Title: HAIR CARE COMPOSITION

Abstract: A kit for colouring hair comprising: (i) a composition comprising at least one metal ion in the form of salt/and/or complex in which the metal is selected from iron, copper, zinc, manganese or mixtures thereof and a cleansing surfactant mix comprising from 3 wt% to 50 wt% of the total shampoo composition of a nonionic surfactant in which the nonionic surfactant comprises condensation products of aliphatic (C₄-C₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides and is the major component by weight of the surfactant mix and (ii) a second composition, which comprises from 0.05 wt% to 10 wt % of the total second composition of a polyphenol.
Hair Care Composition

The present invention relates to kits and methods for colouring hair.

5 **Background**

Polyphenol compound mordanted with metal ions have been known to dye human hair for many years.

10 EP0327345 (Beecham) discloses a hair colouring shampoo containing an Fe(II) salt and a second component is applied which contains a metal ligand including ortho substituted phenols.

Two part colouring systems in which one part comprises a metal salt are disclosed in WO2010/135237 (Advance Cosmetic Technologies); WO/2007/130777; WO 2000/29036 (Henkel).

However, there remains the need for a colourant that can be used routinely and which delivers an effective level of colouring to hair.

20 **Description of the Invention**

Accordingly the present invention provides a kit for colouring hair comprising:

(i) A kit for colouring hair comprising:

25 (i) a composition comprising at least one metal ion in the form of a salt and/or complex in which the metal is selected from iron, copper, zinc, manganese or mixtures thereof and a cleansing surfactant mix comprising from 3 wt% to 50 wt% of the total shampoo composition of a nonionic surfactant in which the nonionic surfactant comprises condensation products of aliphatic (C₈ - C₁₈) primary or secondary linear or branched
chain alcohols or phenols with alkylene oxides and is the major component by weight of the surfactant mix and 
(ii) a second composition, which comprises from 0.05 wt% to 10 wt% of the total second composition of a polyphenol.

Also described is a method of colouring hair comprising the steps of applying to hair sequentially in any order:
(i) a composition comprising at least one metal ion in the form of a salt and/or complex in which the metal is selected from iron, copper, zinc or manganese and a cleansing surfactant mix comprising from 3 wt% to 50 wt% of the total shampoo composition of a nonionic in which the nonionic surfactant is the major component by weight of the surfactant mix and
(ii) a second composition, which comprises from 0.05 wt% to 10 wt% of the total second composition of a polyphenol.

**Detailed Description of the Invention**

**Composition 1**

Composition 1 is preferably a shampoo compositions of the invention are generally aqueous, i.e. they have water or an aqueous solution or a lyotropic liquid crystalline phase as their major component. Suitably, the composition will comprise from 50 to 98%, preferably from 60 to 90% water by weight based on the total weight of the composition.
Metal Salt/Complex

Shampoo compositions of the invention comprise at least one metal ion in the form of a salt and/or complex in which the metal ion is selected from iron, copper, zinc or manganese. The level of metal ion is preferably from 0.01 wt% to 5 wt% of the total shampoo composition more preferably 0.2 wt% to 3 wt%.

The level of metal ion in the formulation may be determined by quantitative elemental analysis.

For the avoidance of doubt, if the formulation contains 2 wt% of the complex

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\text{With molecular weight of 446.14, then it will contain } \frac{55.84}{446.14} \times 2 = 0.25\text{wt\% of Fe(II)} \text{ (2 decimal places). If the formulation contained 1 wt\% of the salt FeCl}_2 \text{ then}
\]

the it will contain \( \frac{55.84}{126.75} \times 1 = 0.44\text{wt\% of Fe(II)} \text{ (2 decimal places).}

The metal ion is preferably selected from Fe(II), Fe(III) and Cu(II), most preferably Fe(II).

