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HAIR DYE COMPRISING DIAMINOPYRIDINES

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8 Claims. (Cl. 167—88)

The present invention relates to a composition and method for dyeing hair and, more particularly, the present invention is concerned with imparting to hair a red, green or blue color or color component such as is frequently desirable for modifying the other dye components in order to give the hair the desired color and usually also a more natural appearance.

The present application is a continuation-in-part of my co-pending application Serial No. 180,867, filed March 19, 1962, now abandoned, and entitled, "Composition and Method for Dyeing Hair."

For the dyeing of hair, dye intermediates may be used which upon oxidation will be developed to form the respective dye. Usually oxidation of the dye intermediate is carried out shortly before or during the dyeing of the hair. In most cases, the dye intermediates are aromatic amines which in an alkaline, preferably ammoniacal, medium and possibly with the addition of an oxidizing agent will give to the hair the desired more or less naturally looking color.

In order to obtain the desired final coloring of the hair, it is usually required that the colors yellow, red, blue and green are available in order to achieve the desired color tone. This is somewhat similar to the requirements with respect to the dyeing of textiles.

In order to obtain a strong color tone or tint, it is necessary that the above mentioned basic colors achieve a deep and full coloring of the hair. Furthermore, it is important that the desired color of the dyed hair, once it is obtained, will not be changed by subsequent mechanical or chemical treatment of the hair.

The use of so-called shading dyes or "modifiers" has been suggested in order to obtain more natural hair coloring or certain fashionable shades of hair coloring.

Such "modifiers" may consist for instance of 1,2 dioxybenzene, 1,3 dioxybenzene, 1,4 dioxybenzene and 1,2,3, trioxybenzene. The above mentioned compounds will modify the color of dyed keratin fibers, particularly of living hair, i.e., the natural hair of a human being, however, only in the direction towards yellow or orange.

Other compounds such as m-diaminobenzene, m-diamino-anisole, m-diaminophenetole, alpha-naphthol and beta-naphthol which are also known as "modifiers" will yield only blue, violet and bluish-red color tones. Furthermore, the last mentioned compounds upon being subjected to an acidic medium will change from blue to red. This turning of the blue color to or towards red also will occur upon an acidic after-treatment of the hair or, after some time, as the result of nearly inevitable contact with acidic sweat, it is a serious disadvantage of the last mentioned compounds.

It also has been proposed to improve the color fastness of hair dyes by combining oxidation dyestuffs with 3,4-diaminobenzoic acid or salts thereof. However, this combination is suitable only for blond and light brown color tones but is not effective for medium brown, dark brown or black hair dyes. It is also impossible by employing diaminobenzoic acid or its salts to obtain the fashionable bluish shading, nor is it possible in this manner to produce a green hair color which is desired as modifier or complementary color to counteract the undesirable reddish tone or dyed hair.

A clear green color can be obtained with salts of weak organic acids, for instance acetates of 4-amino-diphenylamine which, in the "3" position has been substituted with an alkoxy group. However, these salts are split by hydrolysis and thereby the free base is formed. Thus only a weak slightly green dyeing of the hair is achieved in this manner.

The green hair color, however, is a very important shading or modifying color due to the fact that it is the complementary color to the undesirable reddish tinge so frequently occurring in the dyeing of hair.

A reddish color tone is required, for instance, in order to obtain a fashionable color of dyed, originally dark, hair, as a complementary color for overcoming a greenish tinge and to achieve several nuances of blond.

It has been proposed to obtain yellow to orange color-tones on hair by applying various nitrobenzene derivatives such as 2-amino-4-nitrophenol, 4-amino-2-nitrophenol, 4-nitro-1,2-phenylenediamine, 2-nitro-1,4-phenylenediamine or 4,6-dinitro-2-aminophenol, however, these are directly acting and not oxidation dyestuffs. Due to the fact that the last mentioned dyestuffs are water soluble, the thus obtained hair color is not of the desired permanency, particularly upon washing of the hair. A further disadvantage of these nitrobenzene derivatives is that hair of varying degree of porosity will be unevenly dyed.

