(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 February 2015 (12.02.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/018596 A1

(51) International Patent Classification:
A61K 8/34 (2006.01) *A61Q 5/10* (2006.01)
A61K 8/46 (2006.01) *A61K 8/19* (2006.01)
A61K 8/63 (2006.01) *C07J 1/00* (2006.01)

(21) International Application Number:
PCT/EP2014/064906

(22) International Filing Date:
11 July 2014 (11.07.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13179235.0 5 August 2013 (05.08.2013) EP

(71) Applicant *(for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; a company registered in England and Wales under company no. 41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).

(71) Applicant *(for US only)*: **CONOPCO, INC., D/B/A UNILEVER** [US/US]; 800 Sylvan Avenue, AG West, S. Wing, Englewood Cliffs, New Jersey 07632 (US).

(72) Inventors: **BALAKRISHNAN, Lalitha**; Hindustan Unilever Ltd, Research Centre, 64 Main Road, Whitefield, Bangalore 560 066 (IN). **LAHORKAR, Praful, Gulab, Rao**; Hindustan Unilever Ltd, Research Centre, 64 Main Road, Whitefield, Bangalore 560 066 (IN). **MAJUMDER, Suman**; Uttara Co-operative Hsg., Society, Flat-6C, 13 Broad Street, Kolkata 700 019 (IN).

(74) Agent: **CORSTEN, Michael**; Unilever Patent Group, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(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, BN, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2015/018596 A1

(54) Title: A METHOD AND A KIT FOR COLOURING KERATINOUS FIBERS

(57) Abstract: The invention relates to a method and a kit for colouring keratinous fibers especially human hair. The invention more particularly relates to generating black coloured hair while minimising the off odour generated when a conventional penetration agent like cysteine is used in such methods.

A METHOD AND A KIT FOR COLOURING KERATINOUS FIBERS

Field of the invention

The invention relates to a method and a kit for colouring keratinous fibers especially human hair. The invention more particularly relates to generating black coloured hair while minimising the off odour generated when a conventional penetration agent like cysteine is used in such methods.

Background of the invention

Presently, the number of people wishing to have their hair coloured has increased. In order to obtain a uniform colour over the hair, permanent hair colours are used more often than temporary and semi-permanent hair colours. There are several permanent hair colouring methods.

One is the so called oxidative dye approach. This is based on the oxidation of a p-phenylenediamine or p-aminophenol by hydrogen peroxide, in the presence of various couplers. This has been in use for a very long time and is used to generate a wide range of shades that are both lighter and darker than natural hair colour. Since the final coloured molecules are quite large, these hair colours are resistant to removal by shampooing. Such permanent oxidative dyes are usually marketed as two component systems – one containing the dye precursors in an alkaline base, and the other is a solution of hydrogen peroxide.

Another class of dyes are based on metal complexes with polyphenols. These generally come in two parts: a metal salt solution and a developer solution. This method is preferred over the oxidative dye approach since they involve use of mostly materials of natural origin. People generally perceive that synthetic chemicals have a damaging effect on their hair. They also believe that use of dyes involving synthetic actives can cause allergenic reactions in some people in addition to damage to structure of hair fibre. Thus, more and more people are opting for colourant systems that use actives obtained from natural sources.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of the

common general knowledge in the field. A method of colouring hair comprising contacting hair with an iron or copper salt followed by contacting with gallic acid or an ester thereof, is known. Most methods and compositions to colour hair usually require harsh conditions like high alkalinity (with use of materials like ammonia) or oxidants like hydrogen peroxide in order to ensure penetration of the colourant into the hair and thereby provide high colouring efficacy. Alternately an amino acid, cysteine has been used. The issue with cysteine is that when used in hair dyes, an offensive odour due to generation of volatile sulphur compounds is produced. This has been overcome in the present invention by derivatising cysteine with various specific agents that on the one hand retains its penetration efficacy while minimizing the formation of volatile sulphur compounds. The present invention thus provides an odour free hair dying method and kit with high colouring efficacy. Further, potential damage to hair that have been reported to occur due to use of cysteine is avoided. Yet another advantage of the present invention is that it enables formulating over a wider range of pH conditions depending on the type of derivatisation.

US5104413 (Kao, 1992) discloses a hair dye composition comprising the following three components (A), (B) and (C): (A) one or more cysteine derivatives and glutathione, or a salt thereof; (B) an aromatic alcohol and/or a compound represented by the following general formula R_2 -OCH_2 CH_2 OCH_2 CH_2 OH wherein R 2 represents an alkyl group carrying one to five carbon atoms; and (C) a dye. The above patent publication does not disclose the cysteine derivatives claimed in the present invention and is further directed to shampoo fastness.

