

## **PATENT SPECIFICATION**

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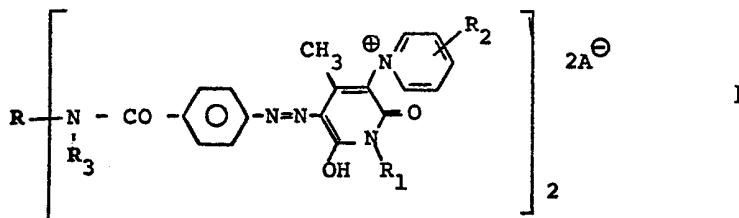


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(54) BISCATIONIC DISAZO DYESTUFFS BASED ON BIS(AMINO BENZOYLAMINO) ALKANES AND PYRIDONES

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The invention relates to biscationic diazo compounds. The invention provides compounds of formula I,



10 wherein R is a straight chain  $C_{2-4}$ alkylene radical, preferably 1,2-ethylene, each  $R_1$ , independently, is hydrogen;  $C_{1-4}$ alkyl, unsubstituted or substituted by a hydroxy group; or a radical  $—NR_4R_5$ , where  $R_4$  and  $R_5$ , independently, are unsubstituted straight chain  $C_{1-4}$ alkyl,  
each  $R_2$ , independently, is hydrogen; straight chain  $C_{1-4}$ alkyl, unsubstituted or substituted by a hydroxy group; or  $C_{1-4}$ alkoxy,  
each  $R_3$ , independently, is hydrogen or unsubstituted  $C_{1-4}$ alkyl, and

The compounds of formula I fall within the scope of Claim 1 of our accepted patent application no. 27014/76. (Serial No. 1 547 900)

Any unsubstituted alkyl as  $R_1$  is preferably methyl or ethyl, more preferably methyl, any hydroxy substituted alkyl is preferably 2-hydroxyethyl, 2-hydroxypropyl

or  $\text{CH}_2\text{CHCH}_2\text{OH}$  and any  $-\text{NR}_1\text{R}_2$  group is preferably  $-\text{N}(\text{CH}_3)_2$ .

Any unsubstituted alkyl as  $R_2$  is preferably methyl, any hydroxyalkyl is preferably 2-hydroxyethyl and any alkoxy is preferably methoxy.

Any unsubstituted alkyl as  $R_3$  is preferably methyl or ethyl.

In the compounds of formula I,  $R_1$  is preferably  $R_1'$ , i.e. hydrogen, methyl, ethyl,

2-hydroxyethyl, 2-hydroxypropyl,  $-\text{N}(\text{CH}_3)_2$  or  $\text{CH}_3\text{CHCH}_2\text{OH}$ , more preferably  $\text{R}_1''$ , i.e. hydrogen or methyl.

$R_2$  is preferably  $R_2'$ , i.e. hydrogen, methyl, methoxy or 2-hydroxyethyl, more preferably  $R_2''$ , i.e. hydrogen or methyl.

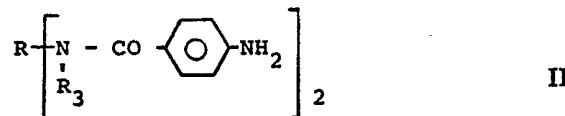
Thus, as a preferred class of compounds may be given those wherein  $R_1$  is  $R_1'$ , i.e. hydrogen.

Thus, as a preferred class of compounds, may be given those wherein  $R_1$  is  $R_1'$ ,  $R_2$  is  $R_2'$  and  $R_3$  is  $R_3'$  and as a more preferred class may be given those wherein  $R_1$  is  $R_1''$ ,  $R_2$  is  $R_2''$  and  $R_3$  is  $R_3''$ ,  $R$  in such compounds being 1,2-ethylene.

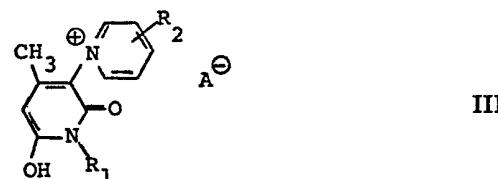
The symmetrical compounds are preferred.

