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SOLVENT DYEING OF HUMAN HAIR

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This application is a continuation-in-part of co-pending application Serial No. 658,911 filed April 19, 1957 (now abandoned).

The present invention relates to improvements in hair dyeing compositions, and to the dyeing of human hair therewith. The invention is particularly concerned with the dyeing of human hair in vivo.

In the dyeing of live human hair, the temperatures which can be used are low compared to those which can and are normally employed for dyeing other fibrous materials, such as wool, cotton and synthetic fibres. Many dyes which are used, for example on wool, require a much higher temperature than is possible in live-hair dyeing in order to achieve satisfactory effects. Consequently, the number of dyes available hitherto for the dyeing of human hair in vivo has been relatively small compared with those available for the dyeing of textile fibres generally.

It is an object of the present invention to provide a method of dyeing human hair in vivo in which many of the conventional dyes used for dyeing wool may be utilised. It is a further object of the present invention to provide a method by means of which the dyeing of human hair can be effected at room temperature. Another object of the invention is to provide a method which enables many coloured substances which are insoluble in water to be used for the dyeing of human hair in vivo. Yet another object of the present invention is to provide hair-dyeing compositions which fulfil the objects set forth above. Further and other objects will be apparent from the description which follows.

The invention is predicated on the surprising discovery that the transfer of dyes from aqueous media onto and into human hair in vivo can be greatly facilitated by the presence of the aqueous media of relatively small quantities of certain organic compounds. Further, it has been surprisingly found that with many dyes, the temperature for effective (i.e substantially fast to shampooing) dyeing is markedly reduced by the presence of such organic compounds. By the use of these organic compounds, therefore, it is possible to use dyes for the dyeing of human hair in vivo which hitherto have been unsuitable for this purpose owing to the relatively high temperature necessary to produce effective dyeing. Again, it has been found that the presence of such organic compounds makes possible the use of water-soluble pigments in the dyeing of human hair in vivo.

To be useful in the method of the present invention, the organic compounds must possess certain definite properties:

(1) The organic compound must be absorbed by human hair from the hair dyeing composition at a temperature below 120° F. and preferably at or below blood temperature.

(2) The organic compound must be a solvent for the dye at or below 120° F. and preferably at or below blood temperature.

(3) The dyes used must be absorbed by human hair from a solution thereof in the organic compound at a

temperature below 120° and preferably at or below blood temperature.

(4) The organic compound must have a straight aliphatic chain or an aliphatic ring of at least four carbon atoms.

(5) The organic compound must be insoluble or only slightly soluble in water.

Where the organic compound contains a benzene ring, for the purposes of this disclosure, the said benzene ring is to be regarded as being equivalent to a straight aliphatic chain of three carbon atoms.

The amount of the organic compound contained in the hair dyeing composition must not be more than 20% by volume, based on the total volume of the composition. In most cases, considerably less, e.g. from 3% to 8% of organic compound is required.

The invention provides hair dyeing compositions which comprise an aqueous liquor containing a coloured substance selected from the group consisting of dyes and pigments and up to 20% by volume, preferably 3% to 8% by volume based on the total volume of the composition, of an organic compound which is no more than sparingly soluble in water, is absorbed by human hair from the hair dyeing composition at a temperature below 120° F. and which is a solvent for the coloured substance at a temperature below 120° F. and from which the said coloured substance is absorbed by human hair at a temperature below 120° F.

In general, for a given dye there will be one or more organic compounds which possess the basic properties listed above, which render it useful for the method of the present invention. Similarly for a given organic compound there will be a number of dyes which are soluble therein and which can be effectively used in the method of the invention for dyeing human hair in vivo.

The amount of organic compound contained in the hair dyeing composition varies according to the nature of the organic compound, the nature of the dyestuff, the concentration in the composition and the temperature to be used. In general, however, for a given temperature and concentration of dyestuff, there is an optimum value usually in the range of from 3% to 8% by weight, for the amount of the organic compound which should be used, at which value maximum efficiency of the dyeing operation is achieved. For a given concentration of dyestuff, as the amount of organic compound present is increased, the efficiency of dyeing rises to a maximum and then decreases again as the amount of organic compound present is further increased.

