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PATENT SPECIFICATION

(11) 1 580 660

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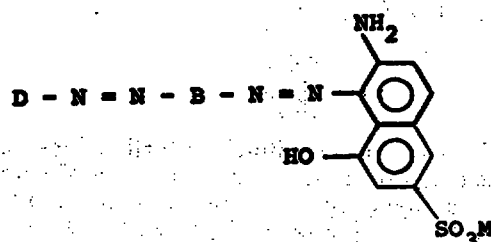


(54) DISAZO DYESTUFFS CONTAINING 2-AMINO-8-HYDROXY NAPHTHALENE-6-SULPHONIC ACID

(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:

The present invention relates to azo compounds and mixtures thereof, their production and use.

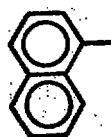
Accordingly, the present invention provides azo compounds of formula I,



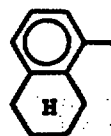
in which D is the radical of a diazo component of formula (a), (b) or (c),



(a)



(b)



(c)

in which

R_1 is trifluoromethyl, $-\text{COOM}_1$, $-\text{COOR}_2$; or a group of formulae $-\text{NHR}_3$, $-\text{NR}_3\text{R}_4$ or $-\text{NR}_3\text{COR}_5$ in a position meta or para to the azo group; ring A being optionally further substituted by a total of up to two further substituents selected from halogen, (C_{1-4}) alkyl (preferably methyl), (C_{1-4}) alkoxy (preferably methoxy) and trifluoromethyl (only one further trifluoromethyl group), R_2 is (C_{1-12}) alkyl,

each of

R_3 and R_4 , independently, is (C_{1-8}) alkyl, R_5 is hydrogen or (C_{1-4}) alkyl, R_6 is (C_{1-8}) alkyl, (C_{1-8}) alkoxy or (C_{1-8}) alkyl mono-substituted by chlorine or methoxy, B is a divalent radical of the 1,4-phenylene, 1,4-naphthylene or 1,2,3,4-tetrahydronaphthylene-5,8 series, and each of M and M_1 , independently, is hydrogen or an equivalent of a non-chromophoric cation, with the proviso that the molecule contains a single $-\text{SO}_3\text{M}$ group, and mixtures thereof, which compounds and mixtures are useful as anionic dyestuffs.

The alkyl radicals as R_2 , R_3 , R_4 , R_5 and R_6 may be straight- or branched-chain. R_2 is preferably (C_{1-8}) alkyl. More preferably, R_2 is R'_2 , where R'_2 is (C_{1-4}) alkyl.

Each of R_3 and R_4 , independently, is preferably (C_{1-4}) alkyl, more preferably R_3 and R_4 are R'_3 and R'_4 , respectively, where each of R'_3 and R'_4 , independently, is methyl or ethyl, especially methyl.

Any alkyl as R_5 is preferably methyl. Preferably, R_5 is R'_5 , where R'_5 is hydrogen or methyl, especially hydrogen.

Any unsubstituted alkyl as R_6 is preferably a (C_{1-4}) alkyl, more preferably methyl or ethyl, especially methyl. Any substituted alkyl as R_6 is preferably ω -chloro- or methoxy-substituted (C_{1-3}) alkyl. Any alkoxy group as R_6 is preferably (C_{1-4}) alkoxy, with methoxy being most preferred.

R_6 is preferably R'_6 , where R'_6 is (C_{1-4}) alkyl, ω -chloro- or methoxy-substituted (C_{1-3}) alkyl or (C_{1-4}) alkoxy. More preferably R_6 is R''_6 , where R''_6 is methyl, ethyl, methoxy, 2-methoxyethyl or 3-methoxypropyl. Most preferably, R_6 is R'''_6 , where R'''_6 is methyl or methoxy, with methyl being especially preferred.

R_1 is preferably R'_1 , where R'_1 is trifluoromethyl, $-\text{COOR}'_2$, $-\text{NHR}'_3$, $-\text{NR}'_2\text{R}'_4$ or $-\text{NR}'_2\text{COR}'_4$. More preferably R_1 is R''_1 , where R''_1 is $-\text{COOR}'_2$ or $\text{NR}'_2\text{COR}'_4$. Most preferably, R_1 is R'''_1 , where R'''_1 is $-\text{NR}'_2\text{COR}'_4$ with $-\text{NHCOCH}_3$ being especially preferred.

