Hair is colored by treating it with a solution containing a transition metal compound having a valence less than the maximum and then oxidizing the compound to an insoluble form. Colors so imparted and colors imparted to other procedures using transition metal compounds may be removed by treatment with a reducing agent or a chelating agent.

14 Claims, No Drawings
PERMANENT BUT REMOVABLE HAIR-COLORING SYSTEM

The art of imparting color to hair is an ancient one whose origin is lost in antiquity. In addition to natural vegetable dyes such as henna and synthetic materials such as coal tar dyes, various metallic compounds have been employed, principally based on lead, silver or copper, but also including the transition metals, particularly cobalt, iron, nickel and manganese. See "Cosmetics — Science and Technology" (1957) pp. 515–524. Prior metal coloring systems depended for the most part on the formation of metal sulfides, either by reaction of the dying solution with the keratinous sulfur in the hair itself or with sulfur from some external source; or on the reduction of the metal from a higher valence state to a lower state, as for example by the reduction of a permanganate to manganese dioxide. None of these techniques have been particularly successful. Moreover there was no practicable technique for removing the color from the hair once it had been developed.

The present invention provides a novel method of hair coloring which will give a wide range of shades permanent to normal washing but whose coloration is readily removed if desired. The invention also provides methods of removing hair color applicable to hair dyed in accordance with the invention and also to hair colored in more conventional ways.

In accordance with the invention, hair is dyed by contacting it with a solution of a transition metal compound in which the metal is in a first valence state less than the maximum, to deposit the compound on the hair, and then oxidizing the compound to form an insoluble oxide in which the metal has a higher valence state. Further, in accordance with the invention, color so imparted to hair may be removed by treating the hair with a suitable reducing agent or with a chelating agent. This removal technique, it will be recognized, may also be used where the original color was imparted by oxides formed by reduction of transition metal compounds in accordance with known dying techniques; and, if a chelating agent is used, where the color was imparted by deposition of certain transition metal sulfides.

The transition metals used for dyeing in accordance with the invention are those forming water soluble compounds capable of being oxidized to form an insoluble, colored oxide. Manganese, iron and cobalt are of principal interest, and of these manganese is preferred. The form in which the metal is initially applied to the hair is not important, so long as it is in a lower state of oxidation. Various salts, e.g., the halides (especially the chlorides), sulfates, or nitrates may be used, as may soluble salts of organic acids, such as the acetates. Manganese is preferably used in the form of manganous salts such as manganous sulfate or chloride. Iron and cobalt are used as the corresponding ferrous or cobaltous salts.

The conditions under which the metallic compounds are applied to the hair are capable of considerable variation. Normally the compounds will be applied as aqueous solutions, 0.26 to 1.05 normal, at moderate temperature, say from about 10° to about 40°C, and at a pH of from about 4 to about 10. Where the initial metal solution is followed by a separate oxidizing solution, it will be allowed to remain on the hair for say 5 to 30 minutes before the oxidizing solution is applied, so that the metal may penetrate into the interior of the hair.

At this point it may be pointed out that dyeing according to the invention can be carried out using a single solution containing an alkali metal peroxydisulfate, e.g., sodium peroxydisulfate, as the oxidizing agent. In this instance a metal salt solution, e.g., a solution of MnCl₂, is mixed with a solution of peroxydisulfate just before it is applied to the hair. The efficacy of the peroxydisulfate as an oxidizing solution depends on its decomposition according to the reaction

$$2\text{SO}_4^{2-} + 2H_2O \rightarrow 4\text{HSO}_4^- + O_2$$

This reaction, however, is relatively slow, permitting the manganous ions to penetrate the hair filaments before they are oxidized.

Where a single step technique, as described above, is used, the solution applied to the hair will normally have a metal compound concentration of 0.05 to 0.50 gram formula weight (GFW)/liter, a peroxydisulfate concentration of 0.08 to 0.60 mols/liter and a pH of between about 8.0 and about 10.0. It may be applied at temperatures of say about 10° to about 40°C, and is left in contact with the hair for between about 5 and about 60 minutes.

