The invention relates to a method and a kit for providing brown colour to keratinous fibres while reducing the blueness generally obtained with such types of colouring methods. The invention relates to giving a high pH of 9 to 12 treatment to the hair after it has been treated with a specific metal-polyphenol complex.
A METHOD OF COLOURING KERATINOUS FIBERS

Technical Field

The invention relates to a method and a kit for providing brown colour to keratinous fibres. The invention more particularly relates to a method and a kit for providing brown colour to hair and reducing the blueness generally obtained with such types of colouring methods.

Background of the invention

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.

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. These types of temporary and semi-permanent hair colours do not give any control to the consumer over the amount of colour deposited. Hence most people prefer the permanent hair colours.

There are several permanent hair colouring compositions which generally come in two parts: a dye solution and a developer solution. People generally perceive that synthetic chemicals have a damaging effect on their hair. They also believe that use of these dyes can cause allergenic reactions in some people in addition to damage to structure of hair fiber. Therefore, more and more people are opting for colourant systems that use actives extracted from natural sources.

A method of colouring hair comprising contacting hair with an iron salt followed by contacting with gallic acid or an ester thereof, is known. Such a method gives a
bluish tinge to the hair which is not liked by some consumers. Consumers generally prefer a more brownish tinge which they believe gives one a natural look. The present inventors have found that giving a high pH treatment to the well known two step process of colouring hair provides the much needed brownish tinge.

Two step process of colouring hair is known e.g. EP0394930 (Kao, 1990), JP04208214 (Seihou Kikaku KK, 1992) and EP0327345 (Beecham, 1989).

EP2399567 (Zhejiang Yangshengtang, 2011) discloses a mordant for hair dyeing comprising an effective amount of ferrous salt, antioxidant and water and a hair dyeing product comprising three parts: a softening agent, a dyeing agent and the mordant.

EP2446876 (Zhejiang Yangshengtang, 2012) discloses a combination of the hair dyeing agent and a softener for dyeing hair where the hair dyeing agent comprises a dye active, a mordant active, a stabilizer, water and a carrier and/or an excipient.

Many of the hair colouring compositions including those mentioned above disclose that the metal-polyphenol complex are applied on the hair at a pH of 3-6 which may be followed by rinsing with water or washing with shampoos where the pH is in the range of 3.5 to 8. It is heretofore not known that giving a high pH of 9 to 12 treatment to the hair after it has been treated with a specific metal-polyphenol complex ensures better brown tinge to the hair which is the invention claimed in the present application.

It is thus an object of the present invention to develop a method of colouring keratinous fibers that enhances the brown tinge.
It is another object of the present invention to develop a method of colouring keratinous fibers that enhances the brown tinge and uses material derivable from natural sources.

5 Summary of the invention

According to the first aspect of the present invention, there is provided a method of colouring keratinous fibers comprising the steps of

(a) contacting the keratinous fibers with a complex of an iron salt with gallic acid or an alkyl ester of gallic acid or a mixture thereof at a pH in the range of 3 to 6; followed by
(b) contacting the keratinous fibers with a composition at a pH in the range of 9 to 12.

According to another aspect of the present invention there is provided a kit for colouring keratinous fibers comprising

(a) an iron salt present as 0.1 to 10% aqueous solution;
(b) gallic acid or an alkyl ester of gallic acid or a mixture thereof present as 0.1 to 10% aqueous solution;
(c) a composition having a pH in the range of 9 to 12; and
(d) instructions for use.

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 fibers 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 a state where the keratin content is low to a colour which may include black or brown. Preferred colour to be achieved as per the present invention is brown with a minimal blue tint. 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.

The first aspect of the invention provides for a method of colouring keratinous fibers comprising the steps of (a) contacting the keratinous fibers with a complex of an iron salt with gallic acid or an alkyl ester of gallic acid or a mixture thereof at a pH in the range of 3 to 6; followed by (b) contacting the keratinous fibers with a composition at a pH in the range of 9 to 12.

