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## METHOD OF USING DIPHENYL AZO COMPOUNDS AS DIRECT DYES IN ALKALINE MEDIA ON HUMAN HAIR

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This invention relates to the dyeing of hair and other keratinous fibres and to dyes for use thereon.

It is known to dye live hair by means of oxidation dyes consisting of benzene polyamine or hydroxyamine derivatives. The commonest method of application is to mix an aqueous solution of these products with hydrogen peroxide immediately before application to the hair. Such dyes may give intense natural shades but have a number of disadvantages which are well known to the users.

These disadvantages includes, first of all, the poor utilization of the polyamine or hydroxyamine derivative; only a part of the derivative is converted into dye in the hair, the remainder being oxidized in the bath and eliminated in the rinsing.

Another disadvantage arises out of the fact that it is necessary to carry out the mixing of the two solutions immediately before application to the hair during use since otherwise the dyeing mixture rapidly oxidizes and gives very inferior results.

Finally, the most useful and the most frequently employed of these derivatives tend to give rise to allergic reactions on some people, which is a serious disadvantage and necessitates certain precautions in their application. Indeed, such dyes must be tested before being used in order to determine whether the person to be treated is sensitive to the dye which it is desired to use.

It is possible to use for the dyeing of hair a preformed dye which becomes fixed on the hair in the state in which it is present in the dyeing solution at the time of use. Dyes of this type generally do not have the disadvantages of dyes of the type referred to above, but they have other disadvantages owing to which they have rarely been used for dyeing hair.

Although there are a large number of direct dyes which can be used for dyeing textile fibres, it has hitherto been very difficult to find dyes which are suitable for the dyeing of hair. In particular, azo dyes, which are the most numerous, give only very mediocre results in this particular application. Some of them have been used but they give only faint shades.

According to a first feature of the present invention there are provided novel azo compounds for use in dyeing hair and other keratinous fibres, which are azobenzenes which contain as substituents in one of the benzene rings at least two hydroxy groups or an amino group and at least one hydroxy group, and the other benzene ring of which carries no substituents or may carry at least one hydroxy substituent.

According to a second feature of the invention there are provided compositions for dyeing hair or other keratinous fibre which comprise aqueous solutions of azobenzenes as just defined.

According to a third feature of the invention there is provided a method of dyeing hair or other keratinous fibre which comprises applying thereto a composition containing an azobenzene as just set forth.

In contrast to the azo dyes hitherto suggested for use in dyeing hair, the dye solutions of the present invention color hair very strongly, especially in the presence of

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ammonia, and at pH 7 or higher, i.e. under the conditions normally employed in hair dyeing. However, it is possible in the case of some dye solutions according to the invention to effect the dyeing of the hair at a pH below 7.

The azobenzene dyes according to the invention may be used in mixture with one another or even with other coloring agents which effect dyeing under similar conditions.

The dyeing solutions according to the invention may conveniently be prepared by dissolving the substituted azobenzene either in water or in an aqueous solution of alkali salts of weak acids of pH between 7 and 11. Alternatively the substituted azobenzene may be dissolved in ammonia or in a caustic alkali solution diluted with water and then, if necessary, there may be added to the resulting solution a product capable of lowering its pH, such as an acid or an acid salt such as sodium bicarbonate or monosodium phosphate. If the substituted azobenzene is dissolved in aqueous caustic alkali without a subsequent addition of a product lowering the pH, it is essential that the quantity of this alkali be lower than that necessary for saturating the hydroxyl groups of the substituted azobenzene so as not to impair the keratinic fibre which it is desired to dye.

Examples of substituted azobenzenes which may be utilised in the invention are:

2:3:4-trihydroxyazobenzene,  
3:4:5-trihydroxyazobenzene,  
2:4:6-trihydroxyazobenzene,  
2:4:2'-trihydroxyazobenzene,  
2:4:4'-trihydroxyazobenzene,  
2-amino-4:2'-dihydroxyazobenzene,  
4-amino-2:2'-dihydroxyazobenzene,  
2-amino-4:4'-dihydroxyazobenzene,  
4-amino-2:4'-dihydroxyazobenzene,  
2:4:6:4'-tetrahydroxyazobenzene.

These substituted azobenzenes may be prepared by coupling a salt of diazobenzene or of a hydroxy-substituted diazobenzene with a polyhydroxyl derivative of benzene or with an amino, mono- or polyhydroxyl, derivative of benzene.

In some cases, there is obtained by this process a mixture of isomers which it may be desirable to separate.

The dyeing solutions according to the invention may contain, in addition to the substituted azobenzene, various ingredients which it is known to use in hair dyes, more especially wetting agents, foaming products, thickeners, and products intended to swell the keratinic fibre and to increase the penetration of the dye.

The following examples will serve to illustrate the invention:

### Example I

0.5 g. of 2-amino-4:4'-dihydroxyazobenzene (obtained by coupling diazotized p-aminophenol with m-aminophenol) is dissolved with the aid of 3 cc. of ammonia solution (22° Bé.) and then made up to 100 cc. with water. The pH of the solution is about 10.5. Naturally white hair which has undergone no previous dyeing or permanent waving treatment is impregnated with the aid of a brush with the solution obtained, and then rinsed for 20 minutes. The hair is thereafter treated by a shampoo of standard type and then again rinsed and dried. It is dyed an intense reddish-yellow colour.

### Example II

The procedure of Example I is followed, using 0.5 g. of a mixture of 2-amino-4:2'-dihydroxyazobenzene and 4-amino-2:2'-dihydroxyazobenzene (this mixture having been obtained by coupling diazotized o-aminophenol with m-aminophenol). The hair is dyed an intense yellow color.

