United States Patent Office 2,848,369 Patented Aug. 19, 1958

2,848,369

HAIR DYE COMPOSITION OF AN ANIONIC DYESTUFF-CATION ACTIVE LIPOPHILIC MATERIAL COMPLEX SOLUBILIZED BY NON-IONIC ETHYLENE OXIDE CONDENSATION PRODUCT

John Robert Seemuller, Maisons-Laffitte, France, assignor to Société Anonyme: Societe Monsavon-l'Oreal, Paris, France, a corporation of France

No Drawing. Application June 14, 1955
Serial No. 515,519

Claims priority, application France November 4, 1954

9 Claims. (Cl. 167—88)

The present invention relates to the preparation of hair dyes and it is an object of the invention to produce dyes which may be applied directly to the hair at normal room temperatures.

It is known that many anionic dyestuffs employed for dyeing textile fibres, more especially animal fibres, may be precipitated from their aqueous solutions by adding a molecularly equivalent quantity of basic substances such as substituted guanidines, amino-pyrazolones and dicyclohexylamine. The new dyestuffs thus obtained are very frequently sufficiently soluble in organic solvents to be suitable for use in the colouring of varnishes.

It is also known that live hair can be dyed at room temperatures by means of the anionic dyestuffs usually employed for dyeing textile and animal fibres, provided that the hair has previously been impregnated with solutions of products known in the textile industry as "active cation" products. This process enables the hair to be dyed but the dyes are only fixed on the surface, because the dyestuff in contact with the fibre impregnated with active-cation product is immediately precipitated on the surface so that the colour obtained is only moderately resistant to friction and to moisture. Furthermore, the operation must be carried out in two stages.

It has now been found possible to dye hair directly at room temperatures in a single operation and with a lasting effect by impregnating the hair with a composition containing an anionic dyestuff resulting from the coupling of a diazo compound of an amine of the benzene series with a 2-naphthaleno 8-phenylamino 6-hydroxysulphonic acid (hereinafter referred to as phenyl gamma acid), an active-cation product in equimolecular proportion to the anionic dyestuff so as to neutralize the latter, a nonionic solubilizing agent in exactly sufficient quantity to permit of bringing the anion-cation complex formed into solution in water for the purpose of promoting the pnenetration of the dye into the hair.

Further investigation has shown that the process of preparing a dye from the aforesaid anionic dyestuffs derived from phenyl gamma acid may be generally applied to anionic dyestuffs.

According to the present invention, therefore, a process for the production of a hair dye suitable for direct dyeing of hair at room temperatures comprises neutralizing an anionic dyestuff with an organic base having at least 6 carbon atoms in the molecule and solubilizing the product obtained (hereinafter referred to as "the dyestuff complex") with a non-ionic solvent miscible with water in quantity not substantially in excess of that required for complete solution.

A suitable anionic dyestuff is the above mentioned dyestuff obtained by coupling a diazo compound of an amine of the benzene series with phenyl gamma acid as hereinbefore defined, but any anionic dyestuff may be employed in carrying out the invention provided it will give a definite acid reaction in aqueous solution. In

other words, any dyestuff, the acidity of which is due to at least one free sulphonic acid, carboxylic acid, or hydroxyl group, is suitable for carrying out the present invention.

The organic base chosen may with advantage be one in which the nitrogen is either trivalent (amine having high molecular weight) or pentavalent (product containing quaternary ammonium). Thus, the molecule of the organic base may be characterised by a lipophilic chain containing inter alia, for example, from 12 to 14 carbon atoms attached to a hydrophilic amine chain.

The non-ionic solvents which may be employed as solubilizing agents include, more especially, the alcohols and the products of the condensation of ethylene oxide on alcohols, phenols, or naphthols.

In a modified embodiment of the process according to the invention, the quantity of solubilizing agent (non-ionic solvent) added may be reduced or even omitted by attaching certain solubilizing groups to the organic base so that the latter simultaneously performs the function of a solubilizing agent with respect to the dyestuff complex and of a neutralizing agent for the anionic dyestuff when forming the complex.