Step (a) in the method above may be carried out by contacting the hair using a complex 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 way of achieving this is to include the iron salt in a first composition and the gallic acid or the alkyl ester thereof in a second composition. The complex may be prepared insitu on the keratinous fibers by contacting the fibers first with the composition comprising the gallic acid or alkyl ester thereof followed by contacting the fibres with the iron salt. In a preferred aspect the fibers are first contacted with the iron containing composition followed by contacting the fibers with the gallic acid or alkyl ester thereof. When either of the sequential sub-steps of step (a) are carried out the sub-steps are preferably carried out not more than 30 minutes, preferably not more than 10 minutes apart.

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

The iron salt is preferably selected from iron chloride (II), iron chloride (III), iron gluconate (II), iron sulphate, iron ascorbate, or iron tartrate, more preferably from iron chloride (II), or iron gluconate (II). The iron salt is preferably used as an aqueous composition at 0.1 to 10 wt%, preferably 0.5 to 5 wt% by weight of said aqueous composition.

Gallic acid and its esters have the structure:

![Gallic acid, Methyl gallate, Ethyl gallate, Propyl gallate](image)

The alkyl ester of gallic acid preferably has the alkyl chain length of 1 to 4 carbon atoms of which ethyl, methyl or propyl gallate is preferred. Of these, methyl or propyl gallate are further more preferred. The gallic acid or the alkyl ester thereof
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.

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.

The complex is formed ex-situ or insitu by reaction of an iron salt with gallic acid
or alkyl ester of gallic acid. In this the preferred iron salts are iron chloride (II), iron
chloride (III), iron gluconate, iron sulphate, iron ascorbate, or iron tartrate. Of
these iron salts iron chloride (II), iron chloride (III), or iron gluconate are more
preferred. The iron salt is preferably present in aqueous solution at a pH in the
range of 2 to 6, more preferably 3 to 5. The aqueous solution of the iron salt is
preferably at a concentration of 0.5 to 5%. Once the iron salt - gallate complex is
formed the pH is in the range of 3 to 6.

It is an essential aspect of the present invention to carry out step (b) which
comprises contacting the keratinous fibers with a composition having a pH of 9 to
12. In conventional methods the hair is rinsed with water or with a conditioner
composition which generally has a pH in the range of 3.5 to 8. The dramatic
increase in the browness of the hair and reduction in the blueness is achieved by
carrying out this step of contacting the hair with a high pH composition. This high
pH composition may be prepared by included alkaline substances e.g. sodium
hydroxide, potassium hydroxide, or cationic polymers like polyethylene imine in this composition. It is essential that the step (b) is carried out after step (a) and the order of this sequence is important. The present inventors have carried out experiments where step (b) is carried out first followed by step (a) and this order does not provide the benefits afforded by the present invention.

There are various ways to enable the method of the invention. The step (a) may comprise a composition that is left on hair for a pre-specified period of time from a leave-on composition. Alternately it may be included as a wash-off composition e.g. a shampoo composition. Step (b) may also be a leave-on or wash-off composition. When compositions of step (a) and step (b) are leave-on compositions, it is preferred that the hair is finally rinsed off after a desired period of time. Of the various possibilities envisaged above, the most preferred combination is that step (a) comprises contacting hair with a wash off shampoo composition and step (b) comprises contacting hair with a wash off conditioner composition.

Step (a) of the method of the invention may be achieved by including the iron-gallate complex in a shampoo composition. Alternately the iron salt and the gallic acid / alkyl ester of gallic acid may be kept in separate compartments of a two compartment container and are mixed some time prior to use, to prepare the desired complex. The contents of the two-compartment container may be mixed to prepare a desired shampoo composition which may be used on hair to provide cleaning as well as colouring benefits. The iron-gallate complex, when in the form of a shampoo is generally in emulsion form. Other suitable forms in which the complex may be delivered are the cream, or gel form. When the iron salt and the gallic acid / alkyl ester of gallic acids are included in separate compartments of a two compartment container, the individual compositions may be in the form of emulsion, gel, or cream form.
Composition at a pH in the range of 9 to 12 used for rinsing the hair after step (a) may be a conditioner composition with alkaline ingredients included to ensure a pH of 9 to 12. It is particularly preferred that the pH of the rinse composition has a pH in the range of 9 to 11. More preferably the pH of the rinse composition is more than 9 but less than 11.

According to another aspect of the present invention there is provided a kit for colouring keratinous fibers comprising:
(a) an iron salt present as 0.1 to 10% aqueous solution;
(b) gallic acid or an alkyl ester of gallic acid or a mixture thereof present as 0.1 to 10% aqueous solution;
(c) a composition having a pH in the range of 9 to 12; and
(d) instructions for use.