Preferably any halogen on ring A is chlorine or bromine, with chlorine being most preferred.

The ring A is preferably further unsubstituted or further substituted by a total of up to two substituents selected from chlorine, methyl and methoxy.

Where the ring A bears one substituent in addition to R_1 , the 2 substituents are preferably in the 2,4-, 2,5- and 3,4-positions, with the 3,4-positions being especially preferred.

Where the ring A bears two substituents in addition to R_1 , the three substituents are preferably in the 2,3,5-, 2,4,5- or 2,4,6-positions, with the 2,4,5- and 2,4,6-positions being most preferred.

Preferably the group (a) is (a_1) ,

(a₁)

wherein the ring A is further unsubstituted or further substituted by a total of up to two substituents selected from the group consisting of halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and trifluoromethyl (only one trifluoromethyl), with the substituents chlorine, methyl and methoxy being especially preferred. More preferably R_1 and R'_1 .

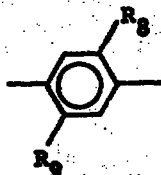
More preferably (a) is (a_2) ,

(a₂)

Wherein R_7 is hydrogen, chlorine, methyl or methoxy, especially hydrogen. In (a_2) most preferably R_7 is hydrogen and R'_1 is $-\text{NHCOCH}_3$, such group being designated as (a_3) hereinafter.

D is preferably (a_1) or (b), more preferably (a_2) , with the group (a_3) being most preferred.

B is preferably 1,4-naphthylene, 1,2,3,4-tetrahydronaphthylene-5,8, or a group of formula (d),



(d)

in which each of R_8 and R_9 , independently, is hydrogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy.

Any alkyl as R_8 and/or R_9 is preferably methyl or ethyl, most preferably methyl.

Any alkoxy as R_8 and/or R_9 is preferably methoxy or ethoxy, most preferably methoxy.

R_8 is preferably R'_8 , where R'_8 is methyl, methoxy or ethoxy, most preferably methoxy.

R_8 is preferably R'_8 , where R'_8 is hydrogen, methyl, methoxy or ethoxy, most preferably R_8 is R'_8 , where R'_8 is methyl or methoxy.

Preferably, the group (d) is (d_1) , where (d_1) is a group of formula (d) where R_8 is R'_8 and R_9 is R'_9 , more preferably (d) is (d_2) , where (d_2) is (d) wherein R_8 is methoxy and R_9 is R'_9 , preferably methoxy.

B is preferably 1,4-naphthylene or a group of formula (d), with (d) being especially preferred. More preferably, B is a group of formula (d_1) , most preferably (d_2) .

Preferred compounds of formula I are those in which D is a group of formula (a) or (b) and B is a group of formula (d) or 1,4-naphthylene.

More preferred compounds of formula I are those where D is a group of formula (a_1) (preferably where R_1 is R'_1) and B is (d) or is 1,4-naphthylene; of these, those compounds where D is a group of formula (a_2) are even more preferred. Most preferred compounds are those wherein D is (a_2) and B is (a_2) .

The non-chromophoric cations as M and M_1 , independently, may be any one of those common the chemistry of anionic dyestuffs. Preferably each M and M_1 , independently, is hydrogen, an alkali metal cation, such as lithium, sodium or potassium, an unsubstituted, lower alkyl substituted- or a hydroxyalkyl substituted-ammonium ion of formula $N^+(R_{10})_4$ in which each R_{10} , independently, is hydrogen, (C_{1-3}) alkyl or 2-3- or 4-hydroxy (C_{1-4}) alkyl. Examples of such ammonium ions are ammonium, triethylammonium, mono-, di-, tri- or tetramethylammonium, mono-, di- or triethanolammonium or mono-, di- or triisopropanolammonium. Preferably M and M_1 are identical. Alkali metal cations are the preferred cations.

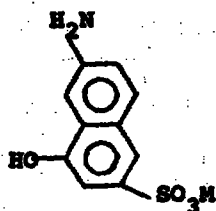
It will be appreciated that the substituted ammonium cation should not contain groups which would cause stability or steric problems, for example tetra-alkanolammonium.

The present invention further provides a process for the production of compounds of formula I, or a mixture thereof, comprising coupling the diazo derivative of an amine of formula II,



II

or a mixture thereof
with a compound of formula III,



III

or a mixture thereof.

The coupling reaction is carried out in acid medium, preferably at a pH value of from 3 to 4.5, in accordance with conventional methods.

