

PATENT SPECIFICATION

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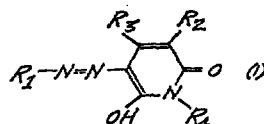


(54) MONOAZO AND DISAZO COMPOUNDS OF LOW SOLUBILITY IN WATER WHICH CONTAIN A DIHYDROXYPYRIDINE RESIDUE, THEIR PRODUCTION AND USE AS DYES

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, 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:—

This invention relates to azo disperse dyestuffs which contain the residue of a dihydroxypyridine coupling component, which are of low solubility in water and which are highly suitable for application as disperse dyes in the dyeing and printing of fibres and textiles of synthetic and semi-synthetic, hydrophobic organic substances of high molecular weight.

The new compounds are free from sulphonic acid groups and have the formula



In this formula

- R_1 stands for the radical of a diazo component,
 R_2 for a cyano or acyl group,
 R_3 for an alkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted,
 R_4 for an alkyl or cycloalkyl radical which is substituted by a halogen atom, or a cyano, acyl or acyloxy group or for a radical of formula



In the specially preferred compounds of formula (I)

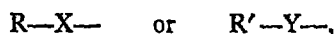
- R_3 stands for an alkyl or cycloalkyl group having 1 to 6 carbon atoms which may be substituted by one or more chlorine or bromine atoms, cyano or alkoxy groups, for a phenyl or benzyl radical which may be substituted by one or more chlorine or bromine atoms, hydroxyl, alkyl, alkoxy, cycloalkyl, nitro, cyano, acyl, acyloxy or acylamino groups, or for a naphthyl, alkoxy-naphthyl, thienyl, methylthienyl, or pyridyl radical, and
 R_4 for an alkyl or cycloalkyl group having 1 to 10 carbon atoms, which is substituted by a chlorine or bromine atom or by a cyano, acyl or acyloxy group.

Examples of suitable radicals R_1 in the diazo component are phenyl, naphthyl, thiazolyl, benzothiazolyl, thiadiazolyl, pyrazolyl, imidazolyl and thienyl radicals. The aliphatic and alkylene radicals are unsaturated or preferably saturated radicals having

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1 to 8 or more particularly 1, 2, 3 or 4 carbon atoms.

The term "acyl" refers to radicals of formulae



where R represents a hydrocarbon radical which may contain one or more substituents and/or may be interrupted by one or more hetero atoms, preferably an alkyl, cycloalkyl or phenyl radical,

X a group of formula $-\text{CO}-$, $-\text{O}-\text{CO}-$ or $-\text{SO}_2-$,

R' a hydrogen atom or R,

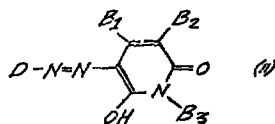
Y a group of formula $-\text{NR}''-\text{CO}-$ or $-\text{NR}''-\text{SO}_2-$,

and R'' a hydrogen atom or R or, together with R' and the N-atom, the atoms needed to form a heterocyclic ring.

The radicals of aromatic character may all bear one or more substituents, e.g. halogen atoms, in particular fluorine, chlorine or bromine atoms, nitro, cyano, thiocyanato, hydroxyl, alkyl, alkoxy, cycloalkyl, phenyl, phenoxy, acyl, acyloxy or acylamino groups.

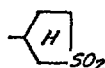
The afore-mentioned alkyl, cycloalkyl, and alkoxy groups generally contain 1 to 8 or more particularly 1, 2, 3 or 4 carbon atoms; they may bear as substituents, e.g., one or more halogen atoms, preferably chlorine or bromine atoms, cyano, thiocyanato, hydroxyl, alkoxy, phenyl, phenoxy, acyl or acyloxy groups. The preferred cycloalkyl radicals are cyclohexyl radicals.

