

UNITED STATES PATENT OFFICE

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DYEING OF HAIR

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This invention relates to dyeing hair, and especially to new compositions and new processes for such purposes. The new processes are especially useful for the dyeing of human hair such as hair on living persons as well as for dyeing animal hair or fur on pelts.

Heretofore, numerous substances having affinity for hair have been proposed as dyes therefor, among which are the metal salts which produce the desired shades by forming oxides or sulfides. Ordinarily these metal oxides or sulfides are formed superficially and do not produce a permanent coloration. In addition some metallic compounds, such as lead or silver, are toxic and users of the dyed fur or hair are subjected to toxic effects. Vegetable dyes, such as hyperic, quercitron, fustic and sumac have been used but these materials ordinarily produce weak dyeings and there is a limited range of shades possible. Combinations of metal salts and vegetable dyes have been used but these combinations have one or all of the disadvantages of their several constituents. There has been extended use of the so-called oxidation dyes which are amino or hydroxy derivatives of aromatic compounds which develop color by the action of oxidizing agents after the amino compound is applied to the hair. The use of the oxidation dyes has generally required preliminary tests to determine the effect of the compound on the hair of the individual since the reaction on the hair of all persons is not the same toward these compounds. Another disadvantage of the oxidation dyes arises from the fact that considerable time, say a day or so, is required after the dyeing has been made to determine whether the ultimate shade or effect of the compound on the hair will be satisfactory or similar to the approximation indicated by the preliminary test. Probably the most serious objection to the use of the oxidation hair dyes is that these compounds are toxic to living persons and that even the least toxic among them is generally harmful to some individual. More recently a composition for hair dyeing was disclosed which comprises the non-poisonous water soluble coal tar dyes with urea, urethane or amides, such as formamide. Still more recently, there was described the process for the dyeing of hair which comprises pre-treating the hair with a cationic active fatty acid-amine condensation product with subsequent application of an aqueous solution of a dyestuff. None of these methods heretofore used has been found to be entirely satisfactory. It is therefore desirable to provide new hair dyes and new methods for their application that will preserve the natural appearance of hair and that will produce a large variety of shades by processes which can be operated easily and conveniently to produce final results in a very

short space of time. Such processes and compositions are especially desirable for the dyeing of hair on pelts and for the dyeing of hair on living persons.

- 5 It is among the objects of the present invention to provide new compositions and processes for dyeing hair. Another object is to provide processes which will produce colored hair having a natural appearance and in a large variety of shades. Another object of the invention is to provide such compositions and processes which will give final results rapidly and satisfactorily at relatively low temperatures. A further object is to provide rapidly acting hair dyes with good fastness properties without deleteriously affecting the natural appearance of the hair. Another object is to provide processes for the coloration of hair which will have good fastness properties but which can be prepared for recoloration by a simple process. Another object of the invention is to provide compositions and processes for the dyeing of furs which will not cause irritation of the skin of the wearers. Still other objects of the invention will be apparent from the following description.

The objects of the invention are attained in general by applying to the hair, and mildly heated, a lake-forming metal salt and a water soluble synthetic organic dye, both of which are in aqueous solution.

The invention will be more fully set forth in the following more detailed description which includes examples that are given as illustrative embodiments of the invention and not as limitations thereof. Parts are expressed in parts by weight unless otherwise noted.

Example 1

- 40 Old gray hair which had been bleached was treated with a 5% mordant solution of ferrous sulfate and an 0.5% solution of the following dye mixture simultaneously for 10 minutes at 110° F.

	Parts
45 Pontachrome Brown G (C. I. 238)	45.5
Pontachrome Yellow SW (C. I. 195 and	
Prototype 56)	9.0
Logwood crystals (C. I. 1246)	45.5

- After this treatment a further application of 50 an 0.5% dye solution was made for 10 minutes at 110° F. The hair came to a final shade in about 20 minutes and was then washed and dried. The hair had a natural appearance in a dark brown shade and had good washing and 55 other properties desired for colored human hair. The penetration of the color was rapid and complete.

- Similarly, lighter shades of brown, such as drabs, can be made by using concentrations of 60 ferrous sulfate as low as an 0.5% solution and dye solutions as low as 0.1%.

