



(51) International Patent Classification:

A61K 8/19 (2006.01) A61K 8/67 (2006.01)
A61K 8/26 (2006.01) A61K 8/97 (2006.01)
A61K 8/27 (2006.01) A61Q 5/10 (2006.01)
A61K 8/365 (2006.01)

(21) International Application Number:

PCT/EP2012/058919

(22) International Filing Date:

14 May 2012 (14.05.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11167451.1 25 May 2011 (25.05.2011) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: HAIR COLOURING PRODUCT COMPRISING METAL IONS AND A COMPONENT FROM THE FRUIT OF THE REDCURRANT OR BLACKCURRANT

(57) Abstract: A kit for colouring hair comprising: (i) a first 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 aluminium; and (ii) a second composition comprising liquefied, puree, pulp, concentrate, extract or juice of the fruit of the redcurrant and/or blackcurrant.



**HAIR COLOURING PRODUCT COMPRISING METAL IONS AND A
COMPONENT FROM THE FRUIT OF THE REDCURRANT OR
BLACKCURRANT**

Hair Care Composition

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

5 Background

The many people who dye their hair desire hair dyes that are naturally obtained and convenient to use.

10 WO/2010/0135237 (ACT) discloses natural sources of dyes, such as plants.

WO/1999/011223 (Unilever) discloses a hair treatment composition suitable for application to dark hair comprising at least one melanin or melanin-type compound derived from hydroglycolic extract of plants selected from: *Vaccinium*
15 *myrtillus*, *Indigofera tinctoria* and *Sarathamnus scoparus*.

WO2010/131049 (Leeds) discloses dye mixtures comprising polyphenolic materials, these materials being obtained from botanical sources. Preferably, the polyphenolic materials comprise anthocyanin compounds.

20

There remains the need for a water soluble colourant that can be simply extracted from a plant and which delivers an effective level of colouring to hair.

The present invention describes naturally derived colourants that are easily
25 obtainable and when applied to the hair provides excellent coloration.

Description of the Invention

Accordingly the invention relates to a kit for colouring hair comprising:

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- (i) a first 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 aluminium; and
- (ii) a second composition comprising liquefied, puree, pulp, concentrate,
5 extract or juice of the fruit of redcurrant and/or blackcurrant.

The invention also relates to a method of colouring hair by applying to the hair sequentially in any order the compositions of the kit described above.

10 **Detailed Description of the Invention**

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
15 % water by weight based on the total weight of the composition.

First Composition

Metal Complex

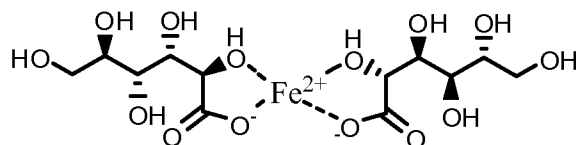
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Compositions of the invention preferably comprise from 0.01 to 10 wt% of the total first composition of at least one metal ion in which the metal is selected from iron, copper, zinc or manganese. More preferably, the level of metal ion is from 0.1 wt% to 5 wt% of the total shampoo composition, most preferably from 0.2 wt% to
25 3 wt%.

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

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

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With molecular weight of 446.14, then it will contain $55.84/446.14 \times 2 = 0.25\text{wt}\%$ of Fe(II) (2 decimal places).

Preferably, the metal ion is Fe(II), Fe(III) or Cu(II), more preferably the metal ion is selected from Fe(II), Fe(III), most preferably Fe(II).

- 10 The metal ion 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^- , primary amines and OH, most preferably COO^- and OH. Organic acids are highly preferred. 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, iron (II) glutamate. The ligand metal complex may be formed in the composition by the addition of an iron salt and the ligand, for example FeCl_2 and sodium lactate. 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

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

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

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

- 5 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.

- 10 The ligand is not a polyamino carboxylic acid, and such ligands 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'',2'''-(Ethane-1,2-diylidinitrilo)tetraacetic acid is a
- 15 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,
- 20 citrate and lactate Particularly preferred are gluconate, lactate or ascorbate.

