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(54) Title: HAIR TREATMENT METHODS AND KITS THEREOF

(57) Abrégé/Abstract:
Method for treating hair wherein a first hair treatment composition is applied to the hair, e.g. the hair roots and a second hair treatment composition is applied to the hair, e.g. the hair lengths and tips, wherein the pH of the second hair treatment composition is higher than the pH of the first hair treatment composition.

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(54) Title: HAIR TREATMENT METHODS AND KITS THEREOF

(57) Abstract: Method for treating hair wherein a first hair treatment composition is applied to the hair, e.g. the hair roots and a second hair treatment composition is applied to the hair, e.g. the hair lengths and tips, wherein the pH of the second hair treatment composition is higher than the pH of the first hair treatment composition.

HAIR TREATMENT METHODS AND KITS THEREOF

FIELD OF THE INVENTION

The invention relates to a method for the treatment of hair such as hair colouring, hair bleaching or hair perming treatment and kits thereof.

BACKGROUND OF THE INVENTION

Consumers desiring to colour their hair typically have two options available namely to use a commercially available retail product or kit or use the services of a professional salon. The latter whilst providing a highly desirable colour outcome, is considerably more expensive than the retail option and thus not available to many consumers particularly those who colour regularly.

For consumers who have previously coloured their hair, the colour and condition of the hair is not homogenous along the entire length. The hair strands will comprise root virgin hair or new growth hair which has not been previously coloured and conversely at the tips hair which has experienced one or multiple hair colouring treatments. The tips of the hair are typically the most damaged portions of the hair and are characterised by an overly deposition of dyes or over-bleaching due to previous oxidative hair colorations. The intermediate hair length is typically a medium between these two extreme conditions. However, the problem with current retail hair colour products is that they do not take into account the differences of properties between the different portions of the hair. It is rather challenging even for experienced home colour users to control the dye deposition or the bleaching provided by a retail hair colour product in order to not overly deposit hair dyes on or over-bleaching hair lengths and tips since the instructions provided in hair colour retail kits are typically imprecise, often not followed and the results achieved are not comparable with those from a salon stylist. The overall colour appearance is typically not as homogeneous as that provided by a salon stylist.

Therefore, there is a need to provide a simple method as well as a simple retail kit for colouring or bleaching hair which gives the user the possibility of obtaining a different hair colour or bleaching effect on different portions of the hair, for example a different colour effect on hair roots vs. hair lengths and tips to provide a smooth root-to-tip transition on hair which has been previously coloured.

SUMMARY OF THE INVENTION

The present invention relates to a method for treating hair comprising the steps of:

i) providing a first hair treatment composition and a second hair treatment composition, wherein the pH of the second hair treatment composition is higher than the pH of the first hair treatment composition;
ii) applying a portion or all of the first hair treatment composition to the hair;
iii) applying a portion or all of the second hair treatment composition to the hair;
iv) optionally rinsing the hair, wherein:
- the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof or
- the method is a method for perming hair wherein each of the first and second hair treatment compositions is a hair perming composition.

The present invention also relates to a hair colouring kit comprising a first dye composition, a second dye composition, a first developer composition and a second developer composition, wherein each of the first and second dye compositions comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and each of the first and second developer compositions comprises one or more oxidizing agent(s), wherein the pH of the second developer composition is higher than the pH of the first developer composition.

Finally, the present invention also relates to a hair colouring kit comprising a first dye composition, a first developer composition and a pH increasing agent wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s) and wherein the first dye composition, the first developer composition and the pH increasing agent are packaged separately.

DETAILED DESCRIPTION OF THE INVENTION

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

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 fibres. Mammalian, preferably human hair is preferred. However wool, fur and other keratin containing fibres are suitable substrates for the compositions according to the present invention. The terms

"root", "hair roots", "root hair line" and "virgin hair" all refer to hair which has not been previously treated with a hair colouring or bleaching composition.

By "hair colouring" composition it is meant a composition suitable for changing the color of hair. The hair colouring composition can comprise oxidative dye precursors, direct dyes or even no, or substantially no, dyes in case of bleaching only compositions where the change of colour is mainly caused by the degradation of the natural melanin contained in the hair shaft by the oxidizing agent. The terms "hair colouring composition" and "method for colouring hair" as used herein also encompasses respectively the terms "hair bleaching composition" and "method for bleaching hair".

In the preferred embodiment according to the present invention, the hair colouring compositions are applied to hair which has already been previously coloured with hair colouring compositions. In such a case, the terms "root", "hair roots", "root hair line" and "virgin hair" all refer to the portion of hair having grown, since the last hair colouration, said portion of hair being virgin, i.e. naturally-coloured and the terms "hair lengths and tips" refer to the remaining portion of hair having been already previously coloured.

By "liquid" it is meant liquid at 25°C and at atmospheric pressure (760 mmHg).

By "solid" it is meant solid at 25°C and at atmospheric pressure (760 mmHg).

All percentages are by weight of the total composition unless specifically stated otherwise. All ratios are weight ratios unless specifically stated otherwise.

Method for treating hair

The present invention relates to a method for treating hair as stated hereinbefore.

The first hair treatment composition may be applied to the hair roots and the second hair treatment composition may be applied to the hair lengths and tips.

Alternatively, the first hair treatment composition may be applied to a strand of hair and the second hair treatment composition may be applied to another strand of hair.

The difference of pH between the second composition and the first composition may be at at least 0.25 or at least 0.5 or at least 1 or at least 2.

The pH of the first and/or second hair treatment compositions may be modified by adding a pH increasing agent to respectively the first and/or second hair treatment compositions.

In step iv) of the method, the hair may be rinsed with water and/or shampoo. After rinsing, they may be further dried and styled as usual. A conditioner composition may be applied to the hair after rinsing, preferably prior to drying and styling.

The present description is not limited to the embodiments wherein only two different hair treatment compositions are applied to the hair, wherein the second hair treatment composition

has a higher pH than the first hair treatment composition. It may be envisaged to apply more than two different hair colouring compositions to the hair wherein each time the pH of the next composition is higher than the pH of the previous composition.

pH increasing agent

According to the present invention, a pH increasing agent is typically a base which is added to a composition to increase the pH of the composition.

The pH increasing agent may be selected from the group consisting of 1,6-hexanediamine, 2-aminobutanol, aminoethyl propanediol, aminomethyl propanediol, aminomethyl propanol, aminopropanediol, ammonia, ammonium bicarbonate, ammonium carbamate, ammonium carbonate, ammonium chloride, ammonium glycolate, ammonium hydroxide, ammonium phosphate, bis-hydroxyethyl tromethamine, butyl diethanolamine,calcium carbonate, calcium glycinate, calcium hydroxide, calcium oxide, copper glycinate, diammonium phosphate, dibutyl ethanolamine, diethyl ethanolamine, dimethyl isopropanolamine, dimethyl mea, dipotassium phosphate, disodium fumarate, disodium phosphate, disodium tartrate, ethanolamine, ethyl ethanolamine, guanidine carbonate, guanidine hcl, imidazole, isopropanolamine, isopropylamine, lithium carbonate, lithium hydroxide, magnesium hydroxide, magnesium oxide, methylethanolamine, pentapotassium triphosphate, pentasodium triphosphate, phenolsulfonphthalein, phenyl mercuric borate, potassium borate, potassium carbonate, potassium citrate, potassium hydroxide, potassium oxide, potassium phosphate, sesquiethoxytriethanolamine, sodium acetate, sodium aluminate, sodium aluminum lactate, sodium bicarbonate, sodium carbonate, sodium formate, sodium fumarate, sodium humate, sodium hydroxide, sodium metaphosphate, sodium metasilicate, sodium oxide, sodium sesquicarbonate, sodium silicate, sodium trimetaphosphate, strontium hydroxide,tea-diricinoleate/ipdi copolymer, tetrahydroxyethyl ethylenediamine, tetrapotassium pyrophosphate, tetrasodium pyrophosphate, triethanolamine, triisopropanolamine, trisodium phosphate, tromethamine, urea, zinc carbonate hydroxide, zinc glycinate, and mixtures thereof. The pH increasing agent may be selected from the group consisting of ammonia, ammonium bicarbonate, ammonium carbonate, ammonium chloride, ammonium hydroxide, ammonium phosphate, calcium carbonate, calcium hydroxide, calcium oxide, diammonium phosphate, dipotassium phosphate, ethanolamine, isopropanolamine, isopropylamine, magnesium hydroxide, magnesium oxide, potassium borate, potassium carbonate, potassium citrate, potassium hydroxide, potassium oxide, sodium bicarbonate, sodium borate, sodium carbonate, sodium hydroxide, sodium sesquicarbonate, sodium silicate, urea and mixtures thereof.

The pH increasing agent may be provided as a solid or a liquid.

In the embodiments wherein the pH increasing agent is provided as a liquid, it may be a solution, an emulsion or a suspension. In these embodiments, the solvent used to form the solution, emulsion or suspension may be water. Alternatively, the solvent may be any solvent with a polarity index of 4.8 or more. The liquid may be encapsulated in a controlled release coating.

In the embodiments wherein the pH increasing agent is provided as a solid, it may be a powder, a precipitate or a crystal. The solid may be encapsulated in a controlled release coating.

Method for colouring hair

The method for treating hair may be a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof.

Whilst not wishing to be bound by theory, it is believed that when the pH of a hair colouring composition comprising one or more oxidative dye precursors is increased, the reaction rate of the colour formation in the composition (i.e. before application to the hair) may become either lower or higher depending on the nature of dye precursors. In the embodiments, wherein the reaction rate of the colour formation in the composition becomes lower due to the increase of the pH, the reaction rate of colour formation on hair may also become lower and therefore the user may apply such a composition to the hair lengths and tips which have been previously coloured and reduce the risk of overly deposition of dyes on portions of hair which were previously coloured. Alternatively, in the embodiments wherein the reaction rate of the colour formation in the composition becomes higher due to the increase of the pH, the increase of the reaction rate may have for consequence that some of the dye precursors may not have the time to diffuse into the hair before the hair colouring reaction has occurred and that therefore such a composition reduces the risk of overly deposition of dyes when applied to portions of hair which have been previously coloured.

Whilst not wishing to be bound by theory, it is believed that when the pH of a hair colouring composition not comprising oxidative dye precursors, i.e. a hair bleaching composition is increased, the concentration of perhydroxyl anions which are involved in the hair bleaching process may become higher and therefore the reaction rate of the bleaching reaction may also become higher and consequently the user may apply such a composition to increase the bleaching of a specific portion of hair.

Therefore, by performing the method according to the present invention, it is possible to provide a different colour and/or bleaching result on different portions of the hair in a simple manner without the need of using the services of a professional salon.

Furthermore, by carrying out the method according to the present invention, wherein the first hair colouring composition is applied to a strand of hair and the second hair colouring composition is applied to another strand of hair, it is possible to obtain strand to strand colour variation.