WO 2012/065576 (NATURAL MEDICINE INST OF ZHEJIANG YANGSHENGTANG CO LTD, 2001-06-14) discloses compositions for dyeing hair. The hair dyeing composition discloses a softening preparation comprising N-acetyl cysteine, a dye preparation comprising tea-polyphenol (comprising epigallo catechin gallate), and a mordant preparation comprising ferrous sulfate and cysteine hydrochloride. The above patent application uses N-acetyl cysteine as a softening agent and not as a penetrating agent and does not address the issue of odour. Further N-acetyl cysteine is expected to show properties which are closer to cysteine and cannot be compared to other cysteine derivatives as such.

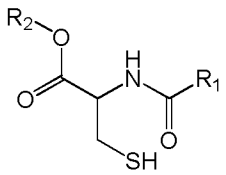
It is an object of the present invention to provide enhanced blackness to hair using polyphenol – metal complex.

It is another object of the present invention to enhance the blackness by ensuring penetration of the dye into the desired keratinous fibers while minimizing off -odours experienced heretofore when agents like cysteine are used.

Summary of the invention

The present invention provides for a method of colouring keratinous fibers comprising the steps of contacting the keratinous fibers with

(i) a penetration enhancer selected from a cysteine derivative of the general formula



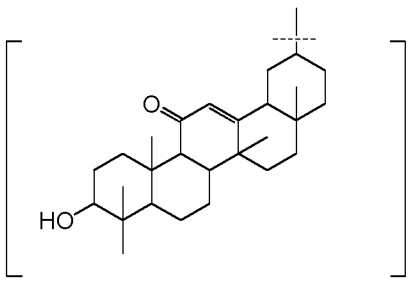
Wherein R_1 and R_2 are combinations selected from any one of:

(a) When R_1 is a C_3 to C_{15} alkyl group, R_2 is a H atom;

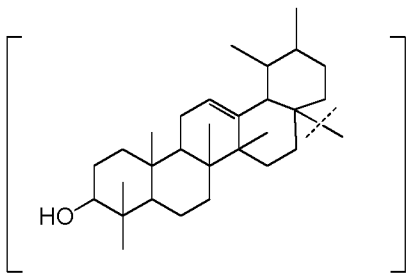
(b) When R_1 is a O-t-butyl group, R_2 is a C_1 to C_{10} alkyl group; and

(c) When R_1 is a sesquiterpene group selected from one of R_3 or R_4 or R_5, R_2 is a C_1 to C_{10} alkyl group;

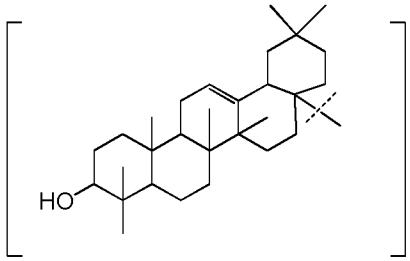
Where R_3 is a glycyrrhetinic acid residue



Where R4 is a ursolic acid residue



Where R5 is a oleanoic acid residue



(ii) a polyphenol and

(iii) a metal ion selected from the group consisting of Cu^{2+}, Cu^{+}, Fe^{2+} and Fe^{3+};

where contacting is in any order

It is particularly preferred that the method comprises the steps of contacting the fibers with a first composition comprising the penetration enhancer and the polyphenol and a second composition comprising the metal ion.

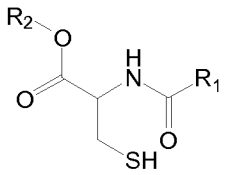
Detailed description of the invention

These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. For the avoidance of doubt, any feature of one aspect of the present invention may be utilized in any other aspect of the invention. The word “comprising” is intended to mean “including” but not necessarily “consisting of” or “composed of.” In other words, the listed steps or options need not be exhaustive. It is noted that the examples given in the description below are intended to clarify the invention and are not intended to limit the invention to those examples per se. Similarly, all percentages are weight/weight percentages unless otherwise indicated. Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word “about”. Numerical ranges expressed in the format "from x to y" are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format "from x to y", it is understood that all ranges combining the different endpoints are also contemplated.

“Keratinous fibres” as used herein, is meant to include fibres which contain keratin of mammals including humans e.g. hair on the body and head. By colouring is meant

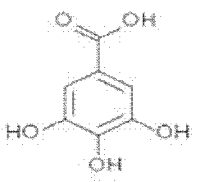
changing the colour generally from grey which is a state where the keratin content is low to a colour which includes black or brown. Preferred colour to be achieved as per the present invention is black or brown with at the most a minimal blue tint. Most preferred colour is black. A composition to achieve this may be generally classified as leave-on or rinse off, preferably rinse off. This may be achieved by including the actives in well known hair care products like shampoo, conditioner and combinations of these.

According to the first aspect of the present invention, there is provided a method of colouring keratinous fibers with a metal ion, a polyphenol, and a penetration enhancer selected from a cysteine derivative of the general formula:

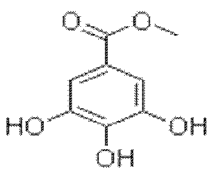


The present invention envisages various polyphenols which may be used. The polyphenol is preferably galic acid or an ester thereof, rosmarinic acid, butein, a hydroxyflavone or the polyphenol is present as an extract of *Glycyrrhiza glabra*.

