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AEROSOL FOAM FOR DYEING HAIR COMPRISING A 5,6- DIHYDROXYINDOLE DERIVATIVE

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(57) Claim

1. An aerosol device containing a dye composition suitable for human keratinous fibres, which composition comprises 5,6-dihydroxyindole and at least 0.1% by weight, relative to the total weight of the composition, of a foam generator in a cosmetically acceptable aqueous medium, wherein the composition is contained under pressure in the aerosol device in the presence of a propellent agent under such conditions that a dyeing foam having a density of up to 0.4 g/cm^3 may be produced therefrom.

18. A process for dyeing human keratinous fibres wherein a dyeing foam as defined in claim 17 is applied to the fibres.

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

AN AEROSOL DEVICE CONTAINING A COMPOSITION BASED ON 5,6-DIHYDROXYINDOLE FOR HUMAN KERATINOUS FIBRES

The following statement is a full description of this invention, including the best method of performing it known to : us

The present invention relates to an aerosol device containing a composition comprising 5,6-dihydroxyindole for dyeing human keratinous fibres, especially hair, and to a process using this composition.

It is well known that natural biosynthesis of eumelanins from tyrosine involves several steps. One of these consists of the formation of 5,6-dihydroxyindole, which is oxidized to yield a pigment which is one of the principal constituents of eumelanin.

Many hair-dyeing processes making use of 5,6-dihydroxyindole, or a derivative thereof, have already been proposed.

Thus French Patent No. 1,166,172, discloses a solution of 5,6-dihydroxyindole at acidic pH which is applied to hair for 5 to 60 minutes and, without rinsing and after rough drying, the colour is developed using an oxidizing agent such as hydrogen peroxide.

According to French Patent No. 1,133,594, an alkaline solution containing 5,6-dihydroxyindole with an oxidizing agent or an oxidation catalyst, if desired, is applied to hair. French Patent Application No. 2,536,993 discloses a dyeing process in several stages separated by rinsings which consists in applying, in one step, a solution

of a metal salt at an alkaline pH and, in another step, a solution of 5,6-dihydroxyindole. After rinsing or shampooing, these two steps may or may not be followed by the application of hydrogen peroxide in order to regulate the final shade by means of lightening.

These processes involve various disadvantages, insofar as they result either in weak shades, or in the production of shades which are strong but require a long exposure time. Other disadvantages of these processes are the need to employ several steps and to store the composition in several separate containers, the contents of which are mixed before use.

We have found that it is possible to dye hair in a single step with a dye composition containing 5,6-dihydroxyindole by packaging and storing the composition in a pressurized aerosol device, in the presence of a propellent agent and a foam generator under conditions such as to form a foam by expansion in free air.

Surprisingly, we have found that the colour strength of the dye, when dispensed in foam form from the aerosol device, is superior to that of the same composition when in conventional solution or emulsion form, which are the forms employed hitherto for dyeing hair with 5,6-dihydroxyindole.

The behaviour of 5,6-dihydroxyindole in a foam is particularly suprising in its specificity.

The dye composition dispensed in foam form from the aerosol device produces shades which do not change after permanent waving; furthermore, it stains the scalp to a lesser extent.

The dyeing power of 5,6-dihydroxyindole is remarkably well preserved on storage in a package of this kind. When dispensed in foam form from a pressurized aerosol device, the composition makes it possible to obtain less selective dyeing and better cover on white hair. Its use is particularly convenient and rapid insofar as it is stored in a single package and is applied in a single step and as the foam generated under pressure is distributed very rapidly and uniformly over hair, dyeing it.

The present invention therefore provides an aerosol device containing a dye composition suitable for human keratinous fibres, which composition comprises 5,6-dihydroxyindole and at least 0.1% by weight, relative to the total weight of the composition, of a foam generator in a cosmetically acceptable aqueous medium, wherein the composition is contained under pressure in the aerosol device in the presence of a propellent agent under such conditions that a dyeing foam having a density of up to 0.4 g/cm^3 may be produced therefrom.

The keratinous fibres are preferably hair.

The present invention also provides a process for dyeing human keratinous fibres, in particular hair, wherein

a dyeing foam dispensed from the aerosol device is applied to the fibres.

5,6-dihydroxyindole is preferably present in the composition in a proportion of from 0.1 to 5%, preferably from 0.5 to 2%, by weight relative to the total weight of the composition.

