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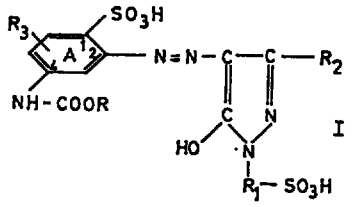
(19)

(54) AZO DYES CONTAINING SULPHONIC ACID GROUPS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4000 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:—

The invention relates to azo dyes containing sulphonic acid groups.

According to the present invention, there are provided compounds of formula I,



I

in which R signifies a substituted or unsubstituted alkyl or cycloalkyl radical,
R_1 signifies a substituted or unsubstituted phenylene or naphthylene radical,
R_2 signifies a substituted or unsubstituted alkyl or aryl radical,
R_3 signifies a hydrogen atom, a substituted or unsubstituted alkyl radical of 1 to 6 carbon atoms or a halogen atom, and
ring A may be further substituted.

Examples of substituted cycloalkyl radicals include e.g. alkylcycloalkyl alkylcyclohexyl.

As used herein, the term "alkyl" signifies a straight or branched chain alkyl radical of 1 to 18 carbon atoms, e.g. of 1 to 12 carbon atoms, particularly of 1 to 6 carbon atoms. Preferred alkyl radicals are from 1 to 4 carbon atoms except that, where R signifies an alkyl radical, such alkyl radical preferably contains 6 to 18 carbon atoms. The alkyl radicals may be substituted by, for example, halogen, hydroxy, cyano, alkoxy or aryl substituents. Suitable aryl substituted alkyl radicals include the benzyl radical. As used herein, the term "alkoxy" signifies an alkoxy radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms.

As used herein, the term "cycloalkyl" signifies a cycloalkyl radical of 5 to 7 carbon atoms.

Examples of aryl include phenyl and naphthyl radicals.

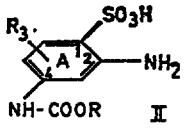
The aromatic rings, for example ring A and R_1, may be substituted, for example, by one or more halogen, cyano, nitro, hydroxy, trifluoroalkyl, trichloroalkyl, substituted or unsubstituted alkyl, cycloalkyl, aryl, alkoxy, carbalkoxy, acylamino, substituted, e.g. mono or disubstituted, or unsubstituted sulphonamido, substituted or unsubstituted alkylsulphonyl, arylsulphonyl, carboxylic acid ester or sulphonic acid ester, substituted or usubstituted carboxylic acid amide or sulphonic acid groups.

By halogen is meant bromine, fluorine, iodine or chlorine, chlorine being preferred.

It is preferred that the compounds of formula I contain no metallizable group in the ortho-position to the —N=N—group in ring A.

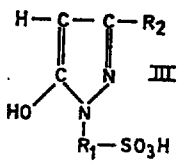
The invention also provides a process for the production of a compound of formula I, stated above, characterised by

a) coupling a diazo derivative of an amine of formula II,



II

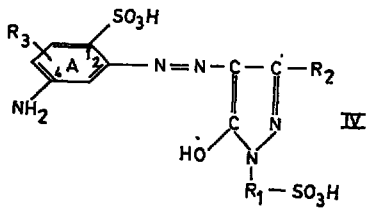
in which R, R_3 and ring A are as defined above, with a compound of formula III,



III

in which R_1 and R_2 are as defined above, or

b) reacting a monoazo compound of formula IV,



IV

in which R_1, R_2, R_3 and ring A are as defined above, with a haloformic acid ester of formula V,

$$R—O—CO—Hal \qquad V$$

in which Hal signifies a fluorine, chlorine, bromine or iodine atom, and R is as defined above.

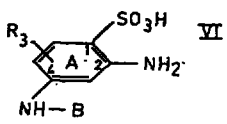
Process a) may be carried out in conventional manner for diazo coupling reactions, for example in an acid medium, e.g. at a pH value of from 2 to 6.

Process b) may, similarly be carried out in conventional manner, for example in water and in the presence of an acid binding agent and at a temperature from 40° to 150°C especially 40° to 100°C and preferably from 60° to 80°C.

Process b) is the preferred process.

The resulting compounds of formula I may be isolated by conventional techniques.

The compounds of formula IV, used as starting materials in process b), may be obtained by coupling a 2-diazo derivative of an amine of formula VI,



VI

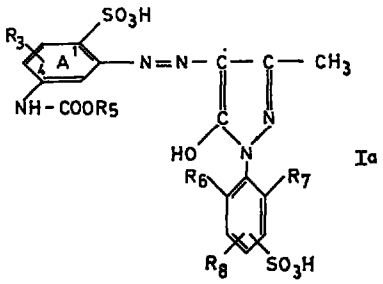
in which R_3 and ring A are as defined above, and

B signifies a hydrogen atom or an acetyl group, with a compound of formula III, stated above, and, where B signifies an acetyl group, deacetylating the resulting product.

The coupling reaction may be carried out in similar manner to process a) described above. The deacetylation may be carried out in conventional manner.

The compounds of formulae II, III, IV, V and VI are known or may be obtained in known manner from available starting materials.

Particular compounds of formula I are the compounds of the following formulae Ia, Ib and Ic.