Preferred dyes have the formula



where D stands for a phenyl radical which may be substituted by one or more chlorine or bromine atoms, hydroxyl, cyano, thiocyanato, nitro, methyl, ethyl, trifluoromethyl, methoxy, ethoxy, formyl, acetyl, propionyl, benzoyl, methylbenzoyl, methoxycarbonyl, ethoxycarbonyl, ethoxycarbonyloxy, benzyloxycarbonyloxy, acetoxyl, propionylloxy, benzoyloxy, methoxyethoxycarbonyl, acetylaminol, propionylaminol, benzoylaminol, methoxycarbonylaminol, ethoxycarbonylaminol, methylsulphonyl, ethylsulphonyl, propylsulphonyl, butylsulphonyl, chloromethylsulphonyl, aminosulphonyl, methylaminosulphonyl, dimethylaminosulphonyl, di-(hydroxyethyl)-aminosulphonyl, cyclohexylaminosulphonyl, phenylaminosulphonyl, chloromethylaminosulphonyl, methoxyphenylaminosulphonyl, benzylaminosulphonyl, N-piperidylsulphonyl, N-morpholinylsulphonyl, methylsulphonyloxy, ethylsulphonyloxy, ethoxyethylsulphonyloxy, propylsulphonyloxy, hexylsulphonyloxy, cyclohexylsulphonyloxy, chloromethylsulphonyloxy, chloroethylsulphonyloxy, cyanoethylsulphonyloxy, phenylsulphonyloxy, aminosulphonyloxy, N-morpholinylsulphonyloxy, methoxyphenylsulphonyloxy, ethylaminosulphonyloxy, methylaminosulphonyloxy, ethylaminosulphonyloxy, propylaminosulphonyloxy, butylaminosulphonyloxy, dimethylaminosulphonyloxy, diethylaminosulphonyloxy, dipropylaminosulphonyloxy, dibutylaminosulphonyloxy, phenylaminosulphonyloxy, N-phenyl-N-methylaminosulphonyloxy, N-phenyl-N-ethylaminosulphonyloxy, methoxyphenylaminosulphonyloxy, phenyl, acetylaminophenyl, phenylaminosulphonylphenylphenylazo or nitrophenylazo groups; for a naphthyl radical which may be substituted by one or more methoxy, ethoxy, phenylazo or dimethylaminosulphonyl groups; for a thiazolyl radical which may be substituted by one or more chlorine or bromine atoms, nitro, cyano, methyl, phenyl, methylsulphonyl or ethylsulphonyl groups; for a benzothiazolyl radical which may be substituted by one or more chlorine or bromine atoms, cyano, nitro, methyl, ethyl, methoxy, ethoxy, methylsulphonyl, ethylsulphonyl, cyanoethylsulphonyl, aminosulphonyl or methylaminosulphonyl groups; for a pyrazolyl radical which may be substituted by one or more cyano, methyl or phenyl groups; for a thiadiazolyl radical which may be substituted by a methyl group; for an imidazolyl radical which may be substituted by one or more nitro or methyl groups; or for a thienyl radical which may be substituted by one or more nitro or acetyl groups;

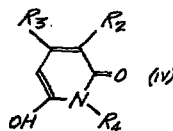
- B_1 for an alkyl radical having 1 to 4 carbon atoms which may be substituted by one or more chlorine or bromine atoms, hydroxyl, cyano, methoxy or ethoxy groups; for a phenyl radical which may be substituted by one or more chlorine or bromine atoms, methyl, methoxy, nitro, methoxycarbonyl, ethoxycarbonyl, methylaminosulphonyl, diethylaminosulphonyl, cyano or acetyl amino groups, or for a naphthyl, methoxynaphthyl, ethoxynaphthyl, thienyl, methylthienyl, furyl, thiazolyl, pyridyl, imidazolyl or benzimidazolyl radical,
- B_2 for a cyano, acetyl, propionyl, methylsulphonyl, ethylsulphonyl, benzoyl, phenylsulphonyl, nicotinoyl, aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, ethylaminocarbonyl or diethylaminocarbonyl group and
- B_3 for an alkyl radical having 1, 2, 3 or 4 carbon atoms which is substituted by one or more chlorine or bromine atoms, cyano, acetyl, propionyl, benzoyl, formyloxy, acetoxy, propionyloxy, methoxypropionyloxy, acryloyloxy, benzoyloxy, methoxycarbonyl, ethoxycarbonyl, ethoxyethoxycarbonyl, cyanomethoxycarbonyl, phenoxy-carbonyl, methoxycarbonyloxy, ethoxycarbonyloxy, phenoxy-carbonyloxy, amino-carbonyl, methylaminocarbonyl, dimethylaminocarbonyl, methylaminocarbonyloxy, ethylaminocarbonyloxy, phenylaminocarbonyloxy, methoxycarbonyloxy, methylsulphonyloxy, ethylsulphonyloxy, phenylsulphonyloxy, vinylsulphonyloxy, phenoxy-sulphonyl, phenylmercaptoethylsulphonyl or vinylsulphonyl groups, or for a radical of formula



