

1 419 312

PATENT SPECIFICATION

(11) 1 419 312

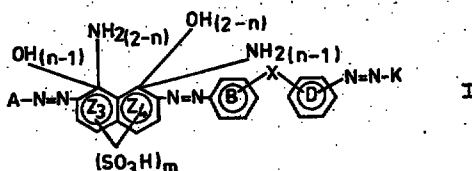
- (21) Application No. 6932/73 (22) Filed 13 Feb. 1973
 (31) Convention Application No. 2181/72
 (32) Filed 15 Feb. 1972 in
 (33) Switzerland (CH)
 (44) Complete Specification published 31 Dec. 1975
 (51) INT CL² C09B 35/46, 43/12; D06P 1/06, 3/32
 (52) Index at acceptance C4P 116 118 120 126 140 3E 3X 9A3A1
 (72) Inventors HERBERT HOLLIGER and HEINZ WICKI



(54) POLYAZO DYES

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

This invention relates to new polyazo naphthalene derivatives.
 The invention provides compounds of formula I,



in which

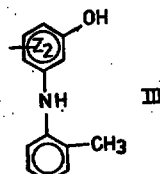
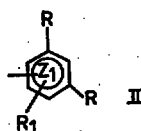
A signifies an unsubstituted phenyl radical or a phenyl radical which is substituted by lower alkyl, alkoxy, S-alkyl, —COOH, —SO₃H, —NO₂, hydroxyl, halogen, or an unsubstituted or substituted sulphonamide, carbonamide, alkylamino, arylamino or acylamino group,

X signifies a bridge member of formula —CS—NH, —CO—NH—, —NHCS— or —NH—CO—,

m signifies the integer 1 or 2,

n signifies the integer 1 or 2 and

K signifies the radical of a coupling component of formula II or III,



in which

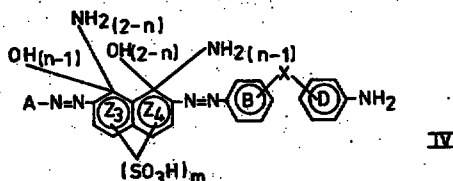
R in each instance signifies —NH₂ or —OH,

R₁ signifies hydrogen or —SO₃H,

the aromatic rings B and/or D and/or Z₁ and/or Z₂ being otherwise unsubstituted or being further substituted once or twice and the aromatic rings Z₃ and Z₄ being otherwise unsubstituted, and water soluble salts thereof.

The invention also provides a process for the production of compounds of formula I, which comprises,

a) coupling the diazo compound from an aminoazo compound of formula IV,



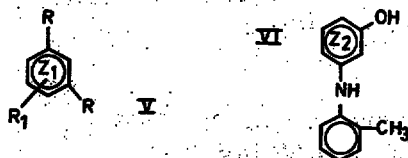
(14)

2

1,419,312

2

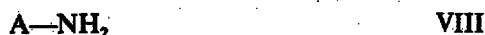
in which A, X, n, m, B, D, Z₃ and Z₄ are as defined above, with one of the coupling components of formulae V or VI,



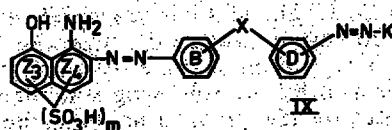
5

in which R, R₁, Z₁ and Z₂ are as defined above,
b) coupling the diazo compound from an amine of formula VIII,

5



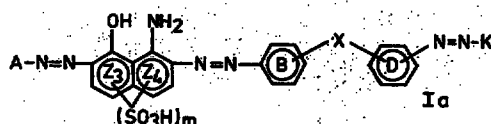
in which A is as defined above, with an azo compound of formula IX,



10

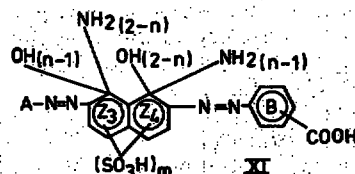
in which m, X, K, Z₃, Z₄, B and D are as defined above, to form a compound of formula Ia,