The metal ion is present as a salt or as a complex with a ligand. Simple salts include sulphates and halides, for instance Fe(II)SO\(_4\) and mixed salts, for instance Fe(II) ammonium sulphate. It is preferred if the metal is present as a complex with a ligand. In the context of this invention a ligand is a molecule that contains more than one organic group, preferably 2 to 4 groups, most preferably 2 groups, that co-ordinate with the metal ion. Groups for co-ordinating with the metal ion are COO\(^-\), OH, ketones, esters, primary amines, secondary amines and tertiary amines, more preferably COO\(^-\), tertiary amines and OH, most preferably COO\(^-\) and OH. Polyphenols are not permitted as multidentate ligands. The ligand-
metal complex may be pre-formed before addition to the shampoo for example iron (II) gluconate. Preferably, the mole ratio of iron ion to ligand is from 1:1 to 1:4, more preferably from 1:1.5 to 1:2.5.

5 Preferably, the metal ion is in the form of a salt and/or complex that is soluble in aqueous solution at the pH of the formulation. Most preferably the metal ion in the form of a salt and/or complex has a solubility in demineralised water at the pH of the formulation of greater than 0.1g/L.

10 The ability of a ligand to complex with a metal ion, $M^{n+}$, may be defined by its $pM^{n+}$ value, wherein

$$pM^{n+} = -\log_{10} [M^{n+}]_{free}$$

15 and the ligand concentration is $10^{-5}$ mol/L and the total metal ion concentration is $10^{-6}$ mol/L and $[M^{n+}]_{free}$ is the molar concentration of uncomplexed metal ions. Preferably, the ligand used has a lower $pM^{n+}$, than gallic acid. Preferably, the $pM^{n+}$ are greater than 8 more preferably greater than 10. $pM^{n+}$ values are most preferably measured at pH=4 in de-mineralised water, with the chloride salt of the metal ion, most preferably ferric chloride.

Polyamino carboxylic acids are preferably present at weight % levels of less than 1/30th of the main ligand, preferably they are absent from the shampoo. A polyamino carboxylic acid is a compound containing two or more amines connected through carbon atoms to two or more carboxylic acid groups. 2,2',2''- (Ethane-1,2-diyl)dinitrilo)tetraacetic acid (EDTA) is a polyamino carboxylic acid. Diethylene triamine pentaacetic acid is a polyamino carboxylic acid. Ethylenediamine-N,N'-disuccinic acid is a polyamino carboxylic acid.
Most preferably the ligands are selected from gluconate, tartrate, ascorbate, citrate and lactate. Particularly preferred are gluconate, lactate or ascorbate.

Particularly preferred are iron (II) gluconate and iron(II) lactate, most preferably iron (II) gluconate.

**Surfactant Mix**

Shampoo compositions of the invention comprise cleansing surfactant, the surfactant is non-ionic in nature, however, other anionic and or amphoteric/zwitterionic surfactants may be present. The fraction of non-ionic surfactant in the surfactant mix ($f_{NI}$) may be defined as

$$f_{NI} = \frac{\text{(Wt\% non-ionic surfactant)}}{\text{(total wt\% of all surfactants)}}.$$

The non-ionic surfactant is the major surfactant component and $f_{NI} > 0.5$, More preferably $f_{NI} > 0.8$, most preferably $f_{NI} > 0.95$.

**Nonionic surfactant**

Shampoo compositions of the invention comprise at least 3 wt% to 50 wt% of the shampoo composition of a nonionic surfactant, preferably from 4 wt% to 20%, more preferably from 5 wt% to 15 wt%.

Nonionic surfactants that are included in the shampoo compositions of the invention include condensation products of aliphatic (C₆ - C₁₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, preferably ethylene oxide and having from 6 to 30 ethylene oxide groups. Alkyl ethoxylates are particularly preferred. Most preferred are alkyl ethoxylates having the formula R-(OCH₂CH₂)ₙOH, where R is an alkyl chain of C₁₂ to C₁₅, and n is 5 to 9.
Other suitable nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:

\[ \text{RO - (G)\textsubscript{n}} \]

wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C\textsubscript{5} to about C\textsubscript{20}. Preferably, R represents a mean alkyl chain length of from about C\textsubscript{8} to about C\textsubscript{12}. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C\textsubscript{5} or C\textsubscript{6} monosaccharide residues, and is preferably a glucoside.

G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably, G is glucose.

The degree of polymerisation, n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies from about 1.1 to about 2. Most preferably the value of n lies from about 1.3 to about 1.5.

