United States Patent Office

3,128,232

Patented Apr. 7, 1964

3,128,232

OXIDATION DYESTUFF AGENT FOR HUMAN HAIR

Hermann Wilmsmann and Eugen Konrad, Darmstadt, Germany, assignors to Wella A.G., Darmstadt, Germany

No Drawing. Filed Mar. 21, 1960, Ser. No. 16,128
Claims priority, application Germany Mar. 21, 1959
11 Claims. (Cl. 167—88)

This application relates to a new oxidation dyestuff for human hair, and more particularly to an oxidation dyestuff for human hair which gives known oxidation dyestuffs a more pronounced color over a wider range of pH values and in general has the effect of improving the action of known dyestuffs.

For the oxidative dyeing of human hair there have been used combinations of primary aromatic amines and their derivatives with so called "toning dyes" or "shade pronouncing dyes" among which may be mentioned resorcin, alpha-naphthol, m-aminophenol, etc. The addition of these "toning dyestuffs" is for the purpose of achieving a specific necessary coloring nuance and is moreover for the purpose of achieving an improved color fastness (note H. Freytag, Haarfaerbemittel, Ullmans Encyclop. d. techn. Chem., 3rd edition, volume 10, pages 736–738).

To obtain the most natural possible action for blond and brown dyeing in the first place combinations of aromatic diamines and aminophenols with resorcinol, chlororesorcinol, 4-nitro-1,2-phenylenediamine and the like have been used. Compounds used for this purpose are found in Colour Index, 2nd edition, volume 3, 1956, under the numbers 76000–76650.

In the case of dyestuff combinations based upon for example p-toluylenediamine with a blond displacing tinting dyestuff such as resorcinol, it is necessary that the concentration of the dyestuff be very low in order to obtain a dark-to-light blond since these dyestuffs have a considerable dye intensity. Because of this very low concentration of dyestuff, in practical dyeing because of the greatly varying quality of the hair (non-dyed second growths as compared to already dyes one time or repeatedly dyed hair portions, the influence of cosmetic preparations such as permanent waving agents, as well as light and air), particularly because of its structure in the case of difficultly dyeable hair, in portions an uneven covering is obtained and therefore an uneven dye color is observable. Attempts have been made by corresponding adjustment of the dyestuff carrier base having well known actions in the textile industry with respect to fiber or dyestuff affinity to use equalizing agents to avoid these disadvantages. In most cases only an unsatisfactory effect has been achieved, however.

Attempts have therefore been made to use such oxidation dyestuffs which in relatively high dyestuff concentrations still have only a relatively slight dye intensity so that even in the case of light blond tones high dyestuff concentrations can be used. For this purpose particularly there have been used 4-aminophenol as well as 4-methyl-aminophenol. These compounds give with hydrogen peroxide a reddish blonde tone and in combination with aromatic p-diamines such as p-toluylenediamine, a lightening of the dye coloring. The combined use of these two oxidation dyestuffs and the dyeing resulting therefrom however have considerable disadvantages. Thus, for example, the light fastness is insufficient. Furthermore, after a time a marked visible shifting of the color towards red occurs. Moreover, the tone of such coloring is dependent on the pH value, particularly when using for a toning dyestuff the above mentioned necessary toning agents for example m-aminophenol, alpha-naphthol, 2,4-diaminotoluene, and 2,4-diaminoanisol. In alkaline pH range the coloring tone is shifted towards blue-green while in acid pH range towards red. This so called "indicator property" is particularly noticeable in an unpleasant manner in the case of hair which has been subjected to usual cosmetic treatments, particularly permanent waving agents (utilizing agents with pH values of 9.5 or 3) and by acid rinses (in the case of the use of alkaline soaps as well as various curling agents).

Attempts have been made to achieve the blond coloring by combinations of aromatic p-diamines with o-aminophenol. This blond coloring, however, is not satisfactory with respect to its fastness to wearing. In the coloring of furs the fastness of the color has been improved by using the o-aminophenol in the form of its copper salts. Heavy metal salts are, however, for the coloring of human hair unsatisfactory not only from the physiological standpoint but also because of catalytic damage to the hair by subsequent treatment with hydrogen peroxide.