10



in which A, K, X, m, Z₃, Z₄, B and D are as defined above,

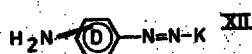
c) reacting a carboxylic acid or a functional derivative of a carboxylic acid of formula XI,



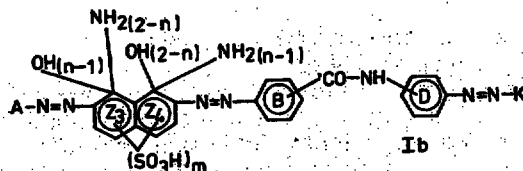
15

15

in which A, n, m, Z₃, Z₄ and B are as defined above, with an aminoazo compound of formula XII,



in which K and D are as defined above, to form a compound of formula Ib,



20

20

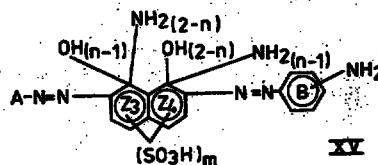
in which A, K, m, n, Z₃, Z₄, B and D are as defined above,
d) reacting a carboxylic acid of formula XIV,



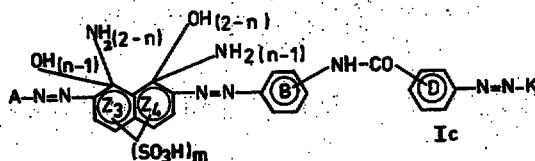
25

in which D and K are as defined above, or a functional derivative thereof, with an aminoazo compound of formula XV,

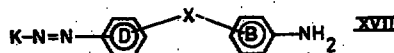
25



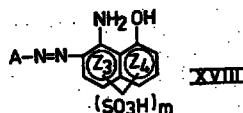
in which A, n, m, B, Z₃ and Z₄ are as defined above, to form a compound of formula Ic,



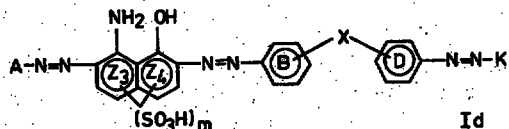
- 5 in which A, m, n, K, Z₃, Z₄, B and D are as defined above,
e) coupling the diazo compound from an amine of formula XVII,



in which K, D, X and B are as defined above, with an azo compound of formula XVIII,



in which A, m, Z₃ and Z₄ are as defined above, to form a compound of formula Id,



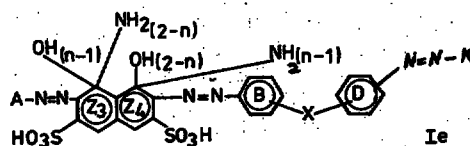
in which A, m, Z₃, Z₄, B, X, D and K are as defined above.

The coupling reactions in process variants a), b) and e) can be carried out according to the conventional methods. For example, the diazo compound can be coupled with a coupling component in aqueous medium at pH values from 4 to 12.

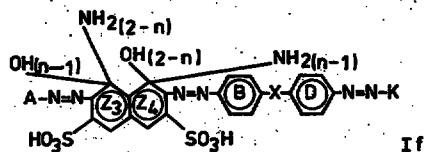
The coupling reactions may be carried out in the presence of coupling accelerants, for example pyridine, urea, guanidine, and generally may be carried out at temperatures from about -10° to +30°C.

The reaction of a compound of formula XI with a compound of formula XII in process variant c) or of a compound of formula XIV with a compound of formula XV in process variant d) are suitably carried out in aqueous medium, in particular with the addition of a condensation accelerant such as sodium hydroxide, and are suitably effected at temperatures ranging from about 20°C to the boil, optionally with the addition of an organic solvent. The compounds of formulae IV to VI, VIII, XI, XII, XIV, XV, XVII and XVIII used as starting materials are known or can be formed in accordance with known methods from known starting materials.