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.
Other sugar-derived nonionic surfactants which can be included in compositions of the invention include the C_{10}-C_{18} N-alkyl (C_{7}-C_{8}) polyhydroxy fatty acid amides, such as the C_{12}-C_{18} N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide.

Anionic Cleansing Surfactant
Shampoo compositions according to the invention may further comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphasuccinates, alkyl ether sulphasuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, and alkyl ether carboxylic acids and salts thereof, especially sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18, preferably from 10 to 16 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether sulphasuccinates, alkyl ether phosphates and alkyl ether carboxylic acids and salts thereof may contain from 1 to 20 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphasuccinate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium lauryl ether sulphasuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium dodecybenzene sulphonate, triethanolamine dodecybenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate, lauryl ether carboxylic acid and sodium N-lauryl sarcosinate.
Preferred anionic cleansing surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n is from 1 to 3), sodium lauryl ether sulphosuccinate(n)EO, (where n is from 1 to 3), ammonium lauryl sulphate, ammonium lauryl ether sulphate(n)EO, (where n is from 1 to 3), sodium cocoyl isethionate and lauryl ether carboxylic acid (n) EO (where n is from 10 to 20). Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.

The total amount of anionic cleansing surfactant in shampoo compositions of the invention generally ranges from 0.5 wt% to 45 wt%, more preferably from 1.5 wt% to 10 wt%, however, when formulated it should be noted that the level of anionic surfactant should not exceed the level of non-ionic surfactant.

Amphoteric/zwitterionic Surfactant
Amphoteric or zwitterionic surfactant can be included in an amount ranging from 0.5 wt% to about 8 wt%, preferably from 1 wt% to 4 wt% of the total shampoo composition.

Examples of amphoteric or zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglucinate, alkyl amphiacetates, alkyl amphopropionates, alkylamphoglucinate, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms.

Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine, lauryl betaine, cocoamidopropyl betaine and sodium cocooamphoacetate.

A particularly preferred amphoteric or zwitterionic surfactant is cocoamidopropyl betaine.
Mixtures of any of the foregoing amphoteric or zwitterionic surfactants may also be suitable. Preferred mixtures are those of cocamidopropyl betaine with further amphoteric or zwitterionic surfactants as described above. A preferred further amphoteric or zwitterionic surfactant is sodium cocoamphoacetate.

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**Further Ingredients**

**Cationic Polymers**

Cationic polymers are preferred ingredients in a shampoo composition of the invention for enhancing performance.

Suitable cationic polymers may be homopolymers which are cationically substituted or may be formed from two or more types of monomers. The weight average ($M_w$) molecular weight of the polymers will generally be between 100,000 and 2 million daltons. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof. If the molecular weight of the polymer is too low, then the conditioning effect is poor. If too high, then there may be problems of high extensional viscosity leading to stringiness of the composition when it is poured.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give polymers having a cationic charge density in the required range, which is generally from 0.2 to 3.0 meq/gm. The cationic charge density of the polymer is suitably determined via the Kjeldahl method as described in the US Pharmacopoeia under chemical tests for nitrogen determination.
Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic polymers include, for example:

- cationic dialkyl quaternary ammonium-containing polymers including, for example, dimethyl diallylammonium chloride homopolymer and copolymers of acrylamide and dimethyl diallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;

- mineral acid salts of amino-alkyl esters of homo-and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);
- cationic polyacrylamides (as described in WO95/22311).

Other cationic polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives.

Cationic polysaccharide polymers suitable for use in compositions of the invention include monomers of the formula:

\[ A-O-[R-N'(R^1)(R^2)(R^3)X] \]

wherein: \( A \) is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. \( R \) is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof. \( R^1 \), \( R^2 \) and \( R^3 \) independently represent alkyl, aryl, alkyaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in \( R^1 \), \( R^2 \) and \( R^3 \)) is preferably about 20 or less, and \( X \) is an anionic counterion.

Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauril dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from the Amerchol Corporation, for instance under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).
A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimethylammonium chloride (commercially available from Rhodia in their JAGUAR trademark series). Examples of such materials are JAGUAR C13S, JAGUAR C14, JAGUAR C15, JAGUAR C17 and JAGUAR C16 Jaguar CHT and JAGUAR C162.

Mixtures of any of the above cationic polymers may be used.