A "foam generator" is a product, which is preferably a surface-active agent or a foaming polymer or a mixture thereof, which, at a concentration of 1% in water by weight, permits the formation of a foam having a density of up to 0.4 g/cm^3.

The density is determined according to the following method:

The cosmetic mixture is packaged in a single-block, bullet-necked aluminium can (45 x 128) with a Precision P 73 valve without a dip tube, having an axial dispenser actuator for a conical collar (021550).

The aerosol can is filled with 90 g of the cosmetic medium to be tested and 10 g of Freon F 114/F 12 propellent gas (43/57). The manipulation is performed 24 hours after the pressurization of the aerosol in a room conditioned at 20°C $\pm$ 1°, the hardware and the sample being at the same temperature. A cylindrical cup is weighed empty (weight P 1), and then immediately filled with the foam produced by the aerosol. Each aerosol can is shaken before use so as to emulsify the propellent gas.

To give a uniform distribution of the foam in the cup, the aerosols are used head down with a rotary and uniform motion.

As soon as the foam has expanded, it is immediately and rapidly levelled with a spatula and the cup is reweighed (weight P 2).

The foam density is determined according to the following formula:

$$\text{density at } 20^{\circ}C = \frac{P\,2 - P\,1}{V}$$

(V is the volume of the cup). Three determinations are carried out for each medium, the value taken being the mean value of these determinations (in g/cm^3).

The surface-active agent is preferably a nonionic, anionic, cationic or amphoteric surfactant, which are well known in the state of the art. These agents are preferably employed in the composition in a proportion of from 0.1 to 55%, preferably from 1 to 40%, by weight, relative to the total weight of the composition.

The foam generator may, for example, be a foaming polymer, for example an anionic, nonionic, amphoteric or cationic polymer or a mixture thereof, preferably with a molecular weight of from 500 to 3,000,000.

Examples of cationic foaming polymers are:

quaternized vinylpyrrolidone/dialkylaminoalkyl

acrylate and methacrylate copolymers, described for example in French Patent No. 2,077,143 such as the products sold by General Aniline under the names "Gafquat 734 or 755" (Trade Marks), cellulose ether derivatives containing quaternary ammonium groups, described for example in French Patent No. 1,492,597 such as the polymers sold by Union Carbide under the names: "JR or LR" (Trade Marks), for example "JR 125", "JR 400", "JR 30 M", "LR 400" or "LR 30 M" (Trade Marks), cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium group such as the products sold by National Starch under the names "Celquat L 200" and "Celquat H 100" (Trade Marks), and polyoxyethylenated polyamines such as those sold by Henkel under the name "Polyquart H" (Trade Mark).

Examples of anionic foaming polymers are:

uncrosslinked polymers of acrylic or methacrylic acid or their salts, crotonic acid/vinyl acetate copolymers grafted onto polyalkylene glycols, such as the product sold by Hoechst under the name "Aristoflex A" (Trade Mark), polymers of maleic acid or anhydride with methacrylic acid or polymers of maleic anhydride and vinyl ether, such as the products marketed by GAF under the names "Gantrez ES or AN" (Trade Marks), and in particular the product sold under the name "Gantrez ES 425" (Trade Mark), and substituted or unsubstituted copolymers of acrylamide and unsaturated carboxylic acids such as N-tert-butylacrylamide/N-hydroxy-

ethylacrylamide/acrylic acid terpolymer described in, for example, French Patent 2,432,528.

Examples of nonionic foaming polymers are partially acetylated polyvinyl alcohols, in particular the product sold by Hoechst under the name of "Mowiol 40.88" (Trade Mark) and their ethers, such as those sold by GAF under the name "Gantrez M" (Trade Mark).

Examples of amphoteric foaming polymers are the methacrylic copolymers of the betaine type, such as the resin sold by Mitsubishi Petrochemical under the name "Amphoset" (Trade Mark) or acrylic terpolymers such as the product sold by National Starch under the name "Amphomer" (Trade Mark).

The foaming polymer is preferably present in the composition in a proportion of from 0.1 to 5% by weight, relative to the total weight of the composition.

The cosmetically acceptable aqueous medium preferably has a pH of from 4 to 11, more particularly from 5 to 9.5. The pH may be adjusted with an alkalifying or acidifying agent usually employed in hair-dye compositions.

In any event, the aqueous cosmetic medium containing a foam generator should permit the formation of a foam having a density of up to 0.4 g/cm^3, determined as indicated above.

