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METHOD AND PREPARATIONS FOR THE PERMANENT DYEING OF KERATINOUS MATERIAL

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The present invention relates to a method and to preparations for the permanent dyeing of keratinous material, such as human or animal hair, wool, fur, feathers and the like, and more particularly to a method and preparations for the permanent dyeing of the hair of living persons.

One object of the present invention is to provide a method for the permanent dyeing of keratinous material with non-toxic coal tar dyes at moderate temperatures and without the use of excessively acid or alkaline solutions.

Another object of the invention is to provide a method for the permanent dyeing of human hair with non-toxic coal tar dyes at temperatures which are easily tolerable for human skin and with neutral or moderately alkaline solutions which are harmless to the hair as well as to the skin.

A further object of the invention is to provide a method for permanently dyeing keratinous material, and particularly human hair, under suitable conditions with non-toxic coal tar dyes, in such a manner that the color is securely fixed in the dyed material and cannot be removed by rubbing, washing or shampooing.

A still further object of the invention is to provide a method for permanently dyeing human hair with non-toxic dyes in a manner to permit permanent waving of the dyed hair without change of the color imparted to the hair and without hair damage.

A still further object of the invention is to provide a method for permanently dyeing human hair with entirely non-toxic and harmless dyes, which method is easy and safe in its application, satisfactory in its results, and does not require either a pre-treatment or an after-treatment of the hair.

Still a further object of the invention is to provide a method of permanently dyeing human hair by means of the dyes which are known as certified colors and which heretofore have not been successfully used for this purpose.

Still another object of the invention is to produce a preparation for the permanent dyeing of keratinous material, and particularly of human hair, which can be applied to the hair in a simple manner and which produces the desired coloring easily and safely and without undesirable or harmful side effects or after effects.

A special object of the invention is to produce a preparation for the permanent dyeing of keratinous material, and particularly of human hair, which consists of two separate solutions to be mixed immediately before application to the material to be dyed, and which yields a mixture producing the desired coloring effect by means of certified colors in a reliable, safe and permanent manner.

Another special object of the invention is to produce a preparation for the permanent dyeing of keratinous material, particularly of human hair, which consists of a dry, powdery mixture of several water-soluble ingredients which, on dissolution in a predetermined amount of water, yield a dye solution applicable directly to the material to be dyed to produce the desired coloring by means of certified colors in a simple and safe manner.

These and other objects, which will appear in more detail as the description proceeds, are accomplished according to my invention by the methods and preparations described hereafter and defined in the appended claims.

Throughout the following description the term "by weight of the solution" is used to indicate that a specified number of parts by weight of solute is present in 100 parts by weight of solution.

Generally, the dyeing method according to my invention comprises the steps of treating the material to be dyed with a freshly prepared neutral to mildly alkaline, aqueous solution containing a small percentage of a water-soluble mercapto compound and, as sole coloring agent, a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, washing the dyed material with an aqueous medium, and drying it.

Heretofore, certified colors could be used for the permanent dyeing of keratinous matter only in strongly acid or strong salt solutions, and at elevated temperatures. As a result, difficulties arose in the use of such dyes for some purposes and, particularly, they could not be employed for the permanent dyeing of the hair of living persons unless the hair was subjected to complicated pre-treatments or after-treatments.

The present invention is based on my discovery that the Ext. D & C, D & C and F D & C certified, non-toxic coal tar dyes are suitable for the permanent dyeing of keratinous material at moderate temperatures and in neutral or mildly alkaline solutions, if a relatively small percentage of water-soluble mercapto compounds is added to the dye solutions immediately before they are used. My invention makes it possible to dye human hair in a simple manner permanently with dye preparations containing exclusively completely harmless and safe ingredients and to produce natural, predictable color shades which are fast to rubbing, washing, shampooing and permanent waving.

While I do not wish to be bound by any specific theory, my experiments seem to indicate that the mercapto compounds facilitate the transport of the dyestuffs directly into the cell structure of the keratinous material to be dyed and thus insure a thorough penetration and fixation of the dyes in the material to be colored.

I have found that hair substance itself, under the action of dissolved mercapto compounds in neutral or weakly alkaline aqueous solutions, absorbs not only water, but other substances dissolved in the aqueous mixture, such as dissolved dyestuffs. The size of the dyestuff molecules and the diffusion velocities of the dissolved substances seem to have little or no influence on their transportation. Even in the presence of relatively small proportions of mercapto compounds, the dyestuffs do not form merely a filter cake on the exterior of the hair shaft, which is removable by rubbing or washing, but pass with the liquid into the interior of the hair. The substances migrating with the water or transported thereby become effectively trapped or imbedded in the hair substance and are not subject to removal by customary treatments, such as rubbing, toweling, washing, shampooing or permanent waving. Microscopic examination has shown the hair fibers to be uniformly stained over the areas between the imbrications.

The expressions "Ext. D & C, D & C and F D & C certified colors" or simply "certified colors" as used in my specification and claims is intended to designate the coal tar dyes which are certified as permissible and pure by the Federal Food and Drug Administration. Such colors are certified as "F D & C" where they are per-

missible in Foods, Drugs and Cosmetics, as D & C where they are permissible in Drugs and Cosmetics, and as "Ext. D & C" where they are permissible in Drugs and Cosmetics for external application only.

It has been found that dye solutions suitable for the dyeing of keratinous material according to my invention may contain preferably between about 0.033 and 6.2% by weight of the solution of such dyestuffs.

