United States Patent

[11] 3,632,290

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[21] Appl. No. **700,701**
[22] Filed **Jan. 26, 1968**
[45] Patented **Jan. 4, 1972**

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[54] **DYEING OF HUMAN HAIR USING ETHYLENE GLYCOL ETHERS**
10 Claims, No Drawings

[52] **U.S. Cl.** **8/10.1,** 8/10, 8/93
[51] **Int. Cl.** **A61k 7/12**
[50] **Field of Search** 8/10.1, 10.2, 93, 10

[56] **References Cited**

UNITED STATES PATENTS

2,095,221	10/1937	Smith	8/93
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1,021,806	3/1966	Great Britain	8/93

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ABSTRACT: Composition and methods for the dyeing of human hair in vivo involving the use of mixtures of aryl and alkyl glycol ethers in aqueous media as carriers and solubilizers for normally water-insoluble dyes. Applicable classes of dyes are basic, solvent soluble, acid, nitro, premetallized, mordant, anionic and direct.

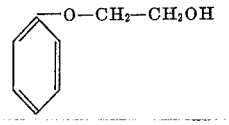
DYEING OF HUMAN HAIR USING ETHYLENE GLYCOL ETHERS

BACKGROUND OF THE INVENTION

In dyeing of human hair in vivo, the temperature that must be used must be low compared to those which an be used for dyeing other fibrous materials such as wool, cotton and synthetic fibers. As is known, many dyes which are used for dyeing fibrous material require a high dyeing temperature. Therefore, in the past it has proven impossible to utilize these dyes in vivo for dyeing of human hair. Because of this the dyes available for utilization for dyeing human hair has been severely limited in number. In view of this it has long been desired to provide a method for dyeing human hair which can utilize the dyes now utilized for dyeing fibrous materials.

SUMMARY OF THE INVENTION

In accordance with this invention it has been found that when ethylene glycol phenyl ether having the formula



is incorporated into an aqueous hair-dyeing composition, the transfer of dyes from the aqueous hair-dyeing composition into the human hair is greatly facilitated. Furthermore, this transfer is effected without the use of high temperature. Hence the use of the ethylene glycol phenyl ether in dyeing compositions allows one to utilize hair-dyeing compositions containing dyes which hereinbefore were considered unusable due to the need to apply high temperature for effective dyeing. A liquid solubilizer or secondary solvent is utilized with the ethylene glycol phenyl ether, such secondary solvent being water soluble and capable of solubilizing a normally insoluble dyes and the ethylene glycol phenyl ether so as to serve as a carrier for increasing the depth of shade of the dye, such secondary solvent being an ethylene glycol ether of the lower alkanols and having the formula $H(C_2H_4O)_mO\ C_nH_{2n+1}$ wherein m and n are integers from 1 to 5.

DETAILED DESCRIPTION

The amount of ethylene glycol phenyl ether contained in the hair-dyeing composition of this invention should not be more than 20 percent by weight, based upon the total weight of the dye composition. In most cases, it is preferred to utilize from about 0.5 to 5 percent by weight of the organic compound, based upon the total dye composition.

The hair-dyeing compositions in accordance with this invention comprise an aqueous system containing a dye and from 0.5 to about 20 percent by weight, preferably 0.5 to 5 percent by weight, based upon the total weight of the dyeing composition of ethylene glycol phenyl ether.

The amount of the ethylene glycol phenyl ether contained in the hair-dyeing composition of this invention can vary according to the nature and concentration of the dyestuff in the composition and the temperature to be used. In general, however, for a given concentration of dyestuff, there is an optimum value in the range of from about 0.5 to 5 percent by weight of the ethylene glycol phenyl ether which should be dyeing operation is achieved. For a given concentration of dyestuff, as the amount of organic compound present is increased, the efficiency of the dyeing rises to a maximum and then decreases again as the amount of the ethylene glycol phenyl ether present is further increased.

In accordance with this invention many dyestuffs which are soluble in water or can be made to be soluble in water by dissolving the dyestuff in an organic solvent which is soluble in water can be applied to human hair. The insolubility of the dyestuff in water also confers upon them good resistance to the shampooing and hence are preferred.

In accordance with this invention a liquid solubilizer or secondary solvent can be utilized such as ethylene glycols ethers of lower alkanols having the formula $H(C_2H_4O)_mO\ C_nH_{2n+1}$ wherein m and n are integers from 1 to 5.