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

- 25 Preferably, the iron is only in a composition which further comprises a cleansing surfactant, such as a shampoo composition.

Surfactant Mix

- Compositions of the first invention comprise surfactant. The surfactant may be
- 30 anionic, non-ionic and or amphoteric/zwitterionic.

- 5 -

Anionic Surfactants

Anionic surfactants may be present from 0.5 wt% to 45 wt%, more preferably from 1.5 to 20 wt% of the first composition.

5

Suitable anionic cleansing surfactants are alkyl ether sulphates, alkyl sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, alkyl ether sulphosuccinates, 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 sulphosuccinates, 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.

10

15

Preferred anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium lauryl ether sulphosuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate, lauryl ether carboxylic acid and sodium N-lauryl sarcosinate.

20

25

Particularly preferred anionic cleansing surfactants are sodium lauryl sulphate, 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).

30

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It is particularly preferred if the anionic surfactant comprises alkyl ether sulphates (AES), more preferably lauryl ether sulphate, most preferred sodium lauryl ether sulfate (SLES). Preferably the SLES has from 1 to 3 ethoxy groups.

- 5 The fraction of AES surfactant in the surfactant mix (f_{AES}) may be defined as

$$F_{AES} = (\text{Wt\% AES surfactant}) / (\text{total wt\% of all surfactants}).$$

Preferably, the AES surfactant is the major surfactant component and $f_{AES} > 0.5$,
More preferably $f_{AES} > 0.8$.

10

The level of alkyl ether sulphate is preferably from 0.5 wt% to 25 wt% of the total first composition, more preferably from 3 wt% to 18 wt%, most preferably from 6 wt% to 15 wt% of the total first composition.

15 **Nonionic surfactant**

Shampoo compositions of the invention may comprise nonionic surfactant, preferably from 0 to 10 wt%, more preferably from 0 to 5 wt%, most preferably no nonionic surfactant is present.

20

Nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic ($C_8 - C_{18}$) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

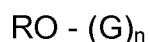
- 25 Alkyl ethoxylates are particularly preferred. Most preferred are alkyl ethoxylates having the formula $R-(OCH_2CH_2)_nOH$, where R is an alkyl chain of C_{12} to C_{15} , and n is 5 to 9.

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Other suitable nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

- 5 Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the 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:

10



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

15

R may represent a mean alkyl chain length of from about C₅ to about C₂₀. Preferably, R represents a mean alkyl chain length of from about C₈ to about C₁₂. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C₅ or C₆ monosaccharide residues, and is preferably a glucoside.

20

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

25

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.

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Other sugar-derived nonionic surfactants which can be included in compositions of the invention include the C₁₀-C₁₈ N-alkyl (C₁-C₆) polyhydroxy fatty acid amides, such as the C₁₂-C₁₈ 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 C₁₀-C₁₈ N-(3-methoxypropyl) glucamide.

Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.

10 **Amphoteric/zwitterionic Surfactant**

Amphoteric or zwitterionic surfactant can be included in an amount ranging from 0 to about 8 wt%, preferably from 1 wt% to 4 wt% of the total shampoo composition.

15 Examples of amphoteric or zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycines, alkyl carboxyglycines, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycines, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms.

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

It is particularly preferred if the shampoo composition comprises from 0.5 wt% to 25 3 wt% of a betaine.

A particularly preferred amphoteric or zwitterionic surfactant is cocoamidopropyl betaine.

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

5

The total amount of surfactant (including any co-surfactant, and/or any emulsifier) in a shampoo composition of the invention is generally from 1 w% to 50 %, preferably from 2 w% to 40 %, more preferably from 5 % to 25% by total weight surfactant based on the total weight of the composition.

10

Further Ingredients

Cationic Polymers

15 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
20 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
25 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.
30 Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd

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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

5 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,
10 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.

15 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
20 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.