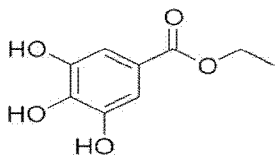
Gallic acid and a few of the commonly occuring esters have the structure given below:



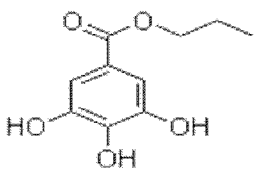
Gallic acid



Methyl gallate



Ethyl gallate



Propyl gallate

Gallic acid and ester of gallic acid preferably having an alkyl chain length of 1 to 4 carbon atoms are preferred for use in the present invention of which ethyl, methyl or propyl gallate is preferred. Of these, methyl or propyl gallate are further more preferred.

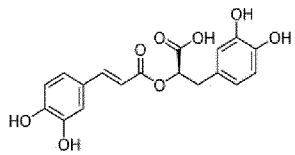
Alternately and as a preferred aspect, the gallic acid is present as an extract of a plant species of the *Terminalia* genus, or an extract of *Embelica officinalis*, *or Mucuna pruriens*. Of these, the extract of the *Terminalia* or *Embelica* species is preferred. The extract is preferably of the leaf, stem, seed, flower or fruit of the above plant. A suitable method of preparing an extract of the plants comprises the steps of

(i) Extracting the plant source with a hydroalcoholic solvent comprising 50 to 90% of a C1 – C3 alcohol at a temperature of 70 to 85° C for 10 to 60 minutes;

(ii) separating the solvent from the mixture; and

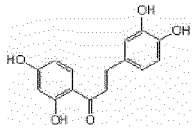
(iii) Concentrating and drying the solvent extract to prepare the desired extract.

Rosmarinic acid, a phenolic compound commonly occurring in the species of *Lamiaceae and Boraginaceae*, has the following chemical structure



Rosmarinic acid may be synthetically prepared or may be extracted from natural sources and purified for use in the present invention. Rosmarinic acid, for use in the present invention is preferably extracted from one or more of the following plants: *Rosmarinus officinalis, Ocimum sanctum, Thymus vulgaris, Melissa officinalis, Salvia officinalis, Anchusa officinalis and Coleus blumei*. The leaves, seeds or roots part of the plant is preferably used for extraction of rosmarinic acid, more preferably the leaf. Of the various plants, *Rosmarinus officinalis and Ocimum sanctum* are most preferred for extraction of Rosmarinic acid for use in the present invention.

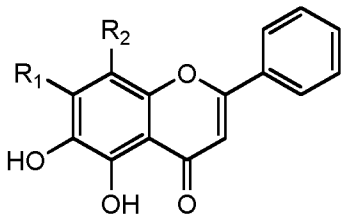
Butein is a compound of the chalcone family and has the chemical structure given below. Butein is specifically a dihydroxychalcone



Butein may be synthetically prepared or may be extracted from natural sources and purified for use in the present invention. Butein, for use in the present invention is preferably extracted from the following plants: *Butea monosperma*, *Rhus verniciflua, Semecarpus anacardium, Dalbergia odorifera, Caragana jubata*.

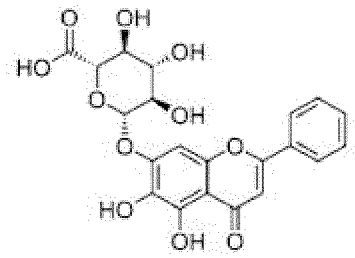
The flower, bark, stem, heartwood or root part of the plant is preferably used for extraction of butein, more preferably the flower part. Of the various plants, *Butea monosperma* is most preferred for extraction of butein for use in the present invention.

Hydroxyflavone compound for use in the first composition of the method of the present invention has the general structure:



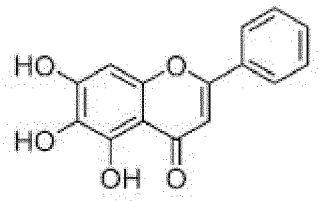
where R_1 is H, OH, OCH_3, or O-Glucose
and R_2 is H, OH, OCH_3, or O-Glucose.

A preferred hydroxyflavone compound of is baicalin, baicalein or mixture thereof. Baicalin has the structure



Thus in Baicalin R_1 is an O-Glucose unit and R_2 is a Hydrogen atom.

Baicalin may be synthetically prepared or may be extracted from natural sources and purified for use in the present invention. A preferred natural source for extraction of baicalin for use in the present invention is preferably *Scutellaria baicalensis.* The leaves, seeds or root of the plant is preferably used for extraction of baicalin, more preferably the root. Alternately, another trihydroxyflavone, baicalein, may be present in carrying out the method of the invention. Baicalein has the structure

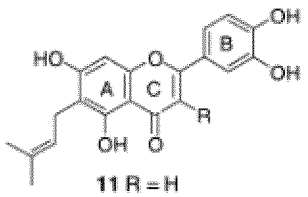


Thus in Baicalein R_1 is an OH group and R_2 is a Hydrogen atom.