The anion  $A^\ominus$  in the compounds of the invention is conveniently one conventional in basic dyestuff chemistry and is preferably non-chromophoric. It may be an organic or inorganic anion and as examples may be given the halide, e.g. chloride or bromide, sulphate, bisulphate, methylsulphate, aminosulphonate, perchlorate, propionate, lactate, succinate, benzenesulphonate, oxalate, maleate, acetate, tartrate, malate, methanesulphonate, tetrafluoroborate and benzoate anions, complex anions such as of zinc chloride double salts and the anions of the acids boric, citric, glycolic, diglycolic and adipic.

The invention also provides a process for the production of compounds of formula I, which process comprises coupling a tetrazo derivative of a diamine of formula II,



with a coupling component of formula III,



preferably in a mol ratio of 1:2.

The diazotisation and coupling may be carried out in conventional manner, coupling suitably taking place in aqueous (acidic, neutral or alkaline) or aqueous/organic medium at a temperature of from  $-10^\circ\text{C}$  to room temperature, optionally in the presence of a coupling accelerator such as pyridine or urea.

The resulting compounds of formula I may be isolated and purified in conventional manner.

By the use of a mixture of two coupling components of formula III, asymmetrical compounds of formula I may be prepared in the form of a mixture with the corresponding two symmetrical compounds. They may be used in the form of the mixtures, or separated for example by chromatographic techniques.

The anion  $A^\ominus$  desired in the compound of formula I may be present already in the pyridone coupling component of formula III or, if desired, having obtained a compound of formula I having a particular anion  $A^\ominus$ , this anion may be exchanged for the desired anion in conventional manner, e.g. using an ion exchanger or by reaction with suitable salts, optionally in several stages, e.g. through the hydroxide or bicarbonate.

The compounds of formulae II and III are either known or may be produced in conventional manner from available starting materials.

The compounds of formula I are useful as dyes for the dyeing of basically dyeable substrates, including paper.

If desired, the compounds may be converted into dyeing preparations. The processing into stable, liquid dyeing preparations may take place in a generally known manner, advantageously by dissolving them in suitable solvents, optionally adding an aid, e.g. a stabilizer; for example in accordance with the description given in French Patent Specification No. 1,572,030.

Suitable liquid preparations are obtained, for example, by dissolving one part by weight of 100% dyestuff in the form of the dyestuff base in 1 to 6 parts by weight of an organic carboxylic acid and in 1.5 to 4 parts by weight of water.

The organic carboxylic acids may be mono-, di- or tri-basic, but advantageously monobasic, low-molecular weight carboxylic acids, such as formic acid, acetic acid or propionic acid.

*Example a* of a liquid preparation: (all parts are by weight)

160 parts of the dyestuff from Example 1, below, as the dyestuff base are dissolved at  $40-60^\circ\text{C}$  in 320 parts of acetic acid and 160 parts of water.

The processing into solid, granulated dye preparations may also take place in a generally known manner, advantageously by granulating in accordance with French Patent Specification 1,581,900.

A granulate preparation contains, for example, 1 part of 100% dyestuff, 0.1 to 0.7 parts of an organic carboxylic acid and 0 to 1.5 parts of a solid, non-ionic diluting or standardising agent, preferably 1 part of dyestuff, 0.25 to 0.65 parts of an organic carboxylic acid and 0 to 1.5 parts of diluting or standardising agent.

The organic carboxylic acids for the production of the granulate may be mono-, di- or tribasic, but advantageously mono- or dibasic, low-molecular weight, saturated or unsaturated carboxylic acids, optionally containing hydroxyl groups, such as formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, malonic acid, fumaric acid, lactic acid, malic acid or citric acid.

The solid, non-ionic diluting or standardising agent may be, for example, dextrin or sugar, such as glucose, fructose or galactose.