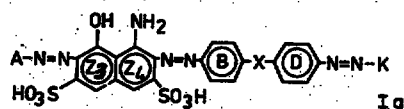
The preferred polyazo compounds comprised in this invention are of formulae Ie, If, Ig and, especially Ih,



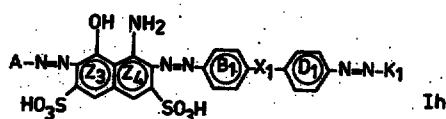
in which A, n, X, B, D, K, Z₃ and Z₄ are as defined above,



in which A, n, X, K, Z₃, Z₄, B and D are as defined above,

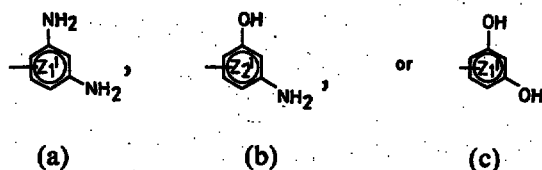


in which A, X, K, Z₃, Z₄, B and D are as defined above, and in particular



in which A, Z₃ and Z₄ are as defined above, and

X₁ signifies a group of formula —CO—NH— or —NH—CO—
K₁ signifies the radical of a coupling component of formula



and the aromatic rings B₁, D₁, Z₁' and Z₂' bear no further substituents.

In particular the present invention comprises polyazo compounds of formula I in which the aromatic rings B, D, Z₁ and Z₂ bear no further substituents.

The aromatic rings Z₁ and Z₂, in addition to the named substituents, may bear one or two further substituents. Suitable substituents are alkyl and alkoxy radicals, preferably lower alkyl and alkoxy radicals having 1 to 4 carbon atoms, halogen, nitro, carboxy, carbalkoxy, sulphonamic acid, cyano, optionally substituted amino and mercapto groups. The alkyl radicals may be substituted by halogen, hydroxyl, cyano or aryl, e.g. phenyl. In the latter case the alkyl radicals signify an aralkyl radical.

By "halogen" is understood in every instance bromine, fluorine or iodine, or preferably chlorine.

The aforementioned substituents may also occur in the aromatic rings B and/or D. Examples of optionally substituted sulphonamide groups are alkylsulphonamides such as monoalkylsulphonamide, dialkylsulphonamide and arylsulphonamide groups. Examples of optionally substituted carbonamide groups are alkylcarbonamide groups such as monoalkylcarbonamide, dialkylcarbonamide and arylcarbonamide groups.

Generally "aryl" signifies an optionally substituted phenyl radical, but it may also signify a naphthyl radical.

The following radicals are specially suitable as radicals A: the aniline radical and the radicals of

1-amino-3-methyl-4-sulphonic acid benzene,
1-amino-3-methyl-6-sulphonic acid benzene,
1-amino-4-methyl-2-sulphonic acid benzene,
1-amino-4-methyl-3-sulphonic acid benzene,
1-amino-2-methyl-4-sulphonic acid benzene,
1-amino-2-methyl-5-sulphonic acid benzene,
1-amino-2-sulphonic acid benzene,
1-amino-3-sulphonic acid benzene,

5	1-amino-4-sulphonic acid benzene, 1-amino-2-carboxylic acid benzene, 1-amino-3-carboxylic acid benzene, 1-amino-4-carboxylic acid benzene, 1-amino-2-methoxybenzene, 1-amino-3-methoxybenzene, 1-amino-4-methoxybenzene, 1-amino-2-nitrobenzene, 1-amino-3-nitrobenzene, 1-amino-4-nitrobenzene, 1-amino-2-chlorobenzene, 1-amino-3-chlorobenzene, 1-amino-4-chlorobenzene, 1-amino-4-methoxy-2-sulphonic acid benzene, 1-amino-2-methoxy-5-sulphonic acid benzene, 1-amino-4-methoxy-3-sulphonic acid benzene, 1-amino-2-nitro-4-sulphonic acid benzene, 1-amino-4-nitro-2-sulphonic acid benzene, 1-aminobenzene-2-sulphonic acid amide, 1-aminobenzene-3-sulphonic acid amide, 1-aminobenzene-4-sulphonic acid amide, 1-amino-2-methoxy-5-methyl-4-sulphonic acid benzene, 1-amino-2,4-dimethyl-6-sulphonic acid benzene, 1-amino-2-chloro-4-methyl-6-sulphonic acid benzene, 1-amino-2-methyl-4-chloro-6-sulphonic acid benzene, 1-amino-2,4-dinitrobenzene.	5
10		10
15		15
20		20
25		25