The water-soluble mercapto compounds to be used in the dye solutions according to my invention are particularly the water-soluble mercapto compounds of the general type useful for hair waving and depilatory purposes. Suitable examples are thioglycolic and thiosalicylic acids in the form of their water-soluble salts, thioglycol, thioglycerol and thiophenol. At present, I prefer in most cases to use thioglycolic acid because it is readily available, has no intense objectionable odor, and is ordinarily entirely harmless in the concentrations in which it is used according to my invention, but I do not limit my invention either to this or to any other particular mercapto compound. The water-soluble mercapto compounds are present in my dye solutions in quantities equivalent with respect to S H group to about 0.1 to 6% by weight of the solutions of thioglycatic acid. For hair dyeing purposes, a mercapto compound content equivalent with respect to S H group to between about 1.2% and about 6% by weight of the solution of thioglycolic acid has been found to give most favorable results.

The temperatures used in my dyeing processes may vary between about 50° and about 110° F. Temperatures of between about 60° and about 80° F. are preferred, particularly in the use of my invention for the permanent dyeing of human hair.

The dye solutions according to my invention are applied to the keratinous material at a pH value between about 6.6 and about 11.3 and preferably at a pH value of between about 9 and 10.2. As basis for the establishment and maintenance of the desired pH values, I have successfully used concentrated aqueous ammonia, sodium hydroxide, sodium carbonate in the presence of ammonium chloride, ethylene diamine, and triethanolamine. Other alkalies could undoubtedly be employed. For most purposes, I prefer to use concentrated aqueous ammonia and sodium hydroxide either separately or in suitable mixtures.

In general, I have found predominantly aqueous solutions of dyestuffs and mercapto compounds well adapted for color transportation into and color fixation in hair. Small additions of water miscible organic solvents, such as propylene glycol, ethyl alcohol, tetra-hydrofurfuryl alcohol or the like may be advantageous in order to improve the solubility of the coal tar dyes.

Useful effects in coloring hair are accomplished at temperatures of between about 60° F. and about 80° F. with relatively weak solutions of mercapto compounds and usually at mild alkalinities. I have found adequate, for example, up to about 4% by weight of the solution of thioglycolic acid at alkalinities corresponding to pH values of not more than about 10.5 during 15 to 25 minutes. Many of my successful hair dyeings, accomplished without evidence of any resultant hair damage have been performed with less than 2.6% by weight of the solution of thioglycolic acid in the form of its sodium salt, with excess of ammonia as free base at pH values of about 9 to 10 at a temperature of about 68° F. within about 15 to 20 minutes. This combination of conditions lies well within allowable extremes and may be adopted as normal. Increase above normal in any of the three principal factors, namely, concentration of mercapto compound, alkalinity in pH terms, and temperature, intensifies not only the resultant coloration, but also the action of the remaining unaltered factors upon the hair substance. With increase toward higher extremes of these factors, and particularly when large increases in two factors occur together, hair substance may tend to absorb excessive

amounts of water with undesirable swelling, distortion and softening of the hair. The fiber may thereby be weakened and actual disintegration of the hair may occur unexpectedly on washing or combing. An unfavorable result caused by the elevation of one factor above normal may often be forestalled by expedient lowering below normal of one or more of the other factors. If considerably high concentrations of mercapto compounds are employed, such as, for instance amounts equivalent with respect to S H group to 4.5 to 6% by weight of the solution of thioglycolic acid, then alkalinity should be adjusted to a lower pH value, for instance, 9.4 or less to preclude irreversible hair damage. If a high temperature is employed, such as, for example, 110° F., then a moderate concentration of mercapto compound, for instance, in the range of up to about 2.5% by weight of the solution of thioglycolic acid, may require lowering of the pH value below 9.3 in order to preclude hair damage. For example, very good hair coloration, without any evidence of hair damage, may be effected with 2.5% by weight of the solution of thioglycolic acid acting upon hair at 110° F. during 15 minutes at a pH of 8.0. Decrease below normal of any of the three factors diminishes the risk of hair damage but weakens correspondingly the resultant coloration. Thus with color solutions, for instance, in the neighborhood of 50° F., coloring action is appreciably less than at 60° to 80° F. for 1.4% by weight of the solution of thioglycolic acid at a pH of 9.4 acting during 20 minutes. With 0.5% by weight of the solution of thioglycolic acid, coloring action is appreciably less than with 1.4% by weight of the solution of thioglycolic acid, other conditions remaining the same for both cases. At a pH value of 7.7, coloring action is appreciably less than at a pH of 8.5 for 2.5% by weight of the solution of thioglycolic acid at 70° F. during 20 minutes. Minima for concentration of mercapto compound, pH, and temperature are not imposed like maxima, by the susceptibility of hair to damage, but are chosen when low values for one or more factors require considerable increase above normal in one or more of the remaining factors for good and intense coloring of the hair.

Contact between hair and dye solution should be maintained for at least several minutes. A period as short as above five minutes may produce appreciable coloration of the hair, but with tinting action during six minutes, the resulting coloring is appreciably weaker than with tinting action during fifteen minutes for 2.5% by weight of the solution of thioglycolic acid at 70° F. and a pH value of 9.4. Ordinarily, it is not necessary or desirable to maintain the hair in contact with the dye solution for more than a maximum time of thirty-five minutes. However, where the pH value of the solution is low or the temperature used is below 70° F., contact times of from 1 to 2 hours may have no detrimental effect on the hair, although generally, after the first thirty minutes, no significant increase in intensity of coloration has been observed.

I have found that in the dyeing of human hair, it is preferable to use solutions containing, in addition to the dissolved dyestuffs, an amount of mercapto compound equivalent with respect to S H group to about 1.2% to 6% by weight of the solution of thioglycolic acid.

Preferably the solutions have a pH value between 6.6 and 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid. The solution is applied to the hair at a temperature of between about 50° F. and 110° F. but not less than 70° F. when both mercapto concentration and pH value approach their minimum values and not higher than 80° F. when both mercapto concentration and pH value approach their maximum values.