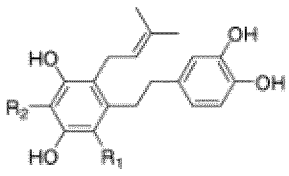
When *Scutellaria baicalensis,* is used for extraction, the extract usually comprises both baicalin and baiclein, the mixture of which is especially preferred for use in the method of the invention.

Other additional hydroxyflavone compounds may be included in carrying out the method of the invention by using an extract of a plant material selected from celery, peppermint, saw thistle, Chinese cabbage, chamomile, thyme or parsley. An especially preferred additional hydroxyflavone compound is apigein.

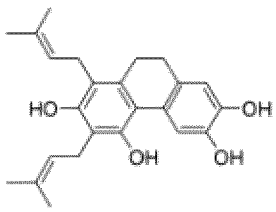
Yet another source of polyphenol for use in the method of the invention is an extract of *Glycyrrhiza glabra.* Licorice (or liquorice), the dried roots and rhizomes of *Glycyrrhiza glabra* (family Leguminosae), has been used as a natural sweetener and a flavorant. Licorice is also one of the oldest and most popular herbal medicines in the world. The chemical compound isolated from licorice are mainly triterpene saponins and flavonoids. The extract of *Glycyrrhiza glabra* for use in the present invention comprises higher than 0.5% total phenols preferably dihydrostilbene or dihydrophenanthrene. They have the following chemical structure



11 R = H
12 R = OH



13 R_1 = -CH_2CH=CMe_2, R_2 = H
14 R_1 = H, R_2 = -CH_2CH=CMe_2

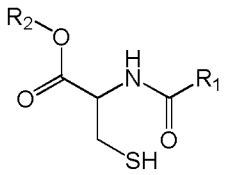


15

The leaves, seeds, roots or stem part of the plant is preferably used for extraction of total phenols from Licorice, more preferably the root.

The polyphenol for use in the first composition of the method of the invention is preferably used as an aqueous composition at 0.1 to 10 wt%, preferably 0.2 to 2 wt% by weight of said aqueous composition.

Another essential element of the method of the invention is a penetration enhancer selected from a cysteine derivative of the general formula:



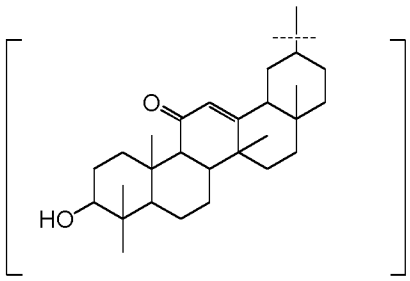
The various possible combinations of R1 and R2 by which the general structure of cysteine may be derivatised are:

(a) When R_1 is a C_3 to C_{15} alkyl group, R_2 is a H atom.

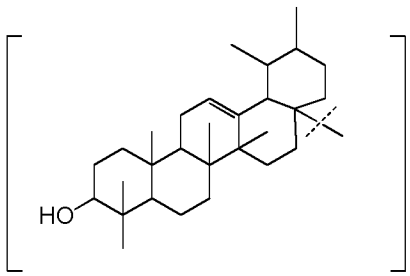
(b) When R_1 is a O-t-butyl group, R_2 is a C_1 to C_{10} alkyl group.

(c) When R_1 is a sesquiterpene group selected from one of R_3 or R_4 or R_5, R_2 is a C_1 to C_{10} alkyl group;

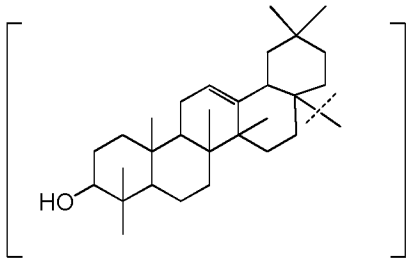
Where R_3 is a glycyrrhetinic acid residue



Where R4 is a ursolic acid residue



Where R5 is a oleanoic acid residue



Of the various possibilities (a), (b) and (c) listed above, the most preferred option is to have R_1 as a C_3 to C_{15} alkyl group and R_2 as a H atom. A further preferred option as per this embodiment is to have R_1 as a C5 to C12 alkyl group and R2 as a H atom. The cysteine derivative for use in the first composition of the method of the invention is preferably present in 0.1 to 15%, more preferably 0.5 to 8% by weight of the first composition. The first composition preferably has a pH in the range of 4 to 10.