The following are suitable as central components, i.e. naphthalene derivatives with rings Z₃ and Z₄:

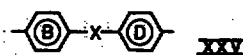
30	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid 1-amino-8-hydroxynaphthalene-4,6-disulphonic acid 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid 1-amino-8-hydroxynaphthalene-4-sulphonic acid 1-amino-8-hydroxynaphthalene-6-sulphonic acid.	30
----	--	----

The new polyazo compounds of formula I possess properties indicating that they are suitable for the dyeing and printing of substrates consisting of or comprising animal, vegetable or synthetic fibres, e.g. natural or synthetic polyamides and polypeptides such as wool, silk, nylon and cotton, and in particular for the dyeing and printing of leather. Conventional techniques may be used for their application to the substrate.

On the named substrates black, blue or green dyeings are generally obtained.

The benzidine dyes, an important group of dyes derived from benzidine, have been found hazardous to health, and consequently they have either been withdrawn from sale or the manufacturers are considering discontinuing their production. This has created a genuine need for other dyes of similar type and shade to replace the high grade benzidine dyes, for the synthesis of which intermediates are required which unlike benzidine are not carcinogenic.

The new compounds of the present invention have the merit as they all contain the bridge member of formula XXV,



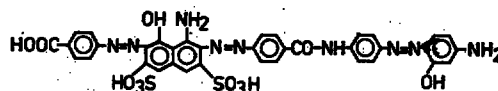
rather than a benzidine derived bridge member.

On leathers of low affinity, e.g. chrome-vegetable and/or chrome-synthetic tanned leathers, the dyes of formula I generally exhibit good build-up.

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

Example 1.

The dye of formula II,



II

can be produced as follows. 319 Parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid are dissolved in water with the addition of sufficient sodium carbonate to give a solution of pH 6 to 6.5. 227 Parts of 4,4'-diaminobenzanilide are tetrazotized with sodium nitrite in the presence of hydrochloric acid in conventional manner. The solution of the 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid is dropped slowly into the solution of the tetrazo component and the unilateral coupling reaction is completed by the addition of sodium acetate.

A diazo solution prepared with 137 parts of 1-amino-4-carboxybenzene, hydrochloric acid and sodium nitrite is coupled at pH 7.5 to 8.5 with the resulting monoazodiaz compound. On completion of the reaction the solution of the disazodiaz compound formed is set with a solution of 109 parts of 1-amino-3-hydroxybenzene in 100 parts of 30% hydrochloric acid and 400 parts of water and the coupling reaction continued to the end-point at pH 5.

The black trisazo dye thus formed is isolated using common salt. It gives deep reddish black dyeings on leather. A dye with comparably good properties but with a greenish black shade is obtained when the final coupling reaction with 1-amino-3-hydroxybenzene is carried out at pH 10 to 12.

Dyeing Example A.

100 Parts of freshly tanned, neutralized chrome grain leather are dyed in a drum dyeing machine for 30 minutes at 55° in a bath of 250 parts of water containing 1 part of the dye of formula Ii. Subsequently the leather is treated in the same bath for 30 minutes with 2 parts of an anionic fat liquor based on sulphonated train oil. On removal it is dried and finished under normal conditions. A very level deep black dyeing of reddish shade is obtained on the leather.

Dyeing Example B.

100 Parts of calf suede leather are wet back in a drum dyeing machine for 4 hours in a bath of 1000 parts of water and 2 parts of ammonia. The suede is then drum dyed for 1 hour 30 minutes at 55° in a fresh bath set with 500 parts of water, 2 parts of ammonia and a solution of 10 parts of the dye of formula Ii. Towards the end of dyeing 4 parts of 85% formic acid are slowly added to exhaust the bath, after which drumming is continued to complete fixation of the dyeing. On removal the suede is rinsed, dried and finished by normal methods and the nap buffed. A very level, deep reddish black dyeing is obtained on the suede.

Dyeing Example C.