According to a preferred embodiment of my inven-

tion, the mercapto content of the solution is kept below about 4% by weight of the solution. This has the advantage that the hair is not appreciably affected by the reducing action of the mercapto compounds and, consequently, no oxidizing after-treatment of the dyed material is necessary. After the dyeing operation itself, the dyed material is simply rinsed with water to remove the excess dye in order to produce a permanent coloring which is fast against rubbing or shampooing. However, it is possible to use solutions containing more than about 4% and up to about 6% by weight of the solution of water-soluble mercapto compounds. In these cases the dyed material, after application of the dye solution thereto, is preferably treated with a mild oxidizing agent, such as hydrogen peroxide.

While most of the certified colors when used in accordance with my invention will produce the desired color values on hair with hair coloring effects which are fast to rubbing, washing, shampooing and permanent waving without any after-treatment, in some cases it may be useful to apply to the dyed hair an after-treatment for the purpose of color development, color intensification or improved color fixation. Mild oxidizing agents, such as hydrogen peroxide, and acids, such as acetic acid, may be used in these cases, which are within the broad scope of my invention, for after-treatment of the dyed hair.

My invention also covers the new preparations for the permanent dyeing of keratinous material to be used in my method. Such preparation may be, for instance, a neutral or mildly alkaline solution containing in an aqueous solvent a small percentage of a water-soluble mercapto compound and, as sole coloring agent, a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof. Preparations which are intended for the dyeing of human hair contain preferably a quantity of water-soluble mercapto compound equivalent with respect to SH group to about 1.2% to 6% by weight of the solution of thioglycolic acid and have a pH value of between 6.6 to 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid.

Since many of the certified colors may deteriorate if they remain in a solution containing mercapto compounds for any length of time, it is essential that the dye components of the solutions are combined with the mercapto components immediately before application to the keratinous material to be dyed. Preferably, the dye-mercapto solutions are freshly prepared from two separate starting solutions immediately before they are used.

Thus, a preparation of the dyeing of keratinous material, and particularly of human hair, may comprise a separate dye solution containing as sole coloring agent a dyestuff selected from the Ext. D & C, D & C and F D & C certified colors and mixtures thereof in an aqueous solvent, and a separate water solution of a water-soluble mercapto compound, the two solutions being adapted to be combined into a mixture for application to the keratinous matter to be dyed, the respective pH values of the two solutions, the total quantity of solvent in both solutions and the relative proportions of the solutions being such that the resulting mixture is neutral or mildly alkaline and contains a small percentage of a water-soluble mercapto compound.

According to another embodiment of my invention, a preparation for the dyeing of keratinous material, and particularly of human hair, may be a substantially dry powder mixture comprising a dry, water-soluble solid mercapto compound, an ammonium salt, a dry, weakly alkaline, water-soluble salt of an alkali metal, and, as sole coloring agent, a dry, water-soluble dyestuff selected from the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, the several ingredients being present in such proportions that, on addition thereof to a predetermined quantity of water, a dye solution is formed which contains a small percentage of mercapto compound and is neutral or mildly alkaline.

The following examples are intended to illustrate the invention without limiting its scope, and to show clearly the absence of transport of dissolved dyesuffs into the hair and other keratinous material in the absence of mercapto compounds in contrast to the immediate activation of such transport of dyestuffs in the presence of small percentages of mercapto compounds under otherwise identical conditions.

Example I

Firm textured, nearly colorless human hair was immersed for 15 minutes at a temperature of 70° F., with exclusion of air, in a solution carrying 0.920 g. of a dyestuff mixture consisting of:

D & C Black #1 (C. I. 246)
D & C Brown #1 (C. I. 234)
Ext. D & C Red #13 (C. I. 252)
4.0 ml. concentrated ammonia water
q. s. water to make 102 ml.
pH—9.9

After 15 minutes the hair was next immersed for 15 minutes in 20 volume hydrogen peroxide in 7 percent acetic acid, then finally shampooed and toweled. The hair retained a pale gray coloration. No appreciable dyeing of the hair had been accomplished.

10 ml. of ammoniacal thioglycolate solution were then added to the previously described solution, the resulting mixture having substantially the following composition:

0.920 g. dyestuff mixture
1.4 g. thioglycolic acid
6.0 ml. concentrated ammonia water
q. s. water to make 112 ml.
pH—9.5

The thioglycolic acid content of the mixture amounted by weight of the solution and the dyestuff content amounted to 0.8% by weight of the solution.

For comparison, hair of the same character was similarly immersed for 15 minutes at 70° F. with exclusion of air in this solution. After 15 minutes, the hair was next immersed for 15 minutes in 20 volume hydrogen peroxide in 7 percent acetic acid, then finally shampooed and toweled. The hair retained a moderate ash blonde coloration, approaching brown, but lacking warmth or redness. A permanent dyeing had resulted.

Example II

Firm textured, nearly colorless human hair was saturated for 3 minutes in a solution containing 3.89 g. of a dyestuff mixture consisting of:

D & C Black #1 (C. I. 246)
F D & C Yellow #5 (C. I. 640)
Ext. D & C Red #8 (C. I. 176)
D & C Red #33 (C. I. 30)
4.0 ml. concentrated ammonia water
q. s. water to make 86 ml.
pH 8.9

The hair was then exposed for 15 minutes to the atmosphere while wet. Cooling of the solution during the exposure period took place, the average temperature being estimated to be about 60° F.

After 15 minutes the hair was in part merely rinsed and blotted, then dried, in part well-shampooed, then rinsed, blotted and dried. The rinsed hair retained a pale pink-violet coloration, the shampooed hair a distinctly paler pink-violet coloration. Most of the pale color adhering to the merely rinsed hair was located superficially and was removable by shampooing. The hair was not permanently dyed.