Diazotization of the compounds of formula II may be carried out in accordance with known methods.

The compounds of formula II are either known or may be prepared in accordance with known methods by coupling the diazo derivative of an amine $D-NH_2$ with a compound of $B-NH_2$ in acid medium.

The compounds of formula III are known.

In general, as a result of the process of production, the compounds of formula I are obtained in salt form, usually in the sodium or potassium salt form and may be isolated as such from the reaction mixture in accordance with known methods. However, they may also be isolated in the form of free acids by adding acid to the reaction mixture. The compounds may be employed for dyeing as such or may be converted into the salt form by the addition of bases such as hydroxides, carbonates, bicarbonates or acetates.

The compounds of formula I and mixtures thereof in the free acid or salt form are useful for dyeing or printing anionic dyable substrates. Examples of suitable substrates are natural and synthetic polyamide fibres, basic modified polyolefins, polyurethanes and leather. Preferred substrates are fibres of natural and synthetic polyamides such as wool, silk and especially nylon. Dyeing may be carried out in

accordance with known methods, especially in accordance with pad dyeing or preferably exhaust dyeing methods. The dyestuffs of formula I and mixtures thereof exhaust from a neutral dyebath.

The dyestuffs according to the present invention are well soluble in water and build up well. The dyeings possess notable wet fastness for example wash- and sweatfastness, notable rubbing fastness and lightfastness. The dyestuffs according to the present invention combine well with other neutral-exhausting dyestuffs, the advantages such as build-up and fastnesses being retained.

The dyestuffs according to the present invention may be employed as such or may be used in the form of liquid or solid preparations. The liquid and solid preparations may be formed in accordance with conventional methods, for example by dissolving in suitable solvents, optionally with the addition of conventional additives such as stabilizers and/or dissolving agents for example, urea with subsequent grinding or granulating. Such preparations may be obtained in accordance with the procedure described in French Patents 1,572,630 and 1,581,900.

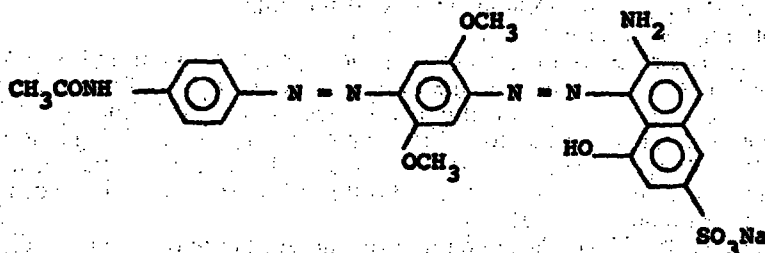
Further, the mixtures according to the present invention may be made up into preparations which are dispersible in cold water. for the preparation of such dispersions the dye mixture may be ground wet or dry to a particle size of less than 20 μ , preferably 1–5 μ , in the presence of one or more conventional anionic dispersing agents and optionally in the presence of a non-ionic dispersing agent, with or without subsequent spray drying. The preparations so obtained are finely dispersed in cold water and are thus easy to handle.

The following Examples further serve to illustrate the invention. In the Examples all parts are by weight and all temperatures are in degrees Centigrade.

Example 1

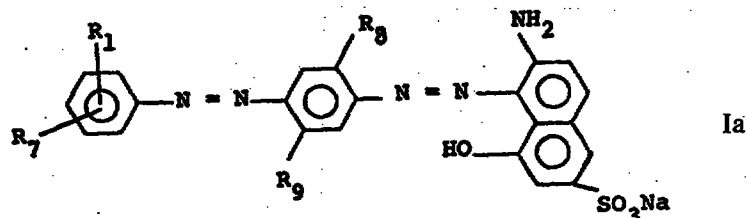
15 parts of 4-aminoacetanilide are diazotised with 24 parts of concentrated hydrochloric acid and 7.0 parts of sodium nitrite in conventional manner. The excess nitrite is decomposed with amidosulphonic acid. 15.3 parts of 1-amino-2,5-dimethoxybenzene are entered into 80 parts of water at 60°, then dissolved by adding 10 parts of concentrated hydrochloric acid and cooled to 0–4° with ice. The above solution of the diazotised 4-aminoacetanilide is added to this solution over the course of half an hour. The pH value is kept at 3.0 to 3.5 by the addition of sodium acetate. Stirring takes place for 2 hours at 0–4°, and then stirring is continued for a further 16 hours at room temperature. The precipitated dyestuff is filtered and washed with a 5% hydrochloric acid solution.