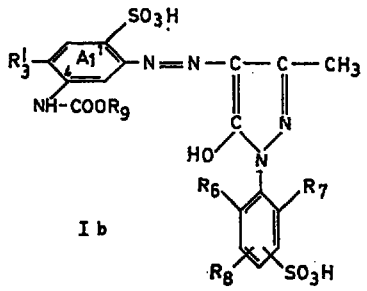


Ia

in which R_3 and ring A are as defined above,

R_5 signifies a substituted or unsubstituted alkyl or cycloalkyl radical, and

R_6, R_7 and R_8, which may be the same or different, each signifies a hydrogen or halogen atom or a substituted or unsubstituted alkyl or alkoxy radical,

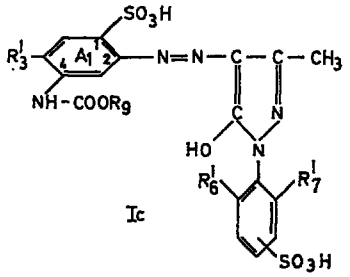


Ib

in which R_6, R_7 and R_8 are as defined above,

R_3' signifies a hydrogen or chlorine atom or a methyl radical,

R_9 signifies a substituted or unsubstituted alkyl radical of 6 to 18 carbon atoms or a substituted, or unsubstituted cyclohexyl radical, and ring A_1 bears no further substituents,



Ic

in which R_3', R_9 and ring A_1 are as defined above,

R_6' signifies a hydrogen or halogen atom or an alkyl radical of 1 to 6 carbon atoms, and

R_7' signifies a hydrogen or halogen atom, an alkyl radical of 1 to 6 carbon atoms or an alkoxy radical of 1 to 6 carbon atoms.

The compounds of formula I may suitably be used for dyeing and printing natural and synthetic polyamide fibres and other textile fibres. In particular, they may be used for exhaust dyeing, pad-dyeing and printing of natural and synthetic polyamide fibres, natural

and regenerated cellulosic fibres and basic dyeable polypropylene fibres, which fibres may be dyed in loose, yarn, fabric or blended form. The compounds of formula I may also suitably be used for dyeing and printing paper and leather.

In exhaust dyeing, the compounds are conveniently applied from a neutral to acid bath at a pH value of 2 to 7, preferably from 4 to 6, in the presence of an acid, e.g. an organic acid such as acetic or formic acid. The dyeings have notable light and wet fastness, e.g. fastness to washing, sea water, perspiration, acid, alkali, aldehyde, potting and milling, and notable fastness to gas fumes. They are also fast to rubbing. The dyes are soluble in water, show satisfactory levelling properties and cover barry nylon.

The compounds of the present invention can be applied alone, in combination with each other or with acid dyes, e.g. of the anthraquinone series, to give dyeings of comparably good light and wet fastness. If the cocpounds of formula I are used in combination with blue dyes, e.g. blue anionic anthraquinone dyes, the dyeings are free from catalytic fading.

For printing with the present dyes known methods can be employed, for instance that described in United States Patent 3,594,112.

Natural polyamide fibres which may be dyed with the dyes of the invention include wool and silk. Synthetic polyamide fibres which may be dyed include those from polymers formed by condensation polymerization of ω-aminocarboxylic acids or their lactams, e.g. the fibres from ω-lauric lactam 11-undecanocarboxylic acid, 7-aminoenanthic acid or ε-caprolactam (polyamides 12, 11, 7 and 6), of dibasic organic acids, e.g. dicarboxylic acids (e.g. adipic, sebacic acid) and diamines (e.g. hexamethylene diamine) (polyamides 66 and 610), or by mixed condensation polymerization, e.g. of ε-caprolactam, adipic acid and hexamethylene diamine (polyamide 66/6).

In comparison with the known dyes, e.g. those disclosed in Swiss Patent 341,586, the compounds of formula I have the advantage of being more suitable for application to natural and synthetic polyamide fibres by printing processes. In addition, they have noteworthy solubility in water.

The following Examples, in which the parts and percentages are by weight and the temperatures in degrees Centigrade. illustrate the invention.

EXAMPLE 1:

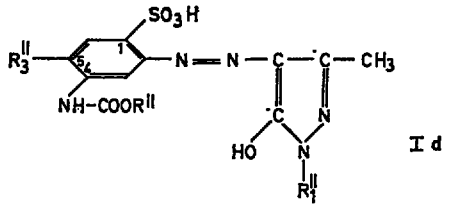
(i) Process a):

20 Parts of 2-amino-4-carbododecyloxy-aminobenzene-1-sulphonic acid (which is obtainable by reaction of 2,5-diaminobenzene-1-sulphonic acid with chloroformic lauryl ester) are stirred into 300 parts of water at room temperature and 6.7 parts of 30% aqueous sodium hydroxide solution are added. 3.5 Parts of sodium nitrite are added and stirring is continued until a solution is obtained. Over 30 minutes, the solution is dropwise added, with stirring, to 30 parts of concentrated hydrochloric acid and 150 parts of water at 0—5°. The resulting suspension is stirred for 1 hour at 0—5° and then added dropwise, to a cooled solution consisting of 14.8 parts of 1-(2'-chloro - 5' - sulpho - phenyl) - 3 - methyl - 5-pyrazolone, 6.7 parts of a 30% aqueous sodium hydroxide solution and 100 parts of water, with care being taken to keep the temperature below 10°. While the diazo suspension is being added, the pH of the coupling mixture is held at 5 by the gradual addition of 10% aqueous soda solution. The coupling mixture is stirred for a further 3 hours. The dye formed settles out and is isolated by filtration, with suction, and is then dried. It is obtained as a yellow powder which, applied from a neutral to weakly acid bath, dyes wool and synthetic polyamide fibres in yellow shades, fast to light, washing and milling.