A simple, though not exhaustive test for establishing the suitability of an organic compound for use in the process of the invention consists in shaking up the compound, whilst in the liquid state, with an aqueous solution or dispersion of the dyestuff and observing the partition of the dye between the resulting phases. If the partition ratio is such that the dyestuff is predominantly found in the organic compound phase, then the organic compound will, in general, be satisfactory for use in the process of the invention, provided that it also has the further properties listed above.

In any given case, relatively simple experiments on a small scale will enable the organic compound best suited for dyeing with a particular coloured substance to be determined.

Many highly coloured substances, because of their insolubility in water, are at present regarded as unsatisfac-

tory for use as dyes. If, however, they are soluble in other solvents, and the solvents in which they are soluble satisfy the above conditions, then the said coloured substances can be applied to human hair by the process of the invention from a dispersion thereof in water in the presence of such a solvent. Their insolubility in water also confers on them good resistance to shampooing.

The hair dyeing compositions of the invention may, of course, include the usual additives commonly used in such compositions, such as detergents, thickeners, etc. The detergents are normally incorporated as cleansing and foaming agents. In the absence of detergent, the dyed hair has a dull appearance due to the presence of a coating of dye on the surface of the hair. The presence of a detergent prevents the formation of this coating, and results in a lustrous appearance. In the method of the present invention, they also have the property of acting as emulsifiers and produce the emulsification of the organic compound as well as assisting the suspension of dyeing materials where the dye is insoluble in water. Most anionic detergents can be used in the method of the present invention, although their incorporation does decrease the amount of dyeing to some extent. A preferred detergent is sodium lauryl sulphate ether. The detergent may be incorporated in a cencentration of from 2% to about 12% by weight, based on the total weight of hair dyeing composition. The amount of detergent added depends on the shade desired. For medium shades about 6% to 10% of detergent is desirable. The addition of larger quantities of detergent, i.e. 12%, will facilitate the production of lighter shades. When deep shades are required, the concentration of detergent should be reduced below 6%, preferably to 2% to 3%. Non-ionic detergents may also be used in the compositions of the invention.

Sodium alginate has been found useful as a thickener except where acetic acid is present in the composition. The preferred thickener, however, is a derivative of cellulose sold under the name "Renose V" Extra, which is effective in the presence of acetic acid. The use of thickeners helps to stabilise the composition, and facilitates its application to human hair, besides reducing the rate of drying out of the solution.

When the compositions of the invention include relatively insoluble dyes, a secondary solvent or solubiliser may be used to bring the otherwise insoluble dyes into solution. Suitable solubilisers are ethyl alcohol (up to 10% by volume) and diacetone alcohol (up to 10% by volume). The preferred solubiliser is glycerol isopropylidene ether (up to 5% by volume). The preferred solubiliser is, however, unstable in acid solution, so that the pH of the hair dyeing composition should be maintained above 7 when this solubiliser is used. A simple way of producing a suitable pH is to add a small quantity of borax to the composition.

The addition of ½% of a 10% solution of glacial acetic acid has been found to improve the dyeing effect in certain cases. Acid should not, of course, be used when any of the additives are not stable in acid solution.

The organic compounds which have been found useful in the method of the invention include amyl alcohol and amyl lactate. A particularly preferred organic compound for use in the method of the present invention is benzyl alcohol. The concentration of this compound in the hair dyeing composition may be from about 3% to about 5% by volume, based on the total volume of the composition, and is preferably 4% by volume. Optimum dyeing is obtained with 4% by volume of benzyl alcohol.

The pH value of the solution including benzyl alcohol is preferably 5 to 9.

The effectiveness of the composition of the present invention over other compositions is illustrated by the following comparative example.

Five hair dyeing compositions were made up as follows:

(1) The following ingredients were mixed together to form a composition:

Dye	0.5
Benzyl alcohol (commercial grade)	4.0
Sodium lauryl sulphate	6.0
Sodium alignate	0.5
Water to 100.	

(2) The ingredients of (1) above were used except that the benzyl alcohol was replaced by isopropyl alcohol.

(3) The ingredients of (1) above were used except that the benzyl alcohol was replaced by 1,2-dichloro propane.

(4) The ingredients of (1) above were used except that the benzyl alcohol was replaced by 1,4-butane diol.

(5) The ingredients of (1) above were used except that the benzyl alcohol was omitted.