Cationic polymer will generally be present in a shampoo composition of the invention at levels of from 0.01% to 5%, preferably from 0.05% to 1%, more preferably from 0.08% to 0.5% by total weight of cationic polymer based on the total weight of the composition.

Suspending Agent

Preferably, an aqueous shampoo composition of the invention further comprises a suspending agent. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives, since these impart pearlescence to the composition. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used; they are available commercially as Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid
esters is Carbopol 1342. All Carbopol (trademark) materials are available from Lubrizol.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

Mixtures of any of the above suspending agents may be used. Preferred is a mixture of cross-linked polymer of acrylic acid and crystalline long chain acyl derivative.

Suspending agent will generally be present in a shampoo composition of the invention at levels of from 0.1% to 10%, preferably from 0.5% to 6%, more preferably from 0.9% to 4% by total weight of suspending agent based on the total weight of the composition.

Preferably, the shampoo composition has a pH of 2 to 8 measured using a calibrated pH meter, more preferably 3 to 6.5.

**Product form**

It is preferred that the shampoo is stored in an air tight container such as a bottle closed with an air tight cap.

**Polyphenol containing composition**

The polyphenol containing composition is preferably an aqueous polyphenol solution. The polyphenol composition preferably comprises from 0.05 wt% to 10 wt% of the total composition, more preferably 0.3 wt% to 3 wt% of polyphenol.
The polyphenol of the invention comprises at least one benzene ring substituted with a first OH group and a second OH or OCH$_3$ group, preferably OH. Preferably the first OH is ortho to the second OH group.

Wherein the aqueous polyphenol solution has a pH preferably of 2 to 7 measured using a calibrated pH meter more preferably 3 to 6.

Polyphenols may be found in the classes of phenolic acid, depsides, Anthocyanin, Anthocyanidin, flavanols, flavanones and gallates. For example flavan-3-ols, flavan-4-ols, flavan-3,4-ols. Gallic Acid, Flavanols and flavanones are preferred. Preferably the polyphenol is not present as a henna based ingredient.

A preferred polyphenol contains a benzene ring substituted in the:
1 position by an X group, wherein X is a carbon containing organic group, preferably selected from an ester group, COOH, chromenes and 3,4 dihydrochromenes.
3 position by a H, OH or OCH$_3$ group, preferably an OH group.
4 position by an OH group.
5 position by an OH or OCH$_3$ group, preferably an OH group.

Preferably the polyphenol is a ortho-dihydroxy benzene derivative.

Most preferably the 2 and 6 positions are substituted by H.

Preferably, the polyphenol has a molecular weight of less than 1,000, more preferably less than 500, most preferably less than 310.

Polyphenols may be suitably found in the wood and bark of trees and in the fruit, seeds and nuts of plants. For example the leaves of *Camilla senesis*, the wood of *Haematoxyllum campechianum*; the bark of *Quercus velutina*; the fruit of *Vitis vinifer*; the fruit of *Olea europaea*; the roots of *Curcuma demoestica*; the trunk and
bark of *Quercus velutina* and *Quercus lusitanica*; the trunk and bark of trees of the genus *Pseudotsuga*; the trunk and bark of *Acacia catechu*. Preferred compounds include gallic acid, methyl gallate, ethyl gallate, propyl gallate caffeic acid, chlorogenic acid, caftaric acid, ellagic acid, ferulic acid, 4-O-galloylgallic acid, nordihydroguaiaretic acid, rosemarinic acid, catechin, epicatechin, catechin gallate, epicatechin gallate, gallocatechin, epigallocatechin, epigallocatechin gallate, curcumin, alizarin, quercetin, quercitrin, myricetin, alizarin, purpurin, morindone, isorhamnetin, pachypodol, rhamnazin, hesperetin, homoeriodictyol, logwood, natural black 1, natural black 2, natural red 24, fisetinidol, robinetinidol, mesquitol. Most preferably haematein, haematoxylin, braziliin, methyl gallate, ethyl gallate, propyl gallate, gallic acid, epigallocatechin, epigallocatechin gallate and gallocatechin. Particularly preferred are methyl gallate, ethyl gallate, propyl gallate and gallic acid.