Blue-red oxidative dyeing of hair can be accomplished with a combination of alpha-naphthol and p-toluylenediamine, or of m-phenylenediamine and p-aminophenol. However, only a bluish red color and not a pure red can be obtained in this manner. Furthermore, the depth of the color obtained by using alpha-naphthol is limited due to the poor solubility and the size of the molecules thereof.

It is therefore an object of the present invention to provide a composition of matter and a method by which a strong green modifier color can be imparted to the hair.

It is another object of the present invention to provide a composition of matter and a method by means of which hair can be dyed red or green or blue in a simple and economical manner.

Additional objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention is concerned with a composition of matter suitable for use in the oxidative dyeing of keratin fibers which comprises at least one dye intermediate adapted to be oxidized into a dye, and at least one diaminopyridine.

More particularly, the present invention also proposes a composition of matter suitable for use in the oxidative dyeing of hair which comprises at least one dye intermediate adapted to be oxidized to form a dye and selected from the group consisting of

p-phenylenediamine,
p-toluylenediamine,
m-phenylenediamine,
m-toluylenediamine,
p-aminophenol,

p-amino-N-dimethylaniline,
4,4'-diaminodiphenylamine,
4-aminodiphenylamine,
4-amino-4'-oxydiphenylamine,
m-diaminoanisole,
m-diethylaminophenol,

and at least one diaminopyridine selected from the group consisting of

2,6-diaminopyridine,
2,3-diaminopyridine,
4-methoxy-2,6-diaminopyridine,
4-ethoxy-2,6-diaminopyridine,
4-methyl-2,6-diaminopyridine,
4-hydroxy-2,6-diaminopyridine,
3-hydroxy-2,6-diaminopyridine,
3-hydroxy-4-methyl-2,6-diaminepyridine,
3-hydroxy-4-methoxy-2,6-diaminopyridine,
6-hydroxy-4-methyl-2,3-diaminopyridine,
6-methoxy-2,3-diaminopyridine,
6-ethoxy-2,3-diaminopyridine,
2,5-diaminopyridine,
2-dimethylamino-5-aminopyridine,
2-methylamino-5-aminopyridine,
2-diethylamino-5-aminopyridine,
2-ethylamino-5-aminopyridine,
2-amino-5-dimethylamino-pyridine,
2-amino-5-methylaminopyridine,
2-methylamino-5-methylamino-pyridine,
5,5'-diamino-bis(2-pyridil)amine and
hydrochlorides thereof.

The present invention also contemplates in a method of dyeing hair, the steps of applying to hair which is to be dyed a dye intermediate adapted to be oxidized into a dye, and at least one diaminopyridine.

According to a preferred embodiment, the method of dyeing hair according to the present invention comprises the steps of applying to hair which is to be dyed a first substance comprising a carrier material having distributed therethrough an alkalizing agent and a dye intermediate adapted to be oxidized into a dye and selected from the group consisting of

p-phenylenediamine,
p-toluylenediamine,
m-phenylenediamine,
m-toluylenediamine,
p-aminophenol,
p-amino-N-dimethylaniline,
4,4'-diaminodiphenylamine,
4-aminodiphenylamine,
4-amino-4'-oxydiphenylamine,
m-diamino-anisole,
m-diethylaminophenol,

and a second substance comprising a carrier material having distributed therethrough an oxidizing agent and at least one diaminopyridine, selected from the group consisting of

2,6-diaminopyridine,
2,3-diaminopyridine,
4-methoxy-2,6-diaminopyridine,
4-ethoxy-2,6-diaminopyridine,
4-methyl-2,6-diaminopyridine,
4-hydroxy-2,6-diaminopyridine,
3-hydroxy-2,6-diaminopyridine,
3-hydroxy-4-methyl-2,6-diaminopyridine,
3-hydroxy-4-methoxy-2,6-diaminopyridine,
6-hydroxy-4-methyl-2,3-diaminopyridine,
6-methoxy-2,3-diaminopyridine and
6-ethoxy-2,3-diamino-pyridine,
2,5 diaminopyridine,
2-dimethylamino-5-pyridine,
2-methylamino-5-aminopyridine,
2-diethylamino-5-aminopyridine,

2-ethylamino-5-aminopyridine,
2-amino-5-dimethylaminopyridine,
2-amino-5-methylaminopyridine,
2-methylamino-5-methylaminopyridine,
5,5'-diamino-bis(2-pyridil)amine and
hydrochlorides thereof.

