United States Patent [19]

Wiskott

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[45] **Jan. 21, 1975**

[54] **2-(DIALKYLAMINO, PYRROLIDINO OR PIPERIDINO)-3-AMINO-5-NITRO PYRIDINES**

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[22] Filed: **Oct. 19, 1973**

[21] Appl. No.: **408,089**

Related U.S. Application Data

[62] Division of Ser. No. 75,305, Sept. 24, 1970.

[30] **Foreign Application Priority Data**

Oct. 2, 1969 Germany 1949750

[52] **U.S. Cl.. 260/293.69,** 260/296 R, 260/247.5 G, 260/268 H

[51] **Int. Cl.** **C07d 29/28**

[58] **Field of Search** ..... 260/293.69, 296 R

[56] **References Cited**

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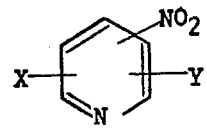
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[57] **ABSTRACT**

A process for the dyeing of living human hair consisting essentially of treating human hair at a temperature of from about 10°C to 40°C with an aqueous solution containing a nitropyridine having the formula



wherein X and Y are amino or substituted amino groups, aqueous dyestuff compositions containing said nitropyridines and novel nitropyridines.

4 Claims, No Drawings

2-(DIALKYLAMINO, PYRROLIDINO OR PIPERIDINO)-3-AMINO-5-NITRO PYRIDINES

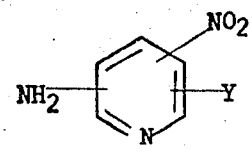
This is a division of Ser. No. 75,305, filed Sept. 24, 1970.

THE PRIOR ART

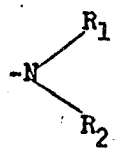
It is known to dye hair with direct dyestuff or so-called oxidation dyestuffs. As oxidation dyestuffs, aromatic amines or phenols are frequently used which form dyes on the hair in the presence of oxidizing agents such as H_2O_2. Furthermore, it has been suggested to use diaminopyridines, where one amino group has been substituted, as oxidation dyestuffs.

OBJECTS OF THE INVENTION

An object of the present invention is the development of a process for the dyeing of living human hair consisting essentially of treating human hair at a temperature of from 10°C to 40°C with an aqueous dyestuff composition containing, as sole dyestuff ingredient, from 0.3 to 5 percent by weight of a nitropyridine having the formula

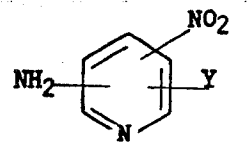


wherein Y is selected from the group consisting of $-NH_2$ and

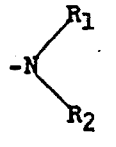


wherein R_1 is a member selected from the group consisting of alkyl having 1 to 8 carbon atoms, alkoxyalkyl having 2 to 8 carbon atoms, hydroxylalkyl having 2 to 8 carbon atoms, aminoalkyl having 2 to 8 carbon atom, cycloalkyl having 5 to 8 carbon atoms, dialkylaminoalkyl having 3 to 12 carbon atoms, alkylaminoalkyl having 2 to 8 carbon atoms, dialkanolaminoalkyl having 5 to 12 carbon atoms and alkanolaminoalkyl having 3 to 8 carbon atoms; R_2 is a member selected from the group consisting of hydrogen and R_1, and R_1 and R_2 taken together are selected from the group consisting of alkylene having 4 to 5 carbon atoms, ethoxyethylene and ethylaminoethylene, and rinsing said hair.

A further object of the present invention is the development of an aqueous composition for dyeing living human hair consisting essentially of at least 40 percent by weight of water, from 0.5 to 55 percent by weight of customary dyestuff adjuvants, no chemical oxidizing agents and from 0.3 to 5 percent by weight of a nitropyridine having the formula

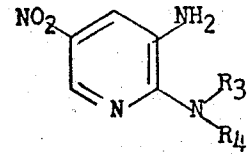


wherein Y is selected from the group consisting of $-NH_2$ and



where R_1 is a member selected from the group consisting of alkyl having 1 to 8 carbon atoms, alkoxyalkyl 2 to 8 carbon atoms, hydroxyalkyl having 2 to 8 carbon atoms, aminoalkyl having 2 to 8 carbon atoms, cycloalkyl having 5 to 8 carbon atoms, dialkylaminoalkyl having 3 to 12 carbon atoms, alkylaminoalkyl having 2 to 8 carbon atoms, dialkanolaminoalkyl having 5 to 12 carbon atoms and alkanolaminoalkyl having 3 to 8 carbon atoms; R_2 is a member selected from the group consisting of hydrogen and R_1, and R_1 and R_2 taken together are selected from the group consisting of alkylene having 4 to 5 carbon atoms, ethoxyethylene and ethylaminoethylene, said aqueous composition having a pH of from about 8 to about 10.

