aminophenol	-	-	1.0	-	-	-	-
3-amino-2,6-dimethylphenol	-	-	2.0	-	-	-	-
2-amino-5-ethylphenol HCl	-	-	1.0	-	-	-	-

Hydroxyethyl-3,4-methylenedioxyaniline HCl	-	-	0.5	-	-	-	-
1,4-diamino-2-(methoxymethyl)-benzene	-	-	1.8	-	4.0	-	-
Phenyl methyl pyrazolone	-	-	0.25	-	-	-	-
1-hydroxyethyl-4,5-diamino pyrazole sulphate	-	-	3.0	-	-	3.0	3.0
4-amino-2-hydroxytoluene	0.1	-	0.5	0.1	1.4	1.0	1.0
m-aminophenol	0.1	0.2	0.5	0.1	-	0.1	-
p-aminophenol	-	-	0.5	-	2.5	-	0.5
Resorcinol	1.2	0.8	1.3	1.2	0.9	-	-
2-amino-6-chloro-4-nitrophenol	-	-	1.0	-	-	-	-
5-amino-6-chloro-o-cresol	-	-	-	-	-	-	1.0
2-methylresorcinol	-	-	1.0	-	-	-	-
1-naphthol	-	-	1.0	-	-	-	-
Lauryl glucoside	-	-	-	-	-	2.0	-
Decyl glucoside	-	-	-	-	-	-	-
Acrylamido propyltrimonium chloride/acrylates copolymer	-	-	-	-	-	1.0	-
Carbomer	-	-	-	-	-	-	0.5
Hydroxyethylcellulose	-	-	-	-	1.5	-	-
Polyquaternium-22	-	-	0.05	-	-	-	0.1
Polyquaternium-10	0.3	0.3	-	0.3	-	-	-

Polyquaternium-7	3.0	3.0	-	3.0	-	-	-
Dimethicone	-	-	-	-	-	-	0.5
Cetareth-12	-	-	-	-	-	0.5	-
Cetareth-20	-	1.0	-	-	-	0.5	-
Cetareth-25	1.0	-	-	1.0	-	-	-
Laureth-12	-	-	-	-	-	-	1.0
Deceth-3	-	-	-	-	-	-	1.0
Oleth-30	-	-	-	-	-	-	1.0
Sodium Laureth Sulphate	2.0	2.0	1.0	2.0	-	-	-
Sodium Lauryl Sulphate	2.0	-	2.0	2.0	-	-	-
Macadamia ternifolia seed oil	-	-	-	-	-	0.1	-
Grape seed oil	-	-	-	-	-	-	0.1
Sodium sulfite	0.4	-	0.2	0.4	-	0.2	-
Sodium metabisulfite	-	0.3	-	-	0.7	-	0.5
Ammonium sulphate	-	0.1	-	-	-	0.1	-
Sodium sulphate	0.5	-	0.5	0.5	-	-	-
Pentasodium pentetate	-	-	-	-	-	-	0.1
Silica dimethyl silylate (nano)	-	-	-	-	-	-	0.1
Sodium silicate	-	-	-	-	-	0.1	-
Etidronic acid	0.2	0.2	-	0.2	-	0.2	-
Disodium EDTA	-	-	0.05	-	0.1	-	-
Titanium dioxide	-	-	-	-	-	-	0.1
Monoethanol amine	-	-	-	-	14.5	-	16
Ascorbic acid	0.2	0.2	0.15	0.2	0.3	0.2	0.2
Lauric acid	-	-	-	-	-	0.15	0.1
Sodium chloride	-	-	-	-	-	0.1	0.1
Potassium hydroxide	-	-	-	-	-	0.2	-
Sodium hydroxide	0.03	-	0.25	0.03	-	-	-
Ammonium hydroxide	2.0	2.3	1.25	2.0	-	2.0	1.5

Perfume	0.25	0.2	0.2	0.25	-	0.2	0.1
Water	QSP	QSP	QSP	QSP	QSP	QSP	QSP
Total	100	100	100	100	100	100	100

The hair coloring composition is mixed with a developer composition at a mixing of 1:1. A suitable developer composition is a commercially available Wella Welloxon™ Perfect Developer Cream, 6% wt. hydrogen peroxide. The resulting mixture is then applied to hair strands of hair (3 g per hair strands). After a leave-on time of 30 min at room temperature (23°C), the hair is rinsed, washed with a standard shampoo, rinsed and then dried.

EXPERIMENTAL

3-sulfopropylacrylate potassium salt (3-SPA) was commercially available from RASCHIG GmbH, Mundenheimer Strasse 100, 67061 Ludwigshafen, Germany, under the tradename RALU®MER SPA.

Hydroxypropyl methacrylate (HPMA) was available from Sigma-Aldrich (CAS 27813-02-1, as a mixture of hydroxypropyl and hydroxyisopropyl methacrylates, containing 180-220 ppm of monomethyl ether hydroquinone as radical inhibitor).

Color properties

The objective is to study the effect of the simultaneous application to hair of oxidative dye precursors with either 3-sulfopropylacrylate potassium salt or hydroxypropyl methacrylate.

Compositions

The following compositions were prepared. The following reference compositions and the hair coloring compositions comprising either 3-sulfopropylacrylate potassium salt or hydroxypropyl methacrylate were prepared:

	Reference A1, D1	Reference B1, E1	Reference C1, F1
Wella™ Koleston Perfect 6/0 (dark blond color)	100%		
Wella™ Koleston Perfect 12/1 (blond color)		100%	
Wella™ Koleston Perfect 66/46 (red color)			100%

The following compositions were prepared:

Each reference composition for the respective hair strands A1, D1, B1, E1, C1 and F1 were prepared by mixing 10 g of a mixture of oxidative dye precursors prepared from a composition comprising 100% wt. (i.e. 10 g) of the respective commercially available Wella™ Koleston Perfect 6/0, 12/1, or 66/46 by total weight of the hair coloring composition with 10 g of a cosmetically acceptable carrier (e.g. water).

The following and respective 12% 3-SPA and 12% HPMA were prepared and comprise the following ingredients:

	12% 3-SPA	12% HPMA
3-sulfopropyl acrylate	12	-
Hydroxypropyl methacrylate	-	12
Cellosize HEC QP 4400 ¹	0.20	0.20
EDTA	0.12	0.12
Keltrol CG-T ²	1.00	1.00
Phenoxethol ³	1.00	1.00
PHB-Methylester ⁴	0.20	0.20
Genapol® C 100 ⁵	0.70	0.70
Cremophor EL ⁶	0.70	0.70
Fragrance	0.30	0.30
Distilled water	QSP	QSP
Total	100	100

The following hair coloring compositions were prepared:

	Hair coloring composition for A3	Hair coloring composition for B3	Hair coloring composition for C3
Reference A1, D1	10 g		
Reference B1, E1		10 g	
Reference C1, F1			10 g
12% 3-SPA	10 g	10 g	10 g

Each hair coloring composition for the respective hair strand A3, B3 or C3 were prepared by mixing 10 g of a mixture of oxidative dye precursors prepared from the respective Reference A1, B1 or C1 composition comprising the respective Wella™ Koleston Perfect 6/0 or 12/1 or 66/46 with 10 g of a 12% of 3-SPA composition.