In addition to water, the compositions may also contain cosmetically acceptable solvents in a proportion

which does not affect foam formation. Examples of such solvents are C_1-C_4 alkanols such as ethanol, isopropanol and tert-butyl alcohol, ethylene glycol monomethyl, monoethyl or monobutyl ethers and ethylene glycol monoethyl ether acetate. These solvents are generally present in a proportion of less than 50%, more particularly less than 20%, by weight, relative to the total weight of the composition.

The composition may, for example, be thickened with a thickening agent such as sodium alginate, gum arabic, guar or carob gum, a heterobiopolymer such as xanthane gum, pectin, a cellulose derivative such as methyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, hydroxypropyl cellulose or carboxymethyl cellulose, a crosslinked acrylic acid derivative having thickening properties or an inorganic thickening agent such as bentonite. The thickening agent is preferably present in a proportion of from 0.1 to 5%, in particular from 0.5 to 3%, by weight, relative to the total weight of the composition.

If desired, the compositions may contain a reducing agent in a small quantity, preferably less than 0.5% by weight relative to the total weight of the composition, such as a thiol acid or ascorbic acid.

The composition may, for example, contain other adjuvants usually employed in hair-dyeing compositions, such as pentrating agents, swelling agents, sequestering agents, film-forming agents, antioxidants, buffers, electrolytes and

perfumes. The adjuvants must be employed in proportions such that they do not prevent foam formation after the pressurized composition has been dispensed from the aerosol device.

The propellent agents employed together with the dyeing composition in the aerosol device are generally volatile hydrocarbons such as butane, isobutane, propane, and are preferably butane, partially or completely fluorinated hydrocarbons such as the products sold by Du Pont de Nemours under the name "Freon" (Trade Mark), and more particularly dichlorodifluoromethane (F12) and 1,2-dichloro-1,1,2,2-tetrafluoroethane, which are employed by themselves or mixed, for example in the form of a 40 : 60 to 80 : 20 mixture.

The pressurized aerosol devices are preferably single-container devices.

The dyeing foam is obtained after expansion, in air, of the pressurized composition defined above, and has a density of up to 0.4 g/cm^3.

The process for dyeing human keratinous fibres, especially hair, consists in aplying to the fibres a foam dispensed from the aerosol device. The fibres may or may not be rinsed after application of the dyeing foam. If they are rinsed, the composition which is applied in foam form is generally kept in contact with the fibres for a period of 5 minutes to 30 minutes, depending on the required shade.

According to a particular embodiment of the invention, a progressive dyeing, that is to say a dyeing in several stages, may be performed by successive applications of the same composition.

We have found that application of the foam is particularly easy, which enables the dye composition to be well distributed.

The examples which follow further illustrate the invention.

EXAMPLE 1

Ethylene glycol monoethyl ether	10 g
5,6-Dihydroxyindole	0.5 g
Mixture of cetostearyl alcohol and sodium lauryl sulphate sold by Henkel under the trade name of "Sinnowax SX"	0.9 g
Polyethoxylated C_{10}-C_{12} alcohol (3 moles of ethylene oxide) sold by Henkel under the trade name of "Mergital AL 309"	1.3 g
Polyethoxylated C_{10}-C_{12} alcohol (5 moles of ethylene oxide) sold by Henkel under the trade name of "Mergital AL 589"	0.9 g
Oleocetyldimethylhydroxyethylammonium chloride	2.3 g
Monoethanolamine q.s. pH : 8.7	
Thioglycolic acid	0.3 g
Water q.s.	100 g

This composition is packaged in a simple single-container aerosol.

Above composition	90 g
Propellant: Freons 12/114 (57/43)	10 g
Total :	100 g

The foam is applied directly to the hair. The foam spreads quickly on being applied. It is left in place for 5 to 10 minutes, and is then rinsed off with water. On light-background hair 90 % of which is white,

repeated application produces a progressive dyeing of the white hair to a natural shade.

EXAMPLES 2-3

Example 1 is repeated:

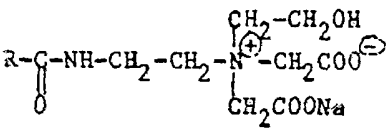
by using 1 g of 5,6-dihydroxyindole instead of 0.5 g, to produce, on medium-background hair 90 % of which is white, a progressive dyeing of the white hair to a natural shade;

by using 1.5 g of 5,6-dihydroxyindole instead of 0.5 g, to produce, by repeated application to dark-background hair 90 % of which is white, a progressive dyeing of the white hair to a natural shade.