ii) Process b):

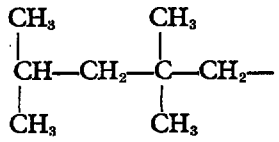
26.5 Parts of the disodium salt form of the monoazo dye obtained by coupling diazotized-2 - amino - 4 - acetylamino - benzene - 1-sulphonic acid with 1-(2'-chloro-5'-sulphophenyl)-3-methyl-5-pyrazolone are dissolved in 300 parts of water and 300 parts of alcohol. Then, 25 parts of concentrated hydrochloric acid are added. The temperature of the solution is raised to 85° and stirred at this temperature for 3 hours. After it has cooled to room temperature, the precipitated deacetylated product is filtered, washed until neutral, and dissolved in 800 parts of water containing 5 parts of soda. The solution is heated to 50° and held at this temperature for 3 hours while 25 parts of chloroformic lauryl ester are dropwise added thereto. Throughout the reaction, the pH is maintained at 7.5—8 by the addition of aqueous soda solution. Subsequently, the solution is cooled, and the dye formed settles out. It is filtered with suction, washed with ice-water and dried. On natural and synthetic polyamide fibres, this dye gives bright greenish yellow dyeings having good light and wet fastness properties.

The following table indicates further dyes of the invention which may be obtained in manner analogous to Example 1, and which are of formula Id,



Id

in which R″, R_1″ and R_3″ have the significances given in the table. The shade of the deings on synthetic polyamide fibre is noted in the final column. In the Table the diisobutyl radical given as a significance for R″ is a radi-



TABLE

Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
2	Dodecyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	H	yellow
3	do.	(2′,5′-dichloro-4′-sulpho)-phenyl	H	do.
4	Decyl	do.	H	do.
5	Undecyl	do.	H	do.
6	Nonyl	do.	H	do.
7	Iso-octyl	do.	H	do.
8	Di-isobutyl	do.	H	do.
9	Heptyl	do.	H	do.
10	2-Ethyl-hexyl	do.	H	do.
11	Cyclohexyl	do.	H	do.
12	*p*-Ethyl-cyclo-hexyl	do.	H	do.
13	3′, 3′, 5′-Tri-methylcyclohexyl	do.	H	do.
14	*p*-Tert-butyl-cyclohexyl	do.	H	do.
15	Benzyl	do.	H	do.
16	2-phenylethyl	do.	H	do.
17	Tridecyl	do.	H	do.
18	n-Tetradecyl	do.	H	do.
19	n-Pentadecyl	do.	H	do.
20	n-Hexadecyl	do.	H	do.
21	n-Heptadecyl	do.	H	do.

TABLE (Continued)

Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
22	Decyl	(2′-Chloro-5′-sulpho)-phenyl	H	yellow
23	Undecyl	do.	H	do.
24	Nonyl	do.	H	do.
25	Iso-octyl	do.	H	do.
26	Di-isobutyl	do.	H	do.
27	Heptyl	do.	H	do.
28	2-Ethyl-hexyl	do.	H	do.
29	Cyclohexyl	do.	H	do.
30	*p*-Ethyl-cyclo-hexyl	do.	H	do.
31	3′, 3′, 5′-Tri-methylcyclohexyl	do.	H	do.
32	p-Tert-butyl-cyclohexyl	do.	H	do.
33	Benzyl	do.	H	do.
34	2-phenylethyl	do.	H	do.
35	Tridecyl	do.	H	do.
36	*n*-Tetradecyl	do.	H	do.
37	*n*-Pentadecyl	do.	H	do.
38	*n*-Hexadecyl	do.	H	do.
39	*n*-Heptadecyl	do.	H	do.
40	Decyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	H	do.
41	Undecyl	do.	H	do.
42	Nonyl	do.	H	do.
43	Iso-octyl	do.	H	do.
44	Di-isobutyl	do.	H	do.
45	Heptyl	do.	H	do.
46	2-Ethyl-hexyl	do.	H	do.

TABLE (Continued)

Example No.	R″	R″$_1$	R″$_3$	Shade of dyeing on synthetic polyamide fibre
47	Cyclohexyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	H	yellow
48	*p*-Ethyl-cyclohexyl	do.	H	do.
49	3′, 3′, 5′-Trimethylcyclohexyl	do.	H	do.
50	p-Tert-butyl-cyclohexyl	do.	H	do.
51	Benzyl	do.	H	do.
52	2-phenylethyl	do.	H	do.
53	Tridecyl	do.	H	do.
54	*n*-Tetradecyl	do.	H	do.
55	*n*-Pentadecyl	do.	H	do.
56	*n*-Hexadecyl	do.	H	do.
57	*n*-Heptadecyl	do.	H	do.
58	Dodecyl	(1′-Sulpho)-2′-naphthyl	H	do.
59	Decyl	do.	H	do.
60	Undecyl	do.	H	do.
61	Nonyl	do.	H	do.
62	Iso-octyl	do.	H	do.
63	Di-isobutyl	do.	H	do.
64	Heptyl	do.	H	do.
65	2-Ethyl-hexyl	do.	H	do.
66	Cyclohexyl	do.	H	do.
67	*p*-Ethyl-cyclohexyl	do.	H	do.
68	3′, 3′, 5′-Trimethylcyclohexyl	do.	H	do.