Preferably, the polyphenols are extracted from a natural source. Preferably, they do not contain any active oxidase enzymes and have been heat treated to destroy any enzyme activity.

To avoid oxidation of the polyphenols by air it is preferred that the composition is stored in an airtight container, preferably a bottle closed with an air tight cap.

The aqueous polyphenol solution contains water, preferably as the dominate ingredient. Auxiliary ingredients may be present for example to increase the viscosity, perfume and help solubilise the polyphenol. Solubilising ingredients include organic solvents and surfactants.

It is preferable if the polyphenol containing composition is a conditioning composition, more preferably a rinse-off conditioning composition. Particularly preferred is a composition that is applied after shampooing.
If present in a conditioner composition comprising a protonating organic acid, the polyphenol is preferably present at a higher molar concentration than the protonating organic acid. In this case the protonating organic acid does not include a polyphenol.

Preferably, the water used to formulate all compositions has a French hardness of from 0 to 36 degrees, more preferably 0 to 24 degrees, most preferably from 0 to 2 degrees.

Preferably, the water used to formulate all compositions contains less than 1ppm of chlorine based bleaching agents such as chlorine dioxide or hypochlorite. Most preferably less than 50ppb.

**Conditioning Agents**

**Silicone Conditioning Agents**

The compositions of the invention can contain, emulsified droplets of a silicone conditioning agent, for enhancing conditioning performance. Silicone conditioning agents may be present in the shampoo or conditioner.

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188.

The viscosity of the emulsified silicone itself (not the emulsion or the final hair conditioning composition) is typically at least 10,000 cst at 25 °C the viscosity of
the silicone itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed $10^9$ cst for ease of formulation.

Emulsified silicones for use in the shampoo compositions of the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10 μm, ideally from 0.01 to 1 μm. Silicone emulsions having an average silicone droplet size of $\leq 0.15$ μm are generally termed microemulsions.

Emulsified silicones for use in the conditioner compositions of the invention will typically have an size in the composition of less than 30, preferably less than 20, more preferably less than 15. Preferably, the average silicone droplet is greater than 0.5 μm, more preferably greater than 1 μm, ideally from 2 to 8 μm.

Silicone particle size may be measured by means of a laser light scattering technique, for example using a 2600D Particle Sizer from Malvern Instruments.

Examples of suitable pre-formed emulsions include Xiameter MEM 1785 and microemulsion DC2-1865 available from Dow Corning. These are emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation.

A further preferred class of silicones for inclusion in shampoos and conditioners of the invention are amino functional silicones. By “amino functional silicone” is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group. Examples of suitable amino functional silicones include: polysiloxanes having the CTFA designation "amodimethicone",
Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166 and DC2-8566 (all ex Dow Corning).

Suitable quaternary silicone polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.

Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC939 Cationic Emulsion and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

It is preferred to use a combination of amino and non amino functional silicones.

The total amount of silicone is preferably from 0.01 wt% to 10 %wt of the total composition more preferably from 0.1 wt% to 5 wt%, most preferably 0.5 wt% to 3 wt% is a suitable level, especially for a shampoo composition.

(ii) Non-silicone Oily Conditioning Components

Compositions according to the present invention may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent. Preferably such non-silicone conditioning oily conditioning agents are present in conditioner compositions.

By "insoluble" is meant that the material is not soluble in water (distilled or equivalent) at a concentration of 0.1% (w/w), at 25°C.
Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof. Straight chain hydrocarbon oils will preferably contain from about 12 to about 30 carbon atoms. Also suitable are polymeric hydrocarbons of alkenyl monomers, such as C$_2$-C$_6$ alkenyl monomers.

Specific examples of suitable hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used.

Suitable fatty esters are characterised by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols.

Monocarboxylic acid esters include esters of alcohols and/or acids of the formula R'COOR in which R' and R independently denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20. Di- and trialkyl and alkenyl esters of carboxylic acids can also be used.

Particularly, preferred fatty esters are mono-, di- and triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C$_1$-C$_{22}$ carboxylic acids. Preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

The oily or fatty material is suitably present at a level of from 0.05 wt% to 10 wt%, preferably from 0.2 wt% to 5 wt%, more preferably from about 0.5 wt% to 3 wt%.
Cationic Conditioning Surfactants

Such conditioner compositions will typically comprise one or more conditioning surfactants which are cosmetically acceptable and suitable for topical application to the hair.