Five samples of white hair, taken from the same head, were each saturated with one of the five compositions set forth above, and allowed to stand at 15° C. for 10 minutes. Each of the wetted samples was then rinsed and examined. All the samples were found to be approximately the same shade of grey. They were then shampooed lightly and again examined. The contrast between the samples dyed in composition (5) and those dyed in compositions (1), (2), (3) and (4) after shampooing was measured by the "Geometric Grey Scale of the Society of Dyers and Colourists for Determining the Degree of Staining in Fastness Testing". The results are set forth below:

Compositions contrasted:	Rating
(5):(1)	2
(5):(2)	5
(5):(3)	5
(5):(4)	5

On the said Geometric Grey Scale the rating 5 is given where there is no significant difference between the two shades. The maximum contrast on the this scale is given the rating 1. It is clear, therefore, that the use of isopropyl alcohol, 1,2-dichloro propane and 1,4-butane diol in the dyeing compositions produces no significant difference in the dying compositions over composition (5) which did not include any organic compound of this type.

It is to be noted that isopropyl alcohol has a chain length of 2, 1,2-dichloro propane has a chain length of 3, and 1,4-butane diol has a chain length of 4. Isopropyl alcohol is miscible in water in all proportions. 1,2-dichloro propane is substantially insoluble in water. 1,4-butane diol is soluble in water. Benzyl alcohol, which has a chain length of 4 (the phenyl group being regarded as 3) is insoluble in water.

The contrast between 1,2-dichloro propane and benzyl alcohol shows the influence of the chain length of the organic compound on their suitability for use in the method of the present invention. Both these compounds are insoluble in water, but whereas 1,2-dichloro propane has 3 carbon atoms in the chain, benzyl alcohol has 4. The contrast between 1,4-butane diol and benzyl alcohol shows the influence of solubility of the organic compounds on their suitability for use in the method of the present invention. Both these compounds have the same chain length of 4, but whereas benzyl alcohol is insoluble in water, 1,4-butane diol is soluble in water.

The above comparative tests clearly show, therefore, that there is a definite improvement in dyeing when the organic compounds according to the present invention are used, and that by using them, dyeing can be achieved which is substantially resistant to shampooing of the hair.

The invention also includes a method of dyeing human hair in vivo which comprises contacting the said human hair at a temperature below 120° F. with an aqueous

liquor containing a coloured substance selected from the group consisting of dyes and pigments and up to 20% by volume, preferably 3% to 8% by volume based on the total volume of the composition, of an organic compound which is no more than sparingly soluble in water, is absorbed by human hair from the hair dyeing composition at a temperature below 120° F. and which is a solvent for the coloured substance at a temperature below 120° F. and from which the said coloured substance is absorbed by human hair at a temperature below 120° F.

The invention also includes a modification of this process in which the aqueous liquid is formed in contact with the hair. This may be effected by applying the organic compound directly to the hair first, either alone or in a solution or emulsion in water, or an organic liquid such as a methyl alcohol, and subsequently applying to the hair an aqueous solution or dispersion of the coloured substance. Alternatively the coloured substance may first be applied to the hair in the form of an aqueous solution or dispersion, and the organic compound applied subsequently to bring about the fixation of the dye to the hair. In all cases the effect of the method is to produce, in contact with the hair, a dyeing composition according to the present invention.

In the preferred method of the invention, both the organic compound and the coloured substances are applied to the hair simultaneously in the form of an aqueous solution or dispersion.

Dyes which have been found useful in the method of the present invention, and which may be used with the organic compounds are:

Dye	Colour Index Reference	Manufacturer
Coomassie Fast Brown RS (Colour Index No. 26550).	C.I. Acid Orange 51	Imperial Chemical Industries, Dyestuffs Division, Manchester, England.
Coomassie Fast Grey 3G (Colour Index No. 65005).	C.I. Acid Black 48	Do.
Sulphonine Red G (Colour Index No. 50315).	C.I. Acid Red 85	Sandoz Chemical Works Inc. New York, U.S.A.
Orasol Yellow 3G (Colour Index No. 12770).	C.I. Solvent Yellow 17	Ciba Co. Inc. New York, U.S.A.
Xylene Fast Blue FF (Colour Index No. 50320).	C.I. Acid Blue 61 (similar to).	Sandoz Chemical Works Inc. New York, U,S.A.