It is therefore a primary object of the present invention to provide a new oxidation dyestuff agent which avoids all of the above enumerated disadvantages of known agents.

It is another object of the present invention to provide a new oxidation dyestuff composition which gives fine color tones in relatively high concentration of dyestuffs and without changing of color at different pH values.

It is another object of the present invention to provide an oxidation dyestuff composition which gives fine dye tones which are color fast, light fast and wear fast.

Other objects and advantages of the present invention will be apparent from a further reading of the specification and of the appended claims.

With the above and other objects in view the present invention mainly comprises as an oxidation dyestuff composition for human hair an oxidation dyestuff and 3,4-diaminobenzoic acid or a salt thereof. The addition of an oxidizing agent such as perborates, percarbonates, perphosphates, hydrogen peroxide or urea peroxide to this composition activates the oxidation dyestuff and the 3,4-diaminobenzoic acid to give a dye composition for human hair which has all of the above enumerated advantages which will be further described and proved below.

In accordance with a further embodiment the present invention comprises a method of dyeing human hair which comprises applying to the hair to be dyed an oxidation dyestuff, 3,4-diaminobenzoic acid or a salt thereof and an oxidizing agent such as hydrogen peroxide or urea peroxide.

It has surprisingly been found that blond as well as light brown tones can be achieved in an entirely satisfactory manner when there is added to the normally utilized oxidation dyestuff such as aromatic p-diamines and aminophenols, as tone dyeing agent 3,4-diaminobenzoic acid. By means of this compound there is obtained by suitable concentrations and also with relatively high dyestuff concentrations light, bright, particularly natural looking blond or brown tones. The colorings obtained according to the present invention are permanent wave fast and have excellent properties as to fastness to wearing. Extremely important is the fact that the colorings achieved according to the present invention do not shift towards red. Most important is the fact that a uniform coloring and coating effect is achieved with hair structures of all varying degrees.

The 3,4-diaminobenzoic acid may be combined with all normal oxidation dyestuffs, as set forth in "Colour Index," 2nd edition, volume 3, pages 3594–3601. For example the blond tones obtained according to the present invention may be used and achieved utilizing the 3,4-diaminobenzoic acid in combination with already known

"tone dyestuffs." The dyeings achieved according to the present invention are insensitive to pH variations. The 3,4-diaminobenzoic acid is easily soluble in alkaline range and suitably can be worked up for use in usual forms of preparations for hair dyestuffs such as liquids, gel-like or thick solutions or emulsions without difficulty.

The following examples are given to more fully illustrate the present invention. It is to be understood that these examples are given for illustrative purposes only and that the invention is not meant to be limited to the specific details of the examples.

EXAMPLE 1

20 g. of cetylalcohol, 2 g. of sodium cetylalcohol sulfate and 5 g. of wool wax are heated to melting and emulsified with 40 g. of water at 70° C. Into this hot emulsion is added a likewise hot solution of:

0.3 g. of toluylenediamine,
0.08 g. of resorcinol,
0.01 g. of m-aminophenol and
0.12 g. of ammonium-3,4-diaminobenzoate in 25 cc. of water.

There is subsequently added to the mixture 10 cc. of 25% ammonia water and stirred until cold.

For coloring purposes 50 g. of this cream are mixed with 50 cc. of 6% hydrogen peroxide and applied to gray human hair. After 30 minutes of coloring time there is obtained a natural looking, very uniform and well covered light blond tone.

EXAMPLE 2

This is a comparative test showing the superior effect of the use of 3,4-diaminobenzoic acid in accordance with the present invention.

Mixtures were made as set forth in the following table of the dyestuff solution constituents (*a–d*) in the combinations and amounts set forth in columns A_1–C_3 with the amounts of aqueous ammonia solution (25%) set forth in the table and then diluted with water to a total of 100.0 g.