	Hair coloring composition for D3	Hair coloring composition for E3	Hair coloring composition for F3
Reference A1, D1	10 g		
Reference B1, E1		10 g	
Reference C1, F1			10 g
12% HPMA	10 g	10 g	10 g

Each hair coloring composition for the respective hair strand D3, E3 or F3 were prepared by mixing 10 g of a mixture of oxidative dye precursors prepared from the respective Reference D1, E1 or F1 composition comprising the respective Wella™ Koleston Perfect 6/0 or 12/1 or 66/46 with 10 g of a 12% of HPMA composition.

Hair strands

Ponytail hair strands having a width of 2.5 cm and a length of 22 cm.

Available from *International Hair Importers & Products*, Glendale, NY

Mass: 3.0 g $\pm$ 0.05g

Characteristics: cysteic acid: 17.4 – 18.1 μ mol/g hair; medullated hair, ϕ : 60-80 μ m

Pre-treatment (Bleaching process)

The hair strands were weighed and then soaked in a mixture of 2.5 g bleaching powder and 7.5 ml Wella Welloxyd™ per 1 g of hair (in a lab basin). It has to be carried out in an extractor hood. The concentration of hydrogen peroxide in Wella Welloxyd™ was 9%. The residence time during the bleaching step was 30 min. The hair strands were turned upside down after each 7.5 min. After bleaching the hair strands were rinsed under tap water (6 L/min, 35°C) for 2 min. The bleaching process was carried out twice in which the second bleaching step followed immediately after the first bleaching step. The hair strands were washed twice with 0.25 ml

standard-shampoo (10% Na-laurylether-sulphate, 4% NaCl) per 1 g hair for 1 minute, rinsed for 1 minute. Then the hair strands were stored in distilled water for 24h. After that the hair strands were rinsed for 2 min under tap water (6 L/min, 35°C). Finally the hair strands were dried at 20°C and 65% relative humidity at least overnight.

Coloring treatment

Fig. 1 represents a photography showing pairs of two hair strands treated by the respective compositions A1-F3.

Each reference composition to be applied to the respective hair strands A1, B1, C1, D1, E1, F1 were mixed with 10 g of a developer composition which was the commercially available Wella™ Welloxon Perfect Developer Cream, 6% wt. hydrogen peroxide.

Each hair coloring composition to be applied to the respective hair strands A3, B3, C3, D3, E, F3 were mixed with 10 g of a developer composition which was the commercially available Wella™ Welloxon Perfect Developer Cream, 6% wt. hydrogen peroxide.

Then, 3 g of each of the above compositions to be tested were applied to two respective pre-treated hair strands A1, B1, C1, D1, E1 or F1, or A3, B3, C3, D3, E3 or F3 with a brush. The color for each hair strand was left for 30 minutes at 30°C. After 30 minutes, each hair strand was rinsed for 2 min under tap water (6 L/min, 35°C) and then blow-dried.

For the hair strands A2, B2 and C2, 3 g of each of the respective hair coloring composition A1, B1 or C1 activated with the developer composition as stated hereinbefore were applied with a brush to two respective pre-treated hair strands A2, B2 or C2. The color for each hair strand was left for 30 minutes at 30°C. After 30 minutes, each hair strand was rinsed for 2 min under tap water (6 L/min, 35°C) and then blow-dried.

Then, 3 g of the 12% 3-SPA composition was applied with a brush to these two respective hair strands A2, B2 or C2. Each hair strand was left for 30 minutes at 30°C. After 30 minutes, each hair strand was rinsed for 2 min under tap water (6 L/min, 35°C) and then blow-dried.

After the hair coloring composition is rinsed off the hair for 2 minutes, the hair is then shampooed with Wella™ Professionals Brilliance, Fine/Normal shampoo commercially available

in Germany in April 2014 and conditioned with Wella™ Professionals Brilliance, Fine/Normal conditioner commercially available in Germany in April 2014 for 1 minute and then blow-dried.

For the hair strands D2, E2 and F2, 3 g of each of the respective hair coloring composition D1, E1, or C1 activated the developer composition as stated hereinbefore were applied with a brush to two respective pre-treated hair strands A2, B2 or C2. The color for each hair strand was left for 30 minutes at 30°C. After 30 minutes, each hair strand was rinsed for 2 min under tap water (6 L/min, 35°C) and then blow-dried.

Then, 3 g of the 12% HPMA composition was applied with a brush to these two respective hair strands. Each hair strand was left for 30 minutes at 30°C. After 30 minutes, each hair strand was rinsed for 2 min under tap water (6 L/min, 35°C) and then blow-dried.

After the hair coloring composition is rinsed off the hair for 2 minutes, the hair is then shampooed with Wella™ Professionals Brilliance, Fine/Normal shampoo commercially available in Germany in April 2014 and conditioned with Wella™ Professionals Brilliance, Fine/Normal conditioner commercially available in Germany in April 2014 for 1 minute and then blow-dried.

Color results when using 3-sulfopropylacrylate potassium salt

The resulted hair strands A1 or A2 provided an overall dark blond color (Fig. 1, photo A). However, when applying to hair, a hair coloring composition A3 comprising oxidative dyes precursors and 3-sulfopropylacrylate potassium salt, the hair strands A3 provided a relatively lighter blond shade than the hair strands of A1 or A2.

The resulted hair strands B1 or B2 provided an overall blond color (Fig. 1, photo B). However, when applying to hair, a hair coloring composition comprising oxidative dyes precursors and 3-sulfopropylacrylate potassium salt, the hair strands B3 provided a slightly lighter blond shade than the hair strands of B1 or B2.

The resulted hair strands C1 or C2 provided an overall red color (Fig. 1, photo C). However, when applying to hair, a hair coloring composition comprising oxidative dyes precursors and 3-sulfopropylacrylate potassium salt, the hair strands C3 provided a lighter red shade than the hair strands of C1 or C2.

When using oxidative dyes precursors mixed with 3-sulfopropylacrylate potassium salt, adverse color effects have been thus observed.

Color results when using hydroxypropyl methacrylate

The resulted hair strands D1 or D2 provided an overall dark blond color (Fig. 1, photo D). The resulting color of the hair strands in D3 was even more vibrant with regard to the resulting color of either the hair strands in D1 or D2.

The resulted hair strands E1 or E2 provided an overall blond color (Fig. 1, photo E). The resulting color of the hair strands in E3 was even more vibrant with regard to the resulting color of either the hair strands in E1 or E2.