A yet further object of the present invention is the obtention of a 3-amino-5-nitropyridine having the formula



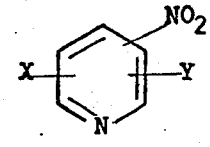
wherein R_3 and R_4 are members selected from the group consisting of alkyl having 1 to 4 carbon atoms, hydroxyalkyl having 2 to 4 carbon atoms, and when taken together, alkylene having 4 to 5 carbon atoms.

These and other objects of the present invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The drawbacks of the prior art have been overcome and the objects of the invention have been achieved by the present invention. It has now been found that certain nitropyridine compounds can be used with excellent results for the dyeing of human hair in the absence of chemical oxidizing agents and other developer or coupling components.

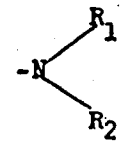
The present invention provides a new method for dyeing human hair with aqueous solutions, emulsions or creams based on direct dyes which is characterized in that the hair is treated at temperatures of 10° to 40°C with nitropyridines of the general formula I



I

wherein X and Y are amino or substituted amino groups, possibly heterocyclic with the nitrogen atom.

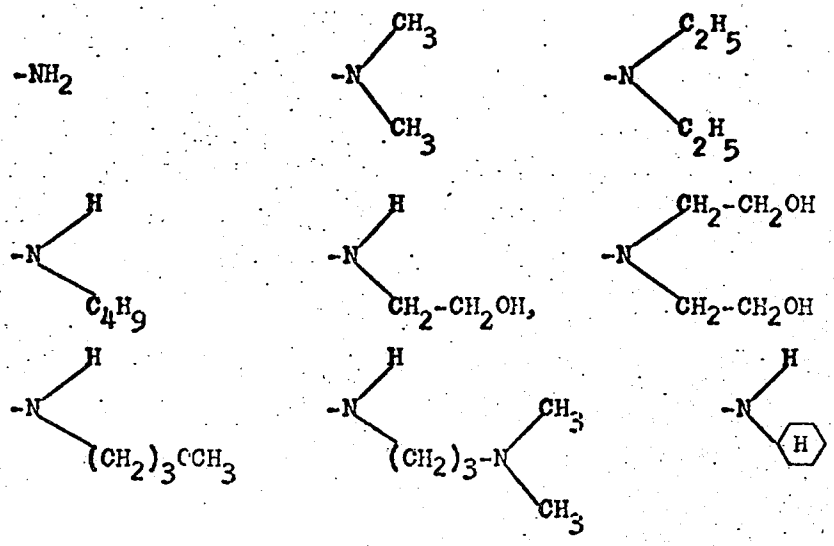
The substituents X and Y can be identical or different. In particular, substituted amino groups of the formula



can be used where R_1 denotes an alkyl radical with 1 to 8, preferably 1 to 4 carbon atoms, which contains, preferably terminal alkyoxy, amino or amino group substituted by alkyl or alkanol radicals, and where the alkyl radical or the alkanol can contain 1 to 4 carbon atoms, and where R_2 denotes a hydrogen atom or a rad-

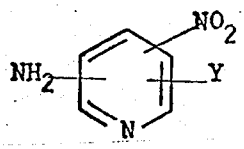
ical as indicated for R_1. R_1 and R_2 can, together with the nitrogen atom, also represent a heterocyclic ring.

Specifically the following groups are mentioned as amino groups for X and Y

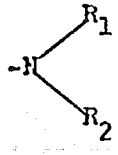


The two amino groups can be identical or different. Suitable substituted amino groups according to the compounds of formula I which contain heterocyclic rings are the pyrrolidino, piperidino, or morpholino groups.

Among the compounds of formula I, preferably a nitropyridine having the formula

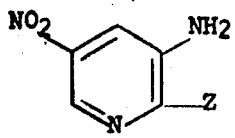


wherein Y is selected from the group consisting of $-NH_2$ and



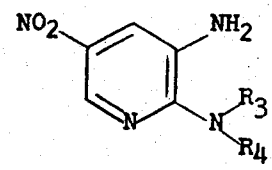
wherein R_1 is a member selected from the group consisting of alkyl having 1 to 8 carbon atoms, alkoxyalkyl having 2 to 8 carbon atoms, hydroxyalkyl having 2 to 8 carbon atoms, aminoalkyl having 2 to 8 carbon atoms, cycloalkyl having 5 to 8 carbon atoms, dialkylaminoalkyl having 3 to 12 carbon atoms, alkylaminoalkyl having 2 to 8 carbon atoms, dialkanolaminoalkyl having 5 to 12 carbon atoms and alkanolaminoalkyl having 3 to 8 carbon atoms; R_2 is a member selected from the group consisting of hydrogen and R_1, and R_1 and R_2 taken together are selected from the group consisting of alkylene having 4 to 5 carbon atoms, ethoxyethylene and ethylaminoethylene, is utilized where X in formula I is $-NH_2$.