Included among these compounds are monoethyl ether of diethylene glycol, the monoethyl ether of triethylene glycol, monopropyl ether of triethylene glycol. The amount of the liquid stabilizer can vary in the dye composition from 1 to 10 percent by weight of the dye composition.

Hair-dyeing compositions of the invention may, of course, include usual additives commonly used in such compositions, such as surface active agents, thickeners, etc. In the method of the present invention, the surface active agents have the properties of acting as emulsifiers which can produce the emulsification of ethylene glycol phenyl ether as well as assisting the suspension of the dyeing materials where the dye is insoluble in water. Any of the conventional anionic, cationic, nonionic, or amphoteric surface active materials or mixtures of these can be utilized in accordance with the present invention. The preferred, commercially available, surface active material in each class is listed below:

Anionic

Sodium lauryl sarcosinate, marketed as Sarkosyl by the Geigy Chemical Company

Cationic

Polyethoxylated quaternary ammonium salt marketed as Ethoquad C/12 by the Armor Chemical Company

Nonionic

Polyoxyethylene sorbitan monolaurate marketed as Tween 20 by the Atlas Chemical Company. Tween 20 has 20 oxy groups per molecule, according to Atlas Cosmetic Bulletin, LD103, Copyright, 1964.

Amphoteric

Lauroylcycloimidinium-1-ethoxy-ethionic acid disodium salt which is described in U.S. Pat. No. 2,773,068 and is marketed as Miranol C2N-SF by the Miranol Chemical Company.

Surface active materials may be incorporated in a concentration of from 0.5 to 10 percent by weight, based upon the total weight of the hair-dyeing composition. Any conventional anionic, cationic, nonionic, or amphoteric surface active material or mixtures of the same can also be used in the composition of this invention.

Hydroxyethyl cellulose has been found useful as a thickener. However, any conventional thickener for dyestuff compositions can be utilized in accordance with this invention. Use of thickeners helps stabilize the composition and facilitates application to human hair, besides reducing the rate of drying out of the solution.

The addition of 0.5 percent of a 10 percent aqueous 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 pH value of the dyeing solution can vary from 4 to 9.5.

Many dyes have been found to be useful in the method of the present invention. These include those dyes known as basic, solvent soluble, acid, nitro, premetallized, mordant and direct. Examples of dyes which have been found useful in the method of the present invention are:

Basic Dyes

Cyper Black 1A—General Aniline and Film Corp., New York, N.Y. C. I. Basic Black No. 3, Color Index Second Edition 1956, Vol. 1, pg. 1,653, very similar to C. I. 11,825.

Genacryl Orange G.—General Dyestuff Corp., New York, N.Y. C. I. Basic Orange No. 21. C. I. 48,035, Color Index Vol. 1, pg. 1628.

Solvent Soluble Dyes

Nigrosene SSB—E. I. DuPont de Nemours & Co., Wilmington, Del. C. I. Solvent Black No. 7—Color Index Vol. 2, pg. 2,900, C. I. 50515

Orosol Red B—Ciba Co., New York, N.Y. C. I. Solvent Red No. 7 Color Index. Vol. 2, pg. 2,845.

Acid Dyes

Erio Anthracene Blue R—Geigy Co., New York, N.Y. C. I. Acid Blue No. 47, Color Index Vol. 1, pg. 1,250, C. I. 62085

Coomassie Fast Brown R—Imperial Chemical Industries, Ltd. Manchester, England. C. I. Acid Orange No. 51. Color Index Vol. 1, pg. 1,076, CI 26550.

Nitro Dyes

Nitro paraphenylenediamine—Lowenstein Dyes & Cosmetics, Brooklyn, N.Y. 95—98 percent pure

Nitro orthophenylenediamine—Lowenstein Dyes & Cosmetics, Brooklyn, N.Y. 97 percent pure.

Premetallized Dyes

Calcofast Wool Blue 2G—American Cyanamid Co., Bound Brook, N.J. C. I. and Blue No. 158, Color Index Vol. 1, pg. 1,299, CI 15050.

Neolan Black WA—Ciba Co., New York, N.Y. C. I. Acid Black No. 52. Color Index Vol. 1, pg. 1,395 CI 15711.