The second composition may produce on the hair a coloration such that the colour variation ΔE_{00}* expressed in the CIE L*a*b* system, between hair coloured with the second composition and hair coloured with the first composition is greater than or equal to 1, as measured according to the colour variation test method. Whilst not wishing to be bound by theory, it is believed that having such a colour variation ΔE_{00}* helps to ensure that the overall colour result obtained with the second composition is significantly different from the overall colour result obtained with the first composition.

The second composition may produce on the hair a coloration such that the colour lightness difference ΔL* expressed in the CIE L*a*b* system, between hair coloured with the second composition and hair coloured with the first composition is greater than 0, as measured according to the colour variation test method. Whilst not wishing to be bound by theory, it is believed that having such a colour lightness difference ΔL* helps to ensure that the second composition provides a lighter colour result when the second composition is applied to the hair than when the first composition is applied to the hair, for example on hair lengths and tips vs. hair roots.

Alternatively, the second composition may produce on the hair a coloration such that the colour lightness difference ΔL* expressed in the CIE L*a*b* system, between hair coloured with the second composition and hair coloured with the first composition is lower than 0, as measured according to the colour variation test method.

The pH of each of the first and second hair colouring compositions may be from 7 to 11. The pH of the first hair colouring composition may be from 7 to 10 and the pH of the second composition may be from 8 to 11.

The method further may comprise the steps of:

a. mixing a first dye composition with a first developer composition to obtain the first composition, wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s);

b. mixing a second dye composition with a second developer composition to obtain the second composition, wherein the second dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the second developer composition comprises one or more oxidizing agent(s).

The pH of the second dye composition may be higher than the pH of the first dye composition. Alternatively, the pH of the second developer composition may be higher than the pH of the first developer composition.

Step b) may be performed between steps ii) and iii).

The method may further comprise the steps of waiting for a time period of from 10 min to 40 min, or from 15 min to 30 min or 20 min, which is performed between steps ii) and iii) and waiting for a time period of from 5 min to 20 min, or of 10 min which is performed between steps iii) and iv).

Alternatively, step b) may be performed immediately after step ii) and step iii) may be performed immediately after step b) and the method may further comprise the step of waiting for a time period of from 5 min to 40 min, or from 20 min to 40 min, or 30 min, which is performed between steps iii) and iv).

The first and second dye compositions may comprise the same or different oxidative dye precursors. The first and second dye compositions may comprise the same or different concentration of dye precursors. The first and the second developer compositions may comprise the same or different oxidizing agents.

Alternatively, the method may further comprises the steps of mixing a first dye composition with a first developer composition to obtain the first composition, wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s) and in step ii), a first portion of the first composition may be applied to the hair, e.g. the hair roots and a second portion of the first composition may be retained and the method may further comprise the step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition. The step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition may be performed between steps ii) and iii).

The method may further comprise the steps of waiting for a time period of from 10 min to 40 min, or 15 min to 30 min, or 20 min, which is performed between steps ii) and iii) and waiting for a time period of from 5 min to 20 min, or 10 min which is performed between steps iii) and iv).

Alternatively, the step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition may be performed immediately after step ii) and immediately before step iii) and the method may further comprise the step of waiting for a time period of from 5 min to 40 min, or 20 min to 40 min, or 30 min, which is performed between steps iii) and iv).

From 90% to 10% or from 80% to 50%, or from 75% to 55% by weight of the first composition may be applied as a first portion to the hair.

The first and/or second dye compositions may be mixed with respectively the first and/or second developer compositions at a mixing ratio of 2:1 to 1:2 or 1:1.

In the embodiments, wherein the pH increasing agent is provided as a liquid, the pH increasing agent:second portion of the first composition mixing ratio may be less than 1:4, or less than 1:10.

In the embodiments wherein the pH increasing agent is provided as a liquid the pH increasing agent:second portion of the first composition mixing ratio may be of 1:4 or more, or 1:4 to 25:1, or 1:4 to 20:1 or 1:4 to 10:1 or 2:1 to 5:1. Whilst not wishing to be bound by theory, it is believed that with such a mixing ratio the pH increasing agent will also act as a diluter which will reduce the overall concentration of actives species such as dye precursors, oxidizing agents such as hydrogen peroxide and alkalizing agents and therefore will also contribute to the reduction of the dye deposition on hair.

The first and/or the second developer compositions may comprise from 1 to 20% by weight of the oxidizing agents. The first and/or the second dye compositions may comprise from 0.01% to 10% by weight of the oxidative dye precursor and/or from 0.1% to 10% by weight of the alkalising agents.

Hair colouring compositions

Other ingredients

The first and/or second hair colouring compositions of the present invention may comprise, in addition to the ingredients indicated above, further ingredients in order to further enhance the properties of the compositions, as long as these are not excluded by the claims.

Suitable further ingredients include, but not limited to: solvents; oxidizing agents; alkalizing agents; oxidative dye precursors, direct dyes; chelants; radical scavengers; pH modifiers and buffering agents; thickeners and/or rheology modifiers; carbonate ion sources; peroxymonocarbonate ion sources; anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, and mixtures thereof; anionic, cationic, nonionic, amphoteric or zwitterionic polymers, and mixtures thereof; fragrances; enzymes; dispersing agents; peroxide stabilizing

agents; antioxidants; natural ingredients (such as proteins, protein compounds, and plant extracts); conditioning agents (such as silicones and cationic polymers); ceramides; preserving agents; opacifiers and pearling agents (such as titanium dioxide and mica); and mixtures thereof.

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

Solvents

The first and/or the second hair colouring compositions according to the present invention may further comprise a solvent. The solvent may be selected from water, or a mixture of water and at least one organic solvent to dissolve the compounds that would not typically be sufficiently soluble in water.

Suitable organic solvents include, but are not limited to: C1 to C4 lower alkanols (such as 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, dipropyleneglocol, polygylcerol); propylene carbonate; and mixtures thereof.

The solvent 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 first and/or the second hair colouring compositions 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 weight of the total composition. Typically, when present, the first and/or the second hair colouring compositions may comprise a total amount of organic solvents ranging from 1% to 30%, by weight of the total composition.

Oxidizing agents

The first and/or the second hair colouring compositions according to the present invention may further comprise at least one source of an oxidizing agent. Any oxidizing agent known in the art may be used. Preferred oxidizing agents are water-soluble peroxygen oxidizing agents. As used herein, "water-soluble" means that in standard conditions at least 0.1g, preferably 1g, more preferably 10g of the oxidizing agent can be dissolved in 1 liter of deionized water at 25°C. The oxidizing agents are 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.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of oxidizing agents ranging from 0.1% to 10%, alternatively from 1% to 7%, alternatively from 2% to 5%, by weight of the total composition.

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

Suitable water-soluble peroxygen oxidizing agents 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 first and/or the second hair colouring compositions may comprise a water-soluble oxidizing agent selected from the group consisting of hydrogen peroxide, percarbonates (which may be used to provide a source of both oxidizing agent and carbonate ions and or ammonium ions), persulphates, and mixtures thereof.

When the first and/or the second hair colouring compositions of the present invention are obtained by mixing a developer composition and a tint composition prior to use, the oxidizing agents may be present in the developer composition. The developer composition may be based on any desired formulation chassis, including any commercial product, for example an oil-in-water emulsion. Typical developer compositions comprise 6% or 9% of the H_2O_2 relative to the total weight of the developer composition. A commercial example is the Welloxon® Emulsion with respectively 6% and 9% H_2O_2, marketed by Wella and comprising as INCI ingredients: Water, H_2O_2, Cetearyl Alcohol, Ceteareth-25, Salicylic Acid, Phosphoric Acid, Disodium Phosphate, Etidronic Acid.

Alkalizing agents

The first and/or the second hair colouring compositions according to the present invention may further comprise one or more alkalizing agents. Any alkalizing agent known in the art may be used.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of alkalizing agents ranging from 0.1% to 10%, alternatively from 0.5% to 6%, alternatively from 1% to 4%, by weight of the total composition.

Suitable alkalizing agents include, but are not limited to: ammonia; alkanolamines (such as monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine); 2-amino-2-methyl-1,3-propanediol, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-1,3-propanediol; guanidium salts; alkali metal and ammonium hydroxides (such as sodium hydroxide); alkali metal and ammonium carbonates; and mixtures thereof. Typical alkalizing agents are ammonia and/or monoethanolamine. Preferably, if present, the ammonium ions and carbonate ions are present in the composition at a weight ratio of from 3:1 to 1:10, alternatively from 2:1 to 1:5.

When the first and/or the second hair colouring compositions of the present invention are obtained by mixing a developer composition and a dye composition prior to use, the alkalizing agent is generally present in the dye composition.

Oxidative dye precursors

The first and/or the second hair colouring compositions according to the present invention may further comprise oxidative dye precursors, which are usually classified either as primary intermediates (also known as developers) or couplers (also known as secondary intermediates). Various couplers may be used with primary intermediates in order to obtain different shades. Oxidative dye precursors may be free bases or the cosmetically acceptable salts thereof.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of oxidative dye precursors ranging up to 12%, alternatively from 0.1% to 10%, alternatively from 0.3% to 8%, alternatively from 0.5% to 6%, by weight of the total composition.

Suitable primary intermediates include, but are not limited to: toluene-2,5-diamine, p-phenylenediamine, *N*-phenyl-p-phenylenediamine, *N*,*N*-bis(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, hydroxypropyl-bis-(N-hydroxyethyl-p-phenylenediamine), 2-methoxymethyl-p-phenylenediamine, 2-(1,2-dihydroxyethyl)-p-phenylenediamine, 2,2'-(2-(4-aminophenylamino)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 sulfate, 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-diaminothane, salts thereof and mixtures thereof.

Suitable couplers include, but are not limited to: resorcinol, 4-chlororesorcinol, 2-chlororesorcinol, 2-methylresorcinol, 4,6-dichlorobenzene-1,3-diol, 2,4-dimethylbenzene-1,3-diol, *m*-aminophenol, 4-amino-2-hydroxytoluene, 2-methyl-5-hydroxyethylaminophenol, 3-amino-2,6-dimethylphenol, 3-amino-2,4-dichlorophenol, 5-amino-6-chloro-o-cresol, 5-amino-4-chloro-o-cresol, 6-hydroxybenzomorpholine, 2-amino-5-ethylphenol, 2-amino-5-phenylphenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol, 5-methyl-2-(methylamino)phenol, 2,4-diaminophenoxyethanol, 2-amino-4-hydroxyethylaminoanisole, 1,3-bis-(2,4-diaminophenoxy)-propane, 2,2'-(2-methyl-1,3-phenylene)bis(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 or 1-acetoxy-2-methylnaphthalene, 4-chloro-2-methylnaphthalen-1-ol, 4-methoxy-2-methylnaphthalen-1-ol, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-pyridinediamine, 3-amino-2-methylamino-6-methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, pyridine-2,6-diol, 5,6-dihydroxyindole, 6-hydroxyindole, 5,6-dihydroxyindoline, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,2,4-trihydroxybenzene, 2-(benzo[d][1,3]dioxol-5-ylamino)ethanol (also known as hydroxyethyl-3,4-methylenedioxyaniline), and mixtures thereof.