TABLE (Continued)

Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
69	*p*-Tert-butyl cyclohexyl	(1′ - Sulpho) - 2′-naphthyl	H	yellow
70	Benzyl	do.	H	do.
71	2-phenylethyl	do.	H	do.
72	Tridecyl	do.	H	do.
73	*n*-Tetradecyl	do.	H	do.
74	n-Pentadecyl	do.	H	do.
75	*n*-Hexadecyl	do.	H	do.
76	*n*-Heptadecyl	do.	H	do.
77	Dodecyl	(2′, 5′-Di-chloro-4′-sulpho)-phenyl	$-CH_3$	do.
78	Decyl	do.	do.	do.
79	Undecyl	do.	do.	do.
80	Nonyl	do.	do.	do.
81	Iso-octyl	do.	do.	do.
82	Di-isobutyl	do.	do.	do.
83	Heptyl	do.	do.	do.
84	2-Ethyl-hexyl	do.fi	do.	do.
85	Cyclohexyl	do.	do.	do.
86	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
87	3′, 3′, 5′, Tri-methylcyclohexyl	do.	do.	do.
88	*p*-Tert-butyl-cyclohexyl	do.	do.	do.
89	Benzyl	do.	do.	do.
90	2-phenylethyl	do.	do.	do.
91	Tridecyl	do.	do.	do.
92	*n*-Tetraecyl	do.	do.	do.
93	*n*-Pentadecyl	do.	do.	do.
94	*n*-Hexadecyl	do.	do.	do.

TABLE (Continued)

Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
95	*n*-Heptadecyl	(2′,5′-Di-chloro-4′-sulpho)-phenyl	$-CH_3$	yellow
96	Dodecyl	(2′-Chloro-5′-sulpho)phenyl	do.	do.
97	Decyl>	do.	do.	do.
98	Undecyl	do.	do.	do.
99	Nonyl	do.	do.	do.
100	Iso-octyl	do.	do.	do.
101	Di-isobutyl	do.	do.	do.
102	Heptyl	do.	do.	do.
103	2-Ethyl-hexyl	do.	do.	do.
104	Cyclohexyl	do.	do.	do.
105	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
106	3′, 3′, 5′-Tri-methylcyclohexyl	do.	do.	do.
107	*p*-Tert isobutyl-cyclohexyl	do.	do.	do.
108	Benzyl	do.	do.	do.
109	2-phenylethyl	do.	do.	do.
110	Tridecyl	do.	do.	do.
111	*n*-Tetradecyl	do.	do.	do.
112	*n*-Pentadecyl	do.	do.	do.
113	*n*-Hexadecyl	do.	do.	do.
114	*n*-Heptadecyl	do.	do.	do.
115	Dodecyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	do.	do.
116	Decyl	do.	do.	do.
117	Undecyl	do.	do.	do.
118	Nonyl	do.	do.	do.

TABLE (Continued)

Example No.	R″	R″$_1$	R″$_3$	Shade of dyeing on synthetic polyamide fibre
119	Iso-octyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	—CH_3	yellow
120	Di-isobutyl	do.	do.	do.
121	Heptyl	do.	do.	do.
122	2-Ethyl-hexyl	do.	do.	do.
123	Cyclohexyl	do.	do.	do.
124	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
125	3′, 3′, 5′-Tri-methylcyclohexyl	do.	do.	do.
126	*p*-Tertbutyl-cyclohexyl	do.	do.	do.
127	Benzyl	do.	do.	do.
128	2-phenylethyl	do.	do.	do.
129	Tridecyl	do.	do.	do.
130	*n*-Tetr. decyl	do.	do.	do.
131	*n*-Pentadecyl	do.	do.	do.
132	*n*-Hexadecyl	do.	do.	do.
133	*n*-Heptadecyl	do.	do.	do.
134	Dodecyl	(1′-Sulpho)-2′-naphthyl	do.	do.
135	Decyl	do.	do.	do.
136	Undecyl	do.	do.	do.
137	Nonyl	do.	do.	do.
138	Iso-octyl	do.	do.	do.
139	Di-isobutyl	do.	do.	do.
140	Heptyl	do.	do.	do.
141	2-Ethyl-hexyl	do.	do.	do.
142	Cyclohexyl	do.	do.	do.

TABLE (Continued)

Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
143	*p*-Ethyl-cyclo-hexyl	(1′-Sulpho)-2′-naphthyl	$-CH_3$	yellow
144	3′, 3′, 5′-Tri-methylcyclohexyl	do.	do.	do.
145	*p*-Tertbutyl-cyclohexyl	do.	do.	do.
146	Benzyl	do.	do.	do.
147	2-phenylethyl	do.	do.	do.
148	Tridecyl	do.	do.	do.
149	*n*-Tetradecyl	do.	do.	do.
150	*n*-Pentadecyl	do.	do.	do.
151	*n*-Hexadecyl	do.	do.	do.
152	*n*-Heptadecyl	do.	do.	do.
153	Dodecyl	2′, 5′-Di-chloro)-4′-sulpho)-phenyl	—Cl	do.
154	Decyl	do.	do.	do.
155	Undecyl	do.	do.	do.
156	Nonyl	do.	do.	do.
157	Iso-octyl	do.	do.	do.
158	Di-isobutyl	do.	do.	do.
159	Heptyl	do.	do.	do.
160	2-Ethyl-hexyl	do.	do.	do.
161	Cyclohexyl	do.	do.	do.
162	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
163	3′,3′,5′-Tri-methylcyclohexyl	do.	do.	do.
164	*p*-Tert-butyl-cyclohexyl	do.	do.	do.
165	Benzyl	do.	do.	do.
166	2-phenylethyl	do.	do.	do.