Lauroyl cysteine, which is one of the most preferred cysteine derivative for use in the method of the invention may be prepared using a process as given below:

Preparation of cysteine derivatives

5 gm of cysteine is taken in a two-necked round bottom flask. 4.3 ml of ethanolamine and 470 ml of methanol are added into it. The mixture is stirred on a magnetic stirrer for 10 minutes. One neck of the flask is connected to a dropping funnel and the other is closed with a stopper. 10 ml of Lauroyl chloride in 40 ml of THF (tetra hydro furan) is added drop-wise using a dropping funnel. The reaction is kept at room temperature (about 25 ^{o}C) for about 24 hours. Solvent from the reaction mixture is removed using rota vapour. Small amount of water is added to precipitate the desired compound Lauroyl cysteine. The desired compound lauroyl cysteine is filtered and dried over vacuum.

According to the present invention preferred metal ions are selected from the group consisting of Cu^{2+}, Cu^{+}, Fe^{2+} and Fe^{3+}. It is preferred that when the metal ion is Cu^{2+} or Cu^{+}, it is delivered through a copper salt. Preferred copper salts are copper chloride, copper formate, copper sulfate, copper tartarate, copper ascorbate or copper gulconate, more preferably copper chloride or copper formate. The copper salt is preferably used as an aqueous solution at 0.2 to 10 wt%, preferably 0.5 to 5 wt% by weight of said aqueous solution.

When the metal ion is iron, it could be in the Fe^{2+} or Fe^{3+} state and it is preferably present as an iron salt. Preferred iron salts are iron chloride (II), iron chloride (III), iron gluconate, iron sulphate, iron formate, iron ascorbate, or iron tartrate more preferably iron chloride (II) or iron chloride (III). The iron salt is preferably used as an aqueous composition at 0.2 to 10 wt%, preferably 1 to 6 wt% by weight of said aqueous composition. Of the various metal ions, $Cu^{2+,}$ Fe^{3+} or Fe^{2+} are preferred for use in the present invention.

The keratinous fiber as per the invention is preferably human or animal hair, preferably human hair. The above method may be carried out by contacting the hair using a complex of the metal salt with polyphenol along with cysteine derivative that has been pre-prepared as a composition. When the complex is pre-prepared, it is preferred that the composition is prepared not more than 60 minutes, preferably not more than 20 minutes, further more preferably not more than 5 minutes before contacting the keratinous fibres. An alternate and preferred way of achieving this is to prepare the complex insitu on the keratinous fibres by contacting the fibres first with a composition comprising the penetration enhancer and the polyphenol followed by contacting the fibres with another composition comprising the metal ion. When the sequential steps mentioned above are carried out, the steps are preferably carried out not more than 30 minutes, preferably not more than 5 minutes apart. When the process is carried out involving the sequential steps as described above, it is preferred that the fibres are rinsed with water between the two steps.

The step of contacting the fibres with the pre-prepared metal complex with polyphenol is preferred over the sequential sub-steps described above.

The composition comprising the polyphenol is preferably present in aqueous solution at a pH at 25 ^{o}C in the range of 4 to 10. The composition comprising the metal ion is preferably present in aqueous solution at a pH at 25 ^{o}C in the range of 4 to 7. Without wishing to be bound by theory, it is believed that the metal ion forms a complex with the polyphenol which imparts the colour to the fibres in an enhanced manner by inclusion of the cysteine derivative. This may be formed insitu on the keratinous fibres by carrying out the reaction on the fibres or the complex may be prepared ex-situ and then applied on to the keratinous fibres. Once the complex is formed, the pH

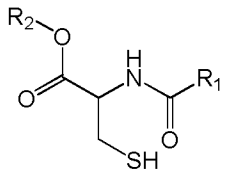
is preferably in the range from 4 to less than 7. Once the fibres have been treated with the complex, they are preferably rinsed with plenty of water to be substantially free of the complex. The complex is preferably applied on the fibres from 5 to 60 minutes, more preferably 15 to 45 minutes in order to obtain maximum efficacy of colour formation.

A suitable way to enable the method of the invention is to carry out the step of contacting the keratinous fibres with the polyphenol by including it in a shampoo composition while the metal ion is included in a conditioner composition. Thus, this aspect will ensure that people first use the shampoo to wash their hair, which is the usual practise. Thereafter people rinse their hair with water followed by applying the conditioner on the hair followed by a further step of rinsing with water.

A more preferred option of delivering the benefits of the invention is that the polyphenol along with the cysteine derivative is included in a composition in the form of a gel/ cream which are of a leave-on nature. After a predetermined period of time of contact of this composition with the desired keratinous fibres, they may be rinsed with water. Thereafter a leave-on composition in the form of a cream or gel containing the metal ion may be applied to the fibres or the metal ion may be included in a wash off composition like a shampoo or a conditioner to enable the method of the invention.

Alternately the metal salt and the polyphenol along with the cysteine derivative are included in two separate compartments of a shampoo composition and are mixed just prior to application on to the keratinous fibres which need to be coloured.