Returning to the two-step procedure, after the metal compound having the metal in a lower valence state has been left in contact with the hair for a time sufficient for the metal ions to have penetrated into the core of the hair filaments, an oxidizing solution is applied. Various oxidizing agents may be used, the criteria being merely that they be effective to convert the soluble, lower valence metallic compound to a higher valence state in a condition under which it becomes insoluble, and not be injurious to the hair or scalp under the effective oxidizing conditions.

Among the oxidizing agents which have been found useful are the permanganes, perborates, persulfates, periodates, perphosphates and monopersulfates, used alone or in combination, as the alkali metal salts, or in the case of the periodates, as the acid (paraperiodic acid, H₃IO₆). Hydrogen peroxide may also be used. The conditions of treatment with the oxidizing agent are, again, subject to considerable variation. In general it will be used in a concentration of say 0.01 to 0.30 GFW/liter at temperatures of say 10° to 40°C, and at a pH of say 7.0 to 10.5. The solution will be left in contact with the hair until the desired shade develops (other things being equal). In general, contact time will be from 1 to 10 minutes.

It will be understood that the shade of dyeing may be varied by varying the kinds of metals used and their proportions as well as by varying the reaction conditions, especially concentration, pH and contact time.

Both the initial metal solutions and the oxidation or fixation solutions may contain various auxiliary materials such as buffers, wetting agents, perfumes and the like.

After the oxidizing solution (or the combined solution) has been left in contact with the hair for the requisite time, the hair may be shampooed using any conventional soap or synthetic detergent composition.

One of the advantages of dyeing in accordance with the invention is that the color may easily be removed, if desired, even though it is permanent under normal washing conditions.
The agencies useful for removing color imparted according to the invention, and as will be explained below, colors imparted by certain prior art metallic coloring systems, are either reducing agents or chelating agents.

In the case of reducing agents, the particular agent selected should be one sufficiently active to convert the oxidized metallic color compound to a soluble lower valence state. The most advantageous materials so far found effective are the alkali metal metabisulfites, e.g., sodium metabisulfite (Na₂S₂O₅). Other equivalent reducing agents such as other reducing salts of the oxy acids based on SO₂, e.g., sodium sulfite (Na₂SO₃), sodium thiosulfate (Na₂S₂O₃) and sodium hydrosulfite (Na₂S₂O₅) may also be used.

The reducing agent is employed in a concentration of say 0.05 to 0.5 mols/liter, normally at say 10° to 40°C, and at a pH of from about 1.5 to about 7. The time of treatment is, of course, dependent on the other conditions. Normally substantially all the color can be removed in a matter of say 0.5 to 20 minutes.

Following treatment with the reducing agent, the hair may be washed in normal manner.

As an alternative to removing color using a reducing agent, color may be removed from hair dyed in accordance with the present invention by using a chelating or complexing agent.

It is well known that various organic compounds form water soluble complexes with transition metal compounds and use may be made of this principle to remove color derived from transition metals from hair. A variety of chelating agents may be used, depending on the metal concerned. Thiourea has been found especially useful, but other materials in which the donor is sulfur may be used as may chelating agents in which the donor is nitrogen, e.g., EDTA, or oxygen, e.g., citric acid.

The conditions under which the chelating agent is used will vary widely depending on the agent and the metal to be removed. In general the concentration of agent will range between about 0.1 and about 1.0 mols/liter. The solution will usually have a pH from say 2.5 to 5.0 and will be applied at temperatures of say 10° to 40°C. Contact time is determined by the speed of the particular reaction. Normally an application of say 1 to 15 minutes will remove substantially all color. However, in certain instances times of an hour or even longer may be required. Sulfide colors generally require longer times or higher temperatures than oxide colors.