TABLE (Continued)

Example No.	R″	R″$_1$	R″$_3$	Shade of dyeing on synthetic polyamide fibre
167	Tridecyl	2′,5′-Di-chloro)-4′-sulpho)-phenyl	—Cl	yellow
168	*n*-Tetradecyl	do.	do.	do.
169	*n*-Pentadecyl	do.	do.	do.
170	*n*-Hexadecyl	do.	do.	do.
171	*n*-Heptadecyl	do.	do.	do.
172	Dodecyl	(2′-Chloro-5′-sulpho)-phenyl	do.	do.
173	Decyl	do.	do.	do.
174	Undecyl	do.	do.	do.
175	Nonyl	do.	do.	do.
176	Iso-octyl	do.	do.	do.
177	Di-isobutyl	do.	do.	do.
178	Heptyl	do.	do.	do.
179	2-Ethyl-hexyl	do.	do.	do.
180	Cyclohexyl	do.	do.	do.
181	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
182	3′,3′,5-Tri-methylcyclohexyl	do.	do.	do.
183	*p*-Tert-butyl-cyclohexyl	do.	do.	do.
184	Benzyl	do.	do.	do.
185	2-phenylethyl	do.	do.	do.
186	Tridecyl	do.	do.	do.
187	*n*-Tetradecyl	do.	do.	do.
188	*n*-Pentadecyl	do.	do.	do.
189	*n*-Hexadecyl	do.	do.	do.
190	*n*-Heptadecyl	do.	do.	do.

TABLE (Continued)

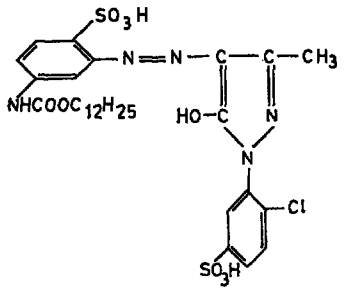
Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
191	Dodecyl	(2′-Chloro-6′-methyl-4′-sulpho)-phenyl	—Cl	yellow
192	Decyl	do.	do.	do.
193	Undecyl	do.	do.	do.
194	Nonyl	do.	do.	do.
195	Iso-octyl	do.	do.	do.
196	Di-isobutyl	do.	do.	do.
197	Heptyl	do.	do.	do.
198	2-Ethyl-hexyl	do.	do.	do.
199	Cyclohexyl	do.	do.	do.
200	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
201	3′,3′,5′-Tri-methylcyclohexyl	do.	do.	do.
202	*p*-Tert-butyl-cyclohexyl	do.	do.	do.
203	Benzyl	do.	do.	do
204	2-phenylethyl	do.	do.	do.
205	Tridecyl	do.	do.	do.
206	*n*-Tetradecyl	do.	do.	do.
207	*n*-Pentadecyl	do.	do.	do.
208	*n*-Hexadecyl	do.	do.	do.
209	*n*-Heptadecyl	do.	do.	do.
210	Dodecyl	(1′-Sulpho)-2′-naphthyl	do.	do.
211	Decyl	do.	do.	do.
212	Undecyl	do.	do.	do.
213	Nonyl	do.	do.	do.
214	Iso-octyl	do.	do.	do.

TABLE (Continued)

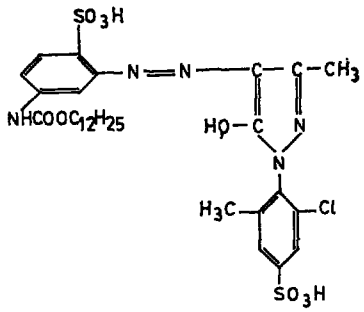
Example No.	R″	R''_1	R''_3	Shade of dyeing on synthetic polyamide fibre
215	Di-isobutyl	(1′-Sulpho)-2′-naphthyl	—Cl	yellow
216	Heptyl	do.	do.	do.
217	2-Ethyl-hexyl	do.	do.	do.
218	Cyclohexyl	do.	do.	do.
219	*p*-Ethyl-cyclo-hexyl	do.	do.	do.
220	3′,3′,5′-Tri-methylcyclohexyl	do.	do.	do.
221	*p*-Tert-butyl-cyclohexyl	do.	do.	do.
222	Benzyl	do.	do.	do.
223	2-phenylethyl	do.	do.	do.
224	Tridecyl	do.	do.	do.
225	*n*-Tetradecyl	do.	do.	do.
226	*n*-Pentadecyl	do.	do.	do.
227	*n*-Hexadecyl	do.	do.	do.
229	Dodecyl	4′-Sulphophenyl	H	yellow
230	Decyl	do.	do.	do.
231	do.	3′-Sulphophenyl	do.	do.
232	Dodecyl	do.	Cl	do.
233	do.	do.	$-CH_3$	do.
234	do.	do.	C_2H_5	do.
235	do.	do.	C_4H_9	do.
236	do.	2′-methoxy-5′-sulphophenyl	H	do.
237	do.	2′,6′-Di-methyl-4′-sulphophenyl	H	do.
238	do.	2′-Sulpho-phenyl	H	do.