The instructions for use preferably includes the instruction to first apply the mixture of aqueous solution of the iron salt and the gallic acid or an alkyl ester of gallic acid followed by the instruction to apply the composition having a pH in the range of 9 to 12.

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

**Examples**

**Comparative Examples A to C:** Methods outside the invention comprising rinsing with a low pH composition.

Several experiments were conducted as described below which involved treating grey hair with a complex of iron and gallic acid / alkyl gallate followed by washing with a low pH composition.

All experiments were performed on white yak hair as the starting substrate. The colour of the white yak 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 yak hair had the following L′a′b′ value

L′ = 74.2, a′ = 1.3, b′ = 7.1

Example A: The white hair was treated with a solution containing 100 mM (~2 wt%) solution of ferrous chloride (FeCl₂) and 50 mM (~1 wt%) gallic acid by incubating for 30 minutes at 25 °C.

Example B: The white hair was treated with a solution containing 100 mM (~1.6 wt%) solution of ferric chloride (FeCl₃) and 50 mM (~1 wt%) gallic acid by incubating for 30 minutes at 25 °C.

Example C: The white hair was treated with a solution containing 100 mM (~4.8 wt%) solution of ferrous gluconate and 50 mM (~1 wt%) gallic acid by incubating for 30 minutes at 25 °C.

The treated hair samples in the above cases were then washed well with shampoo and water (pH in the range of 5 to 7) and dried using a hair drier. The L′a′b′ values of the treated samples were then measured and the values are summarised in Table - 1 below:

<table>
<thead>
<tr>
<th></th>
<th>White hair</th>
<th>Example A</th>
<th>Example B</th>
<th>Example C</th>
</tr>
</thead>
<tbody>
<tr>
<td>L′</td>
<td>74.2</td>
<td>38</td>
<td>46</td>
<td>55</td>
</tr>
<tr>
<td>a′</td>
<td>1.3</td>
<td>3.9</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>b′</td>
<td>7.1</td>
<td>-4.3</td>
<td>-2.1</td>
<td>-1.1</td>
</tr>
</tbody>
</table>
The value desired to be obtained by way of the invention which is perceived as coloured hair with high brownness and low blueness are as follows:

- L* value <50
- b* value to be in the range of -0.5 to 8.0.

The data in Table -1 indicates that using conventional methods outside the invention one does not achieve either the desired L* value or the desired b* value.

**Examples D and E:** Another set of experiments were conducted using conventional method.

**Example D:** An experiment was carried out similar to Example A

**Example E:** An experiment was carried out similar to Example A except that methyl gallate was used instead of gallic acid. The data on the change in colour is summarized in Table - 2.

<table>
<thead>
<tr>
<th></th>
<th>White hair</th>
<th>Example D</th>
<th>Example E</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>74.2</td>
<td>41</td>
<td>40</td>
</tr>
<tr>
<td>a*</td>
<td>1.3</td>
<td>3.9</td>
<td>4.3</td>
</tr>
<tr>
<td>b*</td>
<td>7.1</td>
<td>-2.9</td>
<td>-5.3</td>
</tr>
</tbody>
</table>

The data in Table -2 indicates that using conventional methods (outside the invention) one does not achieve the desired b* value.

**Examples 1 to 4:** Methods as per the invention

Several experiments were conducted as described below which involved treating grey hair with a complex of iron and gallic acid/alkyl gallate followed by washing with a high pH composition.

All experiments were performed on white yak hair as the starting substrate. The white yak hair had the following L*a*b* value
The procedure involved first treating the white hair switches with a solution containing 100 mM (~2 wt%) solution of ferrous chloride (FeCl₂) and 50 mM (~1 wt%) of gallic acid by incubating for 30 minutes at 25 °C. The hairs were then washed well under running water and then dipped in a buffer solution at high pH as listed in Table - 3 for 5 minutes. The buffer solution used was 50 mM Tris buffer adjusted to the desired pH with 1N NaOH.

The hair switches were then washed once with shampoo and then rinsed under running water, dried using hair drier and the colour intensity measured using a chromameter (CR10). The data for the various experiments 1 to 4 (at differing pH rinsing) are summarised in Table - 3.