It will be understood that while it is particularly advantageous to use the removal techniques described above in conjunction with the dyeing procedures described and claimed herein, it is much easier to select the particular removal reagent and conditions with relation to a specific dyeing procedure, the removal techniques themselves represent a separate aspect of the present invention and are capable of being used to remove transition metal oxide or sulfide coloring materials regardless of how they have been applied. Thus, for example, cobalt or nickel salts may be applied to the hair from aqueous solution, and fixed by treatment with a dithionite (hyposulfite) solution. Again, potassium permanganate may be applied to the hair and reduced by the use of sodium sulfide or pyrogallol, to give a color which may be removed either by reduction using metabisulfite, or by a thiourea complexing solution.

The invention is described by the following specific examples which are, of course, only illustrative and are not intended to restrict the invention as it is defined in the claims:

**EXAMPLE I**

A first solution was prepared containing:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl₂</td>
<td>20</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>20</td>
</tr>
<tr>
<td>H₂O</td>
<td>60</td>
</tr>
</tbody>
</table>

And adjusted to pH 8 with NaOH. Human hair was treated with this solution for 30 minutes at room temperature (70°F.) and rinsed with water. It was then treated with an aqueous solution containing 2.1 percent sodium perborate at a pH of 10.2-10.4 for 10 minutes, again at room temperature. After shampooing, the hair had a warm dark brown color.

Varying the pH of the second solution from 10.2 to 2.5 whilst holding the first solution at pH 8 gave a range of colors from dark warm brown through medium and light warm brown to medium and light ash blond. Maintaining the pH of the second solution at 10.2 and varying the pH of the first from 2.5 to 8 with NaOH or NH₄OH gave a range of colors from dark warm brown to light reddish brown.

The procedure just described may be varied in other ways to give varying results. For example, by varying the times of exposure, different shades of brown are obtainable as indicated in the table below:

<table>
<thead>
<tr>
<th>Contact Time (minutes)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 1</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>Color</td>
<td>LB</td>
<td>MB</td>
<td>MB</td>
<td>MB</td>
<td>MB</td>
<td>MB</td>
<td>MB</td>
</tr>
</tbody>
</table>

Where LB is light brown; MD is medium brown and DB is dark brown.

The role of the ammonium chloride in solution 1 is to permit the manganese to be retained in solution after the solution is rendered alkaline. The mechanism appears to be a complex formation.

**EXAMPLE II**

A first solution having the following composition was prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·H₂O</td>
<td>28</td>
</tr>
<tr>
<td>H₂O</td>
<td>62</td>
</tr>
<tr>
<td>Na laurel sulfate</td>
<td>10</td>
</tr>
</tbody>
</table>

The pH of the solution was brought to 6.5 by the addition of NaOH. Human hair was treated with the solution at room temperature for seven minutes and then rinsed with water. Then a second solution, freshly prepared, and containing
3,838,966

EXAMPLE V

The procedure of Example I was repeated, but the first solution was a simple 10 percent aqueous solution of MnCl₂. Treatment with this was at pH 4.7 for 5 minutes at room temperature. The oxidizing solution was an aqueous solution containing 2.1 percent sodium perborate at pH 10.2, and room temperature. After a contact time of 5 minutes, the hair assumed a medium ash brown color. Decreasing the perborate concentration gave lighter colors with a medium ash brown at 1 percent, light ash brown at 0.05 percent and ash blond at 0.25 percent. The colors from these perborate treatments tended, in general, to be more drab than similar treatments using permanganate.

EXAMPLE VI

A solution was prepared containing

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₂·6H₂O</td>
<td>25</td>
</tr>
<tr>
<td>NaBO₃·4H₂O</td>
<td>4</td>
</tr>
<tr>
<td>water</td>
<td>balance</td>
</tr>
</tbody>
</table>

with sufficient 0.5 N HCl to give a pH of 1.6. Three bleached human hair swatches (Nos. 1, 2 and 3) were treated for 45, 10 and 20 minutes respectively and rinsed with water. They were then treated with a 0.44% KMnO₄ solution for 10, 10 and 20 minutes respectively, shampooed and examined. Swatch No. 1, was dark brown; No. 2, very dark brown and No. 3, black.