When the first and/or second hair colouring compositions of the invention are obtained by mixing a dye composition and a developer composition, the primary intermediates and couplers are usually incorporated into the dye composition.

<u>Direct Dyes</u>

The first and/or the second hair colouring compositions according to the present invention may further comprise compatible direct dyes, in an amount sufficient to provide additional coloring, particularly with regard to intensity. Typically, the compositions may comprise a total amount of direct dyes ranging from 0.05% to 4%, by weight of the total composition.

Suitable direct dyes include but are not limited to: Acid dyes such as Acid Yellow 1, Acid Orange 3, Acid Black 1, Acid Black 52, Acid Orange 7, Acid Red 33, Acid Yellow 23, Acid Blue 9, Acid Violet 43, HC Blue 16, Acid Blue 62, Acid Blue 25, Acid Red 4; Basic Dyes such as Basic Brown 17, Basic Red 118, Basic Orange 69, Basic Red 76, Basic Brown 16, Basic Yellow 57, Basic Violet 14, Basic Blue 7, Basic Blue 26, Basic Red 2, Basic Blue 99, Basic

Yellow 29, Basic Red 51, Basic Orange 31, Basic Yellow 87, 4-(3-(4-amino-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)propyl)-4-methylmorpholin-4-ium-methylsulfate, (*E*)-1-(2-(4-(4,5-dimethylthiazol-2-yl)diazenyl)phenyl)(ethyl)amino)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(azanediyl)diethanol, HC Yellow No. 5, HC Red No. 7, HC Blue No.2, HC Yellow No. 4, HC Yellow No. 2, HC Orange No. 1, HC Red No. 1, 2-(4-amino-2-chloro-5-nitrophenylamino)ethanol, HC Red No. 3, 4-amino-3-nitrophenol, 4-(2-hydroxyethylamino)-3-nitrophenol, 2-amino-3-nitrophenol, 2-(3-(methylamino)-4-nitrophenoxy)ethanol, 3-(3-amino-4-nitrophenyl)propane-1,2-diol, HC Yellow No. 11, HC Violet No. 1, HC Orange No. 2, HC Orange No. 3, HC Yellow No. 9, HC Red No. 10, HC Red No. 11, 2-(2-hydroxyethylamino)-4,6-dinitrophenol, HC Blue No. 12, HC Yellow No. 6, HC Yellow No. 12, HC Blue No. 10, HC Yellow No. 7, HC Yellow No. 10, HC Blue No. 9, 2-chloro-6-(ethylamino)-4-nitrophenol, 6-nitropyridine-2,5-diamine, HC Violet No. 2, 2-amino-6-chloro-4-nitrophenol, 4-(3-hydroxypropylamino)-3-nitrophenol, HC Yellow No. 13, 6-nitro-1,2,3,4-tetrahydroquinoxaline, HC Red No. 14, HC Yellow No. 15, HC Yellow No. 14, N2-methyl-6-nitropyridine-2,5-diamine, N1-allyl-2-nitrobenzene-1,4-diamine, HC Red No. 8, HC Green No.1, HC Blue No. 14; Natural dyes such as Annato, Anthocyanin, Beetroot, Carotene, Capsanthin, Lycopene, Chlorophyll, Henna, Indigo, Cochineal; and mixtures thereof.

When the first and/or the second hair colouring compositions are obtained by mixing a dye composition and a developer composition, the direct dyes are usually incorporated into the dye composition.

Chelants

The first and/or the second hair colouring compositions according to the present invention may further comprise chelants (also known as “chelating agent”, “sequestering agent”, or “sequestrant”) in an amount sufficient to reduce the amount of metals available to interact with formulation components, particularly oxidizing agents, more particularly peroxides. Chelants are well known in the art and a non-exhaustive list thereof can be found in AE Martell & RM Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and AE Martell

& RD Hancock, Metal Complexes in Aqueous Solution, Plenum Press, New York & London (1996), both incorporated herein by reference.

Typically, the first and/or the second compositions may comprise a total amount of chelants ranging from at least 0.01%, alternatively from 0.01% to 5%, alternatively from 0.25% to 3%, alternatively from 0.5% to 1%, by weight of the total composition.

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

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

Suitable aminophosphonic acid chelants comprise an aminophosphonic acid moiety (- PO_3H_2) or its derivative - PO_3R_2, wherein R_2 is a C_1 to C_6 alkyl or aryl radical and salts thereof. Suitable aminophosphonic acid chelants include, but are not limited to: aminotri-(1-ethylphosphonic

acid), ethylene-diaminetetra-(1-ethylphosphonic acid), aminotri-(1-propylphosphonic acid), aminotri-(isopropylphosphonic acid), their salts thereof, and mixtures thereof; alternatively aminotri-(methylenephosphonic acid), ethylene-diamine-tetra-(methylenephosphonic acid) (EDTMP) and diethylene-triamine-penta-(methylenephosphonic acid) (DTPMP), their salts thereof, their derivatives thereof, and mixtures thereof.

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

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

When the first and/or the second hair colouring compositions of the invention are obtained by mixing a dye composition and a developer composition, the chelants may be incorporated in the dye composition and/or in the developer composition. A chelant is usually present in the developer composition for stability reason.

Radical scavengers

The first and/or the second hair colouring compositions according to the present invention may further comprise a radical scavenger. As used herein the term "radical scavenger" refers to a species that can react with a radical, preferably a carbonate radical to convert the radical species by a series of fast reactions to a less reactive species. The radical scavenger may be different from the alkalizing agent and/or is present in an amount sufficient to reduce the damage to the hair during the colouring /bleaching process.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of radical scavengers ranging from 0.1% to 10%, alternatively from 1% by weight to 7%, by weight of the total composition.

Suitable radical scavengers include, but are not limited to: alkanolamines, amino sugars, amino acids, esters of amino acids, and mixtures thereof; alternatively 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, their salts thereof, and mixtures thereof; alternatively glycine, sarcosine, lysine, serine, 2 methoxyethylamine, glucosamine, glutamic acid, morpholine, piperdine, ethylamine, 3 amino-1-propanol, and mixtures thereof. As used herein, the term "salts thereof" – in the context of radical scavengers – means particularly potassium salts, sodium salts, ammonium salts, and mixtures thereof.

pH modifier and buffering agents

The first and/or the second hair colouring compositions according to the present invention may further comprise, in addition to the alkalizing agent discussed above, a pH modifier and/or buffering agent in an amount that is sufficiently effective to adjust the pH of the composition to fall within a range from 3 to 13, alternatively from 8 to 12, alternatively from 9 to 11.

Suitable pH modifiers and/or buffering agents include, but are not limited to: ammonia; alkanolamines (such as monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, tripropanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-hydroxymethyl-1,3,-propandiol); guanidium salts; alkali metal and ammonium hydroxides and carbonates; and mixtures thereof.

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

Thickeners and/or rheology modifiers

The first and/or the second hair colouring compositions according to the invention may further comprise a thickener in an amount sufficient to provide the composition with a viscosity so that it can be readily applied to the hair without unduly dripping off the hair and causing mess.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of thickeners ranging from at least 0.1%, alternatively at least 0.5%, alternatively at least 1%, by weight of the total composition.

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

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

fatty-chain unit; cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit; and amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one fatty-chain unit, and mixtures thereof.

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

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

$$CH_2{=}C(R_1)CH_2OB_nR \quad (I)$$

in which R1 is chosen from H and CH3, B is an ethyleneoxy radical, n is chosen from zero and integers ranging from 1 to 100, R is chosen from hydrocarbon-based radicals chosen from alkyl, alkenyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals, comprising from 8 to 30 carbon atoms, and, further, for example, from 10 to 24 carbon atoms and even further, for example, from 12 to 18 carbon atoms.

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

$$CH_2{=}C(R_1)COOH \quad (II)$$

in which R1 is chosen from H, CH3, C2H5 and CH2COOH (i.e. acrylic acid, methacrylic, ethacrylic and itaconic acid units); and wherein the hydrophobic unit of the type such as a (C8-

C30) alkyl ester or (C8-C30) oxyethylenated alkyl ester of an unsaturated carboxylic acid corresponds to, for example, the monomer of formula (III) below

CH2=C(R1)COOBnR2 (III)

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

CH2=C< (IV)

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

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

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

Preferred associative polymers comprise at least one hydrophilic unit which is unsaturated carboxylic acid or its derivatives, and at least one hydrophobic unit which is a C8 to C30 alkyl ester or oxyethylenated C8-C30 alkyl ester of unsaturated carboxylic acid. The unsaturated carboxylic acid is preferably acrylic acid, methacrylic acid or itaconic acid. Commercially available materials include those sold as Aculy-22 by Rohm & Haas; Permulen TR1, Carbopol 2020, Carbopol Ultrez-21 by Noveon, Structure 2001/3001 by National Starch. Other preferred associative polymers include polyether polyurethane, commercially available as Aculyn-44/-46 by Rohm and Haas. Further preferred associative polymers include cellulose modified with

groups comprising at least one C8 – C30 fatty chain, commercially available under the trade name Natrosol Plus Grade 330 CS by Aqualon.

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

Suitable polysaccharides include, but are not limited to: glucans, modified and unmodified starches (such as those derived, for example, from cereals, for instance wheat, corn or rice, from vegetables, for instance yellow pea, and tubers, for instance potato or cassaya), amylose, amylopectin, glycogen, dextrans, celluloses and derivatives thereof (methylcelluloses, hydroxyalkylcelluloses, ethyl hydroxyethylcelluloses, and carboxymethylcelluloses), mannans, xylans, lignins, arabans, galactans, galacturonans, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, alginic acid and alginates, arabinogalactans, carrageenans, agars, glycosaminoglucans, gum arabics, gum tragacanths, ghatti gums, karaya gums, carob gums, galactomannans, such as guar gums, and nonionic derivatives thereof (hydroxypropyl guar) and bio-polysaccharides, such as xanthan gums, gellan gums, welan gums, scleroglucans, succinoglycans, and mixtures thereof. Suitable polysaccharides are described in “Encyclopedia of Chemical Technology”, Kirk-Othmer, Third Edition, 1982, volume 3, pp. 896-900, and volume 15, pp. 439-458, in “Polymers in Nature” by E. A. MacGregor and C. T. Greenwood, published by John Wiley & Sons, Chapter 6, pp. 240-328,1980, and in “Industrial Gums—Polysaccharides and their Derivatives”, edited by Roy L. Whistler, Second Edition, published by Academic Press Inc., all three being incorporated herein by reference. A preferred polysaccharide is a bio-polysaccharide, particularly bio-polysaccharides selected from xanthan gum, gellan gum, welan gum, scleroglucan or succinoglycan; commercially available as Keltrol® T by Kelco and Rheozan® by Rhodia Chimie. Another preferred polysaccharide is hydroxypropyl starch derivative, particularly hydroxypropyl starch phosphate, commercially available as Structure XL® by National Starch.