The granulates are advantageously prepared by comminution from solutions or suspensions, e.g. of the following composition:

15                    1 part of dyestuff 100%,  
                  0.1 to 0.7 parts of the organic carboxylic acid,  
                  0 to 1.5 parts of the non-ionic diluting or standardising agent, and  
                  1.5 to 6 parts of water,  
or preferably

20                    1 part of dyestuff 100%,  
                  0.5 to 0.65 parts of the organic carboxylic acid,  
                  0.0 to 1.5 parts of the diluting or standardising agent, and  
                  2 to 4 parts of water.

*Example b* of a granulate (all parts are by weight).

25                    160 parts of the dyestuff from Example 1, below, as a dyestuff base and 80 parts of dextrin are dissolved at 40—60°C in 47 parts of lactic acid and 320 parts of water, and the mixture is granulated by known methods.

The new dyestuffs are especially suitable for dyeing paper, e.g. for the production of dyed, sized and unsized paper in the stock. However, they may be used similarly for dyeing sheet paper by the steeping method. Conventional techniques may be used.

30                    The compounds of formula I have good solubility properties, and they are particularly soluble in cold water. Furthermore, in the production of dyed paper, they colour the waste water slightly, if at all. They show low mottling on paper and to a great extent are insensitive to pH. The dyeings on paper are brilliant and have good light fastness properties. After lengthy exposure to light, the shade changes tone-in-tone. The dyed papers show good wet fastness properties, not only to water but also to milk, fruit juices and sweetened mineral water, and because of their good fastness to alcohol, they are also resistant to alcoholic drinks. The dyestuffs have a high degree of substantivity, i.e. they are absorbed practically quantitatively; they may be added to the paper pulp directly, i.e. without previous dissolving, as a dry powder or as a granulate, without reducing the brilliance or the yield of colour. The dyed papers are bleachable both by oxidation and by reduction.

35                    The compounds of formula I are also suitable for dyeing, pad-dyeing and printing textile material consisting of acrylonitrile or dicyanoethylene polymers or mixed polymers, or synthetic polyesters which are modified by acid groups, but especially synthetic polyamides which are modified by acid groups, these including in particular the so-called "Differential dyeing polyamide", or mixtures of textile material which consists of a predominant portion of the above-mentioned textile materials or contain these.

40                    The acrylonitrile mixed polymers which are dyed or printed are advantageously co-polymers consisting of 80—95% acrylonitrile and 20—5% vinyl acetate, vinyl pyridine, vinyl chloride, vinylidene chloride, acrylic acid, acrylic acid ester, methacrylic acid, methacrylic acid ester or asymmetrical dicyanoethylene.

45                    The polyester material which is dyed or printed is advantageously of the type described in U.S. Patent Specification 3,379,723, e.g. synthetic polyester as obtained by polycondensation of aliphatic or aromatic dicarboxylic acids or their polyester-forming derivatives

50                    a) with aliphatic or alicyclic diols  
                  b) and optionally aromatic dihydroxy compounds  
                  c) and/or their glycol ethers,  
                  with compounds bearing anionic groups.

55                    Polyester material which is modified by anionic groups may also be equally well dyed or printed, e.g. as described in U.S. Patent Specification 3,018,272, in British Patent Specification 1,406,387, and in Japanese Published Specification No. 10,497/59.

60                    The polyamide material which is modified by anionic groups is advantageously of

the type described in Belgian Patent Specifications 549,179 and 706,104, U.S. Patent Specifications 2,893,816 and 3,890,257 and "Textilveredlung 2" (1967), 11, pages 856—864, so-called Nylon-Dye-Resist types, in "Textilpraxis" 1967, volume 2 (February) pages 737—740 in "Du Pont Preliminary Information" of 14.7.1966 relating to "Type 844 Du Pont BCF Nylon", and 19.9.1966 (Cationic Dyeable Nylon Stable).

5 Textile material consisting of polyacrylonitrile or polyester or polyamide which is modified by anionic groups may be dyed as described in German Published Specification 2,509,095, e.g. by the exhaust method in an aqueous medium, at temperatures of 10 60—100°C or at temperatures of above 100° under pressure, whereby the pH value may vary within a wide range.