Similarly, good dyeings were obtained on pre-bleached medium brown hair.

The advantages of this application are that when the ferrous sulfate solution is added simultaneously with the dye solution in the first operation, deeper and more colorful shades can be made on those gray hairs which are ordinarily difficult to dye.

Example 2

Medium brown hair which had been bleached was wet with a solution containing 1.0% ferrous sulfate and 2.0% of the following dye mixture simultaneously for 10 minutes at 110° F.:

Pontachrome Brown G (C. I. 238)	Parts 67
Logwood crystals (C. I. 1246)	33

The hair came to a final shade in 10 minutes and after about 20 minutes the hair was washed and dried. The hair had a natural appearance in a dark brown shade. It has good washing and other fastness properties desired for colored human hair. Penetration of the color was rapid and complete.

In a similar manner good dyeings were obtained by carrying out the process on old gray hair and on medium brown hair which had not been pre-bleached.

Similarly, lighter shades of browns, such as drabs, can be made by using concentrations of ferrous sulfate as low as 0.25% solution and dye solutions as low as 0.25%.

The advantages of a simultaneous application of ferrous sulfate and dye solution are that it is a single operation and is saving in time and is less troublesome to the person being operated on. It will be obvious that the more quickly the hair is dyed and the less handling required, the better the condition of the dyed hair as well as the comfort of the person attached thereto.

Dry mixtures of ferrous sulfate and the various dye complexes, Pontachrome Brown G, Pontachrome Yellow SW, and logwood crystals, were prepared in various concentrations varying from 20% iron sulfate and 80% dye to 80% ferrous sulfate and 20% dye. These intimate mixtures were stored for four months and at the end of this period trials were made on human hair using 0.5 to 2.0% solutions. The dyeings were carried out for 10 minutes at 110° F. The shades produced were similar to those obtained where the iron and dye solutions were applied separately and where the iron and dye solutions were dissolved separately and applied simultaneously.

Example 3

Old gray hair which had been bleached was wet with a 5.0% solution of ferrous sulfate for 10 minutes at a temperature of 110° F. The hair was squeezed to remove the surplus iron solution. It was then treated with a 1.0% solution of the following dye mixture.

Pontachrome Brown G (C. I. 238)	Parts 27
Pontachrome Yellow SW (C. I. 195 and Prototype 56)	25
Logwood crystals (C. I. 1246)	48

This treatment was carried out for 10 minutes at 110° F. after which the surplus color solution was removed and a further application of a 2.5% ferrous sulfate was applied as in the beginning of this example. The results obtained by this double application of iron solution on old gray hair, which is known to be difficult to dye by hair dyeing operators, produced a black much su-

perior in depth of color to that obtained with only the first application of iron solution. In a similar manner good dyeings were obtained on pre-bleached medium brown hair and it is possible to obtain good blacks with concentrations as low as 0.5% solutions of ferrous sulfate and 0.25% solutions of dye in the first two treatments and 0.25% solutions of ferrous sulfate in the third treatment.

Example 4

Medium brown hair which had been bleached was wet with a 1.0% solution of the following dye mixture for 10 minutes at 110° F. The hair was squeezed free of surplus color and treated for 10 minutes at 110° F. with a 1.0% solution of ferrous sulfate.

Pontachrome Brown G (C. I. 238)	Parts 45.5
Pontachrome Yellow SW (C. I. 195 and Prototype 56)	9.0
Logwood crystals (C. I. 1246)	45.5

The hair came to a final shade in 10 minutes and after about 20 minutes the hair was washed and dried. The hair had a natural appearance in a dark brown shade and had good washing and other fastness properties desired for colored human hair. Penetration of the color was rapid and complete. Similar results were obtained by carrying out the process on old gray hair which had not been pre-bleached. In a similar manner lighter shades of browns, such as drabs, were obtained by using concentrations of dyestuff as low as 0.1% dye solution and 0.25% solution of ferrous sulfate. The predyeing operation can also be carried out by acidulating the dye solution with an organic acid, such as acetic acid or formic acid. This method of application is particularly advantageous to the dyeing of hair of widely different texture and condition found together in that it covers the various hairs more uniformly and evenly.