The present invention also proposes a developer for use in the oxidative dyeing of hair, which comprises an aqueous solution of an oxidizing agent adapted to oxidize an oxidation base of a hair dye, and a diaminopyridine.

Thus, according to the present invention it has been found that stable, strong and acid resistant red, blue and green colorations of hair can be produced by treating the hair with a neutral or slightly alkaline solution, cream or paste containing dye intermediates which may be developed into dyestuffs by being oxidized, and also containing a diaminopyridine.

As oxidizable dye intermediates, primarily those are contemplated which can be used in a neutral or alkaline, preferably slightly alkaline medium.

Preferably, dyeing will be carried out at a pH of between 6.5 and 12, and most preferably at a pH of between 7 and 10.

For instance, a pure oxidative red of surprisingly high resistance against moisture can be obtained by treating hair, in accordance with the present invention, with an ammoniacal solution, cream or paste containing an oxidation base which by oxidation has been developed into the dye, as well as 2,5-diaminopyridine and/or substitution products thereof.

Such dye intermediates which may be oxidized to form a dye are listed for instance under the heading "Oxidation Bases" in the "Colour Index" (second edition, volume 3, pages 3593–3601), under the heading "Bases and Intermediates for Oxidation Dyes," on page 504 of "Cosmetic Science and Technology," by E. Sagarin, and under the heading "Oxidationsfarbstoff," in the Encyklopaedie der technischen Chemie, by Ullmann, volume 13 (1962) pages 109–111.

Preferably, one of the following oxidizable dye intermediates, or salts thereof, is used:

p-phenylenediamine
p-toluylenediamine
m-phenylenediamine
m-toluylenediamine
p-aminophenol
p-amino-N-dimethylaniline
4,4'-diaminodiphenylamine
4-aminodiphenylamine
4-amino-4'-oxydiphenylamine
m-diaminoanisole
m-diethylaminophenol

Of the diaminopyridines, preferably 2,6-diaminopyridine, 2,5-diaminopyridine and 2,3-diaminopyridine, their substitution products and hydrochlorides thereof are used whereby the following groups are particularly suitable as substituting groups:

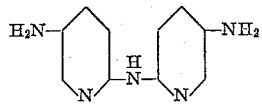
OH
OCH_3
OC_2H_5

Good results are achieved with the following substituted diaminopyridines:

4-methoxy-2,6-diaminopyridine
4-ethoxy-2,6-diaminopyridine
4-methyl-2,6-diaminopyridine
4-hydroxy-2,6-diaminopyridine
3-hydroxy-2,6-diaminopyridine
3-hydroxy-4-methyl-2,6-diaminopyridine
3-hydroxy-4-methoxy-2,6-diaminopyridine
6-hydroxy-4-methyl-2,3-diaminopyridine
6-methoxy-2,3-diaminopyridine
6-ethoxy-2,3-diaminopyridine

2-dimethylamino-5-aminopyridine
2-methylamino-5-aminopyridine
2-diethylamino-5-aminopyridine
2-ethylamino-5-aminopyridine
2-amino-5-dimethylaminopyridine
2-amino-5-methylaminopyridine
2-methylamino-5-methylaminopyridine
5,5'-diamino-bis(2-pyridil)amine of the formula:

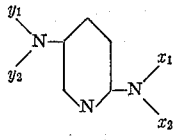
(1)



and substitution products thereof.