Irgalan Dark Brown 5R—Geigy Co., New York, N.Y. C. I. Acid Brown No. 48, Color Index Vol. 1, pg. 1,348.

Irgalan Grey BL—Geigy Co., New York, N.Y. C. I. Acid Black No. 58, Color Index Vol. 1, pg. 1,397.

Mordant Dyes

Calcochrome Brown RH—American Cyanamid Co., Bound Brook, N.J. Mordant Brown No. 33, Color Index Vol. 1, pg. 1,565, CI 13250.

In accordance with the preferred embodiment of this invention, the concentration of the dyestuff in the aqueous hair-dyeing composition is from about 1 to 10 grams per liter based upon the volume of the dyestuff composition.

In accordance with this invention water-soluble anionic dyes such as the Irgalans, Neolans, Pontacyls, Polars, and Pontachromes are suitable for application to human hair provided a cationic surface active agent such as a polyethoxylated quaternary ammonium salt or a quaternary ammonium salt such as lauryl pyridinium chloride is present. It has been found that the useful range of concentration of such cationic agents is from about 0.01 to 5 grams per liter of composition. The anionic dyes and cationic surface active agent together form a very sparingly water soluble anionic-cationic complex, which in the composition of the present invention gives on human hair excellent dyeing.

Anionic dyes have been found useful in the method of the present invention and may be used with ethylene glycol phenyl ether in the composition of this invention.

The invention also includes the method of dyeing human hair in vivo which comprises contacting the said human hair at a temperature below 120°F., preferably from room temperature to 100°F., with an aqueous composition containing a colored substance selected from the group consisting of the dyes and up to 20 percent by weight, preferably from about 0.5 to 5 percent by weight based on the total weight of the composition of ethylene glycol phenyl ether.

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 ethylene glycol phenyl ether directly to the hair first, either alone or in a solution or an emulsion in water or an organic liquid such as methyl or ethyl alcohol and subsequently applying to the hair an aqueous solution or dispersion of the color substance. Alternately the colored substance may be first applied to the hair in the form of an aqueous solution or dispersion and the organic compound applied subsequently thereto to bring about the fixation of the dyestuff in the hair. In the preferred method of the invention, both the ethylene glycol phenyl ether and the colored substances are applied to the hair simultaneously in the form of an aqueous solution or dispersion.

We have found that the effectiveness of this composition can be improved by the addition of certain monomers such as itaconic acid and methacrylamide which are fully described in our U.S. Pat. No. 2,890,094. The concentration of these monomers may vary from 5 to 20 grams per liter with the preferred concentration being from 5 to 10 grams per liter.

The effectiveness of the composition of the present invention is illustrated by the following examples.

The hair-dyeing composition was made up of the following ingredients:

Material	Parts by Weight
Dye C.I. Basic Black No. 3	0.2 g.
Ethylene glycol phenyl ether	3.0 g.
Diethylene glycol monoethyl ether	2.0 g.
Lauroylcycloimidinium-1-ethoxy ethionic acid disodium salt	4.0 g.
Hydroxyethyl cellulose	1.0
Water to a volume of	100 cc.

A sample of white human hair was saturated with the aforementioned composition and allowed to stand at 15°C. for 10 minutes. The wetted sample was then rinsed and examined. After examination the wetted sample was shampooed lightly and again examined. It was seen that there was no color change between the sample before and after shampooing.

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

EXAMPLE 1

A hair-dyeing composition was made of the following ingredients:

Material	Amount
Neolan Black WA (C. I. Acid Black No. 52)	0.5 g.
Ethylene glycol phenyl ether	1.0
Diethylene glycol monoethyl ether	1.0
Itaconic acid	0.5
Ethoquad C/12 (Polyethoxylated quaternary) (ammonium salt of cocoanut fatty acid containing 2 mols of ethylene oxide 75% active)	0.5
Sodium alginate	0.5
Water to a volume of	100 cc.

The hair to be dyed was first shampooed and then rinsed and roughly dried with a towel. The dyeing liquid was 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 grey black 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:

Material	Amount
Irgalan Dark Brown 5R (C. I. Acid Brown No. 48)	0.2 g.
Ethylene glycol phenyl ether	1.0
Diethylene glycol monoethyl ether	1.0
Ethoquad C/12	0.5
Hydroxyethyl cellulose	0.2
Water to a volume of	100 cc.