Suitable conditioning surfactants include those selected from cationic surfactants, used singly or in admixture. Preferably, the cationic surfactants have the formula $N^+R^1R^2R^3R^4$ wherein $R^1$, $R^2$, $R^3$ and $R^4$ are independently (C$_1$ to C$_{30}$) alkyl or benzyl. Preferably, one, two or three of $R^1$, $R^2$, $R^3$ and $R^4$ are independently (C$_4$ to C$_{30}$) alkyl and the other $R^1$, $R^2$, $R^3$ and $R^4$ group or groups are (C$_1$-C$_6$) alkyl or benzyl. More preferably, one or two of $R^1$, $R^2$, $R^3$ and $R^4$ are independently (C$_6$ to C$_{30}$) alkyl and the other $R^1$, $R^2$, $R^3$ and $R^4$ groups are (C$_1$-C$_6$) alkyl or benzyl groups. Optionally, the alkyl groups may comprise one or more ester (-OCO- or –COO-) and/or ether (-O-) linkages within the alkyl chain. Alkyl groups may optionally be substituted with one or more hydroxyl groups. Alkyl groups may be straight chain or branched and, for alkyl groups having 3 or more carbon atoms, cyclic. The alkyl groups may be saturated or may contain one or more carbon-carbon double bonds (e.g., oleyl). Alkyl groups are optionally ethoxylated on the alkyl chain with one or more ethyleneoxy groups.

Suitable cationic surfactants for use in conditioner compositions according to the invention include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride, cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octydimethylbenzylammonium chloride, decyltrimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecylmethylammonium chloride, dioctadecylmethylammonium chloride, tallowtrimethylammonium chloride, dihydrogenated tallow dimethyl ammonium chloride (e.g, Arquad 2HT/75 from Akzo
Nobel), cocotrimethylammonium chloride, PEG-2-oleammonium chloride and the corresponding hydroxides thereof. Further suitable cationic surfactants include those materials having the CTFA designations Quaternium-5, Quaternium-31 and Quaternium-18. Mixtures of any of the foregoing materials may also be suitable. A particularly useful cationic surfactant for use in conditioners according to the invention is cetyltrimethylammonium chloride, available commercially, for example as GENAMIN CTAC, ex Hoechst Celanese. Another particularly useful cationic surfactant for use in conditioners according to the invention is behenyltrimethylammonium chloride, available commercially, for example as GENAMIN KDMP, ex Clariant.

Another example of a class of suitable cationic surfactants for use in the invention, either alone or together with one or more other cationic surfactants, is a combination of (i) and (ii) below:

(i) an amidoamine corresponding to the general formula (I):

\[
R^1\text{CONH(CH}_2\text{)}_m\text{N} \overset{\text{R}^2}{\text{R}^3}
\]

in which \(R^1\) is a hydrocarbyl chain having 10 or more carbon atoms, \(R^2\) and \(R^3\) are independently selected from hydrocarbyl chains of from 1 to 10 carbon atoms, and
\(m\) is an integer from 1 to about 10; and

(ii) an acid.

As used herein, the term hydrocarbyl chain means an alkyl or alkenyl chain.

Preferred amidoamine compounds are those corresponding to formula (I) in which
R\textsuperscript{1} is a hydrocarbyl residue having from about 11 to about 24 carbon atoms, R\textsuperscript{2} and R\textsuperscript{3} are each independently hydrocarbyl residues, preferably alkyl groups, having from 1 to about 4 carbon atoms, and m is an integer from 1 to about 4.

5

Preferably, R\textsuperscript{2} and R\textsuperscript{3} are methyl or ethyl groups.

Preferably, m is 2 or 3, i.e. an ethylene or propylene group.

10 Preferred amidoamines useful herein include stearamido-propyldimethylamine, stearamidopropyl-diethylamine, stearamidoethyl-diethylamine, palmitamidopropyldimethylamine, palmitamido-propyl-diethylamine, palmitamidoethyl-diethylamine, behenamidopropyldimethyl-amine, behenamidopropyl-diethylamine, behenamidoethyl-diethyl-amine, behenamidoethyldimethylamine, arachidamidopropyl-dimethylamine, arachidamidopropyl-diethylamine, arachid-amidoethyl-diethylamine, arachidamidoethyldimethylamine, and mixtures thereof.