Among the nitropyridines of formula I are novel 3-amino-5-nitropyridines of formula II having the formula



II

where Z denotes an amino- or a substituted amino group, which likewise form a heterocyclic ring. In particular, these novel compounds are 3-amino-5-nitropyridines having the formula



wherein R_3 and R_4 are members selected from the group consisting of alkyl having 1 to 4 carbon atoms, hydroxyalkyl having 2 to 4 carbon atoms, and, when taken together, alkylene having 4 to 5 carbon atoms.

The following compounds are mentioned specifically: 2-dimethylamino-5-nitro-3-aminopyridine, 2-pyrrolidine-5-nitro-3-aminopyridine and 2-piperidino-5-nitro-3-aminopyridine. These compounds give excellent dyeing effects on human hair.

The nitropyridines used can be produced in various ways. For example, monohalogen pyridines can be reacted in the presence of dimethyl sulfoxide with the corresponding amines or alkanol amines. Subsequently, two nitro groups are introduced by nitration, of which one is converted to an amino group by reduction, for example, with ammonium sulfide. The corresponding amino halogen-pyridines can also be utilized as starting material, where the amino group can be substituted, if necessary. These compounds are subsequently reacted with the corresponding amines or alkanol amines and the compounds obtained are nitrated or first, the amino halogen pyridines are nitrated and then reacted with amines or alkanol amines.

Other production possibilities consist in nitrating hydroxyaminopyridines substituted on the amino-function, if necessary, chlorinating the hydroxy group with phosphorus oxychloride to obtain nitro-chloro-aminopyridines, and converting the latter as above, for example, in dimethyl sulfoxide with amines or alkanol amines to the desired substituted diamino nitropyridines. The introduction of nitro groups can also be effected in some cases with advantage by nitrosating and subsequent oxidation with ammoniacal hydrogen peroxide.

The dye treatment of the living human hair is preferably for a period of 10 minutes to 1 hour followed by a rinsing of the hair.

The hair dyeing compositions may be applied in the form of aqueous solutions, but especially in the form of creams or emulsions. For this purpose, the nitropyridine compounds are mixed with any optional wetting agents or washing compositions, especially anionic or non-ionic substances. Suitable wetting and washing agents are especially alkylbenzenesulfonates, fatty alcohol sulfates, alkylsulfonates, fatty acid ethanolamides, products of addition of ethylene oxide to fatty acids and fatty alcohols, and fatty alcohol alkyl ether and polyalkyl ether sulfates.

The absorptive capacity of the above-mentioned dyestuffs is also good when they are in admixture with such compositions. Consequently, the hair dyes can be produced in the form of shampoos, especially of cream shampoos, which are much desired in practice.

Further, thickeners such as, for example, methylcellulose, starch, higher fatty alcohols, vaselines, paraffin oil and fatty acids, and also perfume or hair conditioning substances such as, for example, pantothenic acid and cholesterol, may be admixed with the compositions of the invention.

The added substances are used in the amount customary for these purposes. Suitable added amounts of wetting agents are, especially, 0.5 to 30 percent by weight, and of thickeners, are 0.1 to 25 percent by weight, referred in each case to the total composition. The concentration of the dyestuff components is, to a certain extent dependent on the purpose of use and amounts, from 0.3 to 5 percent by weight, preferably 0.5 to 2.5 percent by weight. These quantities are also with reference to the total composition.

The hair dyes are adjusted so that they are alkaline, preferably to a pH value of 8 to 10. The dyeings obtained with the hair dyes described above have good properties with respect to light, washing and rubbing.

The present invention will be further described by way of reference to the following specific examples. These however are not to be deemed limitative of the practice of the invention.