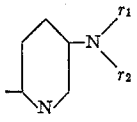
The groups with which 2,5-diaminopyridine may be substituted can be generally described by the following formulae:

(2)



wherein each of x_1, x_2, y_1 and y_2, respectively, may be either hydrogen or an alkyl such as CH_3, C_2H_5 or C_3H_7, preferably with not more than 5 carbon atoms; or each of y_1 and y_2, respectively, will be either hydrogen or an alkyl as described above x_1 will be hydrogen and x_2 will have the formula:

(3)



wherein each of r_1 and r_2, respectively, may be either hydrogen or an alkyl.

The diaminopyridines which are used according to the present invention, for instance, 2,5-diaminopyridine, are physiologically harmless. Even persons who are allergic to the "para" compounds experience no undesirable side effects in connection with these diaminopyridines. In combination with other compatible compounds such as 2,6-dioxypyridine, 2,3-diaminopyridine and 2,6-diaminopyridine, it is possible to produce with 2,5-diaminopyridine practically all desired hair colors without undesirable physiological side effects.

Furthermore, 2,5-diaminopyridine, for instance, may be combined with dyestuff precursors known per se, of the type of aromatic amines and/or amino or hydroxy derivatives of aromatic alcohols, such as p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, m-diaminoanisole, m-diethylaminophenol, 2,3-diaminopyridine, 2,6-diaminopyridine, m-aminophenol, o-aminophenol, alpha-naphthol, 2,6-dioxypyridine, resorcinol, pyrocatechol, pyrogallol, hydroxyquinone, phloroglucinol or 2,7-dioxynaphthalene.

In many cases the oxidative development of the oxidation base may be carried out simply by exposure to the oxygen of the air. However, dyestuff formation can be accelerated by the addition of a chemical oxidizing agent, preferably hydrogen peroxide or compounds including the same.

In the examples described hereinbelow, with the exception of Examples 13 and 14, the incorporation of, per se known, thickening agents, wetting agents, stabilizers, emulsified fats and the like has been omitted. However, it is obviously also within the scope of the present invention

to incorporate such agents in the hair dyeing composition.

The present invention thus closes a gap which up to now limited the results achievable in the dyeing of hair with oxidation bases, inasmuch as it is possible in accordance with the present invention to produce strong, acid resistant blue, red, green oxidation colors. Thereby it is possible to overcome the disadvantages discussed further above and to broaden the color range within which exact shading of the dyed hair can be achieved. In addition, new hair colors differing from those obtainable up to now, can be produced.

It is a further advantage of the present invention that mixtures of diaminopyridine and certain intermediates of oxidation dyes, such as p-aminophenol, wil give after a few minutes a stable blue and/or green hair color, without requiring chemical preparations to serve as oxidizing agents. In other words, the oxygen of the air will suffice for oxidizing such dye intermediate or oxidation base under such conditions.

It is also within the scope of the present invention to incorporate diaminopyridines in developer solutions used in the dyeing of hair. In this manner it is accomplished that the hair dye intermediates which are developed with an oxidizing developer containing a diaminopyridine or substitution product thereof, will maintain their color characteristics for prolonged periods of time, in fact, practically indefinitely. Particularly the slow color change towards red which usually occurs in hair dyed with oxidation dyes, after periods of days or weeks, is prevented by incorporating in the developer solution a 2,6- or 2,3-diaminopyridine.

The components which are required according to the present invention may be used in the form of neutral or slightly alkaline liquids or pastes. Preferably, the dyeing composition is supplied to the consumer in two separate portions, of which one contains the dye intermediate and possibly also a pH controlling agent so as to assure a neutral or slightly alkaline environment during dyeing, while the other portion will contain the diaminopyridine compound and possibly also an oxidizing agent.

It is also possible to supply those portions or components of the dyeing composition in dry state, for instance the oxidation base and the diaminopyridine compound in the form of their solid salts, the oxidizing agent as a hydrogen peroxide-urea adduct, and the pH controlling agent as an alkali-ammonium carbonate or a guanidine carbonate. Furthermore, a thickening agent in dry solid form may be added, such as carboxymethyl cellulose, gelatine or glycerol-monostearate.