The compounds of formula (I) can be produced by diazotizing an amine of formula



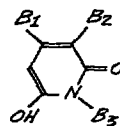
- and coupling the diazonium compound with a compound of formula



The compounds of formula (II) can be produced analogously by coupling a diazotized amine of formula



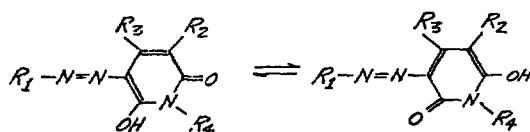
- with a compound of formula



(VI).

The coupling reaction generally takes place in acid, if necessary buffered medium, with cooling. Sodium acetate is a suitable buffering agent.

It is assumed that the compounds of formulae (I) and (II) are present in a tautomeric state, which can be expressed by the following formulae



The coupling components of formulae (IV) and (VI) can be produced in analogy with the method of J. Guareschi, Atti Accademia Reale di Scienze di Torino, 1895/96;

c.f. Berichte der deutschen chemischen Gesellschaft 29 (1896), p. 655, Chem. Zentr. 1896, 1,602 and 1896, II, 46, and Umaprasynna Basu, J. Indian Chem. Soc. Vol. VIII (1931) p. 319—328, by condensation of appropriately substituted acetic acid amides with suitably substituted β -ketocarboxylic acid esters.

It is of advantage to convert the new dyes into dye preparations before application, using the known methods, e.g. grinding in the presence of a dispersing agent and/or fillers, followed by drying in a vacuum or atomizer drier. The resulting dye preparations, after the addition of a suitable amount of water, can be employed for dyeing, padding or printing from long or short baths. From aqueous dispersion the dyes build up excellently on fibres of synthetic and semi-synthetic hydrophobic organic substances of high molecular weight. The dyes are highly suitable for the exhaustion dyeing, pad dyeing and printing of textiles of linear aromatic polyesters, cellulose diacetate, cellulose triacetate and synthetic polyamides. They are also dyeable on polyolefins and polyvinyl compounds.

The known dyeing and printing methods are used, e.g. the process described in U.K. Patent Specification No. 1,114,433. The dyeings obtained are of yellow to red shade and have very good fastness properties, being outstandingly fast to thermofixation, sublimation, pleating, ozone, rubbing and gas fumes. The wet fastness properties including fastness to water, sea water, perspiration, alkali and washing are also very good. Other notable features are the fastness to cross dyeing and light, the reduction stability and the good migration. The dyes are stable to the action of the various forms of permanent press finishing. Their good covering power on barry polyester materials is a further advantage. They are suitable for application to texturized polyester fibres.

In the following Examples the parts and percentages are by weight and the temperatures in degrees centigrade.

EXAMPLE 1

21.6 Parts of 3-dimethylaminosulphonyloxylaniline are dissolved in 280 parts of water and 36 parts of 30% hydrochloric acid. The solution is cooled to 0—5° and a solution of 8 parts of sodium nitrite in 60 parts of water is added for diazotization. For completion of this reaction stirring is continued at 0—5° for 1 hour, after which the excess nitrous acid is decomposed with aminosulphonic acid. For the coupling reaction 20.3 parts of 1- β -cyanoethyl-3-cyano-4-methyl-6-hydroxypyridone-2 are suspended in 250 parts of water and adjusted to pH 4.5 with acetic acid. The diazonium salt solution is added dropwise to the well cooled coupling suspension over 30 minutes, during which time the pH is kept constant with sodium acetate. Stirring is continued for 1 hour, following which the precipitated dye is filtered off. It is obtained as a yellow powder which gives by conventional methods dyeings of yellow shade on synthetic fibres having excellent fastness to light, cross dyeing, washing, water, sea water, perspiration, sublimation, gas fumes, pleating and permanent press finishing. In the following Tables further dyes are listed which can be produced in accordance with the procedure of Example 1. All these dyes have the fastness properties mentioned in the foregoing and give dyeings of yellow to red shade on polyester fibres.