The above methods of delivering the benefits of the invention may be enabled by providing for a kit for colouring keratinous fibres comprising (i) a 'composition A' comprising a penetration enhancer selected from a cysteine derivative of the general formula



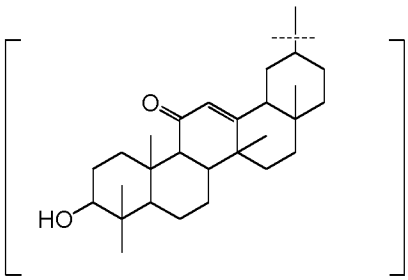
Wherein R_1 and R_2 are combinations selected from any one of:

(a) When R_1 is a C_3 to C_{15} alkyl group, R_2 is a H atom;

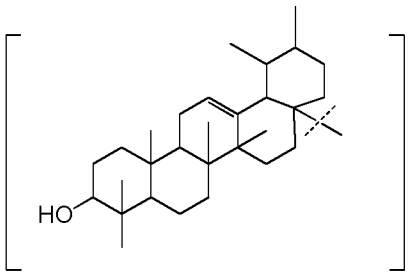
(b) When R_1 is a O-t-butyl group, R_2 is a C_1 to C_{10} alkyl group; and

(c) When R_1 is a sesquiterpene group selected from one of R_3 or R_4 or R_5, R_2 is a C_1 to C_{10} alkyl group;

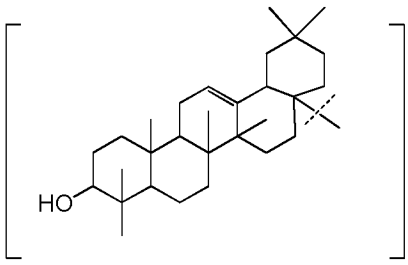
Where R_3 is a glycyrrhetinic acid residue



Where R4 is a ursolic acid residue



Where R5 is a oleanoic acid residue



(ii) a 'composition B' comprising a polyphenol;

(iii) a 'composition C' comprising a metal ion selected from the group consisting of Cu^{2+}, Cu^{+}, Fe^{2+} and Fe^{3+}; and

(iv) instructions for use.

In a preferred aspect the first composition which is a mixture of Composition A and Composition B has a pH in the range of 4 to 10 and the Composition C has a pH in the range of 4 to 7. In the kit either of the compositions may independently be chosen from any one of an oil, a microemulsion, a gel, a cream, a conditioner or a shampoo.

The invention will now be illustrated with the help of the following non-limiting examples.

Examples

Examples A, B and 1-3: Comparision of the colour obtained using the method of the invention as compared to conventional methods

All experiments were performed on switches of white hair as the starting substrate. The colour of the white hair was measured using the following method:

A Minolta CR-10 hand held color reader was used to measure the colour of hair switches. This instrument measures reflected light using 8° illumination/diffuse viewing and gives the colour difference expressed in L*a*b* and dE* or L*C*H* and dE*. For the current studies, measurements were made in L*a*b*.

The white hair had the following L*a*b* value

L* = 79.3, a* = 0.2, b* = 9.3

It is desirous as per the invention to obtain high darkness (blackness of the hair) and this is indicated by an L* value less then 40, preferably less than 30. Experiments on colouring hair were carried out as given below.

To conduct the following experiments a shampoo and a conditioner composition were prepared as below:

Shampoo composition:

Ingredient	Wt%
Sodium laureth sulfate (SLES)	8
Sodium lauryl sulfate (SLS)	7
Cocamide monoethanol amine (CMEA)	2
Cocamidopropyl betaine (CAPB)	2
Glycerine	1
Fragrance	0.7
Water	To 100

Conditioner composition:

Ingredient	Wt%
Cetrimonium chloride	1.0
Cetyl alcohol	2.5
Thickening gum (hydroxy ethyl cellulose)	0.5
Fragrance	0.2
Preservative	0.5
Water	To 100

Example A: In this example propyl gallate was added in the shampoo at 1% and iron gluconate was added in the conditioner at 4%. The white hair was first treated with the shampoo for five minutes and then with the conditioner for 5 minutes. The hairs were then rinsed and dried using a hair drier and the colour intensity was measured using the chromameter.

Example 1: In this example the white hair was first treated with an 8% solution of lauroyl cysteine at pH 9 (adjusted with triethanol amine) followed by the treatment as per Example A.

Example 2: In this example the lauroyl cysteine (at 2.0%) was added in the shampoo composition. The procedure followed was otherwise same as Example A.

Example 3: In this example the lauroyl cysteine (at 2.0%) was added in the conditioner composition. The procedure followed was otherwise same as Example A.

Example B: In this example cysteine was used instead of lauroyl cysteine and the procedure was otherwise same as Example 2.

The data on the colour (L* values) obtained from the various examples are given below in Table -1:

Table -1

Examples	L* Value
Untreated	79.3
Example A	41.1
Example 1	28.8

Example 2	26.7
Example 3	30.1
Example B	27.1

The data in table -1 indicates that the method as per the invention (Examples 1 to 3) gives the desired dark colour comparable to use of cysteine as a penetration enhancer (Example B). However the odour obtained with the method of Example – 2 was compared to Example B and the data is summarized below.

The following samples were tested for odour.