The following examples are given as illustrative only without limiting the invention to the specific details of the examples.

Examples 1–10 describe dyeing compositions, whereby the compositions of Examples 7 and 8 do not require an oxidizing developer, while the composition of Examples 1–6, 9 and 10 are treated with an oxidizing developer.

Example 11 describes an oxidizing developer including a diaminopyridine in accordance with the present invention.

Example 12 compares the results obtained with an oxidation base and a conventional developer, with the results obtained when a diaminopyridine compound is incorporated in the developer.

Example 13 describes a solid product according to the present invention, and Example 14 a product in the form of a cream.

Examples 15–27 describe the use of 2,5-aminopyridines in dyeing hair in accordance with the present invention.

EXAMPLE 1

1.0 gram p-toluylenediamine and 1.0 gram 2,6-diaminopyridine are dissolved in 94.0 grams water and 4 grams of a 25% aqueous ammonia solution are added thereto.

For dyeing hair, 70 grams of the above solution are mixed with 30 cm.^{3} of 6% hydrogen peroxide solution

and the mixture is allowed to contact the hair for 20 minutes at ambient or body temperature, or therebetween. Thereafter, the mixture is rinsed off and it will be seen that the hair has obtained a strong blue color.

EXAMPLE 2

In the manner described in Example 1, a solution is produced of 0.7 gram 4,4'-diaminodiphenylamine, 0.7 gram 2,6-diaminopyridine, 94.6 grams water and 4.0 grams 25% aqueous amomnia. The thus-formed solution mixed with the hydrogen peroxide solution is used to dye living hair as described in Example 1. A blue-green color is obtained.

EXAMPLE 3

The following solution, prepared used and mixed with the hydrogen peroxide solution as described in Example 1, will give a strong turquoise hair color:

	Grams
p-Amino-N-dimethylaniline	0.7
2,6-diaminopyridine	0.7
Water	94.6
25% aqueous amomnia	4.0

EXAMPLE 4

In a similar manner a yellowish-green color is obtained with a solution consisting of:

	Grams
1-methyl-2,4-diaminobenzene	1.0
2,3-diaminopyridine	1.0
Water	94.0
25% aqueous ammonia	4.0

EXAMPLE 5

Similarly, an intensive gray-green hair color is obtained with a solution consisting of:

	Grams
m-Aminophenol	1.3
2,3-diaminopyridine	1.3
Water	93.4
25% aqueous ammonia	4.0

EXAMPLE 6

Again following the procedure outlined in Example 1, a strong green hair color is obtained with a solution consisting of:

	Grams
2,3-diaminopyridine	2.0
2,6-diaminopyridine	2.0
Water	92.0
25% aqueous ammonia	4.0

EXAMPLE 7

A solution is prepared by dissolving 1.0 gram p-aminophenol and 1.0 gram 2,6-diaminopyridine in 95.0 grams water and adding 3.0 grams of 25% aqueous ammonia. The thus formed solution is applied to the hair and rinsed off after 20 minutes. Without using an oxidizing agent, in this manner a lime green coloring of the hair is achieved.

EXAMPLE 8

As described in Example 7, the following solution may be prepared and used for dyeing hair to a natural blonde color without employing an oxidizing agent:

	Grams
2,4-diaminophenol	0.5
p-Aminophenol	0.25
2,6-diaminopyridine	0.25
Water	96.0
25% aqueous ammonia	3.0

EXAMPLE 9

Following the outline of Example 1, an intensive blue-green coloring of the hair is produced with 70 grams of the solution described below mixed with 30 cm.³ of 6% hydrogen peroxide:

	Grams
p-Toluylenediamine	0.8
4-methoxy-2,6-diaminopyridine	0.8
Water	94.4
25% aqueous ammonia	4.0

EXAMPLE 10

Again following the outline of Example 1 and using the oxidizing solution described therein, a strong green hair color is obtained with a solution consisting of:

	Grams
p-Toluylenediamine	0.8
4-ethoxy-2,6-diaminopyridine	0.8
Water	94.4
25% aqueous ammonia	4.0

EXAMPLE 11

0.1 gram ethylenediaminetetra-acetic acid, 0.01 gram 2,6-diaminopyridine and 0.3 gram disodiumpyrophosphate are dissolved under slight heating in 79.59 grams of water. After cooling, 20.0 grams of 30% hydrogen peroxide solution are added.