TABLE I

Composition	Examples					
	4	5	6	7	8	9
5,6-Dihydroxyindole in g%	0.5	0.5	0.5	0.5	0.5	0.5
Sodium lauryl ether sulphate oxyethylenated with 2 moles of ethylene oxide, in g% AS	3	3				
N,N-Diethylaminopolyoxyethyl copra carboxylate lactate with 4 moles of ethylene oxide	-		3	3		
Triethanolamine C_{12}-C_{14} alkyl sulphate, in g% AS					3	
Sodium laurylsarcosinate						3
Ethyl alcohol g	10	10	10	10	10	10
Citric acid q.s. pH	5.5		5.5			
2-Amino-2-methyl-1-propanol q.s. pH		8.5		8.5	8.5	8.5
Water q.s. g	100	100	100	100	100	100

TABLE II

Composition	Examples					
	10	11	12	13	14	15
5,6-Dihydroxyindole in g%	0.5	0.5	0.5	0.5	0.5	0.5
Ricinoleylmonoethanolamide disodium sulphosuccinate	3					
Sodium laureth-13 carboxylate		3				
Oleocetyldimethylhydroxyethylammonium chloride			3			
Octylphenol with 10 moles of ethylene oxide				3		
 R-C(=O) = Copra fatty acid radical					3	
Dodecanediol polyglycerolated with 3.5 moles						3
Ethyl alcohol in g	10	10	10	10	10	10
2-Amino-2-methyl-1-propanol q.s. pH	8.5	8.5	8.5	8.5	8.5	8.5
Water q.s. g	100	100	100	100	100	100

EXAMPLE 16

5,6-Dihydroxyindole	1	g
Hydroxyethyl cellulose copolymer grafted with diallyldimethylammonium chloride, sold by National Starch under the trade name of "Celquat L 200"	0.8	g AS
pH : 5.7 natural		
Water q.s.	100	g

EXAMPLE 17

5,6-Dihydroxyindole	1.5	g
(Tallow)alkyltrimethylammonium chloride sold as a mixture with isopropyl alcohol at a concentration of 50 % by Armak under the trade name "Arquad T 50"	1	g AS
Hydroxyethyl cellulose/epichlorohydrin polymer quaternized with trimethylamine, sold by Union Carbide under the trade name "JR 400"	0.5	g
pH : 5.3 natural		
Water q.s.	100	g

The compositions of Tables I and II and those of Examples 16 and 17 are packaged in a simple single-container aerosol device.

Above composition (4 to 15)	90 g
Freon 12/114 (57/43)	10 g
Total	100 g

The foam is applied to the hair in a similar manner

to that in Example 1. After several applications, the white hair takes up a natural colour.

EXAMPLE 18

5,6-Dihydroxyindole	2 g
Isopropyl alcohol	5 g
Sodium laureth-13 carboxylate	2 g
Sodium laurylsarcosinate	2 g
Water q.s.	100 g
Natural pH : 7	

Aerosol packaging:

Above composition :	90 g
Freon 12/114 (57/43) :	10 g
Total	100 g

The foam is applied to 90% white natural hair. It is left in place for 10 min and is rinsed off with water.

After one application the hair is dyed a natural grey shade.

EXAMPLE 19

5,6-Dihydroxyindole	0.8 g
Ethylene glycol monoethyl ether	4 g
Xanthane gum sold by Rhone-Poulenc under the trade name Rhodopol SC.	0.5 g
Nonionic surfactant produced according to French Patent 71/17,206 by the condensation of 3.5 moles of glycidol with a C_{11}-C_{14} α-diol	1 g

Triethanolamine	q.s. pH:7	
Water	q.s.	100 g

Aerosol packaging:

Above composition:	90 g
Freon 12/114 (57/43):	10 g
Total	100 g

The foam is applied to 90% white natural hair. After one application which is not followed by rinsing, the hair is dyed a natural grey shade.