Example 5

Medium brown hair was treated with a 1% solution containing 90 parts of ferrous sulfate and 10 parts of a sodium salt of a technical dodecyl alcohol sulfate. The treatment was carried out at 110° F. by the same mechanics as for soap shampooing. This preparation combines a cleansing and mordanting operation whereby the natural oils and greases are removed from the hair which is a necessary pretreatment for all hair dyeing operations and at the same time the iron solution becomes fixed to act subsequently as a mordant for a later application of dye solution.

One of the advantages claimed for this treatment is that it eliminates the soap shampoo customarily used before hair dyeing and in some cases the pre-bleaching operations which is usually carried out with hydrogen peroxide before the dyeing. Dry physical mixtures containing 90 parts ferrous sulfate and 10 parts of a sodium salt of a technical dodecyl alcohol sulfate were prepared and stored for 6 months at room temperatures. At the end of this period a solution was used as a mordant to replace the ferrous sulfate solution cited in the foregoing examples. Its behavior was in all respects similar inasmuch as it produced with the foregoing dye solutions, hair having a natural appearance, good luster, and good washing and other fastness properties desired for colored human hair. Penetration of the color was rapid and complete and equal to that in the foregoing examples where iron sulfate

only was used. Similar results were obtained by carrying out the same process on old gray hair and medium brown hair.

Example 6

Old gray hair was treated for 10 minutes at 110° F. with a 2.0% solution of a carbon type of betaine having an alkyl chain of 8-20 carbon atoms at a pH of 8 or over. The hair was then dyed as in the various foregoing examples and it was found that this pre-treatment increased the affinity of mordant and dye solution for the hair. This is particularly advantageous for the dyeing of old gray hair which is more difficult to dye than young, healthy hair. Similarly, improved results were obtained by treatment with an 0.5% solution of a carbon type of betaine.

Example 7

Dyeings were made by all of the methods illustrated in Examples 1 to 6. These dyeings were then subjected to a normal bleaching with hydrogen peroxide such as is commonly used by hair dyeing operations previous to dyeing. Solutions of hydrogen peroxide varying from 5 volume to 20 volume, made slightly alkaline with ammonia, were used for the treatments at a temperature of 110° F. and for a period of 20 minutes. The colors were more or less completely removed from the hair. This property of these synthetic organic dyes being more or less completely removed by bleaching is of great value to the operator inasmuch as it allows the redyeing of hair from one color to another, without the necessity of, as at present, waiting for the hair to grow out again before redyeing. It is also possible, because of this property, to correct mistakes in dyeing which otherwise cannot be corrected satisfactorily for a long period.

Example 8

Medium brown hair was bleached by the application of a 20 volume solution of hydrogen peroxide made slightly alkaline with aqua ammonia for 30 minutes at 110° F. This was applied with a brush resembling a tooth brush. Then in order to insure complete removal of the last traces of peroxide, the hair was dried. A ½% solution of ferrous sulphate containing 10 parts per hundred of a sodium salt of a technical dodecyl alcohol sulphate was then applied to the hair at 110° F. by means of a shampooing operation similar to that for soap shampooing. This treatment was carried on for 20 minutes. The surplus iron solution was then removed by squeezing. A ½% solution of the following dye solution was then applied with a brush for ½ hour at 110° F.

	Parts
Pontachrome Yellow SW (C. I. 195 and Pro-totype 56)-----	10
Pontachrome Brown G (C. I. 238)-----	80
Logwood crystals (C. I. 1246)-----	10
	100

The hair was then shampooed to remove unfixed color and then dried. The hair had a natural appearance in a dark auburn shade, having good luster, good washing and other properties desired for human hair.

Example 9

One part of alum tanned rabbit pelt was treated by immersing in two parts of a 5% solution of a mixture containing 90 parts of ferrous sulphate

and 10 parts of a sodium salt of a technical dodecyl alcohol sulfate for about 30 minutes at 110° F. The pelt was squeezed to remove the surplus solution. It was then treated with a 5% solution of the following dye mixture:

	Parts
Pontachrome Brown G-----	94
Logwood crystals-----	6
	100

This treatment was carried out for 30 minutes at 110° F., after which the surplus dye solution was removed by washing with water. The brown shade produced by this treatment was much deeper and much more level than one which could be produced by a like dye solution or unmordanted tanned rabbit pelt, which is known to be difficult to dye at 110° F. The shade was unusually fast to washing and crocking.