In this manner, an oxidizing developer is produced which may be used for developing oxidation bases of conventional hair dyes which, however, will result in a much more natural hair color which will not tend to develop a reddish tint. Thus, using the above described oxidizing developer according to the present invention will result in a more desirable hair color than that which would be obtained under similar conditions but with a solution of hydrogen peroxide alone, i.e., a solution which does not contain a diaminopyridine compound.

EXAMPLE 12

An oxidation base of a hair dye was prepared by dissolving:

	Gram
p-Toluylenediaminosulfate	0.400
Resorcinol	0.200
2,4-diaminoanisole (1) sulfate	0.004
3-aminophenol	0.030
4,4'-diaminodiphenylaminesulfate	0.004

in 80,000 grams water and 2,000 grams 25% aqueous ammonia, under heating to 50° C. After cooling the solution to 30° C., an additional 3,000 grams of 25% aqueous ammonia and 14.362 grams water were admixed. The thus-formed "dye solution blonde" was then applied in two experiments as described below with a conventional hydrogen peroxide developer, and with the developer described in Example 11.

Experiment A

50 cm.³ of "dye solution blonde" were mixed with 50 cm.³ of 6% hydrogen peroxide solution, and the thus-formed mixture was applied to the living hair for a period of 30 minutes. After rinsing and drying, the hair was found to have obtained a blonde color which after a few days changed to an unnatural reddish appearance.

Experiment B

50 cm.³ of "dye solution blonde" were mixed with 50 cm.³ of the oxidizing developer according to Example 11, and the thus-formed mixture was applied to hair as described in Experiment A. It was found that in this manner highly natural looking stable blonde coloring of the hair was obtained which retained its natural blonde appearance permanently.

EXAMPLE 13

A solid hair dye preparation according to the present invention may be prepared and used as follows:

	Grams
p-Toluylenediaminesulfate	1.0
2,6-diaminopyridinehydrochloride	1.0
Ammonium carbonate powder	4.0
Carbamideperoxide	4.0

are intimately mixed in pulverulent form and then either pressed into tablets or sealed into pockets formed of polyethylene coated foil material.

For use as hair dye, 10 grams of the tablets or pulverulent mixture are dissolved in 90 cm.³ of water and the thus-formed solution is applied to the hair for 20 minutes at ambient or body temperature. After rinsing, the hair will be found to have been dyed a strong blue.

EXAMPLE 14

A cream for hair dyeing is prepared and used as follows:

	Grams
Cetyl alcohol	25.0
Wool wax	2.0
Sodium cetylsulfate	2.0

are molten and emulsified with 40.0 grams of water of 75° C.

The still hot emulsion is mixed with a 70° C. solution of:

	Grams
p-Phenylenediaminesulfate	1.0
2,6-diaminopyridinehydrochloride	1.0
25% aqueous ammonia	3.0
Water	24.0

The thus-formed mixture is stirred until cooled to ambient temperature.

70 grams of the thus-formed cream are mixed with 30 cm.³ 6% hydrogen peroxide and then applied to the hair. After 20 minutes the mixture is rinsed off and after drying, it will be found that the hair has been dyed a strong blue color.

EXAMPLE 15

3.0 grams 2,5-diaminopyridine-hydrochloride are dissolved in 4.0 grams 25% aqueous ammonia and 93.0 grams water.

The thus obtained solution is applied to hair which had previously been treated so as to be of blond color. After contact with the hair for 30 minutes, the hair is freed of solution by rinsing, and dried. In this manner a desirable red color tone of high moisture resistance is obtained on the hair.