The paste of the aminomonoazo dyestuff is dissolved at 80° with 70 parts water and 120 parts of glacial acetic acid then 20 parts of concentrated hydrochloric acid are added and the temperature is set at 0–4° by adding ice. An aqueous solution of 8.0 parts of sodium nitrite is passed in and stirred for 2 hours; the excess nitrite is subsequently decomposed with amidosulphonic acid. 23.9 Parts of 2-amino-8-hydroxynaphthalene-6-sulphonic acid are stirred with 100 parts of water, and dissolved by adding about 12 parts of 30% caustic soda. This solution is added over the course of one hour to the above diazomonoazo solution, whereby the pH is kept at 3.5–4.0 by adding sodium acetate. The reaction mixture is stirred for a further 16 hours at 0°, then set at a pH of 8.5 with caustic soda and stirred at room temperature for 2 hours. The precipitated dyestuff is filtered at this temperature, washed to neutral with a 5% sodium chloride solution and dried. It corresponds to formula



and dyes natural and synthetic polyamide fibres in dark blue shades. The dyeings have notable wet and light fastness.

Further compounds of general formula Ia which may be produced in analogous manner to the above procedure are given in Table 1.



The dyestuffs of Examples 2—5, 7, 8 and 10—34 give dyings of dark blue shades on polyamide fibre, the dyestuffs of Examples 6 and 9 give dyeings of violet shades. The dyeings obtained have comparable properties with the dyeings obtained with the dyestuff of Example 1.

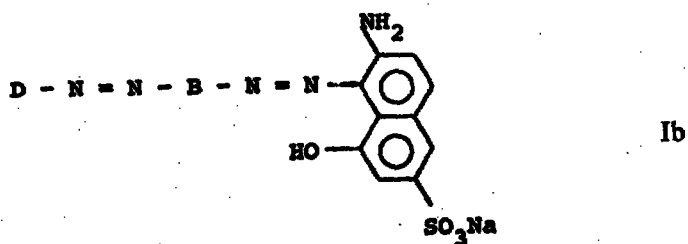
TABLE 1

Example No.	R ₁ (position)	R ₇ (position)	R ₈	R ₉
2	NHCOOCH ₃ (4)	H	OCH ₃	CH ₃
3	NHCOOCH ₃ (3)	H	do.	do.
4	do.	H	do.	OCH ₃
5	NHCOCH ₃ (4)	H	do.	CH ₃
6	do.	H	CH ₃	do.
7	NHCOCH ₃ (3)	H	OCH ₃	OCH ₃
8	do.	H	do.	CH ₃
9	do.	H	CH ₃	do.
10	do.	H	OCH ₃	H
11	do.	CH ₃ (4)	do.	OCH ₃
12	do.	Cl (4)	do.	do.
13	N(CH ₃)COCH ₃ (4)	H	do.	do.
14	N(CH ₃)COCH ₃ (3)	H	do.	do.
15	NHCOCH ₂ Cl (4)	H	do.	CH ₃
16	do.	H	do.	OCH ₃
17	NHCOCH ₂ Cl (3)	H	do.	do.
18	COOC ₂ H ₅ (2)	H	do.	do.
19	COOC ₂ H ₅ (4)	H	do.	do.
20	COO _n C ₄ H ₉ (4)	H	do.	H
21	CF ₃ (3)	H	do.	OCH ₃

TABLE 1 (continued)

Example No.	R ₁ (position)	R ₇ (position)	R ₈	R ₉
22	CF ₃ (2)	Cl (5)	do.	CH ₃
23	NHCOOC ₂ H ₅ (3)	H	do.	H
24	NHCOOC ₂ H ₅ (4)	H	do.	OCH ₃
25	NHCOC ₂ H ₅ (4)	H	OCH ₃	CH ₃
26	NHCOC ₂ H ₅ (3)	H	do.	do.
27	COO _n C ₄ H ₉ (4)	H	do.	OCH ₃
28	NHCOOCH ₂ CH ₂ OCH ₃ (4)	H	do.	CH ₃
29	NHCOOCH ₂ CH ₂ OCH ₃ (3)	H	do.	H
30	NHCOO(CH ₂) ₃ OCH ₃ (4)	H	H	H
31	NHCH ₃ (4)	H	OCH ₃	OCH ₃
32	N(C ₂ H ₅) ₂ (4)	H	do.	do.
33	N(CH ₃)COCH ₃ (4)	H	do.	H
34	NHCOCH ₃ (3)	CH ₃ (4)	do.	CH ₃