For example, ethylene oxide may be condensed with the organic base. The number of ethylene oxide molecules to be condensed depends upon the dyestuff employed.

Furthermore, it is desirable in accordance with the invention to adjust the pH value of the dyeing solution by the addition of an organic acid (e. g. lactic acid) to bring the pH value slightly lower than 7.

Examples of compositions according to the invention will hereinafter be given, these examples not being intended to limit the possible applications of the invention. It should be noted that in all the examples the pH value is preferably between 4.5 and 5.5.

For the sake of simplicity, in all the following examples, the anionic dyestuff will be referred to as the "anion" and the organic base associated therewith as the "cation."

A. AZO DYESTUFFS

Example 1

A dye is prepared by solubilizing the following insoluble anion-cation complex:

	G.
Anion: Dyestuff known under the name "Chlorantine Fast Blue GLI"	2
Cation: Product known under the name "Lissolamine A" (assumed to be octadecylpyridinium bromide)	0.5

with the product known under the name

"Cémulsol 132" (product of condensation of a compound containing a naphthalenic nucleus with ethylene oxide)	1.1
Lactic acid	2.5
Water up to 100 g.	

A light blue tint is obtained on natural white hair.

Example 2

A dye is prepared by solubilizing the following insoluble anion-cation complex:

	G.
Anion: Dyestuff known under the name "Noir diazol E" (Color Index No. 581)	2
Cation: Ester of fatty acid from copra and diethylethanolamine previously condensed on 4.5 mol of ethylene oxide	1.1

With

"Cémulsol 132"	2.5
Lactic acid	2.5
Water up to 100 g.	

A rather distinguished grey-black is obtained on natural white hair.

Example 3

A dye is prepared with the following soluble anion-cation complex:

	G.
Anion: Dyestuff known under the name "Noir diazol E" (Color Index No. 581)	2
Cation: Ester of fatty acid from copra and diethylethanolamine previously condensed with 12 mol. of ethylene oxide	2.5
Lactic acid	2.5
Water up to 100 g.	

In the above example, the condensation of a sufficient number of ethylene oxide molecules on the cation ensures complete water-solubilization of the anion-cation complex and obviates the necessity for using a special solubilizing agent such as Cémulsol 132.

Example 4

A dye is prepared by solubilizing the following insoluble anion-cation complex:

	G.
Anion: Dyestuff known under the name "Rouge Kiton 6 B" (Color Index No. 57)	2
Cation: Ester of fatty acid from copra and diethylethanolamine previously condensed with 4.5 mol. of ethylene oxide	1.7
with	
"Cémulsol 132"	1.9
Acetic acid	1.7
Water up to 100 g.	

A pinkish auburn tint is obtained on natural white or light-blond hair.

Example 5

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Dyestuff obtained by the coupling of the diazo compound of p-nitro-o-anisidine with phenyl gamma acid in an alkaline medium	2
Cation: Lactate of the esters of fatty acids from copra and diethanolamine previously condensed on 4.5 mol. of ethylene oxide	1.8
"Cémulsol 132"	3.9
Lactic acid	8
Water up to 100 g.	

This dye imparts a violet-grey tone to live hair in the cold or at a temperature below 40° S.

Example 6

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Dyestuff obtained by coupling the diazo compound of meta-amino-sulphanilide with phenyl gamma acid in alkaline medium	0.8
Cation: Product known under the name "Lissolamine A" (octadecylpyridinium bromide)	1
"Cémulsol 132"	9
Lactic acid	7
Water up to 100 g.	

The dye imparts a light reddish-brown tone to live hair in the cold or at a temperature below 40° C.

B. AZINE DYESTUFFS

Example 7

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Dyestuff known under the name "Induline B" (Color Index No. 861)	2
Cation: Product known under the name "Lissolamine A" (octadecylpyridinium bromide)	1.3
with	
"Cémulsol 132"	4.75
Lactic acid	2.5
Water up to 100 g.	

A bluish grey is obtained on natural white hair.