Commercially available salt-tolerant thickeners include, but not limited to: xanthan, guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (commercially available as Aquacote), hydroxyethyl cellulose (Natrosol), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (Klucel), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (Natrosol Plus 330), N-vinylpyrollidone (Povidone), Acrylates/Ceteth-20 Itaconate Copolymer (Structure 3001),

hydroxypropyl starch phosphate (Structure ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester such as PEG-150/Decyl/SMDI copolymer (Aculyn 44), PEG-150/Stearyl/SMDI copolymer (Aculyn 46), trihydroxystearin (Thixcin), acrylates copolymer (Aculyn 33) or hydrophobically modified acrylate copolymers (such as Acrylates / Steareth-20 Methacrylate Copolymer as Aculyn 22), acrylates/steareth-20 methacrylate crosspolymer (Aculyn 88), acrylates/vinyl neodecanoate crosspolymer (Aculyn 38), acrylates/beheneth-25 methacrylate copolymer (Aculyn 28), acrylates/C10-30 alkyl acrylate crosspolymer (Carbopol ETD 2020), non-ionic amphophilic polymers comprising at least one fatty chain and at least one hydrophilic unit selected from polyether urethanes comprising at least one fatty chain, blends of Ceteth – 10 phosphate, Di-cetyl phosphate and Cetearyl alcohol (available as Crodafos CES), and mixtures thereof.

Thickeners for use in the first and/or second developer compositions may include acrylates copolymer, hydrophobically modified acrylate copolymers (e.g. Acrylates / Steareth-20 Methacrylate Copolymer) and mixtures thereof. Thickeners for use in the first and/or second dye compositions may include, blends of Ceteth – 10 phosphate, Di-cetyl phosphate and Cetearyl alcohol (as CRODAFOS CES).

<u>Gel network thickener system</u>

The first and/or second hair colouring compositions of the present invention may comprise at at least one gel network thickener system. Said system may comprise at least one low HLB surfactant and/or amphophile having a high melting point, and at least one additional second surfactant as specified hereinafter. Suitable gel network thickener systems are disclosed in PCT application WO2006/060598A1.

Said low HLB surfactant and/or amphophile may have preferably an HLB of 6 or less and melting point of at least 30°C. It may be selected from the group consisting of cetyl, stearyl, cetostearyl or behenyl alcohols, steareth-2, glycerol monostearate and mixtures thereof. Said second surfactant may be anionic, non-ionic or cationic. Anionic surfactants may be selected from the group consisting of alkyl ether phosphates having in average 1-3 ethylene oxide units and comprising an alkyl radical comprising from 8 to 30 carbon atoms. Said non-ionic surfactants may be selected from the group consisting of those comprising one or more polyethyleneoxide chain including polyoxyethylene alkyl ethers having from 100 to 200 ethylene oxide units (e.g. steareth-100, steareth-150). Said cationic surfactant may be selected from the group consisting of behentrimonium chloride, behenamidopropyltrimonium methosulfate, stearamidopropyltrimonium chloride, arachidtrimonium chloride and mixtures thereof. A preferred gel network thickening system comprises fatty alcohols having 14 to 30 carbon atoms

(cetyl and/or stearyl alcohol) and alkyl ether phosphates (e.g. from 1 to 3 ethylene oxide units). The first and/or second hair colouring compositions of the present invention may comprise a total amount of gel network thickening system of from 2% to 10% by weight of respectively the first and/or second hair colouring composition. The weight ratio of the low HLB surfactants to the second specified surfactants is preferably from 10:1 to 1:1.

Carbonate ion sources

The first and/or the second hair colouring compositions 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.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of a carbonate ion source ranging from 0.1% to 15%, alternatively from 0.1% to 10%, alternatively from 1% to 7%, by weight of the total composition.

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

Conditioning agents

The first and/or the second hair colouring compositions according to the present invention may further comprise a conditioning agent, and/or be used in combination with a composition comprising a conditioning agent.

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

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

Particularly useful conditioning materials are cationic polymers. Conditioners of cationic polymer type can be chosen from those comprising units of at least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part of the main

polymer chain, or be borne by a side substituent that is directly attached to the main polymer chain, described hereinafter.

Suitable silicones include, but are not limited to: polyalkylsiloxane oils, linear polydimethylsiloxane oils containing trimethylsilyl or hydroxydimethylsiloxane endgroups, polymethylphenylsiloxane, polydimethylphenylsiloxane or polydimethyldiphenylsiloxane oils, silicone resins, organofunctional siloxanes having in their general structure one or a number of organofunctional group(s), the same or different, attached directly to the siloxane chain and mixtures thereof. Said organofunctional group(s) may be selected from: polyethyleneoxy and/or polypropyleneoxy groups, (per)fluorinated groups, thiol groups, substituted or unsubstituted amino groups, carboxylate groups, hydroxylated groups, alkoxylated groups, quaternium ammonium groups, amphoteric and betaine groups. The silicone can either be used as a neat fluid or in the form of a pre-formed emulsion. Suitable silicones also include: silicones containing groups that may be ionized into cationic groups, for example aminosilicones containing at least 10 repeating siloxane ($Si(CH_3)_2–O$) units within the polymer chain, with either terminal, graft, or a mixture of terminal and graft aminofunctional groups. Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutly, aminopropyl. In the case of graft polymers, the terminal siloxane units can be $(CH_3)_3Si–O$, $R_{12}(CH_3)_2Si–O$, where R_{12} can be either OH or OR_{13}, where R_{13} is a C1-C8 alkyl group, or a mixture of both terminal groups. These silicones are also available as preformed emulsions. Commercially available aminosilicones include those sold as DC-2-8566, DC 7224, DC-2-8220 by Dow Corning; SF1708, SM2125 by GE Silicones; Wacker Belsil ADM 653/ADM 1100/ADM 1600/ADM 652/ADM 6057E/ADM 8020 by Wacker Silicones; DC929, DC939, DC949 by Dow Corning; SM2059 by GE Silicones. Suitable aminosilicones may also contain additional functional groups, particularly additional functional groups including polyoxyalkylene, the reaction product of amines and carbinols, and alky chains. Commercially available materials are known as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone (e.g. Abil Soft AF100, by Degussa), or as Bis(C13-15 Alkoxy)PG Amodimethicone (e.g. DC 8500, by Dow Corning).

Suitable cationic polymers include, but are not limited to: polymers comprising units of at least one amine group chosen from primary, secondary, tertiary and quaternary amine groups that may either form part of the main polymer chain or be borne by a side substituent that is directly attached to the main polymer chain. Such cationic polymers generally have a number average molecular mass ranging from 500 to 5×10^6, alternatively from 1000 to 3×10^6. Preferably the cationic polymers are selected from polymers of the polyamine, polyamino amide and polyquaternary ammonium type.

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

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

15 (e.g. Rohagit KF 720 F by Rohm), Polyquaternium-30 (e.g. Mexomere PX by Chimex), Polyquaternium-33, Polyquaternium-35, Polyquaternium-36 (e.g. Plex 3074 L by Rhon), Polyquaternium 45 (e.g. Plex 3073L by Rohn), Polyquaternium 49 (e.g. Plascize L-440 by Goo Chemicals), Polyquaternium 50 (e.g. Plascize L-441 by Goo Chemicals), Polyquaternium-52.

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

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

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

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

6) Quaternary diammonium polymers comprising repeat units corresponding to [–N+(R1)(R2) – A1 – N+(R3)(R4) – B1 –] [2X-], in which R1, R2, R3 and R4, which may be identical or different, are chosen from aliphatic, alicyclic and arylaliphatic radicals comprising from 1 to 20 carbon atoms and from lower hydroxyalkylaliphatic radicals, or R1, R2, R3 and R4, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other then nitrogen, or R1, R2, R3 and R4, are chosen from liner or branched C1-C6 alkyl radicals substituted with at least one group chosen from nitrile, ester, acyl and amide groups and groups of –CO–O–R5–D and –CO-NH–R5–D wherein R5 is chosen from alkylene groups and D is chosen from quaternary ammonium groups. A1 and B1, which may be identical or different, are chosen from linear and branched, saturated or unsaturated polymethylene groups comprising 2 to 20 carbon atoms. The polymethylene groups may comprise, linked to or intercalated in the main ring, at least one entity chosen from aromatic rings, oxygen and sulphur atoms and sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary, ammonium, ureido, amide and ester groups, and X- is an anion derived from inorganic and organic acids. D is chosen from a glycol residue, a bis-secondary diamine residue, a bis-primary diamine residue or a ureylene group. Suitable examples include polymers known as Hexadimethrine chloride, where R1, R2, R3 and R4 are each methyl radicals, A1 is (CH2)3 and B1 is (CH2)6 and X = Cl; as polyquaternium-34 where R1and R2 are ethyl radicals and R3 and R4 are methyl radicals and A1 is (CH2)3 and B1 is (CH2)3 and X = Br (e.g. Mexomere PAX by Chimax).

7) Polyquaternary ammonium polymers comprising repeating units of formula [–N+(R6)(R7)–(CH2)r–NH–CO-(CH2)q–(CO)t-NH-(CH2)s–N+(R8)(R9)–A–][2X-], in which R6, R7, R8 and

R9 which may be identical or different, are chosen from a hydrogen atom and a methyl, ethyl, propyl, hydroxyethyl, hydroxypropyl, and –CH2CH2(OCH2CH2)pOH radicals, wherein p is equal to 0 or an integer ranging from 1 to 6, wherein R6, R7, R8 and R9 do not all simultaneously represent a hydrogen atom. R and s which maybe identical or different are each an integer ranging from 1 to 6, q is equal to 0 or an integer ranging from 1 to 34 and X- is anion such as a halide. T is an integer chosen to be equal to 0 or 1. A is chosen from divalent radicals such as –CH2–CH2–O–CH2–CH2–. Suitable examples include: polymers known as polyquaternium-2, where r=s=3, q=0,t=0, R6, R7, R8 and R9 are methyl groups, and A is –CH2–CH2–O–CH2–CH2 (e.g. Ethpol PQ-2 from Ethox; Mirapol A-15 by Rhodia); as polyquaternium-17 where r=s=3, q=4, t=1 R6, R7, R8 and R9 are methyl groups, and A is –CH2–CH2–O–CH2–CH2; as Polyquaternium 18, where r=s=3, q=7, t=1 R6, R7, R8 and R9 are methyl groups, and A is –CH2–CH2–O–CH2–CH2; as the block copolymer formed by the reaction of Polyquaternium-2 with Polyquaternium-17, which are known as Polyquaternium 27 (e.g. Mirapol 175 by Rhodia).

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

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

10) Cross linked methacryloyloxy(C1-C4)alkyltri(C1-C4)alkylammonium salt polymers such as the polymers obtained by homopolymerisation of dimethylaminoethyl methacrylates quaternized with methyl chloride, or by copolymerisation of acrylamides with dimethylaminoethyl methacrylates quaternized with methyl chloride, the homo or copolymerisation being followed by crosslinking with a compound comprising olefinic unsaturation, such as methylenebisacrylamides, including polymers known as Polyquaternium-37 (e.g. Synthalen CN/CR/CU sold by 3V sigma; or as a dispersion in another media such as Salcare SC95/SC96 by Ciba; Rheocare CTH(E) by Cosmetic Rheologies) and polymers known as Polyquaternium-32 (e.g. sold as a dispersion in mineral oil such as Salcare SC92 by Ciba).