The formulae of representative dyes of the foregoing Examples are as follows:

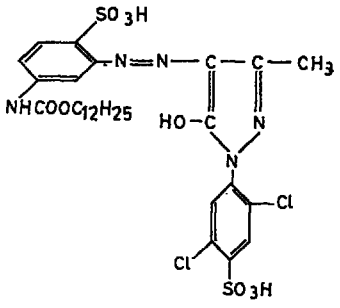
EXAMPLE 1.



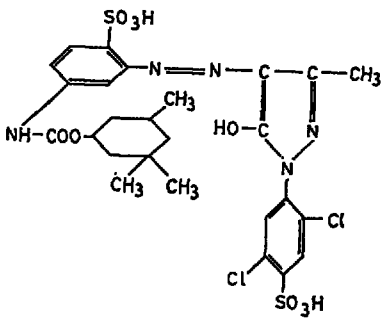
EXAMPLE 2.



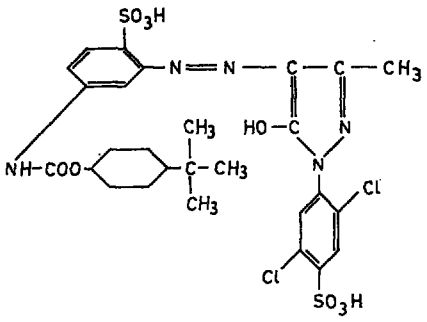
EXAMPLE 3.



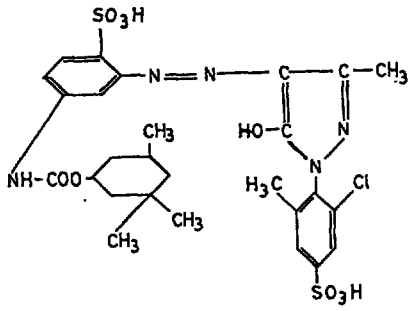
EXAMPLE 13.



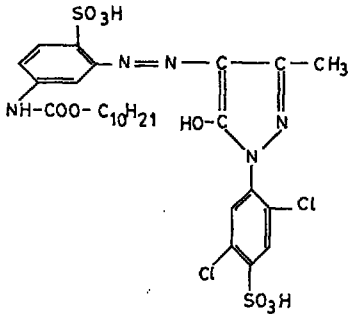
EXAMPLE 14.



EXAMPLE 49.



EXAMPLE 78.



Examples of Application.

Exhaust Dyeing

100 Parts of wool fabric are wet out and entered into a dyebath at 40° and consisting of 4000 parts of water, 10 parts of anhydrous sodium sulphate and 2 parts of the dye of Example 1. The dyebath is raised to the boil in 30 minutes and held at the boil for 1 hour. 4 Parts of glacial acetic acid are then added and dyeing is continued for a further 30 minutes at the boil. During dyeing, the water lost by evaporation is continuously replaced. On removal from the bath, the fabric is rinsed with water and dried. It is dyed a greenish yellow shade.

This method is suitable for dyeing synthetic polyamide fibres with the disclosed dyes, on which they show good light and wet fastness. It is also employable for dyeing polypropylene

fibres modified by the introduction of basic groups, the dyeings on these fibres being of similarly good quality.

Printing

A printing paste is prepared with:

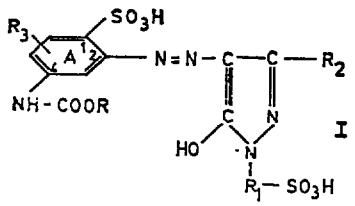
30 parts of the dye of Example 3,
50 parts of thiodiethylene glycol
500 parts of a 30% aqueous crystal gum solution
60 parts of thiourea
60 parts of a 20% aqueous ammoninm sulphate solution and
300 parts of water

1000 parts

The paste is printed on a nylon fabric by one of the standard methods, the fabric dried and the print fixed for 30—45 minutes at 102°. The fabric is then soaped at 60°, washed off and dried. A yellow print with good fastness properties is obtained. An equally good print is obtained when intermediate drying is omitted. On wool and other natural polyamide fibres, prints with similar good properties are obtained by this method.

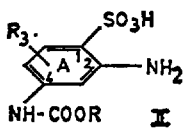
WHAT WE CLAIM IS:—

1. A process for the production of a compound of formula I,



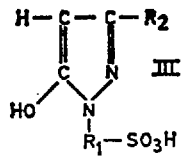
I

in which R signifies a substituted or unsubstituted alkyl or cycloalkyl radical,
R_1 signifies a substituted or unsubstituted phenylene or naphthylene radical,
R_2 signifies a substituted or unsubstituted alkyl or aryl radical,
R_3 signifies a hydrogen atom, a substituted or unsubstituted alkyl radical of 1 to 6 carbon atoms or a halogen atom, and
ring A may be further substituted, characterised by
a) coupling a diazo derivative of an amine of formula II,



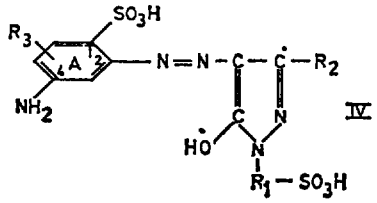
II

in which R, R_3 and ring A are as defined above,
with a compound of formula III,



III

in which R_1 and R_2 are as defined above, or
b) reacting a monoazo compound of formula IV,



IV

in which R_1, R_2, R_3 and ring A are as defined above, with a haloformic acid ester of formula V,

R—O—CO—Hal V

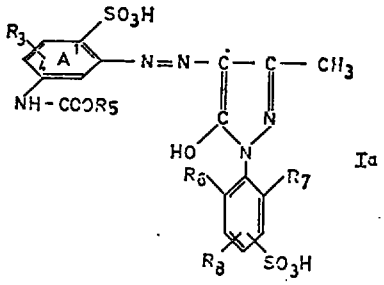
in which Hal signifies a fluorine, chlorine, bromine or iodine atom, and R is as defined above.