10 Dyeing or printing may also take place in the presence of usual dyeing aids, e.g. in the presence of condensation products of naphthalene sulphonic acids and formaldehyde, or reaction products of castor oil and ethylene oxide, etc. Printing of the said 15 textile materials takes place by impregnation with a printing paste which contains the dyestuff, water, an organic acid, e.g. acetic acid, formic acid, and a thickener, with subsequent fixation onto the fibres.

15 The printing paste is applied by stencils or rollers, the print is optionally intermediately dried and the dyestuff is fixed, e.g. by steam-treatment at temperatures of 20 about 100°C, and the print is completed.

20 Fixation of the dyestuff may also take place by the pad-steam process or thermosol process, or by the pad-roll process. Temperatures of above 200°C should, however, be avoided.

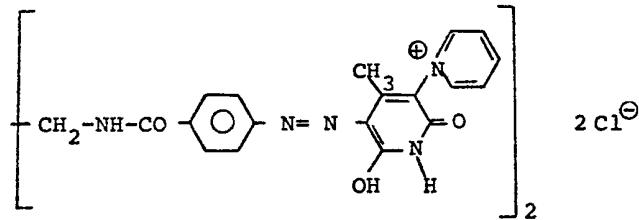
25 The dyestuffs are also suitable for dyeing the said textile materials in the mass, e.g. for gel dyeing by the so-called neocron process, for example in accordance with U.K. Patent Specification No. 673,738.

25 Fast, even dyeings with good fastness properties, for example to light, are obtained on the above-mentioned substrates.

30 The following examples, in which the parts and percentages are by weight and the 30 temperatures in degrees centigrade, illustrate the invention.

Example 1.

35 14.9 Parts of 1,2-bis-(4'-aminobenzoylamino)-ethylene are dissolved at 0° in 100 parts of water and 31 parts of 30% hydrochloric acid, and are then tetrazotised with 6.9 parts of sodium nitrite by known methods. Subsequently, a solution consisting of 25 parts of 3-pyridinium-4-methyl-6-hydroxy-pyridone-2-chloride and 100 parts of water is added to the ice-cold diazo solution, and at the same time 15 parts of crystalline sodium acetate are sprinkled in in portions. After coupling, the reaction mixture is made acid with hydrochloric acid, whereby the dyestuff is precipitated. The dyestuff is 40 filtered off. When dried and ground, a water-soluble powder is obtained, which dyes paper in yellow shades. The dyestuff corresponds to formula:



Dyeing Preparation A.

45 70 Parts of chemically bleached sulphite cellulose (from conifer wood) and 30 parts of chemically bleached sulphite cellulose (from birchwood) are ground in 2000 parts of water in a Hollander. 0.2 Parts of the dyestuff described in Example 1 are 45 sprinkled into this pulp. After mixing for 20 minutes, paper is produced from this pulp. The absorbent paper produced in this manner is dyed yellow. The waste water is practically colourless.

Dyeing Preparation B.

50 0.5 Parts of the dyestuff from Example 1 are dissolved in 100 parts of hot water and cooled to room temperature. This solution is added to 100 parts of chemically bleached sulphite cellulose which has been ground with 2000 parts of water in a Hol-

lander. After mixing thoroughly for 15 minutes, sizing takes place. Paper which is produced from this pulp has a yellow shade of average intensity, with good wet fastness.

Dyeing Preparation C.

An absorbent strip of unsized paper is drawn through a dyestuff solution of the following composition at 40 to 50°:

5      0.5 parts of the dyestuff from Example 1  
0.5 parts of starch and  
99.0 parts of water.

10     The excess dyestuff solution is squeezed out through two rollers. The dried paper strip is dyed yellow.

10     Equally good paper dyeings are obtained using the above dyeing formulae A, B and C, by adding equivalent amounts as in Example a (liquid preparation) or Example b (granulate preparation).

Example 2.