EXAMPLE I

Production of 2-dimethylamino-5-nitro-3-aminopyridine

100 parts by weight of 2-dimethylamino-pyridine were dissolved in 350 parts by volume of concentrated sulfuric acid. Subsequently, a mixture of 134 parts by volume of concentrated sulfuric acid and 114 parts by volume of nitric acid (specific gravity 1.52) was added dropwise to the solution at a temperature maintained below 5°C. The mixture was stirred for one hour while cooling with ice. Then the reaction product was poured into 2500 parts by volume of ice water. The yellow needles obtained were vacuum filtered, washed with water until neutrality, and recrystallized from ethanol. The 2-dimethylamino-3,5-dinitropyridine produced had a melting point of 125° to 126°C. Yield: 110 parts by weight. 30 parts by weight of the dinitro-compound were stirred for 20 hours at room temperature in 1440 parts by volume of methanol and 300 parts by volume of a 40 percent ammonium sulfide solution and then boiled for 1 hour at reflux and vacuum filtered. The solution was concentrated under vacuum to dryness and extracted with chloroform. The extract was subject to chromatography on 200 parts by weight of neutral aluminum oxide and eluted with chloroform. The red fractions yielded on concentration red-brown crystals of 2-dimethylamino-5-nitro-3-aminopyridine (mp = 118° to 121°C).

EXAMPLE II

Production of 2-pyrrolidino-3-amino-5-nitropyridine

74 parts by weight of 2-pyrrolidinopyridine were nitrated as described in Example I. After recrystallization from ethanol, 52 parts by weight of 2-pyrrolidino-3,5-dinitropyridine with a melting point of 130° to 132°C. were obtained. 30 parts by weight of the dinitro-compound were reduced with ammonium sulfide (see Example I) and worked up. The red 2-pyrrolidine-3-amino-5-nitropyridine so obtained melted at 115° to 116°C.

EXAMPLE III

Production of 2-piperidino-3-amino-5-nitropyridine

By nitrating 2-piperidinopyridine according to the method described in Example I, 2-piperidino-3,5-dinitropyridine (mp 147° to 149°C) was obtained. Subsequently, the production solution was reduced with ammonium sulfide, as in Example I, and worked up. The red 2-piperidino-3-amino-5-nitropyridine so obtained melted at 106° to 109°C.

EXAMPLE IV

4 parts by weight of cetyl alcohol, 4 parts by weight of stearyl alcohol, 3 parts by weight of lauryl alcohol and 25 parts by weight of sodium lauryl ether sulfate were melted together at 70°C, and an aqueous alcoholic solution of 1 part by weight of 2,6-diamino-3-nitropyridine was stirred into this mixture. The cream was brought with hot water to 98 parts by weight, cooled to room temperature, adjusted to a pH of 9.5 with concentrated ammonia, to obtain 100 parts by weight.

The dye cream so obtained dyed grey hair an intense yellow when treated at room temperature over a period of 30 minutes. After the dye treatment, the hair was rinsed with water and shampooed.

EXAMPLE V

5 parts by weight of cetyl alcohol, 4 parts by weight of stearyl alcohol, 1 part by weight of lauryl alcohol and 18 parts by weight of a mixture of fatty alcohol sulfates (C_{12} to C_{18}) were melted at 70°C and a solution of 1 part by weight of 2-pyrrolidino-3-amino-5-nitropyridine in some ethyl alcohol was stirred in. The cream was brought with hot water to 98 parts by weight, cooled to room temperature and adjusted to a pH of 9.5 with concentrated ammonia, to obtain 100 parts by weight.

The dye cream so obtained dyed grey hair orange when treated at a temperature of 30°C for 25 minutes.

EXAMPLE VI

A hair dyeing cream was produced as in Example 4, but, as a nitropyridine compound 1 part by weight of 2-dimethylamino-3-amino-5-nitropyridine was utilized.

The cream dyed grey hair yellow when treated at room temperature over a period of 30 minutes.

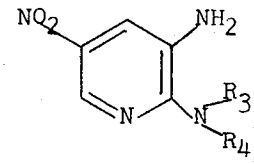
EXAMPLE VII

A hair dyeing cream was produced as in Example 4, but, as a nitropyridine compound 1 part by weight of 2-piperidino-3-amino-5-nitropyridine was utilized. When grey hair was treated with this dye cream for 30 minutes at 30°C a light yellow hair color was obtained.

The preceeding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art may be employed without departing from the spirit of the invention and the scope of the appended claims.

I claim:

1. A 3-amino-5-nitropyridine having the formula



wherein R_3 and R_4 are members selected from the group consisting of alkyl having 1 to 4 carbon atoms, hydroxyalkyl having 2 to 4 carbon atoms, and, when taken together, alkylene having 4 to 5 carbon atoms.

2. The 3-amino-5-nitropyridine of claim **1** wherein R_3 and R_4 are methyl.

3. The 3-amino-5-nitropyridine of claim **1** wherein R_3 and R_4 taken together are butylene.

4. The 3-amino-5-nitropyridine of claim **1** wherein R_3 and R_4 taken together are pentylene.

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