Upon addition of 10 ml. of ammoniacal thioglycolate

solution to this dye solution, a mixture resulted which had the following composition:

3.89 g. of dyestuff mixture
2.5 g. thioglycolic acid
1.1 g. sodium hydroxide
7.41 ml. concentrated ammonia aqua
q. s. water to make 96 ml.
pH—9.25

In this mixture, the thioglycolic acid content amounted to 2.6% by weight of the solution, the dyestuff content to about 4% by weight of the solution.

For comparison, hair of the same character was similarly saturated for 3 minutes and then exposed wet for 15 minutes to the atmosphere under identical temperature conditions estimated on the average to be about 60° F. After 15 minutes, the hair was in part merely rinsed and blotted, then dried, in part well shampooed, then rinsed, blotted and dried. The merely rinsed hair retained a strong violet-brown coloration, the shampooed hair likewise a strong violet-brown coloration, hardly distinguishable from that of the merely rinsed hair. The hair was substantially dyed.

Example III

A solution was prepared containing:

0.320 g. D & C Black #1 (C. I. 246)
0.800 g. D & C Orange #3 (C. I. 27)
0.700 g. Ext. D & C Red #13 (C. I. 252)
Total 1.820 g. dyestuff mixture

25.0 ml. propylene glycol
q. s. water to make 90 ml.

To this solution was added immediately before use 10 ml. of ammoniacal sodium thioglycolate solution containing:

2.5 g. thioglycolic acid
1.1 g. sodium hydroxide
3.4 ml. concentrated ammonia aqua

The resulting 100 ml. solution had a pH of 10.1. The thioglycolic acid content was 2.5% by weight of the solution.

This mixture was immediately applied at a temperature of 68° F. to uncolored human hair, conveniently by a brush. the wet hair was allowed to remain exposed to the atmosphere for 20 minutes at a temperature at which the wet solution was maintained substantially constant at 60° F. Thereafter, the dark excess of dye was rinsed from the hair with warm water until the washings were substantially colorless. The hair was then gently toweled and finally dried with a warm air current. The hair retained a natural and pleasing dark auburn coloration. It was subsequently gently shampooed with only an insignificant change of hair coloration resulting from even the first shampooing.

Example IV

0.800 g. D & C Black #1 (C. I. 246)
0.600 g. D & C Orange #3 (C. I. 27)
0.500 g. F D & C Yellow #6 (a dyestuff obtained by coupling diazotized sulfanilic acid with 2-naphthol-6-sulfonic acid)
1.000 g. Ext. D & C Red 13 (C. I. 252)
Total 3.900 g. dyestuff mixture

25.0 ml. propylene glycol
1.1 g. sodium hydroxide
1.7 ml. of concentrated ammonia aqua were dissolved with water in a volume of 90 mls., pH—12.15

To this solution was added, immediately before use, 10 ml. of substantially neutral ammonium thioglycolate solution, carrying 2.5 g. thioglycolic acid to make 100 ml. solution having a pH of 9.7.

The mixture was immediately applied at a temperature of about 77° to uncolored hair conveniently by a brush. The wet hair was allowed to remain exposed to the atmosphere for 20 minutes at a temperature at which the evaporation of the water caused some cooling down of the solution. The average temperature of 20 minutes exposure time was estimated to be about 75° F.

After 20 minutes, the dark excess of dye was rinsed from the hair with warm water until the washings were substantially colorless. The hair thereafter was gently toweled and finally dried with a warm air current. The hair maintained a permanent, dark brown, very natural coloration.

In some cases, where very intense hair coloration is desired, not all of the dyestuffs participating in the final color-quality remain reliably compatible in high concentrations. In such cases a repeated treatment of the hair with a weaker dye mixture may be convenient, employing in each treatment a dye mixture, with a smaller proportion of mercapto compound. This may be illustrated by the following:

Example V

A mixture was prepared of:

2.4 g. D & C Black #1 (C. I. 246)
1.7 g. D & C Orange #3 (C. I. 27)
2.1 g. Ext. D & C Red #13 (C. I. 252)

Total 6.2 g. dyestuff mixture

25.0 ml. propylene glycol
q. s. water to make 93 ml.

To this mixture is added, immediately before use, 7.0 ml. of ammoniated sodium thioglycolate solution, carrying:

1.75 g. thioglycolic acid
0.78 g. sodium hydroxide
2.4 ml. concentrated ammonia aqua to make 100 ml. solution, pH—10.0

The mixture was at once applied to uncolored hair, conveniently by brief immersion thereof, and the wet hair allowed to remain exposed to the atmosphere at a temperature of 66° F. for 20 minutes. Thereafter, the dark excess of color was rinsed from the hair with warm water, until the washings were substantially colorless. The hair was then gently toweled and dried in a warm air current. The hair retained a dark brown coloration, nearly a black. Immediately thereafter, a portion of the dyed and dried hair was identically treated with an identical mixture of the same quantities of the same dyes as above, freshly mixed with 7 ml. of the same sodium thioglycolate solution. After 20 minutes exposure of the wet hair to the atmosphere at 66° F., the hair was similarly rinsed as above, toweled and dried. The hair retained a black coloration. No hair damage was evident.

Example VI

2.4 g. D & C Black #1 (C. I. 246)
1.7 g. D & C Orange #3 (C. I. 27)
2.1 g. Ext. D & C Red #13 (C. I. 252)

Total 6.2 g. dyestuff mixture was dissolved in a solvent containing:

25.0 ml. propylene glycol
1.5 g. sodium hydroxide
4.0 g. thioglycolic acid
2.86 ml. concentrated ammonia aqua
q. s. water to make 100 ml.
pH—9.45

In the fresh mixture, firm textured, nearly colorless human hair was saturated for 3 minutes at a temperature of about 74° F. and then exposed to the room atmosphere for 20 minutes in wet condition. Over the entire contact period of 23 minutes, the solution had on the average a

temperature of about 66° F. At the end of the 20 minute period, the hair was well rinsed with warm water and dried. The hair retained a beautiful, dark, warm brown coloration, and there was no indication of damage to the hair.