Certain markedly water-soluble anionic dyes such as the Kitons, Procions and Cibacrons are suitable for application to human hair by the method of the present invention provided a cationic surface active agent such as octadecyl pyridinium bromide or a polyamide based on a long chain fatty acid or a polyamine such as tetraethylene pentamine are added to the hair dyeing composition. It has been found that the useful range of concentration of such cationic agents is from 0.007 to 1.0 gm. per liter of composition. The use of more than 1.0 gm. per liter of cationic agent causes undesirable deposition of the dye complex onto the surface of the hair. The anionic dyes and the cationic surface active agent together from a very sparingly water-soluble anionic-cationic complex, which, in the compositions of the invention, gives on human hair excellent dyeing which is substantially fast to shampooing.

Anionic dyes have been found useful in the method of the present invention, and may be used with benzyl alcohol as the organic compound.

The compositions and method of the present invention will be further illustrated by reference to the following specific examples:

Example 1

A hair dyeing composition was made up using the following ingredients, the acid being added last after a gel had formed:

Kiton Fast Orange G (Color Index No. 16,230) C.I. Acid Orange 10	gms.	1.0
2½% solution of octadecyl pyridinium bromide	cc.	0.25
44% solution lactic acid	cc.	2.0
Benzyl alcohol (commercial grade)	cc.	4.0
Sodium lauryl sulphate ether	cc.	2.0
Sodium alginate	cc.	0.5
Water to 100 ccs.		

The hair to be dyed was first shampooed and then rinsed and roughly dried with a towel. The dyeing liquid was then applied evenly to the hair, which was worked with the fingers to produce as much lather as possible. (This was to keep the liquid in close contact with the hair and to prevent it coming into contact with the scalp or face.) After 15 minutes, the hair was rinsed clean. A strong lustrous orange shade was produced which was found to be substantially fast to shampooing.

Example 2

A hair dyeing composition was made up using the following ingredients:

Dye	gms.	1.0
2½% solution of a polyamide formed from tetraethylene pentamine and a long chain fatty acid	cc.	0.25
44% lactic acid	cc.	2.0
Benzyl alcohol (commercial grade)	cc.	4.0
Sodium lauryl sulphate ether	cc.	2.0
Thickener	gm.	1.0
Water to 100.		

Following the procedure of Example 1, a strong lustrous bluish-red shade was produced which was found to be substantially fast to shampooing.

Example 3

A dyeing composition was made up using the following ingredients:

Acid dye	gm.	½
Benzyl alcohol	cc.	4.0
Sodium lauryl sulphate ether	cc.	6.0
Sodium alginate	gms.	0.5
Water to 100.		

The procedure of Example 1 was followed and a light grey lustrous shade was produced which was found to be substantially fast to shampooing.

Example 4

A dyeing composition was made up using the following ingredients:

Acid dye	gm.	1.0
Benzyl alcohol	cc.	4.0
Sodium lauryl sulphate ether	cc.	6.0
Thickener	gm.	1.0
Water to 100 ccs.		

The procedure of Example 1 was followed and a medium brown lustrous shade was obtained which was found to be substantially fast to shampooing.

Example 5

A dyeing composition was made up using the following ingredients:

Dye	gm.	1.0
Benzyl alcohol	cc.	4.0
Glycerol isopropylidene ether	cc.	5.0
Sodium lauryl sulphate ether	cc.	2.0
Sodium alginate	gm.	0.5
Borax	gm.	0.1

Water to 100 ccs.

The procedure of Example 1 was followed and a clear strong lustrous red shade was obtained which was found to be substantially fast to shampooing.

Example 6

A dyeing composition was made up using the following ingredients:

Acid dye	gms.	2.0
Benzyl alcohol	cc.	4.0
Glycerol isopropylidene ether	cc.	5.0
Sodium lauryl sulphate ether	cc.	2.0
Sodium alginate	gm.	1.5

Water to 100 ccs.

The procedure of Example 1 was followed and a full bodied lustrous brown shade was obtained, which was found to be substantially fast to shampooing.

Example 7

A dyeing composition was made up using the following ingredients:

Dye, C.I. acid Black 107	gm.	1.5
Benzyl alcohol	cc.	4.0
Sodium lauryl sulphate ether	cc.	6.0
Sodium alginate	gm.	0.5
10% aqueous lactic acid solution	cc.	0.5

Water to 100 ccs.