Example 8

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Dyestuff known under the name "Induline RAL" (corresponding generally to Color Index No. 861)	2
Cation: Ester of fatty acid from copra and diethylethanolamine previously condensed on 4.5 molecules of ethylene oxide	2.65
with	
"Cémulsol 132"	4.25
Lactic acid	2.5
Water up to 100 g.	

An azure blue lustre is obtained on blond and brown hair.

Example 9

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Product known under the name "Nigrosine LFM" (Color Index No. 865)	2
Cation: Product known under the name "Lissolamine A" (octadecylpyridinium bromide)	1.2
with	
"Cémulsol 132"	3.25
Lactic acid	2.50
Water up to 100 g.	

A bluish-grey tint is obtained on white hair.

C. DYESTUFFS DERIVED FROM XANTHENE

Example 10

A dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Product known under the name "Rouge Kiton Brillant B" (Color Index No. 748)	2
Cation: Product known under the name "Lissolamine A"	0.4
"Cémulsol 132"	0.5
Lactic acid	2.5
Water up to 100 g.	

A pinkish-auburn tint is obtained on all hair.

A thickening agent of known type may be incorporated in a dye according to the invention, notably in order to facilitate the application thereof to live hair, but this thickening agent must be so chosen as not to modify the ionization equilibrium of this dye. The said thickening agent may be either gelatin or a product of condensation of ethylene oxide with an aliphatic alcohol. In the latter case, the condensed ethylene oxide may act as a

solubilizing agent for the equimolecular anion-cation complex, that is to say, it may render unnecessary the use of a non-ionic product such as "Cémulsol 132" indicated in the foregoing examples.

The dye then takes the form of a jelly, a paste or a cream.

Example 11

A cream dye is prepared by solubilizing the following anion-cation complex:

	G.
Anion: Product known under the name "Noir diazol BH" (Color Index No. 401)	2
Cation: Product known under the name "Lissolamine A" (octadecylpyridinium bromide)	0.7

with

Hydroxyethylene cetyl alcohol	15
Lactic acid	5
Distilled water up to 100 g.	

A cream is obtained in which the hydroxyethylene cetyl alcohol acts both as solubilizing agent for the anion-cation complex and as a thickening agent in the cream obtained.

This cream gives a somewhat distinguished grey-black on live hair at a temperature below 30° C.

Example 12

A dye is prepared in the form of a gel by solubilizing the following anion-cation complex:

	G.
Anion: Product known under the name "Violet chlorantine 5 BLL"	2
Cation: Product known under the name "Lissolamine A" (octadecylpyridinium bromide)	0.25

with

"Cémulsol 132"	5.9
Lactic acid	2.5
Gelatin	8
Water up to 100 g.	

The dye takes the form of a jelly and imparts a rather distinguished violet-lilac tint to hair at a temperature below 30° C.

It will be understood that the solubilization of the anion-cation dye complex may be effected cither by adding a non-ionic solubilizing agent or by using a product resulting from the condensation of ethylene oxide on the cation neutralizing the anionic dyestuff, or again by a combination of these two methods.

What I claim is:

1. A composition for dyeing live human hair comprising a complex of a cation active material with an anionic dyestuff wherein said complex is solubilized with a non-ionic solubilizing material, said cationic material being a base selected from the group consisting of an amine and a quaternary ammonium compound and said cationic material containing a lipophilic chain having from about six to eighteen carbon atoms and said anionic dyestuff being characterized by its acidity and the presence of at least one acid group selected from the group consisting of a free sulphonic acid group, a free carboxylic acid group and a free acid hydroxyl group, said non-ionic material being a condensation product of ethylene oxide and a hydroxy containing material selected from the group consisting of an alcohol, a phenol and a naphthol.