Further compounds of formula I which correspond to the general formula Ib,



and which may be prepared in analogous manner to the procedure described in Example 1 are given in Table 2. the dyes of Examples 35—42 and 44—46 give dyeings of a dark blue shade on polyamide fibres and the dyestuff of Example 43 gives dyeings of violet shades on polyamide fibres. The dyeings obtained exhibit similar properties to those of the dyeings obtained with the compound of Example 1.

Table 2

Example No.	D	B
35	<chem>CC(=O)Nc1ccc(cc1)-</chem>	<chem>c1ccc2ccccc2c1-</chem>
36	<chem>CN(C)C(=O)c1ccc(cc1)-</chem>	do.
37	<chem>CC(=O)Nc1ccc(cc1)-</chem>	<chem>c1ccc2c(c1)ccc3ccccc32-</chem>
38	<chem>CN(C)C(=O)c1ccc(cc1)-</chem>	do.
39	<chem>CC(=O)Nc1ccc(cc1)C-</chem>	<chem>c1ccc2ccccc2c1-</chem>
40	<chem>c1ccc2ccccc2c1-</chem>	<chem>COc1ccc(C)cc1-</chem>
41	do.	<chem>COc1ccc(OC)cc1-</chem>
42	<chem>c1ccc2ccccc2c1-</chem>	<chem>COc1ccc(cc1)-</chem>
43	do.	<chem>c1ccc(cc1)-</chem>
44	<chem>CCOC(=O)c1ccc(cc1)-</chem>	<chem>c1ccc2ccccc2c1-</chem>
45	<chem>CC(=O)N(C)c1ccc(cc1)-</chem>	do.
46	<chem>CC(C)C(=O)c1ccc(cc1)-</chem>	do.

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Application Example A

100 parts of pre-wetted nylon cloth (nylon 66) are entered at 40° into a dye bath consisting of 4000 parts of water, 10 parts of anhydrous sodium sulphate and 2 parts of the dyestuff from Example 1.

The dye liquor is heated over the course of 30 minutes to boiling temperature, kept at this temperature for 1 hour, then 4 parts of glacial acetic acid are added thereto and dyeing is completed by heating for a further 30 minutes at boiling temperature. During dyeing, the water that evaporates is continuously replaced. The dark-blue dyed nylon cloth is then removed from the liquor, rinsed with water and dried. Wool may also be dyed by the same process.

Dyeings may be made in the same manner using the dyestuffs from Examples 2—46, or mixtures thereof.

The dyeings have notable wet and light fastness.

Application Example B

Polyamide is printed with a printing paste containing:

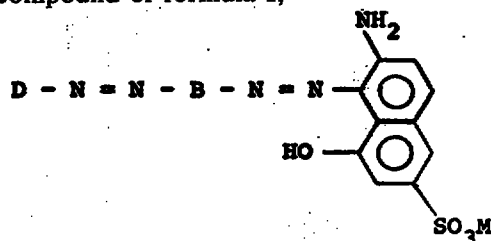
- 30 parts dyestuff of Example 7
- 50 parts urea
- 50 parts dissolving agent (e.g. thiodiethylene glycol)
- 290 parts water
- 500 parts suitable thickening agent (e.g. based on locus bean gum)
- 20 parts acid donating agent (e.g. ammonium tartrate)
- 60 parts thio urea

The printed textile goods are steamed for 40 minutes at 102° (saturated steam), then rinsed with cold water, subsequently washed at 60° with a dilute solution of a conventional detergent and rinsed again with cold water. A dark-blue print having notable light and wet fastness is obtained.