The resulted hair strands F1 or F2 provided an overall red color (Fig. 1, photo F). The resulting color of the hair strands in F3 was even more vibrant with regard to the resulting color of either the hair strands in F1 or F2.

No adverse color effects have been observed when mixing oxidative dye precursors with hydroxypropyl methacrylate in a hair coloring composition in comparison with 3-SPA. The similar color is obtained within the hair strands of D, E or F groups. When applying to hair either a hair coloring composition comprising hydroxypropyl methacrylate or a hair coloring composition comprising hydroxypropyl methacrylate and oxidative dyes precursors, no adverse color effects have been observed. Also, an improvement of the vibrancy of the resulting color was observed when applying to the hair, a hair coloring composition comprising hydroxypropyl methacrylate and oxidative dyes precursors.

Stiffness properties

The objective is to study the effect of the application of hydroxypropyl methacrylate to hair versus 3-sulfopropylacrylate potassium salt in terms of hair stiffness.

Hair Stiffness Test Method

The hair Stiffness Test Method is based on the European Patent Application EP 14182793.1 which is completely incorporated by reference.

The objective of the Hair Stiffness Test Method as disclosed herein is to measure the surface properties of the hair fibres, in terms of hair stiffness when the hair fibres have been treated with specific hair compositions.

Description of the apparatus

Fig. 2 is a schematic representation of a device 1 suitable for the Hair Stiffness Test Method. The device comprises six rods 3. A hair strand 2 is not depicted. The device 1 comprises a plurality of rods 3. The plurality of rods 3 are for bending the fibre(s) of a hair strand 2. The rods 3 are capable of freely rotating; wherein each rod 3 has a proximal end and a distal end 5; wherein the distal end 5 is free. The plurality of rods 3 are arranged such that the distal ends 5 are arranged on the same side of the device 1.

The rods 3 are capable of freely rotating. Herein “freely rotating” means rotation is hindered as little as possible. All rods 3 are cylindrical.

The proximal end of each rod 3 is connected to a support 6. Two fibre-guiding means 7 are mounted on each rod. The fibre-guiding means 7 is firmly attached to its rod 3, or immovably attached to its rod 3 during use. The firm attachment is useful in preventing unnecessary friction fluctuations caused by rotation of the fibre-guiding means 7 around the rod 3. This ensures a negligibly small level of friction of the fibre(s) against the fibre-guiding means 7 with very low friction fluctuation. The fibre-guiding means 7 are located either side of the hair strand of fibres such that the fibre-guiding means 7 are from 100% to 150% of the hair strand width apart.

The proximal end of each rod 3 is connected to a support 6. The support 6 of the device 1 provides a solid base for the rods 3.

Measurements using the device 1 may be performed in a rotational mode, where the rods (and their attached fibre-guiding means 7) freely rotate. In the rotational mode, the device can be used to measure fibre bending force and fibre-fibre friction. Since the rods 3 and fibre-guiding means 7 freely rotate when the device 1 is in the rotational mode, the difference between force in stationary and rotational modes can be used to calculate the friction force on rods 3.

Fig. 3 shows the device of Fig. 2 with a fibre-pulling means which is pulling the fibres of a hair strand 2. The fibres of a hair strand 2 are passed through the device 1 using a fibre-pulling means 10. The fibre-pulling means 10 is able to pull at a constant rate and simultaneously measure force. Commercially available load extension measurement system Instron[®] model No. 3343 was used.

Description of the method

For conducting the Hair Stiffness Test Method, a device 1 was provided as described hereinbefore. Fibres of a hair strand 2 were provided by threading the fibres of the hair strand 2 through the plurality of rods 3 between the fibre-guiding means 7. Then, by use of a fibre-pulling means 10, the fibres of the hair strand 2 were passed through the device 1 and the force required to do this was simultaneously measured. In order to measure the hair stiffness of the fibres of the hair strand 2, the device 1 operates in rotational mode; wherein during the rotational mode, the rods 3 freely rotate.

Protocol experimental for each hair strand to be tested:

Each hair strand was passed in a S-shape between the rods of the device 1 (as illustrated in Fig. 2-3) comprising six rods by means of an Instron® model No. 3343 at an extension of 400 mm/min. The measurement is executed 5 times in rotational mode. The forces exerted are calculated as total work (energy in mJ). The work in the rotational mode relates to the hair stiffness. For each composition to be tested, the hair stiffness of five hair strand replicates were measured and averaged.

Measurements and calculations

The device was used to measure the rotational work of pulling ($W^{rotational}$). The rotational work of pulling ($W^{rotational}$) that is measured measures the sum of the work of fibre-fibre friction ($W^{fibre-fibre\ friction}$) and work of fibre stiffness ($W^{fibre\ stiffness}$). The work of fibre stiffness is the work caused by bending a fibre(s). The rotational work of pulling ($W^{rotational}$) that is measured corresponds to the hair stiffness (in mJ).

Comparative data with 3-SPA

The effect of a styling treatment on hair fibre stiffness in the context of a hair strand of fibres is tested.

Hair strands

Ponytail hair strands having a width of 5 cm and a length of 22 cm.

Available from *International Hair Importers & Products*, Glendale, NY

Mass: 6.0 g $\pm$ 0.05g

Characteristics: cysteic acid: 17.4 – 18.1 μ mol/g hair; medullated hair, ϕ : 60-80 μ m

All hair strands used are double pre-treated (see bleaching process as stated hereinbefore) prior to use in order to improve normalisation i.e. consistency of hair quality. For each experiment sample, 5 hair strands are used. The hair stiffness is then an average of five measured hair stiffness.

“Untreated” corresponds to an untreated hair strand.

A placebo composition and styling compositions “X% 3-SPA”, respectively, were prepared before application to the hair and comprise the following ingredients:

	Placebo	X% 3-SPA composition
3-sulfopropyl acrylate	-	X = 4, or 8, or 12 or 16
Cellosize HEC QP 4400 ¹	0.20	0.20
EDTA	0.12	0.12
Keltrol CG-T ²	1.00	1.00
Phenoxethol ³	1.00	1.00
PHB-Methylester ⁴	0.20	0.20
Genapol® C 100 ⁵	0.70	0.70
Cremophor EL ⁶	0.70	0.70
Fragrance	0.30	0.30
Distilled water	QSP	QSP
Total	100	100

KEY: 1 = Hydroxyethylcellulose; 2 = Xanthan gum (high molecular weight heteropolysaccharide gum produced by a pure-culture fermentation of a carbohydrate with *Xanthomonas campestris*); 3 = 2-(phenoxy)ethanol; 4 = methyl paraben; 5 = Coceth-10 (Coconut oil alcohol, ethoxylated); 6 = PEG-35 Castor Oil.