B1: 8% cysteine solution

B2: hair treated with 8% cysteine solution

B3: 8% cysteine solution in shampoo

2A: 8% lauroyl cysteine solution

2B: hair treated with 8% lauroyl cysteine solution

2C: 8% lauroyl cysteine solution in shampoo

The odour of the above samples were evaluated by ten volunteers who scored the samples on a scale of 0-9 (with 0 being least acceptable and 9 being most acceptable). The average odour scores given by the ten volunteers for each of the ten samples is given in the Table -2 below

Table-2

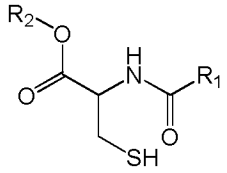
Examples	Average score
B1	0
B2	0.2
B3	2.0
2A	4.1
2B	4.8
2C	4.8

The data in Table-2 above indicates that use of cysteine derivative provides a more acceptable odour as compared to cysteine.

CLAIMS

1. A method of colouring keratinous fibers comprising the steps of contacting the keratinous fibers with

(i) a penetration enhancer selected from a cysteine derivative of the general formula



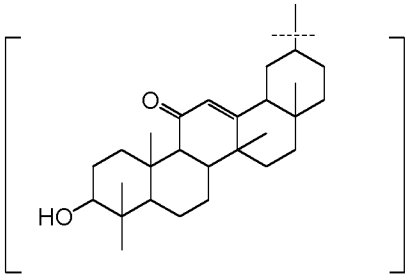
Wherein R_1 and R_2 are combinations selected from any one of:

(a) When R_1 is a C_3 to C_{15} alkyl group, R_2 is a H atom;

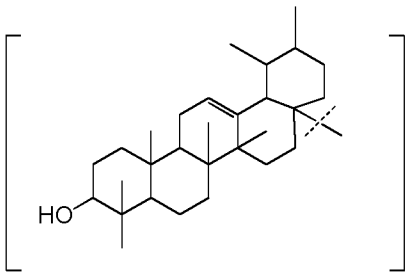
(b) When R_1 is a O-t-butyl group, R_2 is a C_1 to C_{10} alkyl group; and

(c) When R_1 is a sesquiterpene group selected from one of R_3 or R_4 or R_5, R_2 is a C_1 to C_{10} alkyl group;

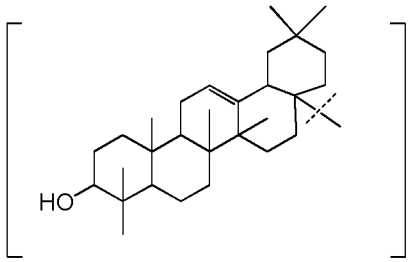
Where R_3 is a glycyrrhetinic acid residue



Where R4 is a ursolic acid residue



Where R5 is a oleanoic acid residue



(ii) a polyphenol and

(iii) a metal ion selected from the group consisting of Cu^{2+}, Cu^{+}, Fe^{2+} and Fe^{3+};

where contacting is in any order

2. A method as claimed in claim 1 comprising the steps of contacting the fibers with a first composition comprising the penetration enhancer and the polyphenol and a second composition comprising the metal ion.

3. A method as claimed in claim 1 or 2 wherein said polyphenol is gallic acid or an ester thereof, rosmarinic acid, butein, a hydroxyflavone or said polyphenol is present as an extract of *Glycyrrhiza glabra*.

4. A method as claimed in any one of the preceding claims wherein said keratinous fiber is human or animal hair.

5. A method as claimed in any one of the preceding claims wherein the penetration enhancer, the polyphenol and the metal ion are not mixed more than 0 to 60 minutes prior to application on the keratinous fibers.

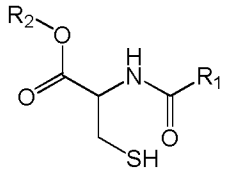
6. A method as claimed in any one of the preceding claims 2 to 5 comprising a sequential treatment comprising a first step of contacting the keratinous fibers with the first composition and a second step of contacting the fibers with the second composition.

7. A method as claimed in claim 6 comprising a step of rinsing the fibers with water between the first step and the second step.

8. A method as claimed in any one of the preceding claims wherein said metal ion is present as an aqueous solution of a chloride, sulphate, gluconate, formate, ascorbate or tartarate salt.

9. A method as claimed in claim 8 wherein the concentration of the solute in the aqueous solution ranges from 0.2 to 10 weight %.