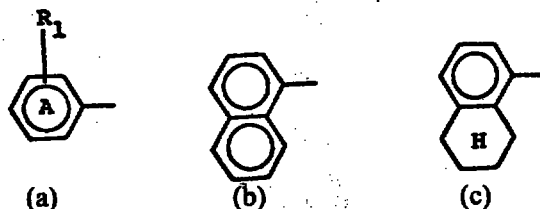
In analogous manner printing pastes may be made employing the dyestuffs of Examples 1—6 or 8—46 or mixtures of dyestuffs of Examples 1—46, such pastes may be employed for printing in accordance with the above given procedure:

WHAT WE CLAIM IS:—

1. An azo compound of formula I,



in which D is the radical of a diazo component of formula (a), (b) or (c),



in which

R_1 is trifluoromethyl, $-\text{COOM}_1$, $-\text{COOR}_2$; or a group of formulae $-\text{NHR}_3$, $-\text{NR}_3\text{R}_4$ or $-\text{NR}_5\text{COR}_6$ in a position meta or para to the azo group; ring A being optionally further substituted by a total of up to two further substituents selected from halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and trifluoromethyl (only one further trifluoromethyl group,

R_2 is (C_{1-12}) alkyl, each of

R_3 and R_4 , independently, is (C_{1-8}) alkyl, R_5 is hydrogen or (C_{1-4}) alkyl, R_6 is (C_{1-8}) alkyl, (C_{1-8}) alkoxy or (C_{1-8}) alkyl mono-substituted by chlorine or methoxy, B is a divalent radical of the 1,4-phenylene, 1,4-naphthylene or 1,2,3,4-tetrahydronaphthylene-5,8 series, and each of M and M_1 ,

(16)

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Application Example A

100 parts of pre-wetted nylon cloth (nylon 66) are entered at 40° into a dye bath consisting of 4000 parts of water, 10 parts of anhydrous sodium sulphate and 2 parts of the dyestuff from Example 1.

5 The dye liquor is heated over the course of 30 minutes to boiling temperature, kept at this temperature for 1 hour, then 4 parts of glacial acetic acid are added thereto and dyeing is completed by heating for a further 30 minutes at boiling temperature. During dyeing, the water that evaporates is continuously replaced. The dark-blue dyed nylon cloth is then removed from the liquor, rinsed with water and dried. Wool may also be dyed by the same process.

10 Dyeings may be made in the same manner using the dyestuffs from Examples 2-46, or mixtures thereof.

The dyeings have notable wet and light fastness.

Application Example B

15 Polyamide is printed with a printing paste containing:

30 parts dyestuff of Example 7

50 parts urea

50 parts dissolving agent (e.g. thiodiethylene glycol)

290 parts water

20 500 parts suitable thickening agent (e.g. based on locus bean gum)

20 parts acid donating agent (e.g. ammonium tartrate)

60 parts thio urea

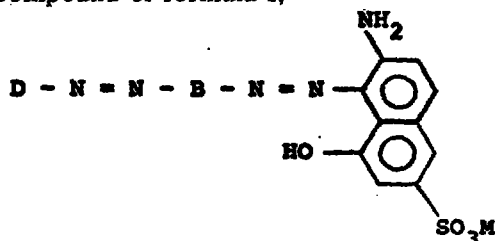
25 The printed textile goods are steamed for 40 minutes at 102° (saturated steam), then rinsed with cold water, subsequently washed at 60° with a dilute solution of a conventional detergent and rinsed again with cold water. A dark-blue print having notable light and wet fastness is obtained.

In analogous manner printing pastes may be made employing the dyestuffs of Examples 1-6 or 8-46 or mixtures of dyestuffs of Examples 1-46, such pastes may be employed for printing in accordance with the above given procedure.

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WHAT WE CLAIM IS:—

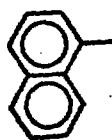
1. An azo compound of formula I,



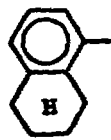
in which D is the radical of a diazo component of formula (a), (b) or (c),



(a)



(b)



(c)

35 in which

R_1 is trifluoromethyl, $-\text{COOM}_1$, $-\text{COOR}_2$; or a group of formulae $-\text{NHR}_3$, $-\text{NR}_3\text{R}_4$ or $-\text{NR}_3\text{COR}_5$ in a position meta or para to the azo group; ring A being optionally further substituted by a total of up to two further substituents selected from halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and trifluoromethyl (only one further trifluoromethyl group,

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R_2 is (C_{1-12}) alkyl,

each of

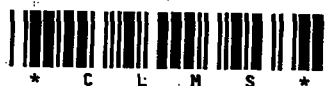
R_3 and R_4 , independently, is (C_{1-6}) alkyl, R_5 is hydrogen or (C_{1-4}) alkyl, R_6 is (C_{1-6}) alkyl, (C_{1-6}) alkoxy or (C_{1-6}) alkyl mono-substituted by chlorine or methoxy, B is a divalent radical of the 1,4-phenylene, 1,4-naphthylene or 1,2,3,4-tetrahydronaphthylene-5,8 series, and each of M and M_1 ,

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independently, is hydrogen or an equivalent of a non-chromophoric cation, with the proviso that the molecule contains a single $-\text{SO}_3\text{M}$ group, or mixtures thereof.