The dyes listed in Table 1 are of formula

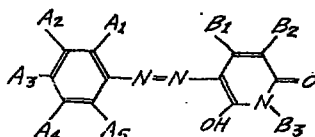


TABLE 1

Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
2	H	H	-OCOOC ₂ H ₅	H	H	-CH ₃	-CN	-CH ₂ CH ₂ COOCH ₃
3	H	H	-NO ₂	H	H	-C ₆ H ₅	do.	-C ₂ H ₄ CN
4	H	-NO ₂	H	H	H	-CH ₃	do.	-C ₂ H ₄ Cl
5	-NO ₂	H	H	H	H	do.	do.	do.
6	-CN	H	-NO ₂	H	-CN	-C ₂ H ₅	-COCH ₃	do.
7	H	-NO ₂	H	H	H	-CH ₃	-CN	-CH ₂ CH ₂ O.COCH ₃
8	H	do.	H	H	H	do.	do.	-CH ₂ CH ₂ O.COC ₆ H ₅
9	H	do.	H	H	H	do.	do.	-CH ₂ CH ₂ O.COC ₂ H ₅
10	H	do.	H	H	H	do.	do.	-CH ₂ CH ₂ O.COC ₃ H ₇
11	H	H	-NO ₂	H	H	do.	do.	-CH ₂ CH ₂ O.COOC ₂ H ₅
12	H	H	do.	H	H	do.	do.	-CH ₂ CH ₂ O.COOC ₆ H ₅
13	-NO ₂	H	H	H	H	do.	do.	-CH ₂ CH ₂ COOCH ₃
14	-Cl	H	-NO ₂	H	H	do.	do.	-CH ₂ CH ₂ O.COCH=CH ₂
15	H	H	-COOCH ₃	H	H	do.	do.	-CH ₂ CH ₂ COOC ₆ H ₅
16	-Cl	H	-SO ₂ CH ₃	H	H	do.	do.	-CH ₂ CH ₂ COCH ₃
17	H	H	-NHCOC ₆ H ₅	H	H	do.	do.	do.

TABLE I (Continued)

Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
18	H	H	-NHCOC ₆ H ₅	H	H	-CH ₃	-COCH ₃	-CH ₂ CH ₂ COCH ₃
19	H	H	-NHCOCH ₃	H	H	do.	do.	do.
20	H	-O-SO ₂ -N(CH ₃) ₂	H	H	H	do.	CN	-CH ₂ CH ₂ O.COCH ₃
21	H	do.	H	H	H	do.	do.	-CH ₂ CH ₂ Cl
22	H	H	-OCH ₃	H	H	do.	do.	-C ₂ H ₄ COC ₆ H ₅
23	H	H	(H ₃ C) ₂ NCO-	H	H	do.	do.	do.
24	H	-OSO ₂ CH ₃	H	H	H	do.	do.	do.
25	H	H	H ₂ NSO ₂	H	H	do.	do.	do.
26	H	-NO ₂	H	H	H	do.	do.	-C ₂ H ₄ SO ₂ CH=CH ₃
27	H	do.	H	H	H	do.	do.	
28	H	H	-CO.OCH ₃	H	H	-CH ₃	-CN	-C ₂ H ₄ OSO ₂ C ₂ H ₅
29	-NO ₂	H	-CH ₃	H	H	-C ₂ H ₅	do.	do.
30	-NO ₂	H	do.	H	H	-C ₃ H ₇	do.	do.
31	-NO ₂	H	do.	H	H	dc	do.	-C ₂ H ₄ CONH ₂
32	-NO ₂	H	do.	H	H	do.	do.	-C ₂ H ₄ COOC ₂ H ₄ O.COCH ₃
33	Cl	H	H	-Cl	H	-CH ₃	do.	-C ₂ H ₄ COOCH ₂ CN
34	Cl	H	H	-Cl	H	do.	do.	-CH ₂ CHOHCH ₂ CN
35	Cl	H	H	-Cl	H	do.	do.	-CH ₂ SO ₂ C ₂ H ₄ SC ₆ H ₅
36	Cl	H	H	-Cl	H	do.	do.	-C ₂ H ₄ SO ₂ OC ₆ H ₅