11) Further examples of cationic polymers include polymers known as Polyquaternium 51 (e.g. Lipidure-PMB by NOF), as Polyquaternium 54 (e.g. Qualty-Hy by Mitsui), as Polyquaternium

56 (e.g. Hairrol UC-4 by Sanyo chemicals), as Polyquaternium 87 (e.g. Luviquat sensation by BASF).

12) Silicone polymers comprising cationic groups and/or groups which may be ionised into cationic groups. Suitable examples include cationic silicones of the general formula (R10-N+(CH3)2–R11–(Si(CH3)2–O)x–R11–(N+(CH3)2–R10), where R10 is an alkyl derived from coconut oil, and R11 is (CH2CHOCH2O(CH2)3 and x is a number between 20 and 2000, including polymers known as Quaternium 80 (e.g. Abil Quat 3272/3474 sold by Goldschmidt); silicones containing groups which may be ionised into cationic groups, for example aminosilicones containing at least 10 repeating siloxane –(Si(CH3)2–O) units within the polymer chain, with either terminal, graft or a mixture of terminal and graft aminofunctional groups. Example functional groups are not limited to aminoethylaminopropyl, aminoethylaminoisobutly, aminopropyl. In the case of graft polymers, the terminal siloxane units can either be (CH3)3Si–O or R12(CH3)2Si–O, where R12 can be either OH or OR13, where R13 is a C1-C8 alky group, or a mixture of both functional terminal groups. These silicones are also available as preformed emulsions. Polymer with terminal siloxane units of (CH3)3Si–O examples includes polymers known as trimethylsilylamodimethicone (e.g. DC-2-8566, DC 7224, DC-2-8220 by Dow Corning; SF1708, SM 2125 GE Silicones; Wacker Belsil ADM 653 by Wacker silicones). Further examples include polymers with terminal siloxane units of (R12O)(CH3)2Si–O where R12 can be either OH or OR13, where R13 is a C1-C8 alky group, or a mixture of both functional terminal groups, known as amodimethicone (e.g. Wacker Belsil ADM 1100/ADM 1600/ADM 652/ADM 6057E/ADM 8020 by Wacker Silicones; DC929, DC939, DC949 by Dow Corning; SM2059 by GE silicones). Silicones containing groups which may be ionised into cationic groups – for example silicones containing at least 10 repeating siloxane –(Si(CH3)2–O) units within the polymer chain, with either terminal, graft or a mixture of terminal and graft aminofunctional groups, together with additional functional groups. Additional functional groups can include polyoxyalkylene, the reaction product of amines and carbinols, alky chains. For example products known as methoxy PEG/PPG-7/3 Aminopropyl Dimethicone (e.g. Abil Soft AF100 by Degussa). For example products known as Bis (C13-15 Alkoxy) PG Amodimethicone (e.g. DC 8500 by Dow Corning).

The cationic polymer may be selected from the group consisting of polyquaternium 37, polyquaternium 7, polyquaternium 22, polyquaternium 87, and mixtures thereof; particularly from the group consisting of polyquaternium 37, polyquaternium 22, and mixtures thereof.

<u>Surfactants</u>

The first and/or the second hair colouring compositions according to the present invention may further comprise a surfactant. Suitable surfactants generally have a lipophilic chain length of from 8 to 30 carbon atoms and can be selected from anionic surfactants, nonionic surfactants, amphoteric surfactants, cationic surfactants, and mixtures thereof.

Typically, the first and/or the second hair colouring compositions may comprise a total amount of surfactants ranging from 1% to 60%, alternatively from 2% to 30%, alternatively from 8% to 25%, alternatively from 10% to 20%, by weight of the total composition.

The first and/or the second hair colouring compositions may comprise a mixture of an anionic surfactant and an amphoteric surfactant with one or more nonionic surfactants. The compositions may comprise a total amount of anionic surfactant ranging from 0.1% to 20%, alternatively from 0.1% to 15%, alternatively from 5% to 15%, by weight of the total composition; and a total amount of amphoteric and/or nonionic components, which may range independently from each other from 0.1% to 15%, alternatively from 0.5% to 10%, alternatively from 1% to 8%, by weight of the total composition.

Suitable anionic surfactants include, but are not limited to: salts (such as alkaline salts, for example, sodium salts, ammonium salts, amine salts, amino alcohol salts and magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylarylpolyether sulphates, monoglyceride sulphates; alkyl sulphonates, alkyl phosphates, alkylamide sulphonates, alkylaryl sulphonates, a-olefin sulphonates, paraffin sulphonates; alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamide sulphosuccinates; alkyl sulphosuccinamates; alkyl sulphoacetates; alkyl ether phosphates; acyl sarcosinates; acyl isethionates; N-acyltaurates; and mixtures thereof. The alkyl or acyl radical of all of these various compounds, for example, comprises from 8 to 24 carbon atoms, and the aryl radical, for example, is chosen from phenyl and benzyl groups. Among the anionic surfactants, which can also be used, mention may also be made of fatty acid salts such as the salts of oleic, ricinoleic, palmitic and stearic acids, coconut oil acid or hydrogenated coconut oil acid; acyl lactylates in which the acyl radical comprises from 8 to 20 carbon atoms. Weakly anionic surfactants can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated (C_6-C_{24}) alkyl ether carboxylic acids, polyoxyalkylenated (C_6-C_{24}) alkylaryl ether carboxylic acids, polyoxyalkylenated (C_6-C_{24}) alkylamido ether carboxylic acids and their salts, for example, those comprising from 2 to 50 ethylene oxide groups, and mixtures thereof. Anionic derivatives of polysaccharides, for example carboxyalkyl ether of alkyl polyglucosides, can be also used.

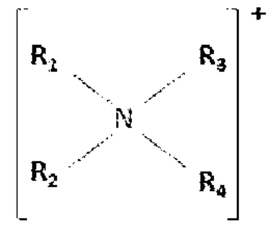
Nonionic surfactants are compounds that are well known (see, for example, in this respect "Handbook of Surfactants" by M. R. Porter, published by Blackie & Son (Glasgow and London),

1991, pp. 116-178). Suitable non-ionic surfactants include, but are not limited to: polyethoxylated, polypropoxylated and polyglycerolated fatty acids, alkyl phenols, α-diols and alcohols comprising a fatty chain comprising, for example, from 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene oxide groups to range, for example, from 2 to 200 and for the number of glycerol groups to range, for example, from 2 to 30. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide and their momoethanolamine and diethanolamine derivatives, polyglycerolated fatty amides, for example, comprising on average from 1 to 5, and such as from 1.5 to 4, glycerol groups; polyethoxylated fatty amines such as those containing from 2 to 30 mol of ethylene oxide; oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as (C_{10}-C_{14})alkylamine oxides or N-acylaminopropylmorpholine oxides.

Suitable amphoteric surfactants include, but are not limited to: aliphatic secondary and tertiary amine derivatives in which the aliphatic radical is chosen from linear and branched chains comprising from 8 to 22 carbon atoms and comprising at least one water-soluble anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); mention may also be made of (C_8-C_{20})alkylbetaines, sulphobetaines, (C_8-C_{20})alkylamido(C_1-C_6)alkylbetaines or (C_8-C_{20})alkylamido(C_1-C_6)alkylsulphobetaines. Among the amine derivatives, mention may be made of the products sold as Miranol, as described, for example, in U.S. Pat. Nos. 2,528,378 and 2,781,354 and having the structures of: R_2-CON HCH_2CH_2—$N^+(R_3)(R_4)(CH_2COO^-)$, (VI) in which: R_2 is chosen from alkyl radicals derived from an acid R_2-COOH present in hydrolysed coconut oil, and heptyl, nonyl and undecyl radicals, R_3 is a β-hydroxyethyl group and R_4 is a carboxymethyl group; and of R_5-$CONHCH_2CH_2$—N(B)(C) (VII) wherein B represents —CH_2CH_2OX', C represents —$(CH_2)_z$—Y′, with z=1 or 2, X′ is chosen from the —CH_2CH_2—COOH group and a hydrogen atom, Y′ is chosen from —COOH and —CH_2—CHOH—SO_3H radicals, R_5 is chosen from alkyl radicals of an acid R_5-COOH present in coconut oil or in hydrolysed linseed oil, alkyl radicals, such as C_7, C_9, C_{11} and C_{13} alkyl radicals, a C_{17} alkyl radical and its iso form, and unsaturated C_{17} radical. These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium

caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid, and cocoamphodipropionic acid. Salts of diethyl aminopropyl cocoaspartamid can be also used. Suitable cationic surfactants include, but are not limited to, the quaternary ammonium salts A) to D) as defined hereinafter:

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



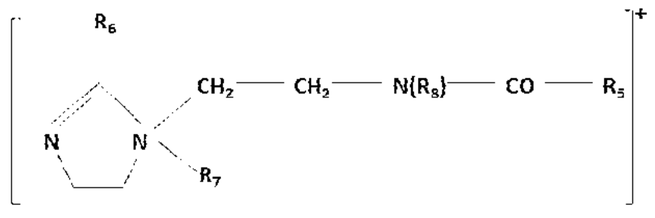
(VIII)

wherein X^- is an anion chosen from halides (chloride, bromide and iodide), (C_2-C_6)alkyl sulphates, such as methyl sulphate, phosphates, alkyl and alkylaryl sulphonates, and anions derived from organic acids, such as acetate and lactate, and wherein R_1 to R_4 are as below in i) or ii).

i) Radicals R_1 to R_3, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals may comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals may be chosen from: alkyl, alkoxy and alkylamide radicals. R_4 is chosen from linear and branched alkyl radicals comprising from 16 to 30 carbon atoms. A suitable cationic surfactant is, for example, a behenyltrimethylammonium salt (for example chloride).

ii) Radicals R_1 and R_2, which may be identical or different, are chosen from linear and branched aliphatic radicals comprising from 1 to 4 carbon atoms, and aromatic radicals such as aryl and alkylaryl. The aliphatic radicals may comprise at least one hetero atom such as oxygen, nitrogen, sulphur and halogens. The aliphatic radicals may be chosen from alkyl, alkoxy, alkylamide and hydroxyalkyl radicals comprising from 1 to 4 carbon atoms. Radicals R_3 and R_4, which may be identical or different, are chosen from linear and branched alkyl radicals comprising from 12 to 30 carbon atoms, the said alkyl radicals comprise at least one function chosen from ester and amide functions. R_3 and R_4 may be chosen from (C_{12}-C_{22})alkylamido(C_2-C_6)alkyl and (C_{12}-C_{22}) alkylacetate radicals. A suitable cationic surfactant is, for example, a dicetyldimethyl ammonium salt (for example chloride);

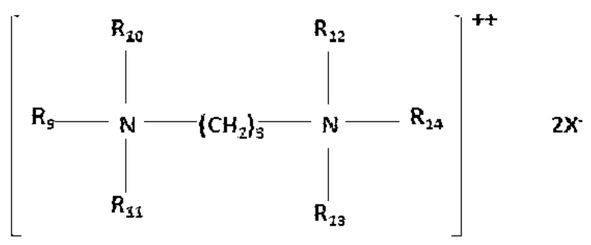
B) Quaternary ammonium salts of imidazolinium of formula (IX) below:



(IX)

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

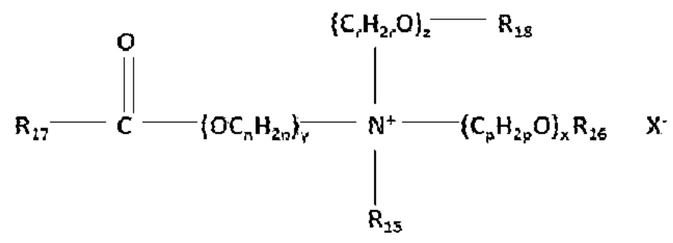
C) Diquaternary ammonium salts of formula (X):



(X)

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

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



(XI)

in which: R15 is chosen from C1-C6 alkyl radicals and C1-C6 hydroxyalkyl and dihydroxyalkyl radicals; R16 is chosen from: a radical R19C(O)-, linear and branched, saturated and unsaturated C1-C22 hydrocarbon-based radicals R20, and a hydrogen atom, R18 is chosen from: a radical R21C(O)-, linear and branched, saturated and unsaturated C1-C6 hydrocarbon-based radicals R22, and a hydrogen atom, R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21 hydrocarbon-based radicals; n, p and r, which may be identical or different, are chosen from integers ranging from 2 to 6; y is chosen from integers ranging from 1 to 10; x and z, which may be identical or different, are chosen from integers ranging from 0 to 10; X– is an anion chosen from simple and complex, organic and inorganic anions; with the proviso that the sum x+y+z is from 1 to 15, that when x is

0, then R16 is R20 and that when z is 0, then R18 is R22. In one embodiment, the ammonium salts of formula (XI) can be used, in which: R15 is chosen from methyl and ethyl radicals, x and y are equal to 1; z is equal to 0 or 1; n, p and r are equal to 2; R16 is chosen from: a radical R19C(O)-,methyl, ethyl and C14-C22 hydrocarbon-based radicals, and a hydrogen atom; R17, R19 and R21, which may be identical or different, are chosen from linear and branched, saturated and unsaturated C7-C21, hydrocarbon-based radicals; R18 is chosen from: a radical R21C(O)- and a hydrogen atom. Such compounds are commercially available as Dehyquart by Cognis, Stepanquat by Stepan, Noxamium by Ceca, and Rewoquat WE 18 by Rewo-Witco.

Ionic strength

The first and/or the second hair colouring compositions of the present invention may further have an ionic strength as defined herein of less than 1.35 mole/kg, alternatively from 0.10 to 0.75 mole/kg, alternatively from 0.20 to 0.60 mole/kg. Whilst not being bound by theory, it is believed that the ionic strength value may also affect the resultant viscosity and root adhesion properties of the composition. The ionic strength can be affected by salt resources such as the dyes, sodium sulphate, ammonium carbonate anti-oxidants and chelants such as EDDS. The dye tends to have the greatest effect on the ionic strength and thus the amounts added in order to provide any particular shade need to be considered in terms of ionic strength as well as dye outcome in order to prevent viscosity and root adhesion problems.

The ionic strength of the composition is a function of the concentration of all ions present in that solution and is determined according to the formula:

$$I = \frac{1}{2}\sum_{i=1}^{n} m_i z_i^2$$

where m_i = molality of ion i (M = mol·/Kg H_2O), z_i = charge number of that ion, and the sum is taken over all ions in the solution. For example, for a 1:1 electrolyte such as sodium chloride, the ionic strength is equal to the concentration, but for $MgSO_4$ the ionic strength is four times higher. Generally multivalent ions contribute strongly to the ionic strength.

For example the ionic strength of a mixed 0.050 M Na_2SO_4 and 0.020 M NaCl solution is: I = $1/2((2 \times (+1)^2 \times 0.050) + (+1)^2 \times 0.020 + (-2)^2 \times 0.050 + (-1)^2 \times 0.020) = 0.17$ M.

Foam

The first and/or the second hair colouring compositions of the invention may be provided in the form of foam which is applied to the hair. Foam formation is typically achieved by the use of a foaming agent incorporated within the mixed composition (typically present in either the oxidizing composition or the dye composition or both) in combination with a manually operated

foaming device. Such manually operated foaming devices are known in the art and include aerosols devices, squeeze foamers and pump foamers.

Suitable foaming agents includes surfactants such as anionic, nonionic and amphoteric surfactants, nonionic surfactants being preferred; polysaccharides (as described herein); polyvinyl pyrrolidone and copolymers thereof; acrylic polymers such as Acrylates copolymer (Aculyn 33) and Acrylates/Steareth-20 methacrylates (Aculyn 22); C12-C24 fatty acids such as stearates and mixtures thereof.

Viscosity

The developer compositions and the dye compositions may be, independently from one another, prepared as so called thin liquids or creams.

Each of the first and second hair colouring compositions may have a viscosity which induces a shear stress of from 20 to 200 Pa at 10 s^{-1} as measured according to the viscosity test method.

The first hair colouring compositions may have a viscosity which induces a shear stress of from 20 to 200 Pa at 10 s^{-1} as measured according to the viscosity test method and the second hair colouring composition may have a viscosity which induces a shear stress of from 20 to 180 Pa at 10 s^{-1} as measured according to the viscosity test method, for example in embodiments wherein the pH increasing agent is provided as a liquid, wherein the pH increasing agent:second portion of the first composition mixing ratio is of 1:4 or more, or 1:4 or more, or 1:4 to 25:1 or 1:4 to 20:1, or 1:4 to 10:1 or 2:1 to 5:1.

Each of the first and second hair colouring compositions may have a viscosity which induces a shear stress of from 20 to 60 Pa at 10 s^{-1}, when the first and second hair colouring compositions are applied to the hair with a container to which a nozzle or a separate applicator device such as a comb or a brush is attached.

The first hair colouring composition may have a viscosity which induces a shear stress of from 30 to 200 Pa at 10 s^{-1}, or from 100 to 200 Pa at 10 s^{-1}, or from 130 to 180 Pa at 10 s^{-1} when the first hair colouring composition is applied to the hair with a brush and bowl applicator. The second hair colouring composition may have a viscosity which induces a shear stress of from 20 to 180 Pa at 10 s^{-1}, or from 40 to 180 Pa at 10 s^{-1}, or from 70 to 170 Pa at 10 s^{-1}, when the second hair colouring composition is applied to the hair with a brush and bowl applicator or with the hands or fingers of the user.

Whilst not being bound by theory, it is believed that the provision of the first hair colouring composition having viscosity values as described hereinabove enables the first hair colouring composition to be applied directly to the roots without any dripping or running down

the hair lengths and also enables the second hair colouring composition to be easily applied and distributed along the entire remaining hair length with minimal to no dripping from the hair.

Application means

Both the first and/or second hair colouring composition may be applied to the hair with a brush and bowl applicator. Alternatively, the first hair colouring composition may be applied to the hair with a brush and bowl applicator whereas the second hair colouring composition may be applied to the hair with the hands and fingers of the user.

Alternatively, both the first and/or second hair colouring compositions may be applied to the hair with a container to which a nozzle or a separate applicator device such as a comb or a brush is attached.

The application means may also include means which assist in achieving particular effects such as highlighting such as highlighting combs, brushes and tools, foils and highlighting caps. Additional application means technology can be used to assist in the penetration of the product into the hair. Examples of such technology include heating devices, ultraviolet light devices and ultrasound devices.

Method for perming hair

The method for treating the hair may be a method for perming hair wherein each of the first and second hair treatment compositions is a hair perming composition.

The classic technique for implementing permanent hair restructuring involves a first stage in which the disulfide bonds of the hair keratin are opened with the aid of a reducing composition comprising a reducing agent (restructuring agent); the hair is then changed to the desired form, and, subsequently, the disulfide bonds are linked back together again using an oxidative composition comprising an oxidative agent (fixing agent). Sulfites, mercaptoacetic acid, thiolactic acid, 3-mercaptopropionic acid, mercaptocarboxylic acid ester, and cysteine are used in particular as reducing agents. These agents are either acidic (sulfite, bisulfite, and mercaptocarboxylic acid ester) or alkaline (alkali and ammonium salts of mercaptocarboxylic acids). In the case of alkaline reducing agents, the required alkalinity is obtained primarily by adding ammonia, organic amines, ammonium or alkali carbonate, and ammonium or alkali hydrogen carbonates. Liquids containing hydrogen peroxide or bromate are particularly used as oxidative compositions.

The first and second hair perming compositions may be reducing compositions comprising a reducing agent.

In case alkaline reducing agents are used, the pH of each of the first and second reducing compositions may be from 7 to 13.5. The pH of the first reducing composition may be from 7 to 12.5 and the pH of the second reducing composition may be from 8 to 13.5.

The method of perming hair may comprise the step of:

a. applying a first portion of the first composition to the hair and retaining a second portion of the first composition;

b. adding a pH increasing agent to the second portion of the first composition to obtain the second composition

Whilst not wishing to be bound by theory, it is believed that for example in the case of alkaline reducing agents, when the pH of a reducing composition is increased, the efficacy of the reducing agent comprised in this composition is also increased and therefore the percentage of the disulfide bonds of the hair keratin which is opened by the reducing agent is also increased. Therefore, such a composition may be applied by the user to increase the perming intensity on a specific portion of hair.

Hair colouring kit

The present invention also relates to a hair colouring kit which may be used for carrying out the method for colouring hair described hereinbefore. The compositions comprised in the kit may comprise any of the ingredients disclosed in the hair colouring compositions section of this application.

The kit may comprise a first dye composition, a second dye composition, a first developer composition and a second developer composition, wherein each of the first and second dye compositions comprises one or more oxidative dye precursors and/or one or more alkalising agents and each of the first and second developer compositions comprises one or more oxidizing agents, wherein the pH of the second developer composition is higher than the pH of the first developer composition.

Alternatively, the kit may comprise a first dye composition, a first developer composition and a pH increasing agent wherein the first dye composition comprises one or more oxidative dye precursors and/or one or more alkalising agents and the first developer composition comprises one or more oxidizing agents and wherein the first dye composition, the first developer composition and the pH reducing agent are packaged separately. In these embodiments, the pH increasing agent may be provided as a solid or a liquid.

The developer composition may comprise from 1 to 20% by weight of the oxidizing agents and the dye compositions may comprise from 0.01% to 10% by weight of the oxidative dye precursor(s) and/or from 0.1% to 10% by weight of the alkalizing agent.

The kit may further comprise a shampoo for use in rinsing the hair after colouring and/or a conditioner composition.

The kit may also comprise a color refresher composition. Such colour refresher composition may comprise at least one pre-formed dye and may be applied to the hair immediately after the oxidative colour. This is typically during the next wash cycle(s) from 1 day to 60 days after the original oxidative application. This colour refresher composition can be used to increase the initial colour obtained and/or boost the colour during the wash and style cycle until the next oxidative colouring or bleaching event.