2. A process for the production of a compound of formula I stated in claim 1, substantially as herein before described with reference to any one of the foregoing Examples 1 to 238.

3. A compound of formula I, stated in claim 1, whenever produced by a process according to claim 1 or claim 2.

4. A compound of formula I, stated in claim 1.

5. A compound of formula Ia,



Ia

in which R_3 and ring A are as defined in claim 1,
R_5 signifies a substituted or unsubstituted alkyl or cycloalkyl radical, and
R_6, R_7 and R_8, which may be the same or

fibres modified by the introduction of basic groups, the dyeings on these fibres being of similarly good quality.

Printing

A printing paste is prepared with:

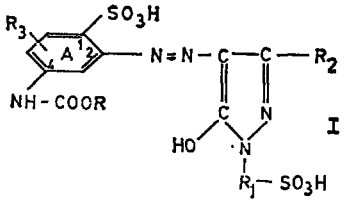
30 parts of the dye of Example 3,
50 parts of thiodiethylene glycol
500 parts of a 30% aqueous crystal gum solution
60 parts of thiourea
60 parts of a 20% aqueous ammoninm sulphate solution and
300 parts of water

1000 parts

The paste is printed on a nylon fabric by one of the standard methods, the fabric dried and the print fixed for 30—45 minutes at 102°. The fabric is then soaped at 60°, washed off and dried. A yellow print with good fastness properties is obtained. An equally good print is obtained when intermediate drying is omitted. On wool and other natural polyamide fibres, prints with similar good properties are obtained by this method.

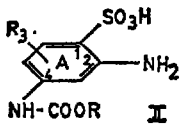
WHAT WE CLAIM IS:—

1. A process for the production of a compound of formula I,



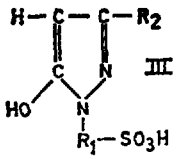
I

in which R signifies a substituted or unsubstituted alkyl or cycloalkyl radical,
R_1 signifies a substituted or unsubstituted phenylene or naphthylene radical,
R_2 signifies a substituted or unsubstituted alkyl or aryl radical,
R_3 signifies a hydrogen atom, a substituted or unsubstituted alkyl radical of 1 to 6 carbon atoms or a halogen atom, and
ring A may be further substituted, characterised by
a) coupling a diazo derivative of an amine of formula II,



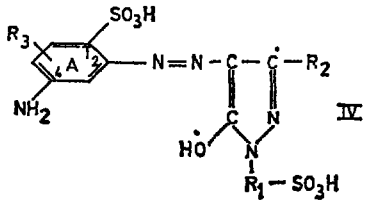
II

in which R, R_3 and ring A are as defined above,
with a compound of formula III,



III

in which R_1 and R_2 are as defined above, or
b) reacting a monoazo compound of formula IV,



IV

in which R_1, R_2, R_3 and ring A are as defined above, with a haloformic acid ester of formula V,

R—O—CO—Hal V

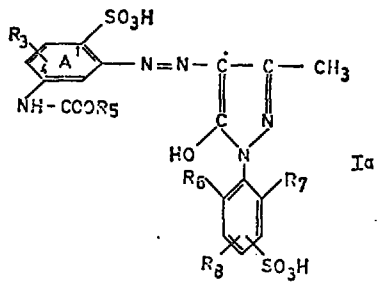
in which Hal signifies a fluorine, chlorine, bromine or iodine atom, and R is as defined above.

2. A process for the production of a compound of formula I stated in claim 1, substantially as herein before described with reference to any one of the foregoing Examples 1 to 238.

3. A compound of formula I, stated in claim 1, whenever produced by a process according to claim 1 or claim 2.

4. A compound of formula I, stated in claim 1.

5. A compound of formula Ia,



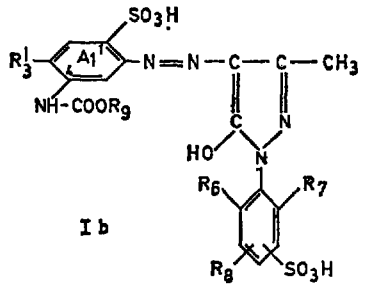
Ia

in which R_3 and ring A are as defined in claim 1,
R_5 signifies a substituted or unsubstituted alkyl or cycloalkyl radical, and
R_6, R_7 and R_8, which may be the same or

* C L M S *

different, each signifies a hydrogen or halogen atom or a substituted alkyl or alkoxy radical.