TABLE I (Continued)

35	Cl	H	H	—Cl	H	do.	—CH ₂ SO ₂ C ₂ H ₄ SC ₆ H ₅
36	Cl	H	H	—Cl	H	do.	—C ₂ H ₄ SO ₂ OC ₆ H ₅

TABLE I (Continued)

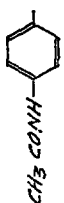
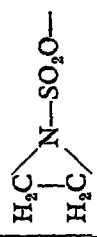
Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
37	H	H	H ₃ CO·CONH—	H	H	—CH ₃	—CN	—C ₂ H ₄ CN
38	H	H	CH ₃ OC ₂ H ₄ O·CO—	H	H	do.	do.	do.
39	H	H		H	H	do.	do.	do.
40	—NO ₂	H	—Cl	H	H	—CH ₃	—CN	—C ₂ H ₄ O·COCH ₃
41	—NO ₂	H	—NO ₂	H	H	do.	do.	do.
42	H	H	—Cl	H	H		do.	—C ₂ H ₄ Cl
43	H ₃ CSO ₂ —	H	do.	H	H	—C ₂ H ₅	do.	—C ₂ H ₄ CN
44	H	H	H ₃ C—SO ₂ —	H	H	—CH ₃	do.	—C ₂ H ₄ Cl
45	H	—Cl	—Cl	H	H	do.	—COOC ₂ H ₅	—C ₂ H ₄ O·CONHC ₆ H ₅
46	—NO ₂	H	—NO ₂	NHCOCH ₃	H	do.	do.	—C ₂ H ₄ COOCH ₂ CN
47	H	H		H	H	do.	—CN	—C ₂ H ₄ SO ₂ C ₂ H ₄ SC ₆ H ₅

TABLE I (Continued)

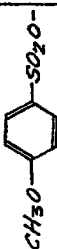
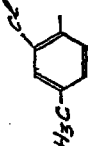
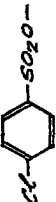
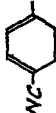
Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
48	H	H ₃ C ₆ N(CH ₃) SO ₂ O—	H	H	H	—CH ₃	—CN	—CH ₂ CHOHCH ₂ CN
49	H	H	(HOC ₂ H ₄) ₂ NSO ₂	H	H	—C ₆ H ₅	—CN	—C ₂ H ₄ COOCH ₂ CN
50	H	—Cl	—Cl	—Cl	H		—COCH ₃	—C ₂ H ₄ O.COC ₂ H ₄ OCH ₃
51	—CH ₃	H	—CH ₃	H	—NO ₂		—CN	C ₂ H ₄ O.COCH=CH ₂
52	—OCH ₃	H		H	H		—CONHC ₂ H ₅	—C ₂ H ₄ O.COCH ₃
53	H	—CH ₃		—CH ₃	H		—CON(CH ₃) ₂	—C ₂ H ₄ O.COC ₂ H ₅

TABLE I (Continued)

TABLE I (Continued)

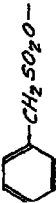
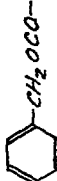
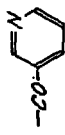
Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
54	H	—CH ₃	—OSO ₂ C ₆ H ₅	H	H	—C ₃ H ₇	—CN	—C ₂ H ₄ COOC ₂ H ₅
55	H		—CH ₃	H	H	—CH ₃	do.	do.
56	—CN	H	H	—Cl	H	do.	—COCH ₃	—C ₂ H ₄ O.COC ₆ H ₅
57	—Cl	H	CH ₃ SO ₂ —	H	H	do.	—CN	do.
58	—Cl	H	do.	H	—Cl	do.	do.	—C ₂ H ₄ SO ₂ OC ₆ H ₅
59	H	H	H ₃ COC ₂ H ₄ OCO—	H	H	—CH ₃	—SO ₂ CH ₃	—C ₂ H ₄ COOC ₂ H ₄ O.COCCH ₃
60	H	H		H	H	do.	—CN	—C ₂ H ₄ OSO ₂ C ₆ H ₅
61	—OCH ₃	H	—NO ₂	H	H	do.	—CON(CH ₃) ₂	do.
62	H	—NO ₂	H	H	H	do.		—C ₂ H ₄ CONH ₂