The present invention may be utilized in a variety of packaging and dispensing devices. These dispensing devices can come in the form of separate devices which may be used independently or in combination with one another. Typically, the hair colouring or bleaching compositions are contained within separate single or multi compartment containers so that the compositions can be stored separately from one another before use. The compositions are then mixed together by a mixing means and then applied to the consumer's hair by an application means.

The developer composition(s), the dye composition(s) and the pH increasing agent may provided in separate containers in the kit. The developer composition(s), the dye composition(s) and the pH increasing agent may be provided in a bottle, a tube, an aerosol, or a sachet.

The consumer may mix the developer composition(s) and the dye composition(s) by any means. This may simply involve the use of a mixing bowl into which the compositions are dispensed and then mixed, preferably using a mixing means such as a tool. Alternatively, it may involve the addition of one of the compositions into the container comprising the other composition (typically the dye composition is added to the developer composition), followed by manual shaking or mixing with a tool. Another system involves the perforation or displacement of a seal located between the separate compartments of the dye composition and developer composition within a single container or sachet followed by manual mixing within the container or in a separate and/or additional container.

The hair colouring kit may further comprise an applicator. The applicator may be a brush and bowl applicator. Alternatively, the applicator may be a nozzle which may be attached to one of the containers comprised in the kit in case the developer composition, the dye composition and the pH increasing agent are provided in separate containers in the kit or a separate applicator device such as a comb or a brush. Such combs and brushes can be adapted in order to achieve particular effects, whether it is quick and even coverage or root/hairline touch up, or highlights or streaks.

Alternatively, one of the containers may be provided with a comb attached to or instead of the dispensing nozzle whereby the product is dispensed through hollow tines and dispensing apertures located in the comb tines. The comb tines may be provided with single or multiple openings along the tines to improve product application and evenness especially root to tip. Product dispensation can be achieved by mechanical pressure applied to the container for example delaminating bottles or any of the mechanisms described hereinabove. The comb may be provided on the container such as to facilitate easy application and may be positioned vertically (so called verticomb) or at an angle to allow the consumer to access all areas.

The volume of developer composition in the kit may be 10 mL to 120 mL, preferably 40 mL to 70 mL, more preferably 55 mL to 65 mL. The volume of dye composition in the kit may be 10 mL to 120 mL, preferably 40 mL to 70 mL, more preferably 55 mL to 65 mL.

The compositions of the kit can be manufactured utilizing any one of the standard approaches, these include a) 'Oil in water' process, b) 'Phase Inversion' process and c) 'One-pot' process. For example, when using "oil in water" process, surfactants of the present invention are added to approximately 50% of total water amount of the compositions at 90°C, homogenized for 15 to 30 min, then cooled to room temperature to form a premix; this premix is then mixed cold with remaining amounts of water, other optional components and/or oxidizing agents, thus forming the developer composition and dye composition of the above described colouring kit.

The kit may further comprise a set of instructions comprising instructing the user to colour its hair according to the method defined hereinbefore.

For the embodiments, wherein the kit comprises a first and second developer composition and a first and second dye composition, the set of instruction may comprise:

i) mixing the first dye composition with the first developer composition to obtain a first hair colouring composition;
ii) applying a portion or all of the first hair colouring composition to the hair;
iii) mixing the second dye composition with the second developer composition to obtain a second hair colouring composition;
iv) applying a portion or all of the second hair colouring composition to the hair;
v) optionally rinsing the hair.

For the embodiments, wherein the kit comprises a first dye composition, a first developer composition and a pH increasing agent, the set of instruction may comprise:

i) mixing the first dye composition with the first developer composition to obtain the first hair colouring composition;

ii) applying a first portion of the first hair colouring composition to the hair and retaining a second portion of the first hair colouring composition;

iii) adding a pH increasing agent to the second portion of the first hair colouring composition to obtain the second hair colouring composition,;

iv) applying a portion or all of the second hair colouring composition to the hair;

v) optionally rinsing the hair.

The set of instructions may comprise any additional step which is disclosed hereinbefore in the method for colouring hair section of the application.

Hair perming kit

The kit may comprise a first reducing composition, a second reducing composition and an oxidizing composition, wherein each of the first and second reducing compositions comprises a reducing agent and wherein the oxidizing composition comprises an oxidizing agent, wherein the pH of the second reducing composition is higher than the pH of the first reducing composition.

Alternatively, the kit may comprise a first reducing composition, an oxidizing composition and a pH increasing agent, wherein the first reducing composition comprises a reducing agent and the oxidizing composition comprises an oxidizing agent. In these embodiments, the pH increasing agent may be provided as a solid or a liquid.

Viscosity test method:

The viscosity of a composition is measured using a TA Instruments AR 2000 Rheometer or equivalent device equipped with a Peltier plate and a 6cm flat acrylic plate with cross hatchings. The instrument is calibrated according to the manufacturer's instructions and the Peltier plate is set at 25.0°C. The cone is raised to a position approximately 4.5 cm above the plate.

Immediately after the mixing, approximately 10g of the mixture is transferred gently onto the centre of the Peltier plate using a spatula. The cone is lowered to obtain the specified gap between the tip of the cone and the upper surface of the Peltier plate. The gap setting is specified by the manufacturer of the cone and is typically approximately 1000 microns. The rheometer is programmed to operate in rotational mode with the shear stress ramped from 0.1 to 600 Pa over a period of 4 minutes, termination at 1000 reciprocal seconds. Rotation is initiated immediately after the specified gap is established. Viscosity data collected during the measurement period are shear stress (Pa) plotted as a function of shear rate (s^{-1}).

Colour variation test method

The colorimetric parameters in the CIE L* a* b* system are measured using an Ocean Optics USB 2000+ spectrophotometer. (illuminant D65, angle 10°, specular component included) in which L* represents the lightness of the colour, a* indicates the green/red colour axis and b* the blue/yellow colour axis. The L*, a* and b* values are average values, the measurement being performed on about 80 different positions of a hair switch by the spectrophotometer.

3g of the hair colouring composition available from International Hair Importers & Products, Glendale, NY to be tested is applied with a brush to a 0.75g, 4 inch hair switch of uncoloured natural white hair and left for 30 minutes at 30°C. After 30 minutes the hair colouring composition is rinsed off the hair for 2 minutes and the hair is then shampooed with Wella Professionals Brillance, Fine/Normal shampoo commercially available in Germany in April 2014 and conditioned with Wella Professionals Brillance, Fine/Normal conditioner commercially available in Germany in April 2014 for 1 minute and then blow-dried.

Calculated parameters (ΔL^* and ΔE_{00}^*):

ΔL^* and ΔE_{00}^* parameters which respectively correspond to the colour lightness difference and the colour variation between hair coloured with the second hair colouring composition according to the present invention and hair coloured with the first hair colouring composition according to the present invention are calculated.

ΔL^* is obtained from the following formula:

$\Delta L^* = L_2^* - L_1^*$, wherein L_1^* represents the lightness of the colour measured on hair coloured with the first hair colouring composition according to the present invention and L_2^* represents the lightness of the colour measured on hair coloured with the second hair colouring composition according to the present invention.

ΔE_{00}^* is a well established parameter. This parameter is calculated based on the colorimetric parameters in the CIE L* a* b* system which are measured for the first and the second hair colouring compositions. The method for calculating this parameter is disclosed in Publication 142-2001 of the CIE (International Commission on Illumination)

Experimental Data:

All concentrations are listed as weight percent, unless otherwise specified.

Dye compositions:

Dye composition 1: Wella Koleston Perfect Vibrant Reds 55/46 commercially available in Germany in April 2014

Dye composition 2:

2-Methoxymethyl-p-phenylenediamine	0.357
Perfume	0.25
Resorcinol	0.2
2-Methylresorcinol	0.05
m-Aminophenol	0.015
Ammonium hydroxide 25%	7.5
Hair colouring chassis	Up to 100

Dye composition 3:

Toluene-2,5-diamine sulfate	1.230
Resorcinol	0.5271
1-naphthol	0.0025
m-Aminophenol	0.05
2-Amino-4-hydroxyethylaminoanisole sulfate	0.014
2-Methylresorcinol	0.053
4-Amino-2-hydroxytoluene	0.009
Ammonium hydroxide 25%	7.7
Hair colouring chassis	Up to 100

Developer compositions:

Developer composition 1: Wella Welloxon Perfect, 6% H_2O_2 commercially available in Germany in April 2014

Developer composition 2: Wella Welloxon Perfect, 9% H_2O_2 commercially available in Germany in April 2014

Developer composition 3:

Water Purified	Up to 100
Disodium EDTA	0.04
Etidronic Acid	0.08
Thickeners	9.05

Hydrogen peroxide solution, 50%	12.00
Simethicone Emulsion	0.0054

In a first experiment, 10 different hair colouring compositions (compositions C1 to C10) were prepared by mixing dye composition 1 with developer composition 1 at a mixing ratio of 1:1 in a bowl (5g of dye composition 1 + 5g of developer composition 1). The pH of the different hair colouring compositions which were obtained was adjusted by adding either sodium hydroxide (50% solution) or phosphoric acid (ACS reagent grade) except for one composition (blank sample) to obtain different compositions having different pHs.

In a second experiment, 10 different hair colouring compositions (compositions C11 to C20) were prepared following the same experimental protocol as for the first experiment, replacing dye composition 1 with dye composition 2 and developer composition 1 with developer composition 2.

In a third experiment, 10 different hair colouring compositions (compositions C21 to C30) were prepared following the same experimental protocol as for the first experiment, replacing dye composition 1 with dye composition 3 and developer composition 1 with developer composition 3.

Compositions prepared in the first, second and third experiments:

Addition of H_3PO_4 or NaOH 50%	Composition	pH value	Composition	pH value	Composition	pH value
600µl H_3PO_4	**C1**	2.42	**C11**	2.45	**C21**	2.13
500µl H_3PO_4	**C2**	2.77	**C12**	2.95	**C22**	2.43
400µl H_3PO_4	**C3**	4.61	**C13**	5.25	**C23**	3.19
300µl H_3PO_4	**C4**	5.31	**C14**	5.85	**C24**	5.04
200µl H_3PO_4	**C5**	6.6	**C15**	7.2	**C25**	6.11

100µl H_3PO_4	**C6**	9.05	**C16**	9.35	**C26**	8.54
Blank sample	**C7**	9.78	**C17**	10.02	**C27**	9.78
100µl NaOH 50%	**C8**	10.25	**C18**	10.42	**C28**	10.2
200µl NaOH 50%	**C9**	10.79	**C19**	10.83	**C29**	10.76
300µl NaOH 50%	**C10**	11.26	**C20**	11.17	**C30**	11.2

The L*, a*, b* parameters have been measured for the different compositions C1 to C30 according to the colour variation test method and the ΔL^* and ΔE_{00}^* parameters have been calculated for some of the compositions according to the colour variation test method.