6. A compound of formula IB,



Ib

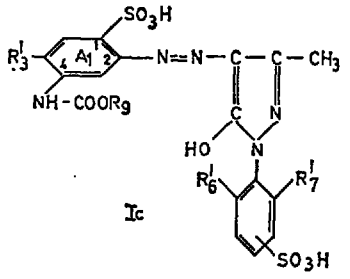
in which R_6, R_7 and R_8 are as defined in claim 5,

R_3' signifies a hydrogen or chlorine atom or a methyl radical,

R_9 signifies a substituted alkyl radical of 6 to 18 carbon atoms or a substituted or unsubstituted cyclohexyl radical,

and ring A_1 bears no further substitution.

7. A compound of formula Ic,



Ic

in which R_3', R_9 and ring A_1 are as defined in Claim 6,

R_6' signifies a hydrogen or halogen atom or an alkyl radical of 1 to 6 carbon atoms, and

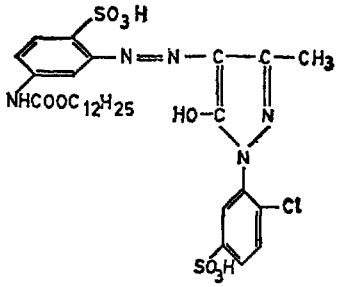
R_7' signifies a hydrogen or halogen atom or an alkyl or alkoxy radical of 1 to 6 carbon atoms.

8. A compound according to any one of Claims 5 to 7, in which any substituted alkyl radical is substituted by a halogen atom, a hydroxy, cyano, alkoxy or aryl group, and any substituted cycloalkyl radical bears up to three alkyl groups.

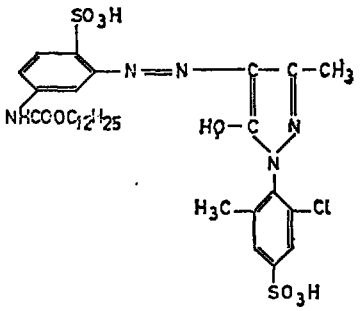
9. A compound according to Claim 8, in which any aryl-substituted alkyl radical is a phenyl-substituted-alkyl radical.

10. A compound according to Claim 4 or 5, in which ring A bears no metallisable group in the ortho-position to the —N=N—group.

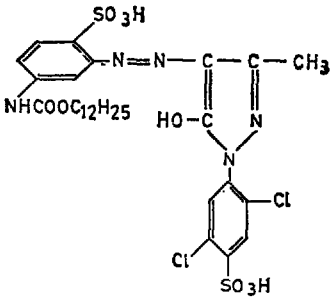
11. A compound of formula



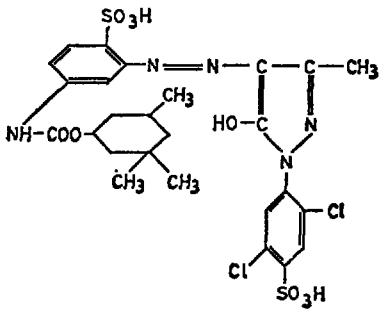
12. A compound of formula



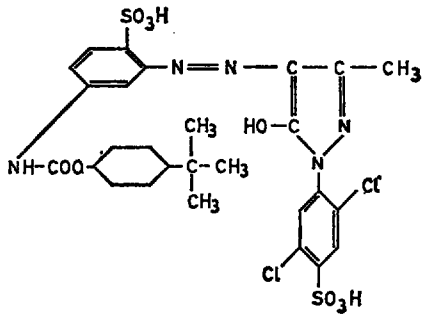
13. A compound of formula



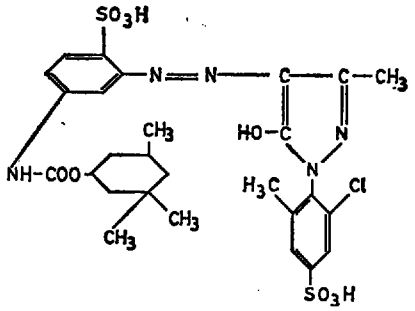
14. A compound of formula



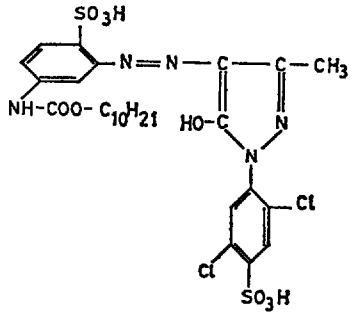
15. A compound of formula



16. A compound of formula



17. A compound of formula



18. A process for dyeing or printing natural and synthetic polyamide fibres, natural and regenerated cellulosic fibres or basic dyeable polypropylene fibres, which comprises applying a compound of formula I, stated in claim 1.

19. A process according to claim 18, substantially as hereinbefore described with reference to any one of the Examples.

20. A process for dyeing or printing paper or leather which comprises applying a compound of formula I, stated in claim 1.

21. Natural or synthetic polyamide fibres, natural or regenerated cellulosic fibres or basic dyeable polypropylene fibres, whenever dyed or printed by a process according to claim 18 or 19.

22. Paper or leather, whenever dyed or printed by a process according to claim 20.

23. A compound of formula I, stated in claim 1, according to any one of Examples 4 to 12, 15 to 48, 50 to 77 and 79 to 238.

24. A compound according to claim 5, in which R_6 has a significance other than hydrogen and R_3 signifies a hydrogen atom.

25. A compound of formula I, stated in Claim 1, according to any one of Examples 1 to 11, 13, 15, 16, 22 to 29, 31, 33, 34, 40 to 47, 49, 51, 52, 58, 59, 62, 65 or 68.

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