25

Suitable cationic polymers include, for example:

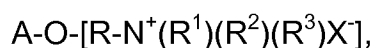
- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers

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of acrylamide and dimethyldiallylammonium 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).
- 10 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:



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, alkylaryl, 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 lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These

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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 0.03 % to 1%, more preferably from 0.05 % 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,

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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,
5 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
10 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.

15

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.

20

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.

25

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

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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.

5

Second Composition

Blackcurrants and Redcurrants are fruit of the plant of the genus *Ribes*.

- 10 The second composition comprises liquefied, puree, pulp, concentrate, extract or juice of the fruit of the currant, more preferably the juice or concentrate, most preferably the juice.

- 15 The juice/concentrate is preferably filtered to remove solid matter. Proteins, carbohydrates and aliphatic organic acids may be removed from the juice, however this is not preferred.

It is preferable if anthocyanin is removed from the fruit of the currant.

- 20 Preferably the juice/concentrate is spray-dried with a water soluble carrier material, such as a sugar before addition to the composition.

- 25 Preferably the second composition comprises from 0.1 wt% to 100 wt% of the total second composition of liquefied, puree, pulp, concentrate, extract or juice of the fruit of the currant with a Karl Fischer water level of 50wt%, or equivalent thereof, more preferably 0.5 wt% to 10wt%.

The Karl Fischer titration is preferably done according to ASTM E203 - 08 (Standard Test Method for Water Using Volumetric Karl Fischer Titration available

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from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA).

Blackcurrants are the fruit of the plant *Ribes nigrum*. There are many cultivars of
5 blackcurrant, including: Amos Black, Ben Alder, Ben Avon, Ben Connan, Ben Dorain, Ben Gairn, Ben Hope, Ben Lomond, Ben Loyal, Ben More, Ben Sarek, Ben Tirran, Big Ben, Boskoop Giant, Cotswold Cross and Wellington XXX.

Redcurrants are the fruit of *Ribes rubrum*, *Ribes spicatum*, *Ribes alpinum*, *Ribes schlehtendalii*,
10 *Ribes multiflorum*, *Ribes petraeum* and *Ribes triste*. Preferably, *Ribes rubrum*.

Ripe berries of the currant are preferred.

15 Polyphenols may be added to the second composition. Preferred polyphenols are selected from gallic acid, methyl gallate, ethyl gallate, propyl gallate, catechin, epicatechin, catechin gallate, epicatechin gallate, gallocatechin, epigallocatechin, epigallocatechin gallate, curcumin, natural black 1, natural black 2, natural red 24. When present the level of polyphenol is preferably from 0.05 to 5wt%.

20

Preferably, the composition has a pH of 2 to 7 measured using a calibrated pH meter more preferably 3 to 6.

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

The composition contains water, preferably as the dominate ingredient. Auxillary ingredients may be present for example to increase the viscosity, perfume and help solubilise the juice etc. Solubilising ingredients include organic solvents and
30 surfactants.

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It is preferable if the currant containing composition is a conditioning composition, more preferably a rinse off conditioning composition. Particularly preferred is a composition that is applied after shampooing.

- 5 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.
- 10 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.
- 15

Conditioning Agents

Silicone Conditioning Agents

20

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.

- 25 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

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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 $\leq 0.15 \mu\text{m}$ 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

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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
5 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.

10

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
15 DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

With some shampoos it is preferred to use a combination of amino and non amino functional silicones

20 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

25

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.

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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 C₂-C₆ 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 C₁-C₂₂ 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 5wt%, 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 (eg, oleyl). Alkyl groups are optionally ethoxylated on the alkyl chain with one or more ethyleneoxy groups.

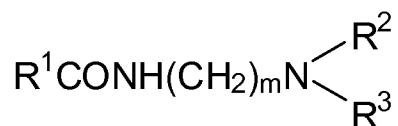
Suitable cationic surfactants for use in conditioner compositions according to the invention include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride, cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallowtrimethylammonium chloride, dihydrogenated tallow dimethyl ammonium chloride (eg, Arquad 2HT/75 from

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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
5 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
10 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:

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



20 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

25 (ii) an acid.