TABLE I (Continued)

Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
63	—CH ₃	H	OH	H	H	—C ₃ H ₇	—CN	—C ₂ H ₄ O·CONHC ₂ H ₅
64	—OCH ₃	H	H	H	H	—C ₆ H ₅	—COOC ₆ H ₅	—C ₂ H ₄ OSO ₂ C ₆ H ₅
65	H	—OCH ₃	H	H	H	—C ₄ H ₉	—SO ₂ —C ₆ H ₅	—C ₂ H ₄ OSO ₂ CH ₃
66	H	H	—COCH ₃	H	H	—C ₃ H ₇	—COC ₂ H ₅	—C ₂ H ₄ CONH ₂
67	—OH	H	H ₂ NSO ₂ —	H	H	—C ₃ H ₇	—CN	—C ₂ H ₄ COC ₂ H ₅
68	H	—CN	H	H	H	—CH ₃	do.	—C ₂ H ₄ COCH ₃
69	H	H	—OC ₂ H ₅	H	H	do.	do.	—C ₂ H ₄ SO ₂ CH=CH ₂
70	—Cl	H	H	Cl	H	do.	do.	
71	H	H ₂ NSO ₂ —	H	H	H	—C ₆ H ₅	do.	—CH ₂ CHOHCH ₂ Cl
72	H	H	—CF ₃	H	H	do.	do.	—CH ₂ CHOHCH ₂ CN
73	H ₂ NSO ₂ —	H	do.	H	H	—CH ₃	do.	—CH ₂ CHClCH ₂ CN
74	H	H ₃ CNHSO ₂ —	H	H	—CH ₃	—CH ₃	—COCH ₃	—C ₂ H ₄ O·CONHC ₆ H ₅
75	H ₃ C ₂ OC ₂ H ₄ NHSO ₂ —	H	H	—Cl	H	—CH ₃	—CN	—C ₂ H ₄ COCH ₃
76	H		H	H	—Cl	do.	do.	—C ₂ H ₄ Cl

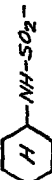
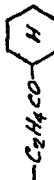
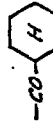
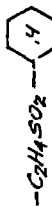
Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
77	H		H	-CH ₃	H	-CH ₃	-CN	-C ₂ H ₄ CN
78	H	$\text{C}_6\text{H}_5\text{-CH}_2\text{-NH-SO}_2\text{-}$	H	H	H	do.	do.	-C ₂ H ₄ COOC ₂ H ₅
79	-Cl	H		H	H	do.	do.	-C ₂ H ₄ O.COC ₂ H ₅
80	-CN	H	-NO ₂	H	Br	do.	do.	-C ₂ H ₄ CN
81	H	H	do.	H	H	do.	-CM	-C ₂ H ₄ CON(CH ₃) ₂
82	-Cl	H	do.	H	H	-CH ₂ CH ₂ OH	-CONHC ₆ H ₅	
83	-SO ₂ CH ₃	H	do.	H	H	-CH ₂ CH ₂ CN	-CON(CH ₃)C ₆ H ₅	-C ₂ H ₄ SO ₂ CH ₃
84	-SO ₂ C ₂ H ₅	H	do.	H	H	-CH ₂ CH ₂ CONH ₂		

TABLE I (Continued)