Following the procedure of example 1, a red-brown shade was produced which was found to be completely removed on shampooing.

EXAMPLE 3

A dyeing composition was made up using the following ingredients:

Material	Amount
Nigrosene SSB (C. I. Solvent Black No. 7)	0.2 g.
Ethylene glycol phenyl ether	3.0
Diethylene glycol monoethyl ether	2.0
Lauroylcycloimidinium-1-ethoxy ethionic acid disodium salt	2.0
Polyoxyethylene sorbitan monolaurate	2.0
Ethoquad C/12	0.2
Hydroxyethyl cellulose	1.0
Water to a volume of	100 cc.

Following the procedure of example 1, a strong dark grey, almost black, shade was produced which was found to be substantially fast to shampooing.

EXAMPLE 4

A dyeing composition was made up using the following ingredients:

Material	Amount
Calcochrome Brown RH (C. I. Mordant Brown No. 33)	0.1 g.
Ethylene glycol phenyl ether	3.0
Diethylene glycol monoethyl ether	2.0
Lauroylcycloimidinium-1-ethoxy ethionic acid disodium salt	2.0
Ethoquad C/12	0.2
Methacrylamide	1.0
Hydroxyethyl cellulose	1.0
Water to a volume of	100 cc.

The procedure of example 1 was followed and a fairly deep yellow brown was obtained which was found to be substantially fast to shampooing.

EXAMPLE 5

A dyeing composition was made up using the following ingredients:

Material	Amount
Benzo Fast Black LA Extra (C. I. Direct Black No. 51)	0.2 g.
Ethylene glycol phenyl ether	1.0
Diethylene glycol monoethyl ether	1.0
Ethoquad C/12	0.5
Hydroxyethyl cellulose	0.2
Water to a volume of	100 cc.

The procedure of example 1 was followed and a black shade was obtained which was completely removed on shampooing.

What is claimed is:

1. A hair-dyeing composition comprising an aqueous medium containing 1 to 10 grams per liter a dyestuff, from 0.5 to 20 percent by weight of ethylene glycol phenyl ether and 1 to 10 percent by weight of di-ethylene glycol mono-ethyl ether.

2. A hair-dyeing composition comprising an aqueous medium containing 1 to 10 grams per liter of a water insoluble dyestuff dissolved in an alcohol selected from the group consisting of methyl alcohol and ethyl alcohol and from 0.5 to 5 percent by weight of ethylene glycol phenyl ether.

3. A hair-dyeing composition which comprises an aqueous medium containing from 1 to 10 grams per liter of said composition of a water soluble dye, from 0.01 to 5 grams per liter of said composition of a cationic quaternary ammonium salt and from 0.5 to 5 percent by weight of said composition of ethylene glycol phenyl ether.

4. The hair-dyeing composition of claim 7, wherein said cationic quaternary ammonium salt is selected from the group consisting of a polyethoxylated quaternary ammonium salt and lauryl pyridinium chloride.

5. A method of dyeing human hair in vivo which comprises contacting said human hair at a temperature below 120° F. with an effective amount of a hair-dyeing composition comprising an aqueous medium containing 1 to 10 g./liter of a dye and 0.5 to 20 percent by weight of ethylene glycol phenyl ether.

6. The method of claim 5 wherein said ethylene glycol phenyl ether is present in said dye composition in an amount of from 0.5 to 5 percent by weight of said composition.

7. A method of dyeing human hair in vivo, comprising the steps of contacting said human hair with an effective amount of an aqueous medium containing therein from about 1 to 10 grams per liter of a water-insoluble dye, a sufficient quantity of a water-soluble alcohol selected from the group consisting of methyl alcohol and ethyl alcohol to render said dye soluble in said medium, and 0.5 to 5 percent of ethylene glycol phenyl ether based on the total weight of material contacting said human hair.

8. A method of dyeing human hair in vivo, comprising the steps of contacting said human hair with an effective amount of an aqueous medium containing from 1 to 10 grams per liter of a water-soluble dye, from 0.01 to 5 grams per liter of quaternary ammonium salt and 0.5 to 20 percent by weight of ethylene glycol phenyl ether based on the total volume of material contacting said human hair.

9. The method of claim 8 wherein said cationic quaternary ammonium salt is a poly ethoxylated quaternary ammonium salt.

10. The method of claim 8 wherein said composition is applied to the human hair at ambient temperature.

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