Each respective composition Placebo and X% 3-SPA compositions (75 g, X can be either 4%, or 8%, or 12% or 16%) is mixed with 12.5 g of Kadus I-Motion Ready Fix 1.9% Peroxide as commercially available from Wella™ (6:1) to lead to an activated Placebo or X% 3-SPA composition.

1.2 g of the above activated Placebo or X% 3-SPA composition per 1 g hair is applied on each hair strand and massaged in for 10 seconds. After 30 minutes at room temperature, the respective composition is wiped off with the fingers. Each hair strand is rinsed with tap water for 1 min (6 L/min, 35°C) and adjusted to a residual humidity of 50% by weight.

Then 0.25 ml Pantene™ Clarifying Shampoo per 1 g hair is applied and massaged in for 1 min. Afterwards, the hair strand is rinsed with tap water for 1 min (6 L water/min, 35°C). All treated hair strands are combed 10 times with a metal comb (5 times with the coarse side and 5 times with the fine side). The hair strands have a residual humidity of 50% per weight. The hair strands are placed in stretched condition in a lab dish. The tip ends are weighed down with a plastic spatula to prevent the bending of the hair strands. Finally, the hair strands are dried in the climatic chamber overnight (20°C, 65% Relative Humidity (RH)).

Each hair strand is passed in a S-shape between the rods of the device 1 as described hereinbefore comprising six rods by means of an Instron® model No. 3343 at an extension of 400 mm/min. The measurement is executed 5 times in stationary mode and 5 times in rotational mode. The forces exerted are calculated as total work (energy). The work in the rotational mode relates to the hair stiffness.

Results

Fig. 4 shows the hair stiffness of the fibres when treated with different compositions of 3-SPA. The presence of 3-sulfopropyl acrylate in the 4%-16% 3-SPA compositions versus the placebo causes an increase in stiffness of the hair fibres, as shown in Fig. 4. 3-sulfopropyl acrylate is a monomer that polymerises to form a polymer inside the hair shaft. This concept has been discussed in WO2009/088520A, WO2012/100006A, WO2012/100007A and EP2295029A. From the present data it is demonstrated that the polymer causes a change in the mechanical properties of the hair fibre – here, hair fibre stiffness increase is demonstrated.

Data with hydroxypropyl methacrylate

The effect of a styling treatment on hair fibre stiffness in the context of a hair strand of fibres is tested.

Hair strands

Ponytail hair strands having a width of 5 cm and a length of 22 cm.

Available from *International Hair Importers & Products*, Glendale, NY

Mass: 6.0 g $\pm$ 0.05g

Characteristics: cysteic acid: 17.4 – 18.1 μ mol/g hair; medullated hair, ϕ : 60-80 μ m

All hair strands used are double pre-treated (see bleaching process as stated hereinbefore) prior to use in order to improve normalisation i.e. consistency of hair quality. For each experiment sample, 5 hair strands are used. The hair stiffness is then an average of five measured hair stiffness.

“Untreated” corresponds to an untreated hair strand.

A placebo 1 composition and styling compositions “X% HPMA”, respectively, were prepared before application to the hair and comprise the following ingredients:

	Placebo 1	X% HPMA composition
Hydroxypropyl methacrylate	-	X = 1, or 4, or 8 or 12
Cellosize HEC QP 4400 ¹	0.20	0.20
EDTA	0.12	0.12
Keltrol CG-T ²	1.00	1.00
Phenoxethol ³	1.00	1.00
PHB-Methylester ⁴	0.20	0.20
Genapol® C 100 ⁵	0.70	0.70
Cremophor EL ⁶	0.70	0.70
Fragrance	0.30	0.30
Distilled water	QSP	QSP
Total	100	100

KEY: 1 = Hydroxyethylcellulose; 2 = Xanthan gum (high molecular weight heteropolysaccharide gum produced by a pure-culture fermentation of a carbohydrate with *Xanthomonas campestris*); 3 = 2-(phenoxy)ethanol; 4 = methyl paraben; 5 = Coceth-10 (Coconut oil alcohol, ethoxylated); 6 = PEG-35 Castor Oil.

Each respective composition Placebo 1 and X% HPMA compositions (75 g, X can be either 1%, or 4%, or 8% or 12%) is mixed with 12.5 g of Kadus I-Motion Ready Fix 1.9%

Peroxide as commercially available from Wella™ (6:1) to lead to an activated Placebo 1 or X% 3-HPMA composition.

1.2 g of the above activated Placebo 1 or X% HPMA composition per 1 g hair is applied on each hair strand and massaged in for 10 seconds. After 30 minutes at room temperature, the respective composition is wiped off with the fingers. Each hair strand is rinsed with tap water for 1 min (6 L/min, 35°C) and adjusted to a residual humidity of 50% by weight.

Then 0.25 ml Pantene™ Clarifying Shampoo per 1 g hair is applied and massaged in for 1 min. Afterwards, the hair strand is rinsed with tap water for 1 min (6 L water/min, 35°C). All treated hair strands are combed 10 times with a metal comb (5 times with the coarse side and 5 times with the fine side). The hair strands have a residual humidity of 50% per weight. The hair strands are placed in stretched condition in a lab dish. The tip ends are weighed down with a plastic spatula to prevent the bending of the hair strands. Finally, the hair strands are dried in the climatic chamber overnight (20°C, 65% RH).

For “Placebo 2 + Booster”, 1.2 g of the above activated Placebo 1 composition per 1 g hair is applied on each hair strand and massaged in for 10 seconds. After 30 minutes of dwell time at room temperature, a 10% aqueous solution of sodium thiosulphate (0.25 g, commercially available from Sigma-Aldrich) per 1 g of hair is applied on each hair strand and massaged in for 10 seconds. After 30 minutes at room temperature, the respective composition is wiped off with the fingers. Each hair strand is rinsed with tap water for 1 min (6 L/min, 35°C) and adjusted to a residual humidity of 50% by weight.

Then 0.25 ml Pantene™ Clarifying Shampoo per 1 g hair is applied and massaged in for 1 min. Afterwards, the hair strand is rinsed with tap water for 1 min (6 L water/min, 35°C). All treated hair strands are combed 10 times with a metal comb (5 times with the coarse side and 5 times with the fine side). The hair strands have a residual humidity of 50% per weight. The hair strands are placed in stretched condition in a lab dish. The tip ends are weighed down with a plastic spatula to prevent the bending of the hair strands. Finally, the hair strands are dried in the climatic chamber overnight (20°C, 65% RH).

For “12% HPMA + Booster”, 1.2 g of the above activated 12% HPMA composition per 1 g hair is applied on each hair strand and massaged in for 10 seconds. After 30 minutes of dwell time at room temperature, a 10% aqueous solution of sodium thiosulphate (0.25 g, commercially available from Sigma-Aldrich) per 1 g of hair is applied on each hair strand and massaged in for

10 seconds. After 30 minutes at room temperature, the respective composition is wiped off with the fingers. Each hair strand is rinsed with tap water for 1 min (6 L/min, 35°C) and adjusted to a residual humidity of 50% by weight.