15     20 Parts of the dyestuff of Example 1 and 80 parts of dextrin are ground in a powder mill for 4 hours. The same dyestuff preparation may be formed by forming the components into a paste using 100 parts of water and finally spray drying.

20     One part of the obtained preparation is mixed with one part of 40% acetic acid, 200 parts of demineralised water are poured onto the paste and the whole heated. Dilution takes place with 7000 parts of demineralised water, 2 parts of glacial acetic acid are added and, at 60°, 100 parts of a polyacrylonitrile material are added to the bath. The polyacrylonitrile material may be pretreated in a bath containing 8000 parts of water and 2 parts of acetic acid for 10—15 minutes at 60°.

25     The bath is raised in the course of 30 minutes to 98°—100°, boiled for 1½ hours at this temperature and then the substrate rinsed. A yellow dyeing with good light and wet fastness is obtained.

Example 3.

30     20 Parts of the dyestuff of formula 1 are mixed with 80 parts of dextrin in a ball mill for 48 hours. One part of the obtained preparation and 1 part of 40% acetic acid are intimately mixed. 200 Parts of demineralised water are poured on and the whole heated. With this stock solution dyeing is carried out as follows.

35     a) The solution is diluted with 7000 parts of demineralised water, then 21 parts of calcined sodium sulphate, 14 parts formic acid and 15 parts of a carrier based on the reaction product of ethylene oxide with dichlorophenols are added and, at 60°, 100 parts of acid modified polyester material are entered into the bath. The polyester material may be pretreated in a bath containing 8000 parts of water and 2 parts of acetic acid for 10—15 minutes at 60°.

40     The bath is raised in the course of 30 minutes to 98—100°, boiled at this temperature for one hour and then the substrate removed and rinsed. A level yellow dyeing with good light and wet fastness is obtained.

45     b) The solution is diluted with 3000 parts of demineralised water after which 18 parts of calcined sodium sulphate and 6 parts each of ammonium sulphate and formic acid are added and, at 60°, 100 parts of acid modified polyester material are entered into the bath. The bath is raised to 110° over the course of 45 minutes in a closed vessel. This temperature is held for one hour with agitation of the bath. The bath is then cooled to 60° over the course of 25 minutes and the dyed material rinsed. A level fast yellow dyeing with good wet fastness is obtained.

Example 4.

50     20 Parts of the dyestuff of Example 1 and 80 parts of dextrin are mixed in a ball mill for 48 hours. One part of the obtained preparation and 1 part of 40% acetic acid are intimately mixed, whereafter 200 parts of demineralised water are poured on and the whole heated.

55     The solution is diluted with 7000 parts of demineralised water, 14 parts of formic acid and 15 parts of a carrier based on the reaction product of ethylene oxide and dichlorophenols are added. The liquor is adjusted to pH 6 with an acid buffer solution. At 25° 100 part of acid modified polyamide material are entered into the bath at a liquor ratio of 1:80. The bath is heated to 98° over the course of 45 minutes and boiled for one hour at this temperature. The substrate is then removed and rinsed under running water at 70—80° and finally under cold water. The material may then be spin dried and finally ironed. A yellow dyeing with good fastness is obtained.

## Example 5.

A printing paste is prepared as follows.

5 One part of the dyestuff of Example 1 and 30 parts of acetic acid are intimately mixed and 280 parts of boiling water poured on. To this solution are added 50 parts of benzyl alcohol and 500 parts of a thickener based on carboxymethyl cellulose, which swells to a ratio of 1:4 in water, and 10 parts of a swelling agent.

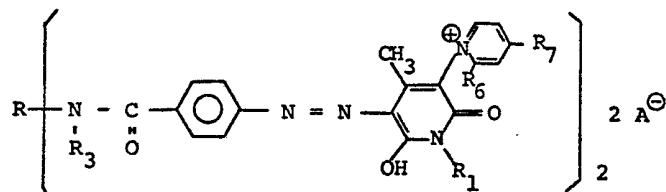
Using this printing paste, a polyacrylonitrile, polyester or polyamide material which has been acid modified, may be printed according to known methods.