When a 1 percent alkaline potassium persulfate solution pH 10.5 is substituted for the permanganate solution a reddish brown to red color is obtained, which can be adjusted by adjusting the pH of the cobalt from 2.5 to 11.0. Adding 1 percent potassium persulfate and 10 percent urea to the cobaltous solution results in an intense red color.

EXAMPLES VII – XVI

These examples are grouped together to illustrate the range of colors which are obtainable in accordance with the invention. In all cases the dyes were performed on dark brown hair which had first been bleached to the pale yellow stage. In all cases the hair was treated with solution 1, as specified in the table below, for the specified time, rinsed with water and then treated with solution 2 for the time specified. Following this, it was washed with a commercial shampoo and dried.

In general, Examples VII – X gave ash colors, while Examples XI – XVI gave warm colors. The intensity of the colors seems proportional to the porosity of the hair, which is increased by bleaching. Lighter colors should therefore be expected when treating hair bleached to a lesser extent. Black may still be obtained under these circumstances by increasing the proportion of perborate in solution 1.
EXAMPLE XVII

A solution was prepared containing, weight percent,

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·H₂O</td>
<td>1.6</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>7.0</td>
</tr>
<tr>
<td>K₂S₂O₅</td>
<td>10.6</td>
</tr>
<tr>
<td>ammonium laurel sulfate (28-30%)</td>
<td>13.3</td>
</tr>
<tr>
<td>NH₄OH (28-30%)</td>
<td>2.5</td>
</tr>
<tr>
<td>water</td>
<td>65.0</td>
</tr>
</tbody>
</table>

It had a pH of about 9.0. The solution was immediately applied to bleached human hair for 60 minutes at room temperature, following which the hair was washed with a commercial shampoo and dried. It had a warm black color.

EXAMPLE XVIII

Hair dyed in accordance with Example XVI was treated with a 1.0 percent aqueous solution of sodium metabisulfite (Na₂S₂O₅) for 5 minutes at room temperature and pH 4.4 and then rinsed with water. The hair samples had the bleached color which they showed before dyeing.

EXAMPLE XIX

Hair dyed in accordance with Example VI was treated with an aqueous solution of sodium metabisulfite at room temperature and pH 4.4 for 5 minutes. Again the hair was restored to its original color.

EXAMPLE XX

A solution was prepared having the following composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>8.0</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>16.0</td>
</tr>
<tr>
<td>Sodium laurel sulfate (28-30%)</td>
<td>50.0</td>
</tr>
<tr>
<td>H₂O (28-30%)</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Hair dyed according to Examples VI, XI and XVI were treated with the above solution for 5 minutes (15 min. for Example XI) at pH 2.5. The color was completely removed in each case.

EXAMPLE XXI

Human hair was treated with a 10 percent solution of nickel acetate (alkalized to pH 9.8 with 28% NH₄OH) at room temperature for 50 minutes. It was then rinsed with water and treated for 10 minutes with a 10 percent sodium dithionite solution at pH 5.7. A black color resulted from the precipitation of nickel sulfide in the hair. If the pH of the nickel solution is left at 9.8 and that of the dithionite is increased to 9.0 a medium brown is obtained. Varying the pH of the nickel in either direction also gives a brown.

Hair treated in accordance with this example was then treated with the thiourea solution of Example XX for 15 minutes at room temperature, with complete removal of color. The same result was obtained in 3 min. at 40°C.

The foregoing examples illustrate that in accordance with the invention hair may be dyed with a wide range of permanent colors, and these colors, as well as colors more conventionally obtained, may be readily removed with simple and inexpensive reagents.

In the examples in which the color is formed by the oxidation of a manganous salt, the color is understood to be due to the formation of manganese dioxide. Similarly where cobaltous or ferrous salts are oxidized the color apparently results from the formation of one or more oxides in which the metal, or some of it, has a valence greater than two.