Results:

The ΔL^* and ΔE_{00}^* parameters which respectively correspond to the colour lightness difference and the colour variation between hair coloured with two different compositions have been calculated according to the colour variation test method. Additional ΔL^* and ΔE_{00}^* parameters can eventually be calculated. As can be seen in the below tables, some of the compositions have a ΔE_{00}^* value greater than or equal to 1.

As explained hereinbefore, whilst not wishing to be bound by theory, it is believed that having such a colour variation ΔE_{00}^* helps to ensure that the overall colour result obtained with the second composition is significantly different from the overall colour result obtained with the first composition.

Furthermore, some of the compositions have in addition a ΔL^* value greater than 0. These compositions may for example be used to provide a lighter colour result when the second composition is applied to the hair than when the first composition is applied to the hair, for example on hair lengths and tips vs. hair roots.

Composition	L*	a*	b*	Composition	L*	a*	b*
C1	59.89	8.35	23.45	C11	61.34	6.82	24.64
C2	57.64	10.1	22.06	C12	59.65	6.46	22.93
C3	43.55	21.61	18.64	C13	55.23	5.45	17.65
C4	28.57	23.87	14.19	C14	40.68	5.21	12.97
C5	22.62	21.57	10.71	C15	35.62	5.78	12.79

C6	20.63	21.01	9.08	C16	40.44	5.8	14.01
C7	18.82	20.57	7.94	C17	35.3	5.89	13.27
C8	19.32	21.32	8.37	C18	38.63	5.58	13.46
C9	21.64	22.47	9.54	C19	45.19	5.19	13.16
C10	22.86	23.75	11.02	C20	49.89	4.99	13.98

Composition	L*	a*	b*
C21	63.57	5.25	24.91
C22	63.16	5.35	25.26
C23	58.86	4.67	22.20
C24	36.10	4.61	9.58
C25	25.34	4.57	7.27
C26	19.72	4.2	5.33
C27	20.71	4.45	5.78
C28	19.78	4.27	5.39
C29	22.05	4.32	5.87
C30	26.47	4.37	5.27

n	$\Delta L^*(C_{n+1}-C_n)$	$\Delta E_{00}^*(C_{n+1}-C_n)$	n	$\Delta L^*(C_{n+1}-C_n)$	$\Delta E_{00}^*(C_{n+1}-C_n)$
1	-2.25	2.6	11	-1.69	0.8
2	-14.09	13.4	12	-4.42	1.0
3	-14.98	7.3	13	-14.55	1.4
4	-5.95	3.1	14	-5.06	1.4
5	-1.99	1.2	15	4.82	0.5
6	-1.81	1.0	16	-5.14	2.2
7	0.5	0.5	17	3.33	0.5
7	2.32	1.2	18	6.56	0.6
9	1.22	1.1	19	4.7	1.6

n	$\Delta L^*(C_{n+1}-C_n)$	$\Delta E_{00}^*(C_{n+1}-C_n)$
21	-0.41	0.2
22	-4.3	2.4
23	-22.76	13.7

24	-10.76	4.6
25	-5.62	2.5
26	0.99	0.5
27	-0.93	0.5
28	2.27	0.9
29	4.42	1.7

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 method for treating hair comprising the steps of:
   i) providing a first hair treatment composition and a second hair treatment composition, wherein the pH of the second hair treatment composition is higher than the pH of the first hair treatment composition;
   ii) applying a portion or all of the first hair treatment composition to the hair;
   iii) applying a portion or all of the second hair treatment composition to the hair;
   iv) optionally rinsing the hair, wherein:
   - the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof or
   - the method is a method for perming hair wherein each of the first and second hair treatment compositions is a hair perming composition.

2. The method according to claim 1, wherein the portion or all of the first composition is applied to the hair roots and the portion or all of the second composition is applied to the hair lengths and tips.

3. The method according to any of the preceding claims, wherein the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof and wherein the second composition produces on the hair a coloration such that the colour variation ΔE_{00}* expressed in the CIE L*a*b* system, between hair coloured with the second composition and hair coloured with the first composition is greater than or equal to 1, as measured according to the colour variation test method.

4. The method according to any of the preceding claims, wherein the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof and wherein the second composition produces on the hair a

coloration such that the colour lightness difference ΔL* expressed in the CIE L*a*b* system, between hair coloured with the second composition and hair coloured with the first composition is greater than 0, as measured according to the colour variation test method.

5. The method according to any of the preceding claims, wherein the difference of pH between the second composition and the first composition is at least 0.25, preferably at least 0.5, more preferably at least 1, even more preferably at least 2.

6. The method according to any of the preceding claims, wherein the pH of each of the first and second compositions is from 7 to 11, preferably wherein the pH of the first composition is from 7 to 10 and the pH of the second composition is from 8 to 11.

7. The method according to any of the preceding claims, wherein the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof and wherein the method further comprises the steps of:

   a. mixing a first dye composition with a first developer composition to obtain the first composition, wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s);
   b. mixing a second dye composition with a second developer composition to obtain the second composition, wherein the second dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the second developer composition comprises one or more oxidizing agent(s),

wherein the pH of the second dye composition is higher than the pH of the first dye composition or the pH of the second developer composition is higher than the pH of the first developer composition.

8. The method according to claim 7, wherein step b) is performed between steps ii) and iii) and:

   - the method further comprises the steps of waiting for a time period of from 10 min to 40 min, preferably 15 min to 30 min, more preferably 20 min, which is performed between

steps ii) and iii) and waiting for a time period of from 5 min to 20 min, preferably 10 min which is performed between steps iii) and iv) or

- step b) is performed immediately after step ii) and step iii) is performed immediately after step b) and the method further comprises the step of waiting for a time period of from 5 min to 40 min, preferably 20 min to 40 min, more preferably 30 min, which is performed between steps iii) and iv).

9. The method according to any of claims 1 to 6, wherein the method is a method for colouring hair wherein each of the first and second hair treatment compositions is a hair colouring composition comprising one or more oxidizing agent(s) and one or more compound(s) selected from the group consisting of oxidative dye precursor(s), alkalizing agent(s) and mixtures thereof and wherein:

- the method further comprises the step of mixing a first dye composition with a first developer composition to obtain the first composition, wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s) and

- in step ii), a first portion of the first composition is applied to the hair and a second portion of the first composition is retained and

- the method further comprises the step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition.

10. The method according to claim 9, wherein the step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition is performed between steps ii) and iii) and:

a. the method further comprises the steps of waiting for a time period of from 10 min to 40 min, preferably 15 min to 30 min, more preferably 20 min, which is performed between steps ii) and iii) and waiting for a time period of from 5 min to 20 min, preferably 10 min which is performed between steps iii) and iv) or

b. the step of adding a pH increasing agent to the second portion of the first composition to obtain the second composition is performed immediately after step ii) and immediately before step iii) and the method further comprises the step of waiting for a time period of from 5 min to 40 min, preferably 20 min to 40 min, more preferably 30 min, which is performed between steps iii) and iv).

11. The method according to any of claims 9 or 10, wherein the pH increasing agent is selected from the group consisting of 1,6-hexanediamine, 2-aminobutanol, aminoethyl propanediol, aminomethyl propanediol, aminomethyl propanol, aminopropanediol, ammonia, ammonium bicarbonate, ammonium carbamate, ammonium carbonate, ammonium chloride, ammonium glycolate, ammonium hydroxide, ammonium phosphate, bis-hydroxyethyl tromethamine, butyl diethanolamine,calcium carbonate, calcium glycinate, calcium hydroxide, calcium oxide, copper glycinate, diammonium phosphate, dibutyl ethanolamine, diethyl ethanolamine, dimethyl isopropanolamine, dimethyl mea, dipotassium phosphate, disodium fumarate, disodium phosphate, disodium tartrate, ethanolamine, ethyl ethanolamine, guanidine carbonate, guanidine hcl, imidazole, isopropanolamine, isopropylamine, lithium carbonate, lithium hydroxide, magnesium hydroxide, magnesium oxide, methylethanolamine, pentapotassium triphosphate, pentasodium triphosphate, phenolsulfonphthalein, phenyl mercuric borate, potassium borate, potassium carbonate, potassium citrate, potassium hydroxide, potassium oxide, potassium phosphate, sesquiethoxytriethanolamine, sodium acetate, sodium aluminate, sodium aluminum lactate, sodium bicarbonate, sodium carbonate, sodium formate, sodium fumarate, sodium humate, sodium hydroxide, sodium metaphosphate, sodium metasilicate, sodium oxide, sodium sesquicarbonate, sodium silicate, sodium trimetaphosphate, strontium hydroxide,tea-diricinoleate/ipdi copolymer, tetrahydroxyethyl ethylenediamine, tetrapotassium pyrophosphate, tetrasodium pyrophosphate, triethanolamine, triisopropanolamine, trisodium phosphate, tromethamine, urea, zinc carbonate hydroxide, zinc glycinate, and mixtures thereof, preferably from the group consisting of ammonia, ammonium bicarbonate, ammonium carbonate, ammonium chloride, ammonium hydroxide, ammonium phosphate, calcium carbonate, calcium hydroxide, calcium oxide, diammonium phosphate, dipotassium phosphate, ethanolamine, isopropanolamine, isopropylamine, magnesium hydroxide, magnesium oxide, potassium borate, potassium carbonate, potassium citrate, potassium hydroxide, potassium oxide, sodium bicarbonate, sodium borate, sodium carbonate, sodium hydroxide, sodium sesquicarbonate, sodium silicate, urea and mixtures thereof.

12. The method according to any of claims 9 to 11, wherein the pH increasing agent is provided as a solid or a liquid.

13. The method according to any of claims 9 to 12, wherein the pH increasing agent is provided as a liquid and

a. the pH increasing agent:second portion of the first composition mixing ratio is of less than 1:4, preferably less than 1:10; or
b. the pH increasing agent:second portion of the first composition mixing ratio is of 1:4 or more, preferably 1:4 to 25:1.

14. The method according to any of claims 7 to 13, wherein:
a. the first and/or the second developer composition comprises from 1 to 20% by weight of the oxidizing agents, and/or
b. the first and/or second dye composition comprises from 0.01% to 10% by weight of the oxidative dye precursors and/or from 0.1% to 10% by weight of the alkalizing agents.

15. The method according to any of claims 9 to 14, wherein from 90% to 10%, preferably from 80% to 50%, more preferably from 75% to 55% by weight of the first composition is applied as a first portion to the hair, preferably the hair roots.

16. The method according to any of the preceding claims, wherein the first and second compositions are applied to the hair with a brush and bowl applicator or a container to which a nozzle or a separate applicator device such as a comb or a brush is attached.

17. A hair colouring kit comprising a first dye composition, a second dye composition, a first developer composition and a second developer composition, wherein each of the first and second dye compositions comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and each of the first and second developer compositions comprises one or more oxidizing agent(s), wherein the pH of the second developer composition is higher than the pH of the first developer composition.

18. A hair colouring kit comprising a first dye composition, a first developer composition and a pH increasing agent wherein the first dye composition comprises one or more oxidative dye precursor(s) and/or one or more alkalizing agent(s) and the first developer composition comprises one or more oxidizing agent(s) and wherein the first dye composition, the first developer composition and the pH increasing agent are packaged separately.