10 The prints are dried and then placed in an autoclave where they are steamed for 30 minutes at 110° under 1.8 atmospheres (one can also steam continuously for 5 to 30 minutes).

15 After rinsing with cold water, unfixed dyestuff may be removed by washing for 5 minutes at 70° with a 0.1% soap solution, (detergent). Finally the prints are rinsed with cold water and dried by known methods. A fast level print with good fastness is obtained.

According to the procedure of Example 4, advantageous dyeings are obtained on differential dyeing polyamide material of the types 844, 845 and 847, (Du Pont).

20 In the following table further dyes are given which can be produced according to the procedure of Example 1. These dyes can be used in the same way as that of Example 1 and correspond to the formula

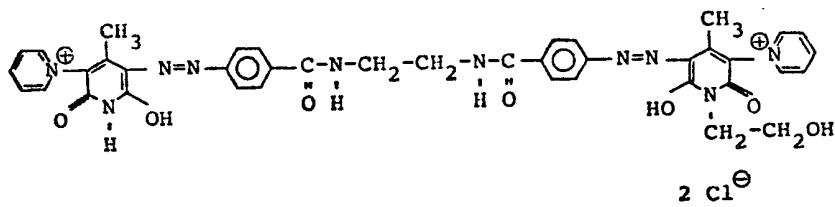


wherein R, R<sub>1</sub>, R<sub>3</sub>, R<sub>6</sub> and R<sub>7</sub> have the meanings given in the table.

The anion A<sup>⊖</sup> may be any one mentioned in the foregoing description.

Example No.	R	R <sub>1</sub>	R <sub>3</sub>	R <sub>6</sub>	R <sub>7</sub>
6	—CH <sub>2</sub> —CH <sub>2</sub> —	H	H	CH <sub>3</sub>	H
7	do.	H	H	H	CH <sub>3</sub>
8	do.	H	CH <sub>3</sub>	H	H
9	do.	CH <sub>2</sub> —CH <sub>2</sub> —OH	H	H	H
10	do.	do.	H	CH <sub>3</sub>	H
11	do.	do.	H	H	CH <sub>3</sub>
12	do.	do.	CH <sub>3</sub>	H	H
13	do.	CH <sub>3</sub>	H	H	H
14	do.	do.	H	CH <sub>3</sub>	H
15	do.	do.	H	H	CH <sub>3</sub>
16	do.	do.	CH <sub>3</sub>	H	H
17	do.	N(CH <sub>3</sub> ) <sub>2</sub>	H	H	H
18	do.	do.	H	CH <sub>3</sub>	H
19	do.	do.	CH <sub>3</sub>	H	H
20	do.	CH <sub>2</sub> —CHOH—CH <sub>3</sub>	H	H	H
21	do.	CH <sub>3</sub> —CH—CH <sub>2</sub> OH	H	H	H

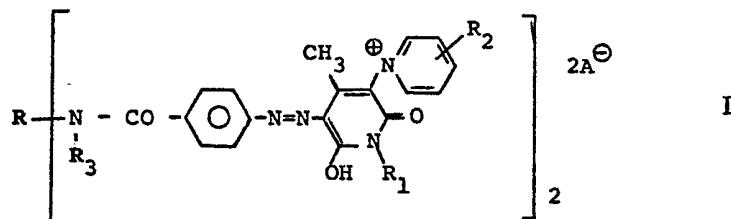
## Example 22.



The dyestuffs of Example 6—22 dye paper, polyacrylonitrile and acid modified polyamide materials in yellow shades.

## WHAT WE CLAIM IS:—

1. A compound of formula I,



5 wherein R is a straight chain  $C_{2-4}$ alkylene radical,  
each  $R_1$ , independently, is hydrogen;  $C_{1-4}$ alkyl, unsubstituted or substituted by a  
hydroxy group; or a radical  $-NR_4R_5$ , where  $R_4$  and  $R_5$ , independently, are unsub-  
stituted straight chain  $C_{1-4}$ alkyl,  
each  $R_2$ , independently, is hydrogen; straight chain  $C_{1-4}$ alkyl, unsubstituted or substi-  
tuted by a hydroxy group; or  $C_{1-4}$ alkoxy,  
10 each  $R_3$ , independently, is hydrogen or unsubstituted  $C_{1-4}$ alkyl, and  
 $A^-$  is an anion.