<table>
<thead>
<tr>
<th></th>
<th>White hair</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>L*</td>
<td>74.2</td>
<td>36.6</td>
<td>36.4</td>
<td>37.0</td>
<td>37.1</td>
</tr>
<tr>
<td>a*</td>
<td>1.3</td>
<td>5.4</td>
<td>6.6</td>
<td>6.6</td>
<td>8.5</td>
</tr>
<tr>
<td>b*</td>
<td>7.1</td>
<td>-0.3</td>
<td>-0.2</td>
<td>-0.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The data in Table - 3 indicates that using the method of the invention, the desired blackness is obtained (as indicated by the L* values of less than 40), as well as the desired reduction in blueness (as indicated by the b* values of between -0.5 to 8).
Example F: Process comprising a different sequence of contact.

Experiments were carried out similar to Example 4 except that the hair was first contacted with a solution at high pH (of 12) followed by contacting the hair with the complex of iron salt with gallic acid. The procedure was thus as follows:

The procedure involved first treating the white hair switches with a buffer solution at high pH (of 12) for 5 minutes. The buffer solution contained 50 mM Tris buffer adjusted to the desired pH with 1N NaOH. The hair switches were then contacted with a solution containing 100 mM (~2 wt%) solution of ferrous chloride (FeCl₂) and 50 mM (~1 wt%) of gallic acid by incubating for 30 minutes at 25 °C. The hairs were then washed well under running water.

The colour intensity of the switches as per Example F and that for Example 4 which was repeated were measured using a chromameter (CR1 0). The data for these samples Example 4 and F are summarised in Table - 4. The data presented below is a mean of two samples.

Table-4

<table>
<thead>
<tr>
<th></th>
<th>White hair</th>
<th>Example 4</th>
<th>Example F</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>74.2</td>
<td>38.6</td>
<td>31.6</td>
</tr>
<tr>
<td>a*</td>
<td>1.3</td>
<td>3.9</td>
<td>4.2</td>
</tr>
<tr>
<td>b*</td>
<td>7.1</td>
<td>2.2</td>
<td>-5.4</td>
</tr>
</tbody>
</table>

The data in Table-4 indicates that although the desired L value is achieved using a method outside the invention (Example F), it is not possible to achieve the desired b value.

The invention thus provides for a method of colouring keratinous fibers where the desired level of blackness is obtained while minimising blueness and enhancing brownness.
CLAIMS

1. A method of colouring keratinous fibers comprising the steps of
   (a) contacting the keratinous fibers with a complex of an iron salt with gallic
   acid or an alkyl ester of gallic acid or a mixture thereof at a pH in the
   range of 3 to 6; followed by
   (b) contacting the keratinous fibers with a composition at a pH in the range
   of 9 to 12.

2. A method as claimed in claim 1 wherein the complex is prepared not more
   than 1 hr before contacting the keratinous fibers.

3. A method as claimed in claim 1 or claim 2 wherein said alkyl ester of gallic
   acid is ethyl, methyl or propyl gallate.

4. A method as claimed in claim 3 wherein said ester is methyl gallate or propyl
   gallate.

5. A method as claimed in claim 1 wherein gallic acid is present as an extract of
   a plant species of the *Terminalia* genus, or an extract of *Embelica officinalis,
   or Mucuna pruriens*

6. A method as claimed in claim 5 wherein gallic acid is an extract of the leaf,
   stem, seed, flower or fruit of the plant.

7. A method as claimed in any one of the preceding claims wherein said iron
   salt is iron chloride (II), iron chloride (III), iron gluconate, iron sulphate, iron
   ascorbate, or iron tartrate.

8. A method as claimed in any one of the preceding claims wherein said
   complex is present at a pH is in the range of 3 to 6.
9. A method as claimed in any of the preceding claims wherein step (b) comprises rinsing the keratinous fibers with a composition having a pH of 9 to 12.

10. A kit for colouring keratinous fibers comprising
(a) an iron salt present as 0.1 to 10% aqueous solution;
(b) gallic acid or an alkyl ester of gallic acid or a mixture thereof present as 0.1 to 10% aqueous solution;
(c) a composition having a pH in the range of 9 to 12; and
(d) instructions for use.