Then 0.25 ml Pantene™ Clarifying Shampoo per 1 g hair is applied and massaged in for 1 min. Afterwards, the hair strand is rinsed with tap water for 1 min (6 L water/min, 35°C). All treated hair strands are combed 10 times with a metal comb (5 times with the coarse side and 5 times with the fine side). The hair strands have a residual humidity of 50% per weight. The hair strands are placed in stretched condition in a lab dish. The tip ends are weighed down with a plastic spatula to prevent the bending of the hair strands. Finally, the hair strands are dried in the climatic chamber overnight (20°C, 65% RH).

Each hair strand is passed in a S-shape between the rods of the device 1 as described hereinbefore comprising six rods by means of an Instron® model No. 3343 at an extension of 400 mm/min. The measurement is executed 5 times in stationary mode and 5 times in rotational mode. The forces exerted are calculated as total work (energy). The work in the rotational mode relates to the hair stiffness.

Results

Fig. 5 shows the hair stiffness of the fibres treated with different composition of hydroxypropyl methacrylate. The presence of hydroxypropyl methacrylate in the 1%-12% HPMA compositions versus the placebo also causes an increase in stiffness of the hair fibres, as shown in Fig. 5. Hydroxypropyl methacrylate is a monomer that polymerises to form a polymer inside the hair shaft. As compared to 3-sulfopropyl acrylate, the hair stiffness properties are improved when using hydroxypropyl methacrylate versus 3-sulfopropyl acrylate. Indeed, the hair stiffness of the hair strands treated by 8% HPMA (see Fig. 5) is higher than the hair stiffness of the hair strands treated by 8% 3-SPA (See Fig. 4).

Furthermore, as we have seen with the 1%-12% HPMA compositions, polymerisation inside the hair deals with two main active ingredients: an ethylenic monomer, i.e. hydroxypropyl methacrylate and a radical-forming agent such as hydrogen peroxide. The peroxide creates radicals which initiate the polymerisation process. However, hydrogen peroxide is rather stable in “clean” conditions i.e. without the presence of a proper redox partner. So, after combining those main active ingredients, the time until the polymerisation starts and how complete the polymerization reaction goes depends on the availability of a redox partner for the hydrogen peroxide inside the hair, i.e. is dependent upon health/history/quality of the particular hair fibre(s)

and therefore hard to predict exact polymerisation start and completion level in view the variability in hair fibre(s) across the human population.

The addition of a redox partner for the hydrogen peroxide such as sodium thiosulphate, as shown in Fig. 5, results in an increased hair stiffness of the hair strands treated with “12% HPMA + Booster” versus “Placebo 2 + Booster” and versus “12% HPMA”. High concentrations of the activating agent can help to lead to a more complete polymerisation.

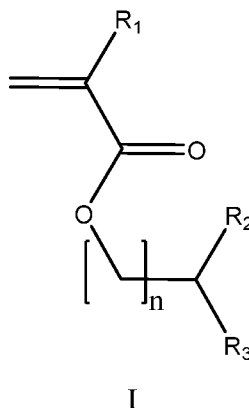
Figs. 1, 4, and 5 clearly show that an acrylate monomer such as hydroxypropyl methacrylate (HPMA) can polymerize inside hair in the presence of a hair coloring composition comprising preferably oxidative dye precursors without adversely affecting the formation of hair color chromophores inside the hair. Fig. 5 also shows that the addition of a redox partner as a “booster compound” can promote the effectiveness and the efficiency of the polymerization inside hair.

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.”

CLAIMS

What is claimed is:

1. A hair coloring composition comprising, in a cosmetically acceptable carrier:
one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or
a mixture thereof:



wherein

R_1 is selected from the group consisting of -H, -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH; and

wherein the hair coloring composition has a pH from 8 to 12.

2. The hair coloring composition of Claim 1, wherein the hair coloring composition comprises oxidative dye precursors comprising one or more couplers and one or more primary intermediates.
3. The hair coloring composition according to any of the preceding claims, wherein the hair coloring composition comprises from 0.5% to 50% of the one or more acrylate monomers by total weight of the hair coloring composition.
4. The hair coloring composition according to any of the preceding claims,
wherein
 R_1 is selected from the group consisting of -H, and -CH₃;
 $n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, and -COOH.

5. The hair coloring composition of Claim 4,
wherein

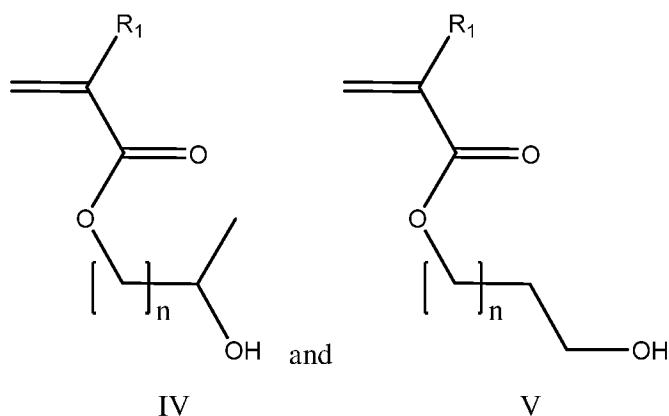
R_1 is selected from the group consisting of -H, and -CH₃;

$n = 1$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, and -COOH.

6. The hair coloring composition of Claim 4, wherein the one or more acrylate monomers comprise a mixture of a first acrylate monomer of Formula IV and a second acrylate monomer of Formula V:



wherein

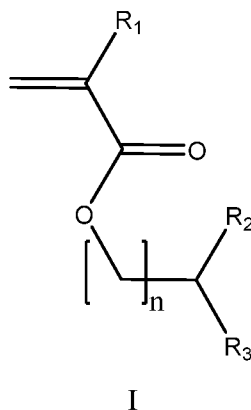
R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$; more preferably $n = 1$.

7. The hair coloring composition according to any of the preceding claims, wherein the composition is substantially free of any initiator of free-radical polymerisation.
8. The hair coloring composition according to any of the preceding claims, wherein the hair coloring composition is substantially free of oxidizing agent.

9. The hair coloring composition according to any of the preceding claims, wherein the composition is substantially free of poly(meth)acrylate polymer which is obtained from the one or more acrylate monomers.
10. The hair coloring composition according to any of the preceding claims, wherein the one or more primary intermediates are selected from the group consisting of 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)ethylazanediyl)diethanol, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol, 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 sulphate, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-ethylpyrazole, 4,5-diamino-1-isopropylpyrazole, 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, 2,3-diamino-6,7-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one dimethosulfonate, 4,5-diamino-1-hexylpyrazole, 4,5-diamino-1-heptylpyrazole, methoxymethyl-1,4-diaminobenzene and mixtures thereof.
11. The hair coloring composition according to any of the preceding claims, wherein the one or more primary intermediates of the hair coloring composition are 1,4-diamino-2-(methoxymethyl)-benzene.
12. The hair coloring composition according to any of the preceding claims, wherein the hair coloring composition further comprises one or more direct dyes, preferably one or more oxidatively stable direct dyes.
13. The hair coloring composition according to claim 12, wherein, the hair coloring composition comprises a total amount of from 0.001% to 4% of the one or more direct dyes by total weight of the hair coloring composition.