Example VII

6.2 g. of dyestuff mixture having the same composition as in the preceding example were dissolved in a solvent containing:

25.0 ml. propylene glycol
2.0 g. sodium hydroxide
5.5 g. thioglycolic acid
3.86 ml. concentrated ammonia aqua
q. s. water to make 100 ml.
pH—9.30

In the fresh mixture, firm textured, nearly colorless human hair was saturated for 3 minutes at about 74° F., then exposed to room temperature for 20 minutes in wet condition. The over-all temperature of the solution throughout the contact time of 23 minutes was about 66° F. At the expiration of the 20 minute period, the hair was rinsed, then treated for 10 minutes at a temperature of about 68° F. with 5 volumes hydrogen peroxide solution carrying 3% of acetic acid. After final rinsing and drying, the hair retained a very dark brown coloration, almost a black. No indication of hair damage appeared at any stage of treatment.

Example VIII

6.2 g. of a dye mixture having the same composition as in the preceding two examples were dissolved in a solvent containing:

25.0 ml. propylene glycol
2.2 g. sodium hydroxide
6.0 g. thioglycolic acid
4.21 ml. concentrated ammonia aqua
q. s. water to make 100 ml.
pH—9.15

In the fresh mixture, firm textured, nearly colorless human hair was saturated for 3 minutes at 79° F. and then exposed to the room atmosphere for 20 minutes in wet condition. The average temperature over the entire 23 minutes of contact was about 66° F.

At the end of 20 minutes exposure, the hair was rinsed, then treated for 10 minutes at room temperature with 5 volumes of hydrogen peroxide solution carrying 3% of acetic acid, finally rinsed and dried. The hair retained a very dark, drab brown coloration, almost a black. There was no indication of hair damage apparent at any stage of the treatment.

Example IX

A solution was prepared carrying:

0.50 g. D & C Violet #1 (C. I. 697)
2.50 g. thioglycolic acid
1.1 g. sodium hydroxide
7.41 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH 10.4

In the fresh solution, firm textured, uncolored human hair was saturated for 3 minutes at about 73° F., then exposed in wet condition to the room atmosphere for 20 minutes. During the entire contact time of 23 minutes, the average temperature of the solution was about 64° F. Thereafter, the hair was well rinsed and dried. It retained a permanent pronounced blue coloration.

Example X

A solution was prepared carrying:

0.50 g. D & C Violet #1 (C. I. 697)
2.50 g. thioglycolic acid
2.55 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH 8.52

In the fresh mixture, firm textured, colorless human hair was saturated for 3 minutes at a temperature of about 76° F. and then exposed in wet condition to the room atmosphere for 20 minutes. The average temperature of the solution throughout the total exposure time of 23 minutes was estimated to be about 68° F.

At the end of the 20 minutes, the hair was well rinsed and dried. The hair retained a pronounced blue coloration, slightly duller and a little more reddish than the final blue of Example IX.

Example XI

A solution was prepared carrying:

0.250 g. D & C Black #1 (C. I. 246)
0.600 g. D & C Orange #3 (C. I. 27)
0.500 g. F D & C Yellow #6 (a dyestuff obtained by coupling diazotized sulfanilic acid with 2-naphthol-6-sulfonic acid)
0.300 g. Ext. D & C Red #13 (C. I. 252)
Total 1.650 g. dyestuff mixture

25.0 ml. propylene glycol
2.5 g. thioglycolic acid
1.1 g. sodium hydroxide
3.41 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH—9.40

The fresh solution was chilled to 50° F. and firm textured, uncolored human hair was immediately immersed therein at 50° F. for 15 minutes. Thereafter the hair was rinsed, blotted, and dried. The hair retained a pale, golden blonde coloration, very natural.

Example XII

A solution was prepared carrying 1.65 g. of a dyestuff mixture having the same composition as in Example XI, and

25.0 ml. propylene glycol
2.5 g. thioglycolic acid
2.95 ml. concentrated ammonia water
q. s. water to make 100 ml. pH—8.0

The fresh solution was warmed to 110° F., and firm textured, uncolored human hair was immediately immersed therein at 110° F. for 15 minutes. Thereafter the hair was rinsed, blotted and dried. The hair retained a dark, warm brown color, very natural. No evidence appeared of hair damage.

Example XIII

A solution was prepared carrying 1.56 g. of a dyestuff mixture having the same composition as in Example XII, and

25.0 ml. propylene glycol
2.5 g. thioglycolic acid
1.95 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH—6.60

The fresh solution was warmed to 110° F. and firm textured, uncolored human hair immediately immersed therein at 110° F. for 15 minutes. Thereafter the hair was rinsed, blotted and dried. The hair retained a brownish, light-auburn coloration, much less intense than the dark, warm brown color retained after identical procedure with a corresponding solution, at pH—8.0 at the same temperature as in Example XII.

Example XIV

A solution was prepared containing:

0.160 g. D & C Black #1 (C. I. 246)
0.750 g. D & C Orange #3 (C. I. 27)
0.600 g. F D & C Yellow #6 (a dyestuff obtained by coupling diazotized sulfanilic acid with 2-naphthol-6-sulfonic acid)
0.140 g. Ext. D & C Red #13 (C. I. 252)
Total 1.650 g. dyestuff mixture

25.0 ml. propylene glycol
2.5 g. thioglycolic acid
1.1 g. sodium hydroxide
3.41 ml. concentrated ammonia squa
q. s. water to make 100 ml. pH—9.40

Firm textured, uncolored human hair was dipped in this solution at 68° F. for three minutes and then exposed to the atmosphere for 5 minutes at 66° F. The hair was then rinsed, blotted and dried. A permanent dyeing of the hair to a light, ash blonde, was obtained.