15 Particularly preferred amidoamines useful herein are stearamidopropyldimethylamine, stearamidoethyl-diethylamine, and mixtures thereof.

20 Commercially available amidoamines useful herein include:

25 stearamidopropyldimethylamine with tradenames LEXAMINE S-13 available from Inolex (Philadelphia Pennsylvania, USA) and AMIDOAMINE MSP available from Nikko (Tokyo, Japan), stearamidoethyl-diethylamine with a tradename AMIDOAMINE S available from Nikko, behenamidopropyldimethylamine with a tradename INCROMINE BB available from Croda (North Humberside, England),
and various amidoamines with tradenames SCHERCODINE series available from Scher (Clifton New Jersey, USA).

A protonating acid may be present. Acid may be any organic or mineral acid which is capable of protonating the amidoamine in the hair treatment composition. Suitable acids useful herein include hydrochloric acid, acetic acid, tartaric acid, fumaric acid, lactic acid, malic acid, succinic acid, and mixtures thereof. Preferably, the acid is selected from the group consisting of acetic acid, tartaric acid, hydrochloric acid, fumaric acid, and mixtures thereof.

The primary role of the acid is to protonate the amidoamine in the hair treatment composition thus forming a tertiary amine salt (TAS) in situ in the hair treatment composition. The TAS in effect is a non-permanent quaternary ammonium or pseudo-quaternary ammonium cationic surfactant.

Suitably, the acid is included in a sufficient amount to protonate more than 95 mole% (293 K) of the amidoamine present.

In conditioners of the invention, the level of cationic surfactant will generally range from 0.01 wt% to 10 wt%, more preferably 0.05 wt% to 7.5 wt%, most preferably 0.1 wt% to 5 wt% of the composition.

Conditioners of the invention will typically also incorporate a fatty alcohol. The combined use of fatty alcohols and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, in which the cationic surfactant is dispersed.

Representative fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 22. Fatty alcohols are typically compounds containing straight chain alkyl groups. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and
mixtures thereof. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

The level of fatty alcohol in conditioners of the invention will generally range from 0.01 % to 10%, preferably from 0.1 % to 8%, more preferably from 0.2 % to 7%, most preferably from 0.3 % to 6% by weight of the composition. The weight ratio of cationic surfactant to fatty alcohol is suitably from 1:1 to 1:10, preferably from 1:1.5 to 1:8, optimally from 1:2 to 1:5. If the weight ratio of cationic surfactant to fatty alcohol is too high, this can lead to eye irritancy from the composition. If it is too low, it can make the hair feel squeaky for some consumers.

Adjuncts

The compositions of the present invention may also contain adjuncts suitable for hair care. Generally such ingredients are included individually at a level of up to 2 wt%, preferably up to 1 wt% of the total composition.

Suitable hair care adjuncts, include amino acids, sugars and ceramides and viscosity modifiers.

Method of use

The method of colouring hair comprising the steps of applying to hair sequentially in any order:

(i) a shampoo composition comprising at least one metal salt and/or complex in which the metal is selected from iron, copper, zinc or manganese and a cleansing surfactant mix comprising from 3 wt% to 50 wt% of the total shampoo composition of a nonionic in which the nonionic surfactant is the major component by weight of the surfactant mix and
(ii) a second composition, which comprises from 0.05 wt% to 10 wt% of the total second composition of a polyphenol.

Preferably the compositions of the invention are applied to wet hair, necessitating the step of wetting the hair before application of the compositions of the invention.

A method preferably comprises the step of rinsing hair between application of the shampoo composition (i) and the second composition (ii). It is highly preferred if the hair is rinsed after application of both compositions of the invention.

Further conditioning and/or styling products may be applied as part of the colouring process.

The level of each composition applied to the head of hair is preferably from 5g to 100g.

Preferably, each composition remains on the hair for 5 to 600 seconds, more preferably 10 to 300 seconds.