Table 1

Agents	Combinations								
	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
p-Toluylenediaminesulfate (*a*)	0.1	0.2	0.4	0.1	0.2	0.4	0.1	0.2	0.4
Resorcinol (*b*)	0.1	0.2	0.4	-----	-----	-----	-----	-----	-----
p-Aminophenol (*c*)	-----	-----	-----	0.1	0.2	0.4	-----	-----	-----
3,4-Diaminobenzoic acid (*d*)	-----	-----	-----	-----	-----	-----	0.1	0.2	0.4
Ammonia solution (25%)	5.08	5.16	5.32	5.08	5.16	5.32	5.08	5.16	5.32

The solid substances were used in the amounts set forth in grams while the ammonia solution was used in the amount set forth in cubic centimeters.

Into 10 cc. each of the above obtained freshly prepared solutions were dissolved 1 g. of urea peroxide and with the resulting solution gray human hair was treated and after 30 minutes of working time the hair was rinsed and dried so that the differences between the already known coloring agents (A and B) and the coloring agents according to the present invention (C) could be observed.

From these dye tests it was apparent that the increasing of the dyestuff concentration (in the groups A, B and C from A_1 to A_3, from B_1 to B_3 and from C_1 to C_3) resulted in a markedly increased dye intensity in the cases of A and B as compared to C. It is observed that in the case of the combination C_3 according to the present invention utilizing four times the dyestuff amount as in the known combination A_1 it is possible to obtain the same depth of color.

The dye tones obtained according to the present invention (C_1–C_3) are a very natural blond.

EXAMPLE 3

This example also relates to comparative tests.

With the compounds given in Table 2 below dyestuff solutions were produced according to combinations D and E and gray human hair was dyed therewith. The production of the solutions as well as the dyeing procedure was analogous to the tests given in Example 2.

Table 2

Agents	Combinations	
	D	E
p-Aminophenol (*e*)	0.4	0.4
m-Aminophenol (*f*)	-----	0.4
3,4-Diaminobenzoic acid (*d*)	0.4	-----
Ammonia solution (25%)	5.0	5.0

The above tests show that with the dyeing agent according to the present invention (combination D) a blond tone is obtained which is practically insensitive to pH variations.

The dye tone obtained according to combination E when wet with dilute acetic acid becomes red-violet and when wet with dilute ammonia becomes blue-green.

Although in the above tests the 3,4-diamino-benzoic acid itself was used it should be understood that the present invention is applicable to the use of this free acid and also to the use of salts thereof particularly alkali metal salts, the ammonium salt, or organic amine salts.

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. Dye composition for human hair, said composition comprising an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

2. Dye composition for human hair, said composition comprising an oxidation dyestuff for human hair, a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof, and an oxidizing agent adapted to oxidize and thereby activate said oxidation dyestuff.

3. Dye composition for human hair, said composition comprising an oxidation dyestuff for human hair, a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof, and an oxidizing agent adapted to oxidize and thereby activate said oxidation dyestuff and being selected from the group consisting of perborates, percarbonates, perphosphates, hydrogen peroxide and urea peroxide.

4. Dye composition for human hair, said composition comprising an oxidation dyestuff for human hair selected from the group consisting of aromatic p-diamines and aminophenols, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

5. Dye composition for human hair, said composition comprising p-toluylenediamine as an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

6. Dye composition for human hair, said composition comprising p-toluylenediamine sulfate as an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

7. Dye composition for human hair, said composition comprising p-amino-phenol as an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

8. Dye composition for human hair, said composition comprising 4-methyl-amino-phenol as an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof.

9. The method of dyeing human hair which comprises applying to such hair to be dyed an oxidation dyestuff for human hair, a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof, and an oxidizing agent adapted to oxidize and thereby activate said oxidation dyestuff.

10. The method of dyeing human hair which comprises applying to such hair to be dyed an oxidation dyestuff for human hair selected from the group consisting of aromatic p-diamines and aminophenols, a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof, and an oxidizing agent adapted to oxidize and thereby activate said oxidation dyestuff and being selected from the group consisting of perborates, percarbonates, perphosphates, hydrogen peroxide and urea peroxide.

11. Dye composition for human hair, said composition comprising an oxidation dyestuff for human hair, and a substance selected from the group consisting of 3,4-diaminobenzoic acid and alkali metal, ammonium and organic amine salts thereof in an amount of one-third to two times the weight of said oxidation dyestuff.

No references cited.