Repeating the same procedure with exposure times of 10, 20 and 30 minutes respectively, the final coloration became progressively more intense, until, with 30 minute exposure, a very natural, dark ash-blonde with red overtones was obtained.

Example XV

A mixture, in powder form, consisting of:

0.250 g. D & C Black #1 (C. I. 246)
0.600 g. D & C Orange #3 (C. I. 27)
0.500 g. F D & C Yellow #6 (a dyestuff obtained by coupling diazotized sulfanilic acid with 2-naphthol-6-sulfonic acid)
0.300 g. Ext. D & C Red #13 (C. I. 252)

Total 1.650 g. dyestuff mixture

3.9 g. calcium thioglycolate, equivalent to 2.4 g. thioglycolic acid
4.5 g. sodium carbonate—c. p., anhydrous
3.0 g. ammonium chloride, U. S. P. was shaken to solution in water to make 100 ml. having a pH=9.4.

In the fresh mixture, firm textured uncolored human hair was saturated for 3 minutes at 70° F., then exposed in wet condition to the room atmosphere for 20 minutes, the average temperature of the solution for the entire contact time being estimated as 66° F. At the end of the 20 minutes, the hair was well rinsed and dried. It retained a beautiful, very natural dark brown coloration.

Example XVI

A solution was prepared carrying:

1.0 g. F D & C Green #2 (C. I. 670)
1.0 g. D & C Red #33 (C. I. 30)

Total 2.0 g. dyestuff mixture

1.23 g. ethylene diamine
2.14 g. 2-mercapto-ethanol (equivalent to 2.53 g. of thioglycolic acid)
q. s. water to make 100 ml.; pH=9.6

Firm textured, uncolored human hair was saturated briefly in the fresh solution and then exposed in wet condition to the room atmosphere for 15 minutes at a temperature to retain the solution at about 66° F. throughout the exposure period. Thereafter, the hair was immersed for 15 minutes in 4% acetic acid solution, finally shampooed, rinsed and dried. The hair retained a strong bluish red permanent coloration.

Example XVII

A solution was prepared carrying:

0.40 g. D & C Red #33 (C. I. 30)
0.40 g. F D & C Blue #1 (C. I. 671 is the ammonium salt)
1.60 g. D & C Orange #3 (C. I. 27)
0.25 g. Ext. D & C Red #13 (C. I. 252)

Total 2.65 g. dyestuff mixture

25.0 ml. propylene glycol
2.63 g. monothioglycerol (1 mercapto-2,3 propane diol), (equivalent to 2.24 g. of thioglycolic acid)
3.14 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH=9.8

Firm textured, uncolored human hair was saturated in the fresh solution at 70° C. for 3 minutes, then exposed in wet condition to the room atmosphere for 20 minutes. During the entire contact period of 23 minutes the temperature of the solution averaged about 66° F. At the end of the 20 minutes, the hair was shampooed, rinsed and dried. The hair retained a coppery red coloration.

Example XVIII

A solution was prepared carrying:

0.250 g. D & C Black #1 (C. I. 246)
0.600 g. D & C Orange #3 (C. I. 27)
0.500 g. F D & C Yellow #6 (a dyestuff obtained by coupling diazotized sulfanilic acid with 2-naphthol-6-sulfonic acid)
0.300 g. Ext. D & C Red #13 (C. I. 252)

Total 1.650 g. dyestuff mixture

25.0 ml. propylene glycol
3.0 g. thiophenol (equivalent to 2.5 g. of thioglycolic acid)
3.44 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH=9.5

Firm textured, uncolored human hair was saturated in the fresh solution at about 74° F. for 3 minutes and then exposed in wet condition to the room atmosphere for 20 minutes. The average temperature during the entire contact time of 23 minutes was about 66° F.

At the end of 20 minutes, the hair was rinsed and dried. It retained a reddish blond coloration.

Example XIX

A solution was prepared containing 1.65 g. of a dye mixture having the same composition as in Example XIX, and:

25.0 ml. propylene glycol
4.18 g. thiosalicylic acid (equivalent to 2.5 g. of thioglycolic acid)
5.3 ml. concentrated ammonia aqua
q. s. water to make 100 ml. pH=9.6

Firm textured, uncolored human hair was saturated in the fresh solution for 3 minutes at 74° F. and then exposed in wet condition to the room atmosphere for 20 minutes. The average temperature of the solution throughout the exposure period of 23 minutes was about 66° F.

After 20 minutes, the hair was rinsed and dried. It retained a light, coppery brown color which was permanent.

In numerous other instances, both with mixtures of certified colors and with single certified colors, I have established by similar comparative tests that a negligible to slight fixation in hair of color from neutral or alkaline solutions in the absence of mercapto compounds, can be transformed into strong and useful fixation in hair of the same colors merely by the added presence in the color solutions of mercapto-compounds. Such further instances include:

Ext. D & C Blue #1 (Methylene Blue) C. I. 922
D & C Violet #1 (Wool Violet 5BN) C. I. 697
D & C Orange #5 Dibromofluorescein
Ext. D & C Yellow #3 (Fast Light Yellow) C. I. 636
F D & C Red #1 (Ponceau 3R) C. I. 80
F D & C Red #2 (Amaranth) C. I. 184
D & C Red #19 (Rhodamine B) C. I. 759
D & C Red #27 (Tetrachlorotetrabromofluorescein)

The following examples are intended to show that

wool can also be permanently dyed with my dye preparations at ordinary temperatures:

Example XX

A solution was prepared containing:

0.300 g. D & C Black #1 (C. I. 246)
0.088 g. D & C Brown #1 (C. I. 234)
0.113 g. Ext. D & C Red #13 (C. I. 252)

Total 0.501 g. of dyestuff mixture

1.0 g. Dupanol C (sodium lauryl sulfate)
q. s. water to make 85 ml. pH=6.25

In this mixture there was immersed for 20 minutes at 80° F. a strip of white all wool fabric, which was thereafter rinsed to nearly colorless with water. Wool is not dyed by brief contact at ordinary temperatures with the nearly neutral dyestuff mixture. To the nearly neutral dye-mixture were next added and well-mixed 2.5 ml. of concentrated ammonia-aqua to make 87–88 ml. pH 11.3. A duplicate strip of white, all-wool fabric was immersed therein for 20 minutes at 76° F. The wool was thereafter briefly dipped in 5 percent acetic acid solution, and finally rinsed with warm tap water. The wool retained a faint grayish color. The wool is incipiently, but weakly, dyed, at ordinary temperatures with the weakly alkaline mixture of dyestuffs.

To the ammoniacal dye mixture was next added, and well mixed, 5 ml. of ammoniacal sodium thioglycolate solution carrying:

1.4 g. thioglycolic acid
0.6 g. sodium hydroxide
0.4 ml. concentrated ammonia aqua, to make 93 ml. pH=9.93

A triplicate strip of white, all wool fabric was immersed for 20 minutes at 76° F. The wool was thereafter briefly dipped in 5% acetic acid solution, then shampooed warm, and warm rinsed. The wool retained an intense, dull black color. Wool is deeply dyed at ordinary temperatures by brief contact with the combination of alkaline mercapto compound with the dyestuffs.

Example XXI

A solution was prepared carrying:

0.300 g. D & C Black #1 (C. I. 246)
0.088 g. D & C Brown #1 (C. I. 234)
0.113 g. Ext. D & C Red #13 (C. I. 252)

Total 0.501 g. of dyestuff mixture

1.0 g. Dupanol C (sodium lauryl sulfate)
2.64 ml. concentrated ammonia aqua
0.1 g. thioglycolic acid
0.03 g. sodium hydroxide
q. s. water to make 100 ml.
pH=11.3

In the fresh mixture a strip of white, all wool fabric was immersed for 20 minutes at 66° F., thereafter dipped for 5 minutes in 5% aqueous acetic acid at 66° F., finally shampooed in warm water, rinsed, and dried. The wool retained a distinct, even, gray color, appreciably stronger than the faint grayish color obtained in the entire absence of thioglycolate, and much weaker, than the dull black color obtained in the presence of the 14–15 times stronger thioglycolate used in Example XX.

Example XXII

Wool was treated with the solution and by the method described in Example XXI at 50° F. for 15 minutes. After subsequent rinsing and drying, the wool retained a pronounced permanent, medium gray coloration without any evident alteration of the texture or strength.

Example XXIII

Wool was treated with the solution and in the manner described in Example XXI at pH 8, and at a temperature of 110° F., for 15 minutes. After rinsing and drying, the wool retained a beautiful velvet black. It had been permanently dyed. No wool damage was evident. The dyed fabric remained soft and pliable.

Example XXIV

Wool was dyed in the solution and by the process described in Example XXI at pH 6.6, and at a temperature of 110° F., for 15 minutes. After rinsing and drying, the wool retained a permanent, very dark reddish brown coloration, noticeably lighter than the velvet black retained after the identical procedure with a corresponding solution at pH 8.0 as described in Example XXIII.

What is claimed is:

1. A method for the permanent dyeing of keratinous material, which comprises treating the material to be dyed with a freshly prepared aqueous solution containing a quantity of a water soluble mercapto compound of low toxicity equivalent with respect to SH group to about 0.1 to about 6% by weight of the solution of thioglycolic acid and, as sole coloring agent, about 0.033 to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified, colors and mixtures thereof, the solution having a pH value between about 6.6 and about 11.3, then washing the dyed material with an aqueous medium and drying the same.

2. A method as claimed in claim 1 in which the material to be dyed is treated with dyestuff solution at a temperature between about 50° F. and 110° F.

3. Method as claimed in claim 1, in which the pH value of the solution is maintained between 9 and 10.2.

4. A method for the permanent dyeing of human hair which comprises the steps of treating the hair to be dyed, at a temperature of between about 50° F. and 110° F., with a freshly prepared aqueous solution of a quantity of a water-soluble mercapto compound of the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol equivalent with respect to SH group to about 1.2% to 6% by weight of the solution of thioglycolic acid and containing, as sole coloring agent, about 0.033% to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, the solution having a pH value between 6.6 and 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid, then washing the dyed hair with an aqueous medium and drying the same.

5. A method as claimed in claim 4, in which the pH value of the solution is maintained between 9 and 10.2.

6. A method as claimed in claim 4, in which the mercapto compound used is thioglycolic acid.

7. A method for the permanent dyeing of human hair which comprises the steps of treating the hair to be dyed with a freshly prepared aqueous solution of a quantity of a water-soluble mercapto compound of the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol equivalent with respect to SH group to about 1.2% to 6% by weight of the solution of thioglycolic acid and containing, as sole coloring agent, about 0.033% to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, said solution having a pH value between 6.6 and 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid, said solution being applied to the hair at a tempera-

ture of between about 50° F. and 110° F. but not less than 70° F. when both mercapto concentration and pH value approach their minimum values and not higher than 80° F. when both mercapto concentration and pH value approach their maximum values.

8. A method as claimed in claim 7, in which the pH value of the solution is maintained between 9 and 10.2.

9. A method as claimed in claim 7, in which the dye solution is left in contact with the hair for a period of about 5 minutes to about 35 minutes.