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*Example III*

The procedure of Example I is followed, using 0.5 g. of 2:4:6-trihydroxyazobenzene (obtained by coupling diazotized aniline with phloroglucinol). The hair is dyed an intense greenish-yellow color.

*Example IV*

The procedure of Example I is followed, using 0.5 g. of 2:4:2'-trihydroxyazobenzene (obtained by coupling diazotized o-aminophenol with resorcinol). The hair is dyed an intense reddish yellow color.

*Example V*

The procedure of Example I is followed, using 0.5 g. of 2:4:4'-trihydroxyazobenzene (obtained by coupling diazotized p-aminophenol with resorcinol). The hair is dyed an intense greenish-yellow color.

*Example VI*

The procedure of Example I is followed, using 0.5 g. of 2:4:6:4'-tetrahydroxyazobenzene (obtained by coupling diazotized o-aminophenol with phloroglucinol). The hair is dyed an intense yellow color.

*Example VII*

The procedure of Example I is followed, using 0.5 g. of a mixture of 2:3:4-trihydroxyazobenzene and 3:4:5-trihydroxyazobenzene (this mixture having been obtained by coupling diazotized aniline with pyrogallol). The hair is dyed a deep greenish-yellow color.

*Example VIII*

1 g. of 2:4:6-trihydroxyazobenzene is made up into a paste in 8 cc. of normal caustic soda solution and then diluted to 100 cc. with water, the mixture thereafter being heated to the neighborhood of boiling point. After cooling the solution obtained, which has a pH of 9.1, naturally white hair which has not previously undergone any dyeing or permanent waving operation is impregnated with the solution by means of a brush and, after a period of contact of 20 minutes, the hair is rinsed and optionally treated with a shampoo and again rinsed. The hair is dyed an intense greenish-yellow color.

*Example IX*

0.5 g. of 2-amino-4:4'-dihydroxyazobenzene is worked up into a paste in 2 cc. of normal caustic soda solution and then diluted to 100 cc. with water and heated to the neighborhood of boiling point. Hair is treated with the cooled solution, which has a pH of about 9.5, as indicated in Example VIII. It is dyed a yellow shade.

*Example X*

0.5 g. of 2:4:6-trihydroxyazobenzene is dissolved in 5 cc. of normal caustic soda solution, and water and 16.5 cc. of sodium bicarbonate solution (85 g. per litre) are added to obtain a total volume of 100 cc. This dyeing solution, which has a pH of about 9.1, imparts a yellow shade verging on green to hair under the conditions indicated in Example VIII.

*Example XI*

A solution is prepared by dissolving 0.5 g. of 2:4:6:4'-tetrahydroxyazobenzene in 4.15 cc. of normal caustic soda solution in the cold. There is then added 8.4 cc. of sodium carbonate (106 g. per litre) and 11 c. of normal hydrochloric acid, and the solution is then diluted with water to a volume of 100 cc. The pH of this dyeing solution is about 8.9. Under the conditions indicated in Example VIII, it imparts to naturally white hair, which has not previously undergone any dyeing or permanent waving operation, a yellow shade.

*Example XII*

0.5 g. of 2:4:6-trihydroxyazobenzene is dissolved in 5 cc. of a mixture of monosodium phosphate and disodium

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phosphate having a pH of 8, and the mixture is diluted with water to a total volume of 100 cc. The dyeing solution thus obtained is buffered and has a pH of 8. Naturally white hair, which has not undergone any dyeing or permanent waving operation, is dyed a yellow-green shade therewith.

*Example XIII*

0.5 g. of 2-amino-4:4'-dihydroxyazobenzene is dissolved in 5 cc. of a solution containing a mixture of sodium carbonate and sodium bicarbonate, of pH 9, and this solution is diluted with lukewarm water to a volume of 100 cc. The dyeing solution thus obtained, after cooling, is buffered and possesses a pH of about 9. Naturally white hair, which has not previously undergone any dyeing or permanent waving operation, is dyed a yellow shade therewith.

What is claimed is:

1. A method of dyeing live human hair, which consists in; bringing said fibres into contact with an aqueous solution containing an azo benzene selected from the group consisting of 2:3:4-trihydroxyazobenzene, 3:4:5-trihydroxyazobenzene, 2:4:6-trihydroxyazobenzene, 2:4:2'-trihydroxyazobenzene, 2:4:4'-trihydroxyazobenzene, 2-amino-4:4'-dihydroxyazobenzene, 4-amino-2:2'-dihydroxyazobenzene, 2-amino-4:4'-dihydroxyazobenzene, 4-amino-2:4'-dihydroxyazobenzene, and 2:4:6:4'-tetrahydroxyazobenzene, said solution being adjusted to a pH of 7 to 11, and being allowed to remain in contact therewith for approximately 20 minutes, then shampooing, rinsing and drying.

2. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2:3:4-trihydroxyazobenzene adjusted to a pH of between 7 to 11, and allowing said hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

3. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 3:4:5-trihydroxyazobenzene adjusted to a pH of between 7 to 11 and allowing the said to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

4. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2:4:6-trihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

5. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2:4:2'-trihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

6. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2:4:4'-trihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

7. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2-amino-4:4'-dihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

8. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 4-amino-2:2'-dihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

9. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous

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solution of 2-amino-4:4'-dihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

10. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 4-amino-2:4'-dihydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

11. A method of dyeing live human hair, which consists in bringing the hair into contact with an aqueous solution of 2:4:6:4'-tetrahydroxyazobenzene, adjusted to a pH of between 7 to 11 and allowing the hair to remain

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in contact therewith for approximately 20 minutes, shampooing, rinsing and drying the hair.

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