2. A compound of Claim 1, wherein R is 1,2-ethylene.

3. A compound of Claim 1 or 2 wherein  $R_1$  is hydrogen, methyl, ethyl, 2-hydroxy-  
ethyl, 2-hydroxypropyl,  $-N(CH_3)_2$  or  $CH_3CHCH_2OH$ .

15 4. A compound of Claim 3, wherein  $R_1$  is hydrogen or methyl.

5. A compound of any one of Claims 1 to 4, wherein  $R_2$  is hydrogen, methyl,  
methoxy, or 2-hydroxyethyl.

6. A compound of Claim 5, wherein  $R_2$  is hydrogen or methyl.

7. A compound of any one of Claims 1 to 6, wherein  $R_3$  is hydrogen, methyl or  
20 ethyl.

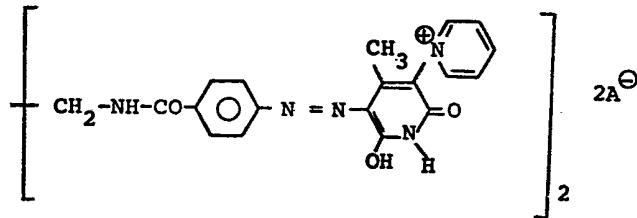
8. A compound of Claim 7, wherein  $R_3$  is hydrogen.

9. A compound of Claim 2, wherein  $R_1$  is as defined in Claim 3,  $R_2$  is as defined  
in Claim 5 and  $R_3$  is as defined in Claim 7.

10. A compound of Claim 9, wherein  $R_1$  is as defined in Claim 4,  $R_2$  is as defined  
in Claim 6 and  $R_3$  is as defined in Claim 8.

15 11. A compound of any preceding claim which is symmetrical.

12. A compound of formula

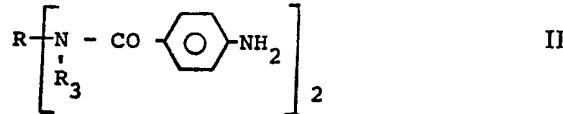


25 wherein  $A^-$  is as defined in Claim 1.

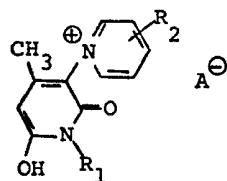
30 13. The compound of Claim 12, wherein  $A^-$  is  $Cl^-$ .

14. The compound of any one of Examples 6 to 22, hereinbefore set forth.

35 15. A process for the production of a compound of formula I, stated in Claim 1,  
comprising coupling a tetrazo derivative of a diamine of formula II,



35 with a coupling component of formula III,



III

16. The process of Claim 15, substantially as hereinbefore described with reference to and as illustrated by any one of Examples 1 and 6 to 22. 5

17. A compound of formula I, stated in Claim 1, whenever obtained by the process of Claim 15 or 16. 5

18. A solid dye composition comprising, as dye component, a compound of any one of Claims 1 to 14 or 17. 5

19. A liquid dye composition comprising, as dye component, a compound of any one of Claims 1 to 14 or 17. 10

20. A process for dyeing a basic dyeable substrate comprising applying thereto a compound of any one of Claims 1 to 14 or 17. 10

21. The process of Claim 20, wherein the substrate is paper. 15

22. The process of Claim 20, wherein the substrate is a textile substrate. 15

23. The process of Claim 22, wherein said substrate is of a homo or mixed polymer of acrylonitrile or dicyanoethylene or an acid modified polyamide or polyester. 15

24. The process of any one of Claims 20 to 23, substantially as hereinbefore described. 15

25. A basic dyeable substrate whenever dyed by the process of any one of Claims 20 to 24.

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