Preferably, the water used to wet and rinse the hair has a French hardness of from 0 to 36 degrees, more preferably 0 to 24 degrees, most preferably from 0 to 2 degrees.

Preferably, the water used to wet and rinse the hair contains less than 1ppm of chlorine based bleaching agents such as chlorine dioxide or hypochlorite. Most preferably less than 50ppb

**Examples**
The invention will now be illustrated by the following non-limiting Examples:
A 0.7g twice bleached platinum blonde hair switch was rinsed for 30 seconds in running demineralised water (861ml/minute). 0.5g of a shampoo containing 0.5w% of Fe(II) gluconate and 12wt% surfactant, was massaged in the hair for 30 seconds, the hair left for 90 seconds and rinsed for 30 seconds in running demineralised water (861ml/minute). The shampoo procedure was then repeated (30 second wash, 90 second stand, 30 second rinse) and following this 0.5g of a 0.33wt% aqueous solution of haematein applied to the hair and massaged into the hair for 60 seconds, then the hair allowed to stand for 240 seconds. The switch was then rinsed for 60 seconds in running demineralised water (861ml/minute), dried in air and the colour measured using a reflectometer (Color i7) and expressed as the CIE L*a*b* values.

A variety of shampoo were tested and the results giving below

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>L*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>63.5</td>
</tr>
<tr>
<td>ANIONIC:</td>
<td></td>
</tr>
<tr>
<td>Sodium lauryl ether sulphate (3EO)</td>
<td>44.3</td>
</tr>
<tr>
<td>ANIONIC:</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulphate</td>
<td>41.5</td>
</tr>
<tr>
<td>NON_IONIC:</td>
<td></td>
</tr>
<tr>
<td>R-(OCH2CH2)nOH, where R is an alkyl chain of C12 to C15, and n is 7</td>
<td>36.3</td>
</tr>
</tbody>
</table>

The non-ionic surfactant provides the greatest colour change to the hair, as shown by the largest drop in L* value.
CLAIMS

1. A kit for colouring hair comprising:
   (i) a composition comprising at least one metal ion in the form of a salt
   and/or complex in which the metal is selected from iron, copper, zinc,
   manganese or mixtures thereof and a cleansing surfactant mix comprising
   from 3 wt% to 50 wt% of the total shampoo composition of a nonionic
   surfactant in which the nonionic surfactant comprises condensation
   products of aliphatic (C₈ - C₁₈) primary or secondary linear or branched
   chain alcohols or phenols with alkylene oxides and is the major component
   by weight of the surfactant mix and
   (ii) a second composition, which comprises from 0.05 wt% to 10 wt% of the
   total second composition of a polyphenol.

2. A kit as claimed in claim 1 in which the metal is in the form of a metal
   complex.

3. A kit as claimed in any preceding claim in which the metal ion is Fe(II),
   Fe(III) and Cu(II).

4. A kit as claimed in claim 3 in which the metal ion is Fe (II).

5. A kit as claimed in any preceding claim in which complex comprises a
   ligand of gluconate, lactate or ascorbate.

6. A kit as claimed in any preceding claim in which the metal salt and/or
   complex is iron (II) gluconate.

7. A kit according to any preceding claim in which the level of metal ion is
   from 0.01 wt% to 5 wt% of composition 1.
8. A composition as claimed in any preceding claim in which the polyphenol is a ortho-dihydroxybenzene derivative.

9. A composition as claimed in any preceding claim in which the polyphenol is methyl gallate, alkyl gallate, propyl gallate and gallic acid.

10. A method of colouring hair comprising the steps of applying to hair sequentially in any order:
   (i) A kit for colouring hair comprising:
   (i) a composition comprising at least one metal ion in the form of a salt and/or complex in which the metal is selected from iron, copper, zinc, manganese or mixtures thereof and a cleansing surfactant mix comprising from 3 wt% to 50 wt% of the total shampoo composition of a nonionic surfactant in which the nonionic surfactant comprises condensation products of aliphatic (C₈ - C₁₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides and is the major component by weight of the surfactant mix and
   (ii) a second composition, which comprises from 0.05 wt% to 10 wt% of the total second composition of a polyphenol.

11. A method according to claim 9 in which further comprises the step of rinsing hair between application of composition 1 (i) and the second composition (ii).