100 Parts of a chrome-vegetable tanned lamb skin are drum dyed for 45 minutes at 55° in a bath consisting of 1000 parts of water, 10 parts of the dye of formula Ii and 1.5 parts of an anionic sperm oil emulsion. The dyeing is fixed by continued drumming for 30 minutes with gradual addition of 5 parts of 85% formic acid. After normal drying and finishing, a leather dyed in a level, deep reddish black is obtained.

Dyeing Example D.

A solution of 20 parts of the dye of formula Ii in 847 parts of water, 150 parts of ethyl glycol* and 3 parts of 85% formic acid is applied to the grain side of a buffed, combination tanned side leather by spraying, padding with a plush pad or flow coating. The leather is dried under mild conditions and finished. A deep reddish black dyeing is obtained which has good fastness properties.

Example 2.

The dye of formula Ii in Example 1 can also be obtained by reacting 1 mol of the compound of formula IX produced from 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and diaminobenzanilide and 1-amino-3-hydroxybenzene, with 1 mol of 1-aminobenzene-4-carboxylic acid, in the pH range of 8 to 12.

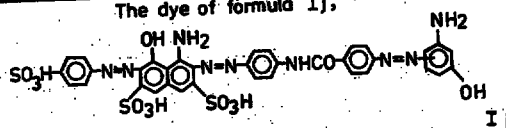
Example 3.

The same dye of formula Ii can be obtained by reaction of the disazo compound of formula XI from 1-aminobenzene-4-carboxylic acid and 1-amino-8-hydroxy naphthalene-3,6-disulphonic acid and 1-amino-4-carboxylic acid chloride with the diazo compound from 1-amino-4,4'-azo-3'-amino-1'-hydroxybenzene of formula XII.

* ethyl glycol ("Cellosolve" Trade Mark) = ethylene glycol monoethyl ester.

Example 4

The dye of formula Ij,

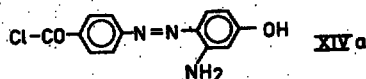


can be produced as follows. 138 Parts of para-nitraniline are diazotized with sodium nitrite and hydrochloric acid by the normal method. A neutral solution of 309 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid in water is allowed to flow into the diazonium solution so that the pH of the reaction solution does not increase to above 2.3.

On completion of the coupling reaction a diazonium compound produced from 173 parts of 1-aminobenzene-4-sulphonic acid, sodium nitrite and hydrochloric acid is entered into the solution of the monoazo compound, and coupling to the disazo compound is carried out at pH 9.5. The disazo compound solution is raised to 40° and the nitro group reduced with 117 parts of sodium sulphide at pH 12. 185.5 Parts of 4-nitrobenzoyl chloride are added to the diazoamino compound, with sodium hydroxide for adjustment to an alkaline pH, and the compound condensed. After condensation a further 117 parts of sodium sulphide are added and the nitro group reduced. The pH is adjusted to 7 and sodium chloride added to isolate the product. The product is stirred into water, the solution adjusted acid to Congo paper with hydrochloric acid and set with sodium nitrite for diazotization. Subsequently a solution of 109 parts of 1-amino-3-hydroxybenzene and sodium hydroxide in water is added and the diazotized compound coupled at pH 9. The trisazo dye of formula Ij formed is isolated with sodium chloride. It is a dark olive-green powder which dissolves in water and dyes leather with excellent fastness properties.

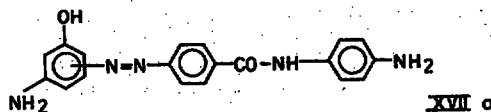
Example 5.

A dye identical with that produced in Example 4 can be obtained when the compound of formula XV produced from 1 mol of 1-aminobenzene-4-sulphonic acid and 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and 1,4-diaminobenzene is reacted with 1 mol of a carboxylic chloride of formula XIVa,



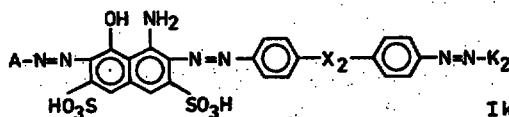
Example 6.