14. Use of one or more acrylate monomers of Formula I, or a cosmetically acceptable salt thereof, or a mixture thereof, in a hair coloring composition:



wherein

R_1 is selected from the group consisting of -H, and -CH₃;

$n = 0, 1, 2, 3$; preferably $n = 1, 2, 3$; more preferably $n = 1$;

R_2 is selected from the group consisting of -H, -CH₃, and -OH;

R_3 is selected from the group consisting of -H, -CH₃, -CH₂OH, -CH₂OCH₃, -CH₂F, -CH₂Cl, -CH₂Br, -Cl, and -COOH for improving the hair stiffness of hair without impacting the hair color.

15. A kit for coloring hair comprising:

(a) a hair coloring composition as defined in claims 1 to 13;

(b) an oxidizing formulation comprising one or more oxidizing agents; and

wherein the hair coloring composition (a) and the formulation (b) are separately packaged.

16. A method of coloring hair comprising:

(a) mixing the hair coloring composition as defined in claims 1 to 13 with an oxidizing formulation comprising one or more oxidizing agents to form a mixture, preferably with sodium thiosulphate; and

(b) applying the mixture onto hair.

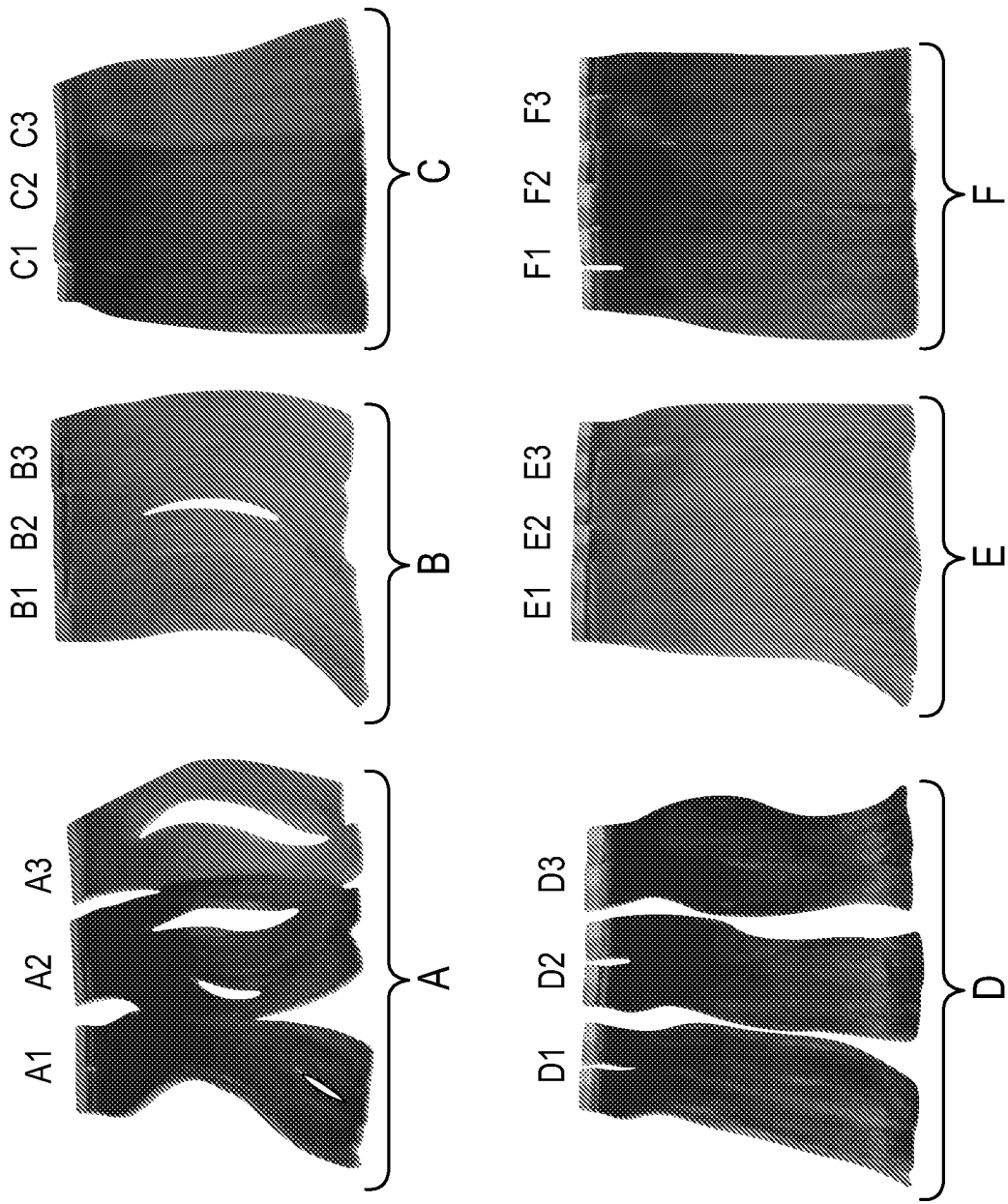


Fig. 1

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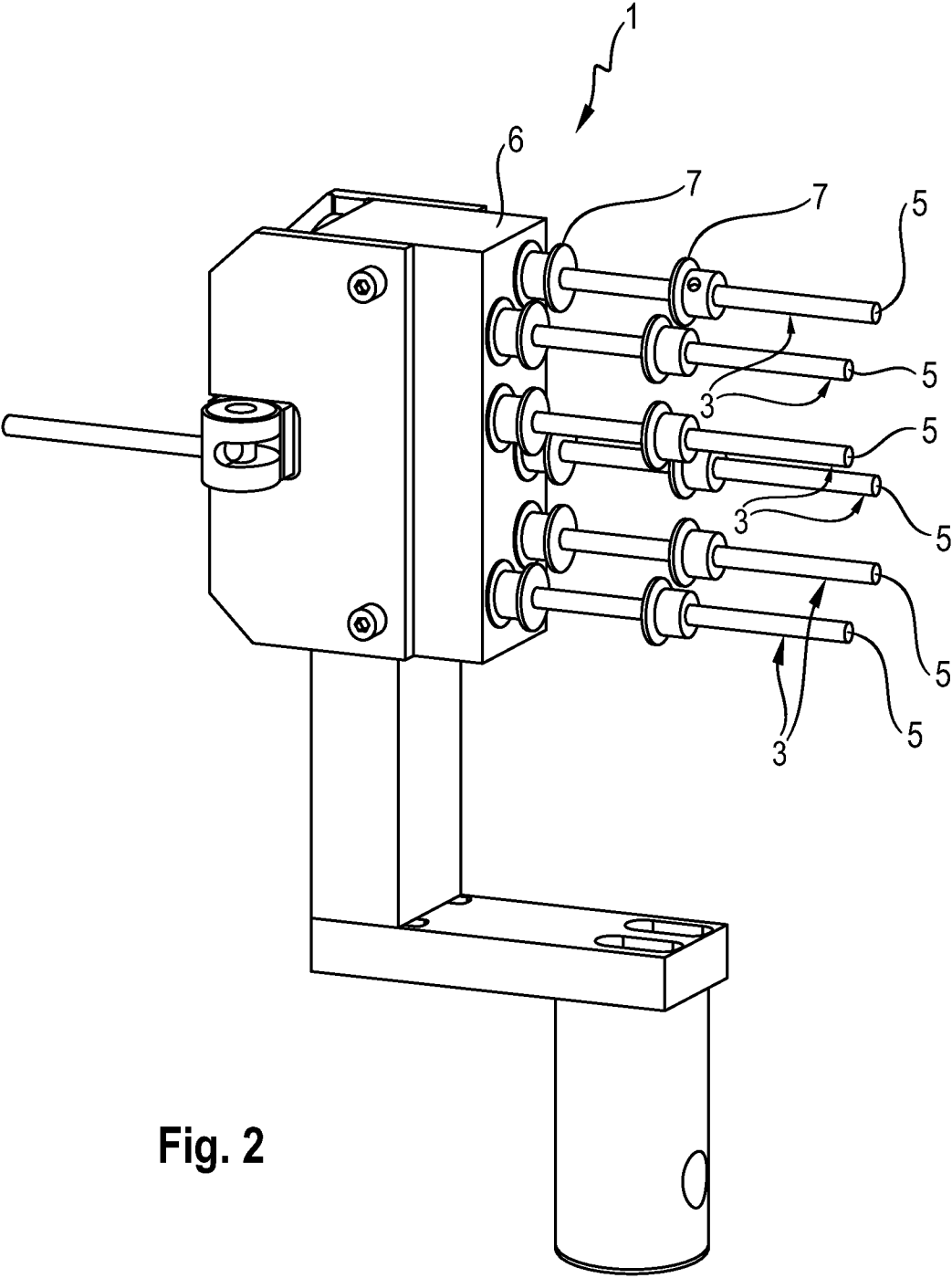
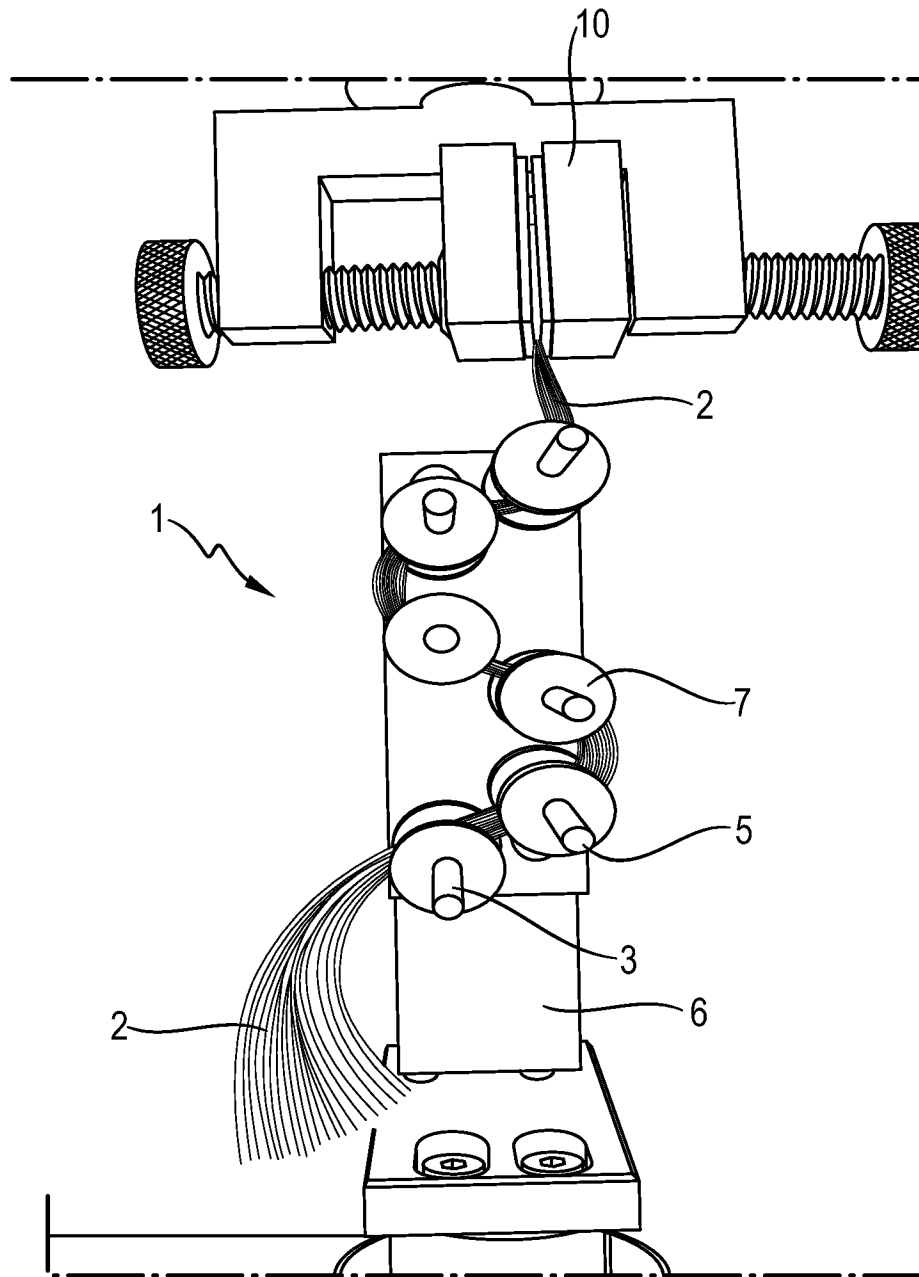