EXAMPLE 16

70 grams of the solution according to Example 15 are mixed with 30 ml. 6% aqueous hydrogen peroxide. After applying the thus formed solution to hair for 20 minutes at ambient or body temperature and subsequent rinsing, the hair will be of intensive red color.

EXAMPLE 17

An initial solution is formed of 0.4 gram 2,5-diaminopyridine, 0.4 gram p-toluylenediamine, 4.0 grams 25% aqueous ammonia and 95.2 grams water. Prior to applications to the hair, 70 ml. of the above solution are mixed with 30 ml. 6% aqueous hydrogen peroxide. After application of the hydrogen peroxide-containing solution to the hair for 20 minutes, the hair is rinsed and will be found to be of chestnut brown color.

EXAMPLE 18

Proceeding in accordance with Example 17, however, with an initial solution of 0.2 gram 2,5-diaminopyridine and 0.2 gram 4-amino-diphenylamine in 4.0 grams 25% aqueous ammonia and 95.6 grams water, a chestnut blond hair color is obtained.

EXAMPLE 19

By replacing the initial solution of Example 17 with a solution of 0.4 gram 2,5-diaminopyridine and 0.4 gram 4,4'-diaminophenylamine in 4.0 grams 25% aqueous ammonia and 95.2 grams water, a violet hair color is obtained.

EXAMPLE 20

By replacing the initial solution of Example 17 with a solution of 0.4 gram 2,5-diaminopyridine and 0.4 gram o-aminophenol in 4.0 grams 25% aqueous ammonia and 95.2 grams water, a titian red hair color is obtained.

EXAMPLE 21

By replacing the initial solution of Example 17 with a solution of 0.5 gram 2,5-diaminopyridine and 0.5 gram alpha-naphthol in 4.0 grams 25% aqueous ammonia and 95.0 grams water, a red-violet hair color is obtained.

EXAMPLE 22

By replacing the initial solution of Example 17 with a solution of 0.6 gram 2,5-diaminopyridine and 0.4 gram 2,6-diaminopyridine in 4.0 grams 25% aqueous ammonia and 95.0 grams water, an orange hair color is obtained.

EXAMPLE 23

By replacing the initial solution of Example 17 with a solution of 0.5 gram 2,5-diaminopyridine and 0.5 gram 2,6-dioxypyridine in 4.0 grams 25% aqueous ammonia and 95.0 grams water, a blue-violet hair color is obtained.

EXAMPLE 24

By replacing the initial solution of Example 17 with a solution of 1.5 grams 2,5-diaminopyridine and 0.5 gram 2,6-dioxypyridine in 4.0 grams 25% aqueous ammonia and 94.0 grams water, a dark brown hair color is obtained.

EXAMPLE 25

By replacing the initial solution of Example 17 with a solution of 0.3 gram 2,5-diaminopyridine, 0.2 gram 2,3-diaminopyridine and 0.2 gram 2,6-diaminopyridine in 4.0 grams 25% aqueous ammonia and 95.3 grams water, a dark blond hair color is obtained.

EXAMPLE 26

By replacing the initial solution of Example 17 with a solution of 0.4 gram 2,5-diaminopyridine, 0.2 gram 2,3-diaminopyridine, 0.2 gram 2,6-diaminopyridine and 0.2 gram 2,6-dioxypyridine in 4.0 grams 25% aqueous ammonia and 95.0 grams water, an ash blond hair color is obtained.

EXAMPLE 27

By replacing the initial solution of Example 17 with a solution of 2.0 grams 2-dimethylamino-5-aminopyridine 0.2 HCl in 4.0 grams 25% aqueous ammonia and 94.0 grams water, a highly intensive wash-fast bordeaux red hair color is obtained.

In the case of hair which has been previously blonded, the initial solution of the present example, without the addition of hydrogen peroxide will result in an intensive, slightly bluish, red hair color of high resistance to washing.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A composition of matter suitable for use in the oxidative dyeing of hair which comprises a carrier material adapted for application to human hair having distributed therethrough an alkalizing agent and at least one diaminopyridine selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino - 5 - aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5'-diamino-bis(2-pyridil)amine and hydrochlorides thereof.