Example 10

One part of chrome tanned shearling (woolled sheepskin) was treated by immersing in two parts of a 5% solution of ferrous sulphate for about 30 minutes at 110° F. The mordanted shearling was squeezed to remove the surplus solution. It was then treated with a 5% solution of the following dye mixture:

	Parts
Pontachrome Brown G-----	94
Logwood crystals-----	6
	100

This treatment was carried out for 30 minutes at 110° F., after which the surplus dye solution was removed by washing with water. The tan shade produced by this treatment was deeper and more level than one which could be produced by a like dye solution on unmordanted tanned shearling, which is known to be difficult to dye at 110° F.

Solutions of various water soluble lake-forming metal salts such as those of copper, aluminum, chromium and iron have been found particularly valuable for the processes of this invention. The iron salts, such as the chlorides, sulfates and acetates and those of water soluble sulfates of ferrous iron such as ferrous sulfate and ferrous ammonium sulfate are preferred. The iron salts work more rapidly at a moderate low temperature than the chromium salts, they produce shades which are more like the natural shades of human hair than the copper salts and they produce somewhat faster dyes, as a general rule, than the aluminum salts. Ordinarily solutions are used which contain from about 0.25% to about 5% of the metallic salt.

A solution of any of the various water soluble synthetic organic dyes selected from the class of chrome, acid, direct, disazo or basic dyes can be used. These dyes operate rapidly and produce a great variety of fast shades which can be varied in a number of ways, as by using a mixture of the dyes. For dyeing human hair the dyes classified as water soluble chrome dyes are preferred and among such dyes are the ones which are devoid of the amine group.

The term chrome dyes refers to the synthetic organic dyes which are generally applied on animal fibers with sodium or potassium bichromate or a neutral chromate by any one of the three methods, i. e., by premordanting with chrome salt, by after chroming with a chrome salt or by dyeing with dye and a chrome salt simultaneous-

ly and in the same bath. The term acid dyes refers to the synthetic organic dyes which are applied on animal fibers in a neutral or acid bath. The term direct dyes refers to the synthetic organic dyes which are generally applied on vegetable or cellulosic fibers and which vary in their animal fiber dyeing properties. The term diazo dyes refers to those synthetic organic dyes which are generally applied on vegetable or cellulosic fibers and which vary in their animal fiber dyeing properties. They can be dyed directly on vegetable fibers and then diazotized on the fiber and coupled with such components as beta naphthol, phenyl methyl pyrazolone, the arylides of beta hydroxy naphthoic acid, beta metatoluylene diamine or other coupling components of similar properties. The term basic dyes refers to those synthetic organic dyes which can be applied on animal fibers in a neutral or acid bath or on vegetable fibers premordanted with a metallic salt or a tannin-bearing organic compound. Ordinarily the synthetic organic dyes of the class described above are applied to cellulosic or animal fibers in dye baths which are heated to temperatures approaching that of the boiling point of water, temperatures which cannot be tolerated by a human being or by pelts which have not been tanned by processes yielding thermally stable leather.

The dyes must be capable of being applied in the form of solutions and the term water soluble dyes in the specification and claims refers to dyes which are readily soluble in water as well as those which can be more conveniently and rapidly put into solution by first dissolving in a water miscible organic solvent, such as alcohol and then diluting with water to the desired strength for use.