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

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Preferred amidoamine compounds are those corresponding to formula (I) in which

R^1 is a hydrocarbyl residue having from about 11 to about 24 carbon atoms,
 R^2 and R^3 are each independently hydrocarbyl residues, preferably alkyl groups,
5 having from 1 to about 4 carbon atoms, and m is an integer from 1 to about 4.

Preferably, R^2 and R^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,
stearamidopropyldiethylamine, stearamidoethyldiethylamine,
stearamidoethyldimethylamine, palmitamidopropyldimethylamine,
palmitamidopropyl-diethylamine, palmitamidoethyldiethylamine,
15 palmitamidoethyldimethylamine, behenamidopropyldimethyl-amine,
behenamidopropyldiethylamine, behenamidoethyldiethyl-amine,
behenamidoethyldimethylamine, arachidamidopropyl-dimethylamine,
arachidamidopropyldiethylamine, arachid-amidoethyldiethylamine,
arachidamidoethyldimethylamine, and mixtures thereof.

20

Particularly preferred amidoamines useful herein are
stearamidopropyldimethylamine, stearamidoethyldiethylamine, and mixtures
thereof.

25

Commercially available amidoamines useful herein include:
stearamidopropyldimethylamine with tradenames LEXAMINE S-13 available from
Inolex (Philadelphia Pennsylvania, USA) and AMIDOAMINE MSP available from
Nikko (Tokyo, Japan), stearamidoethyldiethylamine with a tradename
AMIDOAMINE S available from Nikko, behenamidopropyldimethylamine with a
30 tradename INCROMINE BB available from Croda (North Humberside, England),

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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 conditioner 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, lactic 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 % to 10 %, more preferably 0.05 % to 7.5 %, most preferably 0.1 % to 5 % by weight 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,

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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.

- 5 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
- 10 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

- 15 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

20 viscosity modifiers.

Method of use

The method of colouring hair comprising the steps of applying to hair sequentially

25 in any order:

- (i) a first 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 aluminium; and

- 25 -

- (ii) a second composition comprising liquefied, puree, pulp, concentrate, extract or juice of the fruit of blackcurrants or redcurrants.

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

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

10

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
15 100g.

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

20 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
25 chlorine based bleaching agents such as chlorine dioxide or hypochlorite. Most preferably less than 50ppb

The invention will now be illustrated by the following non-limiting examples.

Examples of the invention are illustrated by a number, comparative examples are
30 illustrated by a letter.

Examples**Example 1**

- 5 An iron containing shampoo was formulated, with the composition shown in the table below.

An iron containing shampoo was formulated, with the composition shown in the table below.

10

Ingredient (INCI name)	Weight%	% active
Iron (II) Gluconate	4	100
Sodium Laureth Sufate	16.5	70
Cocamidopropylbetaine	5.33	30
Carbomer	0.36	100
Sodium Chloride	0.5	100
Ethylene Glycol Distearate	3	30
Methylchloroisothaizolinone Methylisothiazolinone	0.04	1.5
Mica	0.15	100
DMDM Hydantoin	0.1	100
Dimethiconol, TEA-Dodecylbenzenesulfonate	1.7	0.45
Guar Hydroxypropyltrimonium Chloride	0.2	100
Parfum	0.7	100
Aqua	to 100	100

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Example 2

0.7g Yak hair switches were used in the experiment. The switches were wetted and washed for 120 seconds with 0.14g of the iron shampoo of example 1. The switch was then rinsed in water, shampooed again then rinsed once more. The switch was then immersed in a 100 ml 5 wt% aqueous solution of the juice concentrated for 10 mins, removed, rinsed and dried in air.

A reference experiment was performed where the switched were not exposed to iron shampoo, but only immersed in a 100 ml 5wt% aqueous solution of the juice concentrated for 10 mins, removed, rinsed and dried in air.