10. A kit for colouring keratinous fibers comprising (i) a 'composition A' comprising a penetration enhancer selected from a cysteine derivative of the general formula



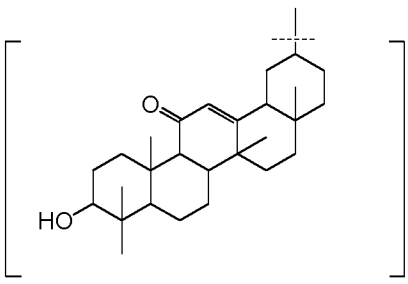
Wherein R_1 and R_2 are combinations selected from any one of:

(a) When R_1 is a C_3 to C_{15} alkyl group, R_2 is a H atom;

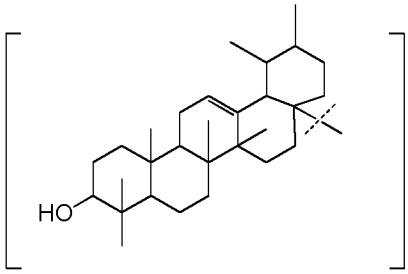
(b) When R_1 is a O-t-butyl group, R_2 is a C_1 to C_{10} alkyl group; and

(c) When R_1 is a sesquiterpene group selected from one of R_3 or R_4 or R_5, R_2 is a C_1 to C_{10} alkyl group;

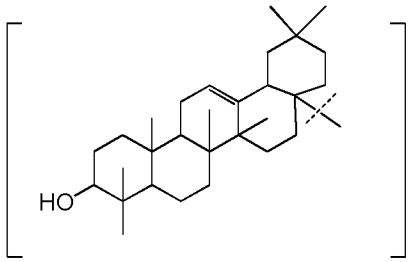
Where R_3 is a glycyrrhetinic acid residue



Where R4 is a ursolic acid residue



Where R5 is a oleanoic acid residue



(ii) a 'composition B' comprising a polyphenol;

(iii) a 'composition C' comprising a metal ion selected from the group consisting of Cu^{2+}, Cu^{+}, Fe^{2+} and Fe^{3+}; and

(iv) instructions for use.

11. A kit as claimed in claim 10 comprising a first composition comprising a mixture of composition A and composition B, said first composition having a pH in the range of 4 to 10.

12. A kit as claimed in claim 10 or 11 wherein the 'composition C' has a pH in the range of 4 to 7.

13. A kit as claimed in any one of claims 10 to 12 wherein the compositions are in the form of an oil, microemulsion, gel, cream, conditioner or shampoo.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/064906

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/34 A61K8/46 A61K8/63 A61Q5/10 A61K8/19
C07J1/00
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 C07J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/065576 A1 (NATURAL MEDICINE INST OF ZHEJIANG YANGSHENGTANG CO LTD [CN]; HU LIU [C) 24 May 2012 (2012-05-24) abstract page 13; example 1	1-13
Y	DE 12 08 450 B (MEAD JOHNSON & CO) 5 January 1966 (1966-01-05) column 1, line 1 - line 38 column 1, line 39 - column 2, line 39	1-13
A	US 5 104 413 A (IKEDA YOSHIO [JP]) 14 April 1992 (1992-04-14) cited in the application column 1, line 53 - column 2, line 16 table 1	1-13

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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	Date of mailing of the international search report
22 September 2014	06/10/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Olausson Boulois, J

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/064906

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2001/003583 A1 (MONTANARI DANIELA [IT] ET AL) 14 June 2001 (2001-06-14) paragraphs [0017] - [0020]	1-12
A	KONDRATENKO R M ET AL: "Synthesis and immunostimulating activity of cysteine-containing derivatives of glycyrrhizic acid", RUSSIAN JOURNAL OF BIOORGANIC CHEMISTRY, M A I K NAUKA - INTERPERIODICA, RU, vol. 30, no. 1, 1 January 2004 (2004-01-01), pages 53-59, XP009156430, ISSN: 1068-1620, DOI: 10.1023/B:RUBI.0000015774.09619.80 page 53	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/064906

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012065576 A1	24-05-2012	CN 102258438 A	30-11-2011
		EP 2641587 A1	25-09-2013
		JP 2013542962 A	28-11-2013
		KR 20140071268 A	11-06-2014
		TW 201223552 A	16-06-2012
		US 2013255009 A1	03-10-2013
		WO 2012065576 A1	24-05-2012
DE 1208450 B	05-01-1966	CH 462386 A	15-09-1968
		DE 1208450 B	05-01-1966
		FR 1375958 A	23-10-1964
		GB 1002889 A	02-09-1965
		NL 6406777 A	16-12-1965
		US 3242052 A	22-03-1966
US 5104413 A	14-04-1992	AT 111344 T	15-09-1994
		DE 69012515 D1	20-10-1994
		DE 69012515 T2	12-01-1995
		EP 0429855 A1	05-06-1991
		JP H0699290 B2	07-12-1994
		JP H03141215 A	17-06-1991
		US 5104413 A	14-04-1992
US 2001003583 A1	14-06-2001	AT 259210 T	15-02-2004
		AU 4775099 A	10-01-2000
		CH 689821 A5	15-12-1999
		DE 69914752 D1	18-03-2004
		DE 69914752 T2	15-07-2004
		DK 1089704 T3	14-06-2004
		EP 1089704 A1	11-04-2001
		ES 2221396 T3	16-12-2004
		PT 1089704 E	31-05-2004
		US 2001003583 A1	14-06-2001
		WO 9966887 A1	29-12-1999