Fig. 2

3 / 5

Fig. 3



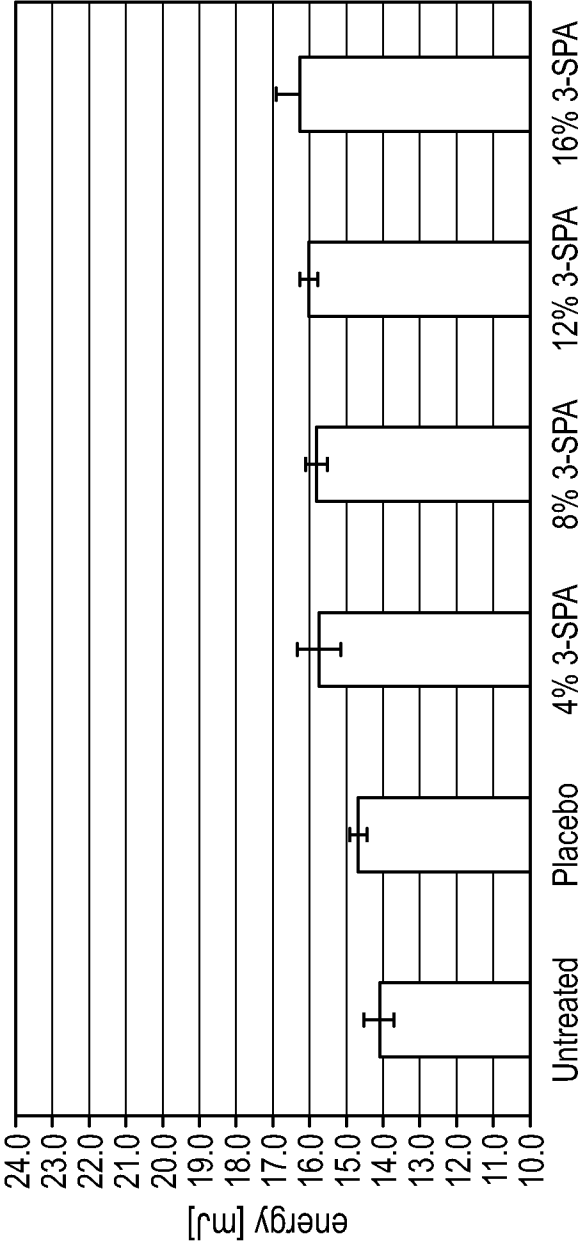


Fig. 4

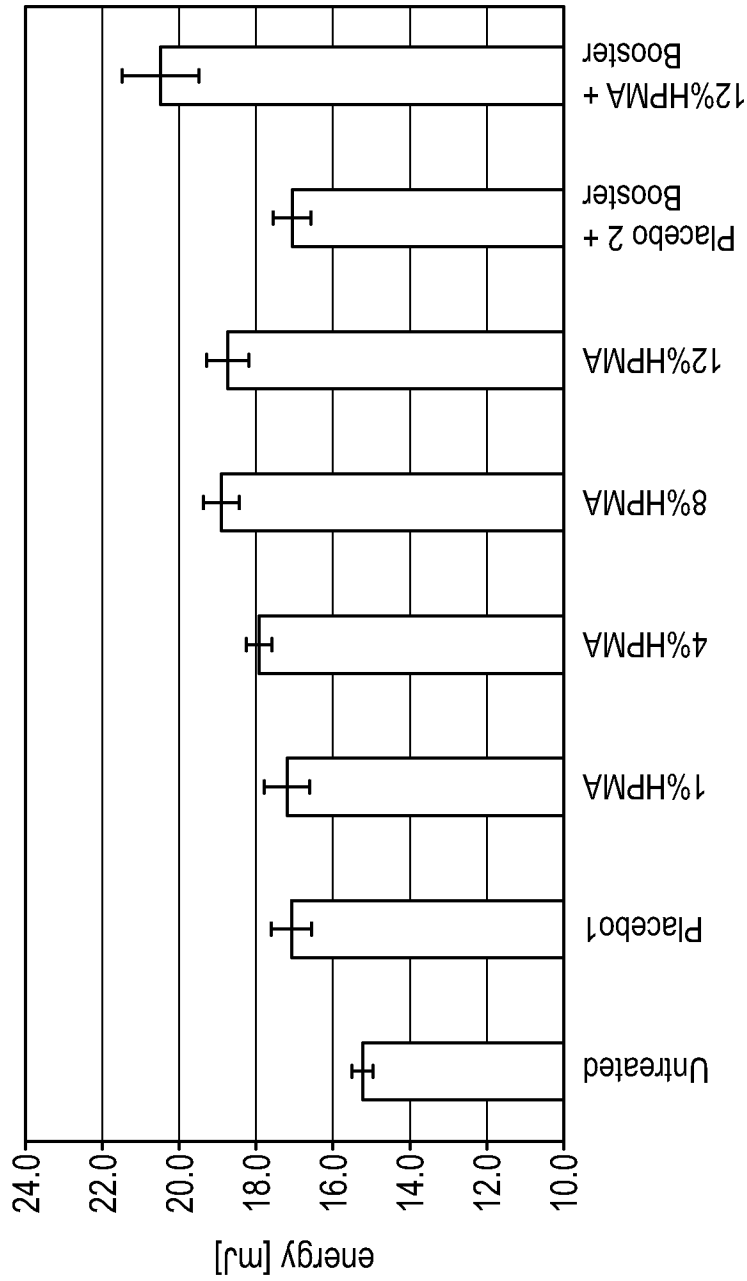


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/064094

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/37 A61Q5/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/053504 A2 (OREAL [FR]) 10 April 2014 (2014-04-10) claim 1 page 66; example 2; table 2 page 0364	1-16
A	----- US 2010/028279 A1 (CARBALLADA JOSE ANTONIO [US] ET AL) 4 February 2010 (2010-02-04) page 1, paragraph 0001 example 1	1-16
A	----- EP 2 561 857 A2 (PROCTER & GAMBLE [US]) 27 February 2013 (2013-02-27) paragraph [0001] claims 1,5	1-16
A	----- EP 2 561 855 A2 (PROCTER & GAMBLE [US]) 27 February 2013 (2013-02-27) claim 1	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/064094

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014053504 A2	10-04-2014	CN 104684533 A EP 2903584 A2 JP 2015531385 A WO 2014053504 A2	03-06-2015 12-08-2015 02-11-2015 10-04-2014
US 2010028279 A1	04-02-2010	US 2010028279 A1 WO 2010014763 A2	04-02-2010 04-02-2010
EP 2561857 A2	27-02-2013	BR 112013011428 A2 CA 2816735 A1 CN 103501756 A EP 2561857 A2 JP 2013543871 A US 2012183486 A1 WO 2012100007 A2	19-07-2016 26-07-2012 08-01-2014 27-02-2013 09-12-2013 19-07-2012 26-07-2012
EP 2561855 A2	27-02-2013	BR 112013011425 A2 CA 2816729 A1 CN 103391763 A EP 2561855 A2 JP 5792822 B2 JP 2013545753 A US 2012180807 A1 WO 2012100006 A2	19-07-2016 26-07-2012 13-11-2013 27-02-2013 14-10-2015 26-12-2013 19-07-2012 26-07-2012