10. A method for the permanent dyeing of human hair which consists of the steps of treating the hair to be dyed at a temperature of between about 50° F. and 110° F. with a freshly prepared aqueous solution of a quantity of a water-soluble mercapto compound of the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol equivalent with respect to SH group to about 1.2% to 4% by weight of the solution of thioglycolic acid and containing, as sole coloring agent, about 0.033% to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, said solution having a pH value of between 6.6 and 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid, then washing the dyed hair with an aqueous medium and drying the same.

11. A method for the permanent dyeing of human hair which consists of the steps of treating the hair to be dyed at a temperature between about 50° F. and 110° F. with a freshly prepared aqueous solution of a quantity of a water-soluble mercapto compound of the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol equivalent with respect to SH group to about 4% to 6% by weight of the solution of thioglycolic acid and containing, as sole coloring agent, about 0.033% to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, said solution having a pH value between 6.6 and 9.4 but not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid, then treating the dyed hair with a mild oxidizing agent, washing the hair with an aqueous medium and drying the hair.

12. A preparation for the permanent dyeing of keratinous material in the form of an aqueous solution having a pH between about 6.6 and about 11.3 and containing a quantity of a water-soluble mercapto compound of low toxicity equivalent with respect to SH group to about 0.1 to about 6% by weight of the solution of thioglycolic acid and, as sole coloring agent, about 0.033 to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof.

13. A preparation for the permanent dyeing of human hair in the form of a freshly prepared aqueous solution containing an amount of a water-soluble mercapto compound selected from the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol equivalent with respect to SH group to about 1.2% to 6% by weight of the solution of thioglycolic acid and, as sole coloring agent, about 0.033% to about 6.2% by weight of the solution of a dyestuff of the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, said solution having a pH value between 6.6 and 10.4 but not higher than 9.4 when the mercapto concentration is equivalent to at least 3% by weight of the solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration is equivalent to at least 5.6% by weight of the solution of thioglycolic acid.

14. A preparation as claimed in claim 13, in which the solution has a pH value of between about 9 and 10.2.

15. A preparation for the permanent dyeing of keratinous material in the form of a substantially dry powdered mixture comprising a dry water-soluble solid mercapto compound of low toxicity, an ammonium salt, a dry, weakly alkaline water-soluble salt of an alkali metal, and, as sole coloring agent, a dry dyestuff selected from the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, the several ingredients being present in such proportions that, on addition of the dry powdered mixture to a predetermined quantity of water, a dye solution is formed which contains about 0.033% to about 6.2% by weight of the solution of dyestuff and a quantity of mercapto compound equivalent with respect to SH group to about 0.1% to about 6% by weight of the solution of thioglycolic acid and which has a pH value of between about 6.6 and 11.3.

16. A preparation for the permanent dyeing of human hair in the form of a substantially dry powdered mixture comprising a dry water-soluble salt of thioglycolic acid, an ammonium salt, a dry, weakly alkaline water-soluble salt of an alkali metal, and, as sole coloring agent, a dry dyestuff selected from the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof, the several ingredients being present in such proportions that, on addition of the dry powdered mixture to a predetermined quantity of water, a dye solution is formed containing about 0.033 to 6.2% b. w. of dyestuff and about 1.2% to 6% by weight of the solution of thioglycolic acid and which has a pH value of between about 6.6 and 10.4 but not higher than 9.4 when the thioglycolic acid concentration is at least 3% by weight of the solution and not higher than 9.15 when the thioglycolic acid concentration is at least 5.6% by weight of the solution.

17. A method for the permanent dyeing of keratinous material, which comprises the steps of preparing separately an aqueous dye solution containing, as sole coloring agent, a dyestuff selected from the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof and a water solution of a water-soluble mercapto compound, the respective pH values of the two solutions, the total quantity of solvent in both solutions, the relative proportions of the solutions, the concentration of mercapto compound in the mercapto solution and the concentration of dyestuff in the dye solution being such that a mixture of the two solutions contains about 0.033% to about 6.2% by weight of the solution of dyestuff and a quantity of mercapto compound equivalent with respect to SH group to about 0.1% to about 6% by weight of the solution of thioglycolic acid and has a pH value between about 6.6 and about 11.3, combining the two separate solutions to form such mixture, applying the freshly prepared mixture to the keratinous material to be dyed, washing the dyed material with an aqueous medium and drying the same.

18. A method for the permanent dyeing of human hair, which comprises the steps of preparing separately an aqueous dye solution containing, as sole coloring agent, a dyestuff selected from the group consisting of the Ext. D & C, D & C and F D & C certified colors and mixtures thereof and a water solution of a water-soluble mercapto compound of the group consisting of thioglycolic acid, thiosalicylic acid in the form of its water-soluble salts, thioglycol, thioglycerol and thiophenol, the respective pH values of the two solutions, the total quantity of solvent in both solutions, the relative proportions of the solutions, the concentration of mercapto compound in the mercapto solution and the concentration of dyestuff in the dye solution being such that a mixture of the two solutions contains about 0.033% to about 6.2% by weight of the solution of dyestuff and a quantity of

mercapto compound equivalent with respect to SH group to about 1.2% to about 6% by weight of the mixed solution of thioglycolic acid and has a pH value of between about 6.6 to 10.4 but not higher than 9.4 when the mercapto concentration in the mixture is equivalent to at least 3% by weight of the mixed solution of thioglycolic acid and not higher than 9.15 when the mercapto concentration of the mixture is equivalent to at least 5.6% by weight of the mixed solution of thioglycolic acid, combining the two separate solutions to form such a mixture, applying the fresh mixture to the hair to be dyed at a temperature about 50° and 110° F., washing the dyed hair with an aqueous medium and drying the same.

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