The procedure of Example 1 was followed and a fairly strong lustrous slate grey shade was obtained, which was found to be substantially fast to shampooing.

We claim:

1. A hair dyeing composition comprising an aqueous liquor containing a dye and up to 20% by volume, based on the total volume of the composition, of an organic compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

2. A hair dyeing composition as claimed in claim **1** in which the organic compound is benzyl alcohol.

3. A hair dyeing composition as claimed in claim **1** in which the organic compound is amyl alcohol.

4. A hair dyeing composition comprising an aqueous liquor containing a dye and from 3% to 5% by volume of benzyl alcohol.

5. A hair dyeing composition which comprises an aqueous liquor containing from 5 to 40 gm. per liter of composition of a water soluble anionic dye and from 0.007 to 1.0 gm. per liter of composition of a cationic surface active agent and an organic compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

6. A hair dyeing composition comprising an aqueous liquor containing from 5 to 40 gm. per liter of composition of a water soluble anionic dye, from 0.007 to 1.0 gm. per liter of octadecyl pyridinium bromide and from 30 to 80 cc. per liter of benzyl alcohol.

7. A hair dyeing composition as claimed in claim **1** which also contains the water miscible organic solvent glycerol isopropylidene ether is present in the composition in an amount up to 5% by volume based on the total volume of the composition.

8. A hair dyeing composition consisting of an aqueous liquor containing a dye, from 30 cc. to 50 cc. per liter of benzyl alcohol, up to 60 cc. per liter of sodium lauryl sulphate and up to 1.5 gm. per liter of sodium alginate.

9. A method of dyeing human hair in vivo which comprises contacting the said human hair at a temperature below 120° F. with a hair dyeing composition comprising an aqueous liquor containing a dye and up to 20% by volume, based on the total volume of the composition, of an organic compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

10. A method of dyeing human hair in vivo which comprises contacting said human hair at a temperature below 120° F. with a hair dyeing composition comprising an aqueous liquor containing a dye and from 3% to 5% by volume of benzyl alcohol.

11. A method of dyeing human hair in vivo which comprises forming in contact with said human hair a composition comprising an aqueous liquor containing from 5 to 40 gm. per liter of composition of a water soluble anionic dye and from 0.007 to 1.0 gm. per liter of composition of a cationic surface active agent and up to 20% by volume based on the total volume of the composition of an organic compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

12. A method of dyeing human hair which comprises contacting said human hair at a temperature below 120° F. with a composition comprising an aqueous liquor containing from 5 to 40 gm. per liter of composition of a water soluble anionic dye, from 0.007 to 1.0 gm. per liter of octadecyl pyridinium bromide and from 30 to 80 cc. per liter of benzyl alcohol.

13. A method of dyeing live human hair with a dyestuff having a proper shade, which comprises applying to the hair at ambient temperature a solution which comprises said dye distributed in an aqueous medium in an amount not exceeding about 20% of the total thereof, of a compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

14. A method of dyeing live human hair with a dyestuff having a proper shade, which comprises applying to the hair at ambient temperature a solution which comprises said dye distributed in an aqueous medium in an amount not exceeding about 3 to 8% of the total thereof, of a compound selected from the group consisting of benzyl alcohol, amyl alcohol and amyl lactate.

15. A method of dyeing live human hair with a dyestuff having a proper shade, which comprises applying to the hair at ambient temperature a solution which comprises said dye distributed in an aqueous medium and an amount not exceeding about 20% of the total thereof, of amyl alcohol.

16. A method of dyeing live human hair with a dyestuff having a proper shade, which comprises applying to the hair at ambient temperature a solution which comprises said dye distributed in an aqueous medium and an amount, not exceeding about 20% of the total thereof, of amyl lactate.

17. The method of claim **13** wherein the solution also contains a detergent.

18. The method of claim **13** wherein the solution also contains a thickener.

19. The method of claim **13** wherein the solution also contains a secondary solvent.

20. A method of dyeing live human hair with a direct dyestuff having a proper shade which comprises applying to the hair at ambient temperature a solution which comprises said dye distributed in an aqueous medium and in an amount not exceeding about 10% of the total thereof of benzyl alcohol.

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