The colour of the swatch was measured using a reflectometer and expressed as the CIE L*a*b* values. The colouration of the switches was expressed as the ΔL value where $\Delta L = L(\text{before treatment}) - L(\text{after treatment})$

Larger L values indicate more colour uptake.

	ΔL	
	With Fe	Reference without Fe
Blackcurrant	17.9	9.3

The blackcurrant juice used was Nutriphys® Blackcurrent (ex Christian Hansen).

The blackcurrant juice provides a much darker colouration with iron present.

CLAIMS

1. A kit for colouring hair comprising:
 - (i) a first 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 aluminium; and
 - (ii) a second composition comprising liquefied, puree, pulp, concentrate, extract or juice of the fruit of the redcurrant and/or blackcurrant.
2. A kit according to claim 1 in which the second composition comprises liquefied, puree, pulp, concentrate, extract or juice of the fruit of the blackcurrant
3. A kit according to claim 1 or claim 2 in which the level of metal salt is from 0.01 to 10 wt% of the total first composition.
4. A kit according to any preceding claim in which the first composition further comprises a surfactant.
5. A kit according to claim 4 in which the surfactant comprises an alkyl ether sulphate.
6. A kit according to claim 4 or claim 5 in which the level of surfactant is from 5 wt% to 25 wt% of the total first composition.
7. A kit as according to any preceding claim in which the metal ion is Fe(II) or Fe(III).
8. A kit according to any preceding claim in which the metal is in the form of a complex comprising a ligand derived from an organic acid.

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9. A kit as claimed in claim 8 in which the complex comprises a ligand of gluconate, lactate or ascorbate.
- 5 10. A kit according to any preceding claim in which the level of liquefied, puree, pulp, concentrate, extract or juice of the fruit of currant is from 0.5 wt% to 10 wt% of the total second composition.
- 10 11. A kit according to any preceding claim in which the shampoo composition further comprises from 0.5 wt% to 3 wt% of a betaine.
12. A kit according to any preceding claim in which the first composition further comprises from 0.1 wt% to 5 wt% of a conditioning silicone.
- 15 13. A kit according to any preceding claim in which the first composition further comprises from 0.05 wt% to 0.5wt% of a cationic deposition polymer,
14. A kit for according to any preceding claim in which the second composition further comprises a cationic surfactant
- 20 15. A method of colouring hair comprising the steps of applying to hair sequentially in any order the compositions of the kit described above.
16. A method according to claim 15 which further comprises the step of rinsing the hair between application of the compositions of the kit.

25

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/058919

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/19 A61K8/26 A61K8/27 A61K8/365 A61K8/67
A61K8/97 A61Q5/10

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

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

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

EPO-Internal, CHEM ABS Data, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 2010/131049 A2 (UNIV LEEDS [GB]; BLACKBURN RICHARD SIMON [GB]; ROSE PAUL MARTIN [GB];) 18 November 2010 (2010-11-18) cited in the application claims 1-5, 11, 27, 28, 37 paragraph [0015] - paragraph [0022] -----	1-16
X	WO 2010/063533 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]; BALAKRIS) 10 June 2010 (2010-06-10)	1,15
Y	claims 1, 2 page 2, line 10 - line 16 examples ----- -/-	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 June 2012

Date of mailing of the international search report

19/06/2012

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/058919

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	claims 1-8 page 2, line 21 - page 3, line 62 examples	1-16
Y	----- BECHTOLD ET AL: "Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry", JOURNAL OF THE SCIENCE OF FOOD AND AGRICULTURE, WILEY & SONS, CHICHESTER, GB, VOL. 86, 2006, pages 233-242, XP002661482, ISSN: 0022-5142, DOI: 10.1002/JSFA.2360 the whole document	1-16
A	----- EP 2 022 469 A1 (KPSS KAO GMBH [DE]) 11 February 2009 (2009-02-11) claims 1-3 paragraph [0005] -----	1-16

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Information on patent family members

International application No

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