In all the examples, except where otherwise specified, the treatments were carried out at approximately room temperature (20°C.), though the temperatures of the solutions themselves may have been somewhat greater in certain cases due to heat of reaction.

The hair treated in the examples, unless otherwise specified, had been bleached with H₂O₂, to remove natural color, before dyeing.

What is claimed is:

1. A method for removing color from hair dyed with a coloring material which is an oxide or a sulfide of a transition metal, which comprises treating said hair with a solubilizing agent which, when the coloring material is an oxide, is a reducing agent or a chelating agent and when the coloring material is a sulfide, is a chelating agent.
2. The method claimed in claim 1 wherein the solubilizing agent is thiourea.
3. The method claimed in claim 1 wherein the hair is dyed with an oxide and the solubilizing agent is a metabisulfite.
4. A method for coloring hair which comprises treating the hair with an aqueous solution of a transition

Hair dyed according to Examples VI, XI and XVI were treated with the above solution for 5 minutes (15 min. for Example XI) at pH 2.5. The color was completely removed in each case.
metal compound in which the metal is present in less than its highest valence state to deposit said compound on the hair and oxidizing said compound to an insoluble compound in which the metal is in a higher valence state, to impart to the hair a color which is permanent under ordinary washing conditions.

5. A method of removing the color from hair colored according to claim 4 which comprises treating the colored hair with a reducing or chelating agent.

6. The method claimed in claim 4 wherein the transition metal is manganese, cobalt or iron.

7. The method claimed in claim 4 wherein the oxidizing agent is a permanganate, persulfate, perborate or periodate.

8. A method of coloring hair which comprises treating the hair with an aqueous solution of a manganous salt to deposit said manganous salt thereon, and treating the so treated hair with an aqueous perborate, persulfate, periodate or permanganate solution to precipitate an insoluble manganese oxide on the hair.

9. A method of coloring hair which comprises treating the hair with an aqueous solution of a cobaltous salt to deposit said cobaltous salt thereon and treating the so treated hair with an aqueous solution of a perborate, persulfate, periodate or permanganate to insolubilize said cobaltous salt.

10. A method of coloring hair which comprises treating the hair with an aqueous solution of a ferrous salt to deposit said salt thereon and subsequently treating the so treated hair with an aqueous solution of a perborate, persulfate, periodate or permanganate to insolubilize said ferrous salt.

11. A method for treating hair which comprises coloring hair by depositing thereon a coloring material which is a sulfide or an oxide of a transition metal and subsequently removing the color by treating the hair with a solubilizing agent which, when the coloring material is an oxide, is a reducing agent or a chelating agent, and when the coloring material is a sulfide, is a chelating agent.

12. The method claimed in claim 11 wherein the transition metal is manganese, nickel, cobalt or iron.

13. The method claimed in claim 11 wherein the solubilizing agent is thiourea.

14. The method claimed in claim 11 wherein the solubilizing agent is a metabisulfite.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,838,966 Dated October 1, 1974

Inventor(s) MYRON BARCHAS and MAGDA OFELIA GUTIERREZ

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, line 5, "to" should read -- by --

Col. 2, line 13, "2S2O8^-++ 2H2O --> 4HSO4^- + O2" should read

-- 2S2O8^- + 2H2O --> 4HSO4^- + O2 --

Col. 5, line 8, "17 .5" should read -- 17.5 --

Col. 5, line 51, "C.Cl2" should be -- CoCl2 --

Col. 7, in the table, "1N^2HCl" should be -- 1N HCl --

"H5I06" should be -- H5I06 --

Col. 8, line 25, "918" should be -- 9.8 --

Col. 10, line 6, "so treated" should be deleted.

Signed and sealed this 28th day of January 1975.

(SEAL)
Attest:

MCCOY M. GIBSON JR. C. MARSHALL DANN
Attesting Officer Commissioner of Patents