2. A compound or mixture according to Claim 1, in which R_2 is (C_{1-9}) alkyl.

5 3. A compound or mixture according to Claim 1 or Claim 2, in which each of R_3 and R_4 , independently, is (C_{1-4}) alkyl. 5

4. A compound or mixture according to any one of Claims 1 to 3, in which R_5 is (C_{1-4}) alkyl, (C_{1-4}) alkoxy or (C_{1-3}) alkyl monosubstituted by chlorine or methoxy.

10 5. A compound or mixture according to any one of Claims 1 to 4, in which R_2 is R'_2 where R'_2 is (C_{1-4}) alkyl. 10

6. A compound or mixture according to any one of Claims 1 to 5, in which R_3 and R_4 are R'_3 and R'_4 , where each of R'_3 and R'_4 , independently, is methyl or ethyl.

7. A compound or mixture according to any one of Claims 1 to 6, in which R_5 is R'_5 where R'_5 is hydrogen or methyl.

15 8. A compound or mixture according to any one of Claims 1 to 7, in which R_6 is R'_6 , where R'_6 is (C_{1-4}) alkyl, (C_{1-4}) alkoxy or ω -chloro- or methoxy-substituted (C_{1-3}) alkyl. 15

9. A compound or mixture according to any one of Claims 5 to 8, in which R_1 is R'_1 , where R'_1 is trifluoromethyl, $-\text{COOR}'_2$, NHR'_2 , $-\text{NHR}'_2\text{R}'_4$ or $\text{NR}'_2\text{COR}'_4$.

20 10. A compound or mixture according to Claim 9, in which R_1 is R''_1 , where R''_1 is $-\text{COOR}'_2$ or $\text{NR}'_2\text{COR}'_4$ where R'_4 is methyl, ethyl, methoxy, 2-methoxyethyl or 3-methoxypropyl. 20

11. A compound or mixture according to Claim 10, in which R_1 is R''''_1 , where R''''_1 is $\text{NR}'_2\text{COR}'_4$, where R'_4 is methyl or methoxy.

25 12. A compound according to any one of the preceding claims in which the ring A is further unsubstituted or further substituted by up to two substituents selected from chlorine, methyl and methoxy. 25

13. A compound or mixture according to Claim 9, in which the group (a) is (a₁).



(a₁)

30 in which R'_1 is as defined in Claim 9, and the ring A is substituted by up to two substituents selected from halogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy and trifluoromethyl (only one further trifluoromethyl substituent). 30

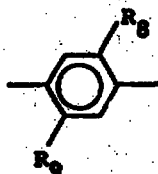
14. A compound or mixture according to Claim 13, in which (a) is (a₂)



(a₂)

35 wherein R''''_1 is as defined in Claim 11 and R_7 is hydrogen, chloride, methyl or methoxy. 35

15. A compound or mixture according to any one of the preceding claims, in which B is 1,4-naphthylene, 1,2,3,4-tetrahydronaphthylene or a group of formula (d)



(d)

40 in which each of R_8 and R_9 , independently, is hydrogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy. 40

16. A compound or mixture according to Claim 15, in which R_8 is R'_8 , where R'_8 is methyl, methoxy or ethoxy and R_9 is R'_9 , where R'_9 is hydrogen, methyl, methoxy or ethoxy.

45 17. A compound or mixture according to Claim 16, in which (d) is a group (d₁), where (d₁) is a group of formula (d) where R_8 is R'_8 and R_9 is R'_9 . 45

18. A compound or mixture according to Claim 15, in which B is 1,4-naphthylene or a group of formula (d).

50 19. A compound or mixture according to Claim 1, in which D is a group of formula (a) or (b) and B is a group of formula (d) as defined in Claim 15, or 1,4-naphthylene. 50

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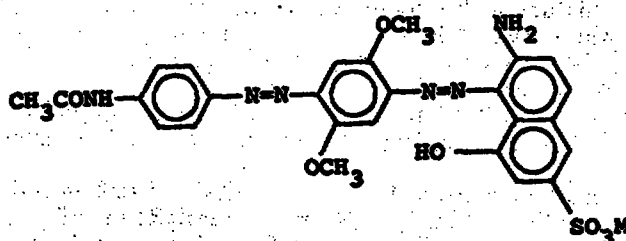
20. A compound or mixture according to Claim 13, in which D is a group of formula (a₁) and B is (d₁), as defined in Claim 17, or 1,4-naphthylene.