EXAMPLE 20

5,6-Dihydroxyindole	2 g
Ethyl alcohol	5 g
Polyoxyethylenated polyamide sold by Henkel under the trade name Polyquart H	1.5 g
NaOH q.s. pH:7	
Water q.s.	100 g

Aerosol packaging:

Above composition :	90 g
Freon 12/114 (57/43):	10 g
Total	100 g

The foam is applied to 90% white natural hair. It is left in place for 10 min. It is rinsed off with water. After 3 successive applications the hair is dyed a natural medium grey shade.

The claims defining the invention are as follows:

1. An aerosol device containing a dye composition suitable for human keratinous fibres, which composition comprises 5,6-dihydroxyindole and at least 0.1% by weight, relative to the total weight of the composition, of a foam generator in a cosmetically acceptable aqueous medium, wherein the composition is contained under pressure in the aerosol device in the presence of a propellent agent under such conditions that a dyeing foam having a density of up to 0.4 g/cm^3 may be produced therefrom.

2. A device according to claim 1 wherein the 5,6-dihydroxyindole is present in a proportion of from 0.1 to 5% by weight relative to the total weight of the composition.

3. A device according to claim 2 wherein the 5,6-dihydroxyindole is present in a proportion of from 0.5 to 2% by weight relative to the total weight of the composition.

4. A device according to any one of claims 1 to 3 wherein the foam generator is an anionic, nonionic, amphoteric or cationic surface-active agent or a mixture thereof.

5. A device according to claim 4, wherein the surface-active agent is present in a proportion of from 0.1 to 55% by weight relative to the total weight of the composition.

6. A device according to claim 5 wherein the surface-active agent is present in a proportion of from 1 to 40% by weight based on the total weight of the composition.

7. A device according to any one of claims 1 to 3 wherein the foam generator is an anionic, cationic, nonionic or amphoteric foaming polymer.

8. A device according to claim 7 wherein the foaming polymer is:

(1) a quaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymer, a cellulose ether derivative containing quaternary ammonium groups, a cellulose copolymer or cellulose derivative grafted with a water-soluble quaternary ammonium group, or a polyoxyethylenated polyamine;

(2) an uncrosslinked polymer of acrylic or methacrylic acid or a salt thereof, a crotonic acid/vinyl acetate copolymer grafted onto a polyalkylene glycol, a polymer of maleic acid or anhydride with methacrylic acid or a polymer of maleic anhydride and vinyl ether, or a substituted or unsubstituted copolymer of an acrylamide unsaturated carboxylic acid;

(3) a methacrylic copolymer in betaine form or an amphoteric acrylic terpolymer; or

(4) a partially acetylated polyvinyl alcohol or polyvinyl alcohol ether.

9. A device according to claim 7 or 8 wherein

the foaming polymer is present in a proportion of from 0.1 to 5% by weight, relative to the total weight of the composition.

10. A device according to any one of claims 1 to 9 wherein the aqueous medium has a pH of from 4 to 11.

11. A device according to claim 10 wherein the pH is from 5 to 9.5.

12. A device according to any one of claims 1 to 10 wherein the medium contains a cosmetically acceptable organic solvent which is a C_1-C_4 alkanol, ethylene glycol monomethyl, monoethyl or monobutyl ether or ethylene glycol monoethyl ether acetate in a proportion of less than 50% by weight, relative to the total weight of the composition.

13. A device according to claim 12 wherein the organic solvent is present in a proportion of less than 20% by weight relative to the total weight of the composition.

14. A device according to any one of claims 1 to 13 wherein the composition additionally comprises a thickening agent in a proportion of from 0.1 to 5% by weight, relative to the total weight of the composition.

15. A device according to any one of claims 1 to 14 wherein the propellent agent is a volatile hydrocarbon which is butane, isobutane, propane or a partially or completely fluorinated hydrocarbon, or a mixture thereof.

16. An aerosol device substantially as hereinbefore described in any one of the Examples.

17. A dyeing foam having a density of up to 0.4 g/cm^3 produced by dispensing the composition from an aerosol device as defined in any one of claims 1 to 16.

18. A process for dyeing human keratinous fibres wherein a dyeing foam as defined in claim 17 is applied to the fibres.

19. A process for dyeing human keratinous fibres wherein a foam dispensed from an aerosol device as defined in any one of claims 1 to 16 is applied to the fibres and a rinsing step is performed after an application time of from 5 to 30 minutes.

20. A process according to claim 18 or 19 wherein the dyeing foam is applied several times in succession.

~~21. A device or process as disclosed herein in all its new and useful aspects.~~

DATED this 16th day of June 1987.

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