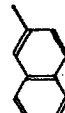
Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
85	H	H	—Cl	H	H	—CH ₃	—COCH ₂ C ₆ H ₅	—C ₂ H ₄ SO ₂ C ₆ H ₅
86	—Cl	H	—Cl	H	H	do.		—C ₂ H ₄ SO ₂ CH ₂ C ₆ H ₅
87	—CN	H	—NO ₂	H	H	do.	—CO—N(CH ₃) ₂	—C ₂ H ₄ OSO ₂ C ₆ H ₅
88	—NO ₂	H	do.	H	H	—C ₆ H ₅	—CONH ₂	
89	—Br	H	do.	H	—NO ₂		—SO ₂ NHC ₃ H ₇	—C ₂ H ₄ CN
90	—Br	H	—NO ₂	H	H	—CH ₃	do.	CH ₃ COOC ₂ H ₄ —
91	H	H	do.	H	H	C ₆ H ₅	do.	do.
92	H	—NO ₂	H	H	H	do.	do.	C ₂ H ₅ COOC ₂ H ₄ —

TABLE I (Continued)

TABLE I (Continued)

Examp. No.	A ₁	A ₂	A ₃	A ₄	A ₅	B ₁	B ₂	B ₃
93	-NO ₂	H	H	H	H	-CH ₃	SO ₂ NHC ₃ H ₇ -	NCCH ₂ COOC ₂ H ₄ -
94	-CN	H	-NO ₂	H	-CN	do.	do.	ClCH ₂ COOC ₂ H ₄ -
95	H	-NO ₂	H	H	H	do.	do.	H ₅ C ₆ COOC ₂ H ₄ -
96	H	do.	H	H	H	do.	do.	H ₅ C ₆ CH ₂ COOC ₂ H ₄ -
97	H	do.	H	H	H	do.	do.	4-H ₃ COH ₃ C ₆ COOC ₂ H ₄ -
98	H	do.	H	H	H	do.	do.	4-ClH ₄ C ₆ COOC ₂ H ₄ -
99	H	do.	H	H	H	do.	do.	2,4-Cl ₂ H ₃ C ₆ COOC ₂ H ₄ -
100	H	H	-NO ₂	H	H	-C ₆ H ₅	do.	C ₃ H ₇ COOC ₂ H ₄ -
101	H	H	do.	H	H	do.	do.	CH ₂ =CHCOOC ₂ H ₄ -
102	-NO ₂	H	H	H	H	-CH ₃	do.	CH ₃ COOC ₂ H ₄ O ₂ COOC ₂ H ₄ -
103	-Cl	H	-NO ₂	H	H	-C ₃ H ₇	do.	CH ₃ COOC ₂ H ₄ -
104	H	H	CH ₃ OCO-	H	H	-CH ₃	do.	C ₄ H ₉ COOC ₂ H ₄ -
105	-Cl	H	-NO ₂	H	-Cl	-C ₂ H ₅	do.	CH ₃ COOC ₃ H ₆ -
106	-NO ₂	H	CH ₃ SO ₂ -	H	H	do.	do.	CH ₃ COOC ₂ H ₄ -
107	-CN	H	H	-Cl	H	-C ₃ H ₇	do.	C ₂ H ₅ COOC ₂ H ₄ -
108	-Cl	H	CH ₃ SO ₂ -	H	H	do.	do.	CH ₃ COOC ₂ H ₄ -
109	H	H	H ₅ C ₆ CONH-	H	H	-C ₆ H ₅	do.	H ₅ C ₆ COOC ₂ H ₄ -

The dyes listed in Table 2 are of formula

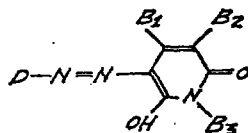


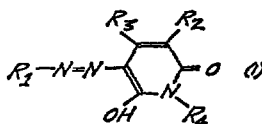
TABLE 2

Examp No.	D	B ₁	B ₂	B ₃
110	4-Phenylazophenyl	-CH ₃	-CN	-CH ₂ CH ₂ COC ₆ H ₅
111	2-Methoxy-4-(4'-(4'-nitrophenylazo)-phenyl	do.	do.	do.
112	4-Phenylazo-naphthyl-1	do.	do.	-CH ₂ CH ₂ CN
113	4-(4'-Acetylamino-phenyl)-phenyl	-CH ₃	-CN	-CH ₂ CH ₂ CN
114	6-Cyanoethyl-sulphonylbenzo-thiazolyl-2	Thienyl-2	-CN	-CH ₂ CH ₂ OCOCH ₃
115	do.	do.	do.	-CH ₂ CH ₂ COOCH ₃

In our copending patent applications Nos. 57025/71 (Serial No. 1,274,943) and 57026/71 (Serial No. 1,274,944) which were divided out of this application we have described and claimed certain azo disperse dyestuffs containing the residues of closely related and similar dihydroxypyridines.