21. A compound or mixture according to Claim 20, in which, in the group of formula (a₁), R₁ is —COOR₂' or NR₂'COR₂'.

22. A compound or mixture according to Claim 21, in which D is a group of formula (a₂) as defined in Claim 14.

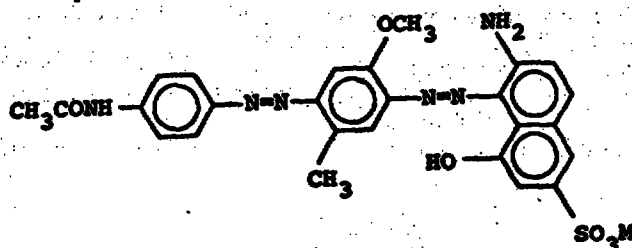
23. A compound or mixture according to Claim 22, in which D is a group of formula (a₂) wherein R₂ is hydrogen and R₂' is —NHCOCH₃, B is (d₂), where (d₂) is (d) wherein R₃ is methoxy and R₃' is methyl or methoxy.

24. A compound of formula



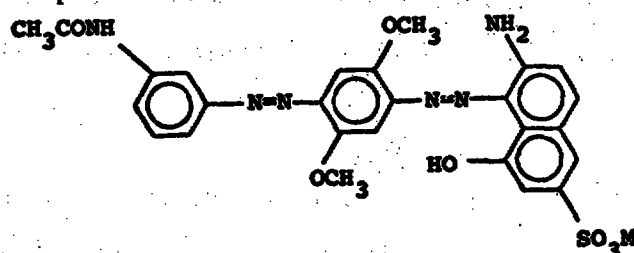
in which M is as defined in Claim 1.

25. A compound of formula



in which M is as defined in Claim 1.

26. A compound of formula



in which M is as defined in Claim 1.

27. A compound according to any one of Examples 2 to 4, 6 or 8 to 46.

28. A compound or mixture according to any one of the preceding claims in which M and, where R₁ is COOM₁, M₁, are, independently, hydrogen or an alkali

metal cation or a group of formula N(R₁₀)₄, in which each R₁₀, independently, is hydrogen, (C₁₋₃)alkyl or 2-, 3- or 4-hydroxy(C₂₋₄)alkyl.

29. A compound or mixture according to Claim 28, in which M and M₁ are the same and signify hydrogen or an alkali metal cation.

30. A compound or mixture according to Claim 1, in which R₁ is other than —COOM₁ and, when R₁ is a group of formula —NR₂'COR₂', R₂ is hydrogen and R₂' is (C₁₋₃)alkyl.

31. A compound or mixture according to Claim 1, in which R₁ is other than —COOM₁.

32. A process for the production of a compound of formula I, as defined in Claim 1, or a mixture thereof, comprising coupling the diazo derivative of an amine of formula II



II



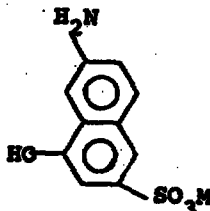
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or a mixture thereof
with a compound of formula III,



III

or a mixture thereof.

33. A process for the production of a compound of formula I, as defined in Claim 1, or a mixture thereof, substantially as hereinbefore described with reference to any one of Examples 1 to 46.

34. A compound of formula I, as defined in Claim 1, or a mixture thereof, whenever obtained by a process according to Claim 32 or Claim 33.

35. A process for dyeing or printing anionic dyeable substrates comprising employing a compound or mixture according to any one of Claims 1 to 31 or 34, as dyeing or printing agent.

36. A process according to Claim 35, in which the substrate consists of natural or synthetic polyamide fibres, basic modified polyolefins, polyurethanes or leather.

37. A process according to Claim 35, in which the substrate consists of wool, silk or nylon.

38. A process for dyeing or printing anionic dyeable substrates substantially as hereinbefore described with reference to Example A or B.

39. Dyed or printed substrates whenever obtained by a process according to any one of Claims 35 to 38.

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