2. A composition of matter suitable for use in the oxidative dyeing of hair which comprises at least one oxidizable dye intermediate which upon oxidation forms a dye and selected from the group consisting of p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, 4-aminodiphenylamine, 4-amino-4'-oxydiphenylamine, m-diaminoanisole, m-diethylaminophenol; and at least one diaminopyridine selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl - 2,6 - diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino - 5 - dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5'-diamino-bis(2-pyridil)amine and hydrochlorides thereof.

3. A composition of matter suitable for use in the oxidative dyeing of hair which comprises at least one oxidation hair dye intermediate, and at least one diaminopyridine selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino - 5 - aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5'-diamino-bis(2-pyridil)amine and hydrochlorides thereof.

4. In a method of dyeing hair, the steps of applying to hair which is to be dyed an oxidation hair dye intermediate, and at least one diaminopyridine, selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy - 4 - methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5' - diamino - bis(2-pyridil)amine and hydrochlorides thereof.

5. In a method of dyeing hair, the steps of applying to hair which is to be dyed an oxidizable dye intermediate which upon oxidation forms a dye and which is selected from the group consisting of p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, 4-aminodiphenylamine, 4-amino-4'-oxydiphenylamine, m-diaminoanisole, m-diethylaminophenol, and at least one diaminopyridine, selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino - 5 - methylaminopyridine, 5,5'-diamino-bis(2-pyridil)amine and hydrochlorides thereof.

6. In a method of dyeing hair, the steps of applying to hair which is to be dyed a first substance comprising a carrier material adapted for application to human hair having distributed therethrough an alkalizing agent and a dye intermediate adapted to be oxidized into a dye and selected from the group consisting of p-phenylenediamine, p-toluylenediamine, m-phenylenediamine, m-toluylenediamine, p-aminophenol, p-amino-N-dimethylaniline, 4,4'-diaminodiphenylamine, 4-aminodiphenylamine, 4-amino-4'-oxydiphenylamine, m-diaminoanisole, m-diethylaminophenol, and a second substance comprising a carrier material having distributed therethrough an oxidizing agent and at least one diaminopyridine, selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl - 2,6 - diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5' - diamino - bis(2-pyridil)amine and hydrochlorides thereof.

7. A developer for use in the oxidative dyeing of hair which comprises an aqueous solution of hydrogen peroxide and of at least one diaminopyridine selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diaminopyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy-2,6-diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino-5-methylaminopyridine, 5,5' - diamino - bis(2-pyridil)amine and hydrochlorides thereof.

8. A developer for use in the oxidative dyeing of hair, which comprises an aqueous solution of an oxidizing agent adapted for application to human hair and also adapted to oxidize an oxidation base of a hair dye, and a diaminopyridine selected from the group consisting of 2,6-diaminopyridine, 2,3-diaminopyridine, 4-methoxy-2,6-diamino-

pyridine, 4-ethoxy-2,6-diaminopyridine, 4-methyl-2,6-diaminopyridine, 4-hydroxy - 2,6 - diaminopyridine, 3-hydroxy-2,6-diaminopyridine, 3-hydroxy-4-methyl-2,6-diaminopyridine, 3-hydroxy-4-methoxy-2,6-diaminopyridine, 6-hydroxy-4-methyl-2,3-diaminopyridine, 6-methoxy-2,3-diaminopyridine, 6-ethoxy-2,3-diaminopyridine, 2,5-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-5-aminopyridine, 2-diethylamino-5-aminopyridine, 2-ethylamino-5-aminopyridine, 2-amino-5-dimethylaminopyridine, 2-amino-5-methylaminopyridine, 2-methylamino - 5 - methylaminopyridine, 5,5'-diamino-bis(2-pyridil) amine and hydrochlorides thereof.

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