2. A composition for dyeing live human hair comprising a complex of an anionic dyestuff and a cation active material solubilized by a non-ionic solubilizing agent, said cationic agent being present in equi-molecular portions to the anionic dyestuff so as to neutralize the latter and the non-ionic solubilizing agent being present in just sufficient quantity to bring the complex into solution in water, said cationic material being a base selected from the group consisting of an amine and a quaternary ammonium compound, said cation active material containing a lipophilic chain of at least six carbon atoms and said anionic dyestuff being characterized by acidity and the presence of at least one acid group selected from the group consisting of a free sulphonic acid group, a free carboxylic group and a free acid hydroxyl group, said non-ionic agent being a condensation product of ethylene oxide and a hydroxy containing material selected from the group consisting of an alcohol, a phenol and a naphthol.

3. A composition as set forth in claim 2 wherein said anionic dyestuff is the reaction product of an amine of the benzene series and 2 naphthaleno, 8 phenylamino, 6 hydroxy-sulphonic acid.

4. A composition as set forth in claim 2 wherein the cation active material contains a lipophilic chain having from twelve to fourteen carbon atoms.

5. A process for the preparation of a hair dye suitable for direct dyeing of hair at room temperatures which comprises neutralizing an anionic acid dyestuff with a cationic organic base selected from the group consisting of an amine and a quaternary ammonium compound, and said base having a lipophilic chain of at least six carbon atoms in the molecule to thereby form a dyestuff complex and solubilizing the thus formed product by introducing the presence of a non-ionic solubilizing group in quantity just sufficient to provide complete solution, said solubilizing group being provided in part by condensing the dyestuff complex with ethylene oxide and in part by adding a separate non-ionic solubilizing material which is a hydroxy containing compound selected from the group consisting of an alcohol, a phenol and a naphthol.

6. A composition for dyeing live human hair comprising a complex of an anionic dyestuff and a cation active material solubilized by a non-ionic solubilizing agent, said cationic agent being present in equi-molecular portions to the anionic dyestuff so as to neutralize the latter and the non-ionic solubilizing agent being present in just sufficient quantity to bring the complex into solution in water, said cationic material being a base selected from the group consisting of an amine and a quaternary ammonium compound, said cation active material containing a lipophilic chain of at least six carbon atoms and said anionic dyestuff being characterized by acidity and the presence of at least one acid group selected from the group consisting of a free sulphonic acid group, a free carboxylic group and a free acid hydroxyl group, said solubilizing agent being a solubilizing group on said cation active material produced by the condensation thereof with ethylene dioxide.

7. A composition as set forth in claim 6 wherein said anionic dyestuff is the reaction product of an amine of the benzene series and 2 naphthaleno, 8 phenylamino, 6 hydroxy-sulphonic acid.

8. A process for the preparation of a hair dye suitable for direct dyeing of hair at room temperatures which comprises neutralizing an anionic acid dyestuff with a cationic organic base selected from the group consisting of an amine and a quaternary ammonium compound, and said base having a lipophilic chain of at least six carbon atoms in the molecule to thereby form a dyestuff complex and solubilizing the thus formed product by introducing the presence of a non-ionic solubilizing group in quantity just sufficient to provide complete solution, said solubilizing group being provided entirely by condensing the dyestuff complex with ethylene oxide in quantity just sufficient to render the condensed reaction product totally soluble in water.

9. A process for the preparation of a hair dye suitable for direct dyeing of hair at room temperatures which comprises neutralizing an anionic acid dyestuff with a cationic organic base selected from the group con-

sisting of an amine and a quaternary ammonium compound, and said base having a lipophilic chain of at least six carbon atoms in the molecule to thereby form a dyestuff complex and solubilizing the thus formed product by introducing the presence of a non-ionic solubilizing group in quantity just sufficient to provide complete solution, said solubilizing group being provided in the form of a water miscible condensation product of ethylene oxide with a hydroxy containing compound selected from the group consisting of an alcohol, a phenol and a naphthol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,208,594	Orelup	July 23, 1940
2,359,783	Orelup	Oct. 10, 1941

FOREIGN PATENTS

1,074,030	France	Mar. 31, 1954
860,689	Germany	Dec. 22, 1952
1,044,113	France	June 17, 1953
216,267	Switzerland	Dec. 1, 1941