As other illustrations of the many synthetic dyes which produce the desired results which can be used alone or in mixtures of dyes similar to those specifically recited in the examples, the following are mentioned as listed by Colour Index, edited by F. M. Rowe and published by the Society of Dyers and Colourists (England), namely, Colour Index Numbers 10, 21, 101, 109, 151, 179, 203, 216, 234, 235, 246, 332, 420, 430, 561, 620, 640, 652, 655, 662, 696, 720, 749, 788, 789, 802, 814, 833, 841, 864, 865, 883, 909, 922, 1034, 1035, 1088 and 1091. Others to which Colour Index numbers have not been assigned are anthranilic acid→1-(o-chlor-m-sulpho - phenyl) - 3 - methyl-5-pyrazalone, para phenylene diamine→1:6 Cleves acid→1:6-Cleves acid→F acid, 2-amino naphthalene-6:8-disulphonic acid→meta toluidine→1:6-Cleves acid→meta toluidine-para amine benzoylated as described in U. S. P. 1,735,924, para nitro aniline→aniline, para nitro aniline→ethyl, hydroxy ethyl aniline, 1-amino-2-methyl anthraquinone, 1-amino-4-hydroxy anthraquinone, di-ortho toluy guanidine salt of C. I. 208 (U. S. P. 1,674,128), di-ortho toluy guanidine salt of amino G→resorcin←amino G acid (U. S. P. 1,674,128) and 4-nitro-2-amino-phenol→mixture of 4 parts of metaphenylene diamine and 1 part metatoluene diamine←Laurents acid.

The dye solution is ordinarily neither strongly alkaline nor strongly acid inasmuch as in general the solubility of the dyes is decreased as the acidity of the solution is increased and the affinity of the dyes is decreased as the alkalinity is increased. Ordinarily dye solutions will be suitable for use if their pH is within the range of about 5 to about 9.

The solution of the lake-forming metal salt and

the dye solution may be applied at a temperature not less than 40° F. but the preferred temperature for dyeing human hair is about 70° F. to about 110° F., since the action of the dye is faster, better quality dyeings are produced at these temperatures and temperatures as high as about 110° F. are not unduly uncomfortable to the scalp. However, any higher temperature, say about 130° F., can be used provided it does not injure the hair, the scalp or the pelt. The term, mildly heated as used in this specification and claims refers to temperatures of about 40° F. to about 130° F. The solutions, which are to be used, are heated and applied to the hair by the means of cotton, a suitable brush or any other applicator in a manner somewhat similar to brush dyeing.

Reasons for the surprising effectiveness of the described processes for the dyeing of hair are not fully understood, particularly because high temperatures are required in the application of direct colors to cellulosic fiber and high temperatures and acid dye baths are usually used in the application of acid colors to animal fibers such as wool. Under the conditions by which acid colors are applied to wool in the absence of acid, high temperatures appear to be necessary for the proper fixation of the dyestuff. The results produced by the process of the invention appear to indicate an unexpected affinity of the hair for the heavy metal salts of the synthetic organic dyestuff. This peculiar affinity of the hair for the heavy metal salt appears to exist independent of whether the salt is formed prior to this application to the hair as in Example 2 or whether it is formed in the hair as illustrated in Examples 1, 3, 4, 5, 6, 7 and 8.

This application is a continuation-in-part of our application Serial No. 324,084, filed March 15, 1940.

From the foregoing disclosure it will be recognized that the invention is susceptible of modification without departing from the spirit and scope thereof and it is to be understood that the invention is not restricted to the specific illustrations thereof herein set forth.

We claim:

1. The process of dyeing hair which comprises applying to the hair a lake-forming metal salt and a water-soluble synthetic organic dye, said salt and dye being in aqueous solution and being heated to a temperature of about 70° F. to about 110° F.
2. The process in accordance with claim 1 in which the dye is a chrome dye.
3. The process in accordance with claim 1 in which the lake-forming metal salt is a ferrous sulfate.
4. The process in accordance with claim 1 in which an aqueous solution of the lake-forming metal salt is applied to the hair and then an aqueous solution of the water-soluble synthetic organic dye is applied while the hair is still moist, said solutions being applied at a temperature of about 70° F. to about 110° F.
5. The process in accordance with claim 1 in which the aqueous solution of the lake-forming metal salt and the aqueous solution of the water-soluble synthetic organic dye are mixed before they are applied to the hair.
6. The process in accordance with claim 1 in which the solution of water-soluble synthetic organic dye is applied to the hair before the solution of the lake-forming metal salt is applied.

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CERTIFICATE OF CORRECTION.

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Patent No. 2,338,746.

January 11, 1944.

WILLARD FREDERICK VAN RIPER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 17, Example 9, for "solution or" read --solution on--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of March, A. D. 1944.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.