WHAT WE CLAIM IS:—

1. Azo disperse dyestuffs which are free from sulphonic acid groups and are of formula



where R₁ stands for the radical of a diazo component,

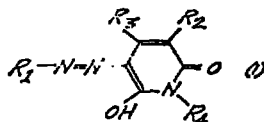
R₂ for a cyano or acyl group,

R₃ for an alkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted,

and R₄ for an alkyl or cycloalkyl radical which is substituted by a halogen atom, a cyano, acyl or acyloxy group or for a radical of formula



2. Azo disperse dyestuffs according to claim 1, of formula



The dyes listed in Table 2 are of formula

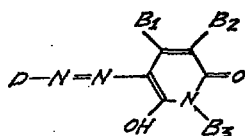


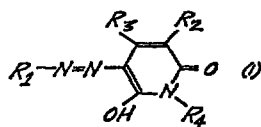
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113	4-(4'-Acetylamino-phenyl)-phenyl	-CH ₃	-CN	-CH ₂ CH ₂ CN
114	6-Cyanoethyl-sulphonylbenzo-thiazolyl-2	Thienyl-2	-CN	-CH ₂ CH ₂ OCOCH ₃
115	do.	do.	do.	-CH ₂ CH ₂ COOCH ₃

In our copending patent applications Nos. 57025/71 (Serial No. 1,274,943) and 57026/71 (Serial No. 1,274,944) which were divided out of this application we have described and claimed certain azo disperse dyestuffs containing the residues of closely related and similar dihydroxypyridines.

WHAT WE CLAIM IS:—

1. Azo disperse dyestuffs which are free from sulphonic acid groups and are of formula



where R₁ stands for the radical of a diazo component,

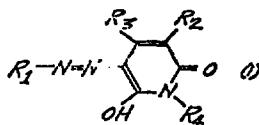
R₂ for a cyano or acyl group,

R₃ for an alkyl, cycloalkyl, aryl or heterocyclic radical which may be substituted,

and R₄ for an alkyl or cycloalkyl radical which is substituted by a halogen atom, a cyano, acyl or acyloxy group or for a radical of formula



2. Azo disperse dyestuffs according to claim 1, of formula



where R_3 stands for an alkyl or cycloalkyl group having 1 to 6 carbon atoms which may be substituted by one or more chlorine or bromine atoms, cyano or alkoxy groups, for a phenyl or benzyl radical which may be substituted by one or more chlorine or bromine atoms, hydroxyl, alkyl, alkoxy, cycloalkyl, nitro, cyano, acyl, acyloxy or acylamino groups or for a naphthyl, alkoxy-naphthyl, thienyl, methylthienyl, or pyridyl radical, and

R_4 for an alkyl or cycloalkyl group having 1 to 12 carbon atoms, which is substituted by a chlorine or bromine atom or a cyano, acyl or acyloxy group or for a radical of formula



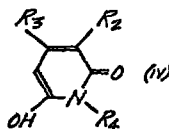
3. The particular azo disperse dyestuffs herein described and illustrated in any of the Examples.

4. A process for the production of an azo disperse dyestuff according to claim 1 which comprises diazotizing an amine of formula



(III)

and coupling the resulting diazonium compound with a compound of formula



where R_1 , R_2 , R_3 and R_4 have the meanings given them in claim 1.

5. A process for the production of an azo disperse dyestuff according to claim 1 substantially as herein described and exemplified.

6. Azo disperse dyestuffs whenever prepared by a process according to claim 4 or claim 5.

7. A dyeing or printing process in which fibres or textiles of synthetic or semi-synthetic hydrophobic organic substances of high molecular weight are dyed or printed with an azo disperse dyestuff according to any one of Claim 1 to 3 or 6.

8. A dyeing process conducted substantially as described in the Application Example.

9. Fibres and textiles of synthetic and semi-synthetic hydrophobic organic substances of high molecular weight dyed or printed by a process according to claim 7.

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