The dye of formula Ii can be obtained when the diazo compound from an amine of formula XVIIa,



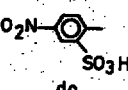
is coupled with the monoazo compound of formula XVIII produced from 1 mol of diazotized 1-aminobenzene-4-carboxylic acid and 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid.

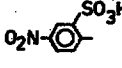
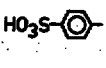
The structural composition of further dyes is given in the following table. They can be produced in similar manner to the compounds of formulae Ii and Ij and agree with the formula Ik,



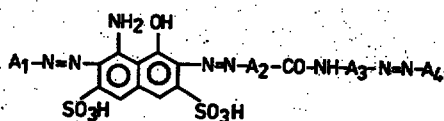
where A, X₂ and K₂ have the significances given in the table. The shade of the dyeings on leather is noted in the final column.

Table I

Example No.	Radical A	X ₂	K ₂	Shade of dyeing on
7		-NH-CO-		green-black
8		-NH-CO-	do.	olive-green
9		-CO-NH-		green-black
10	do.	-NH-CO-	do.	green
11		-CO-NH-		violet-black
12	do.	-NH-CO-	do.	olive
13		-CO-NH-	do.	green-black
14	do.	-NH-CO-	do.	olive
15		-CO-NH-	do.	red-black
16	do.	-NH-CO-	do.	olive
17		-CO-NH-	do.	blue-black

Example No.	Radical A	X ₂	K ₂	Shade of dyeing on leather
18		-NH-CO-		olive
19		-NH-CO-	do.	olive
20		-CO-NH-		olive
21	do.	-NH-CO-	do.	olive
22		-CO-NH-	do.	dark green
23	do.	-NH-CO-	do.	blue

The structural composition of further dyes is given in the following table. They can be produced in similar manner to the compounds of formulae Ii and Ij and agree with the formula II,



II

where A₁, A₂, A₃ and A₄ have the significances given in the table. The shade of the dyeings on leather is noted in the final column.

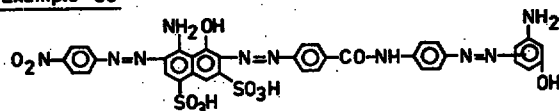
Table II

Example No.	Radical A ₁	A ₂	A ₃	A ₄	Shade of dyeing on leather
24					black
25		do.	do.		do.
26		do.	do.		do.
27		do.	do.		do.
28		do.	do.		do.
29		do.	do.		do.
30		do.	do.		do.
31		do.	do.		do.
32		do.	do.		do.
33		do.	do.		do.

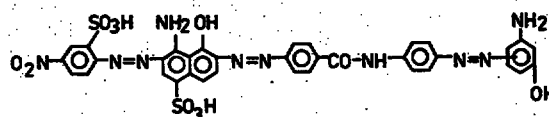
Example No.	Radical A ₁	A ₂	A ₃	A ₄	Shade of dyeing on leather
34					black
35	do.	do.		do.	do.
36					do.
37	do.	do.		do.	greenish black
38		do.			do.

The following dyes also can be produced in similar manner to the compounds of formulae II and Ij. They give black dyeings on leather.

Example 39

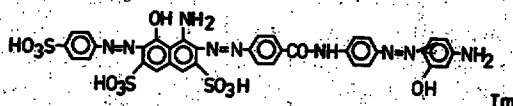


Example 40



Example 41

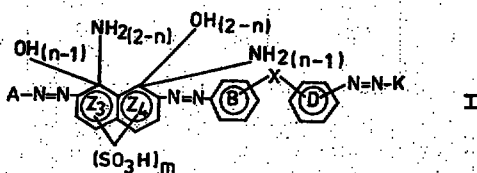
The dye of formula I m,



can be produced as follows. 22.7 Parts of 4,4'-diaminobenzanilide (4-aminobenzoyl-4'-aminoanilide) are tetrazotized with 60 parts of 30% hydrochloric acid, 30 parts of ice and 13.8 parts of sodium nitrite by the normal method. A neutral solution of 31.9 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid in 100 parts of water is added dropwise to the tetrazonium compound at 0—5° and unilateral coupling at pH 2 to 2.6 brought to completion by stirring sodium bicarbonate into the solution. On completion of the reaction the diazo compound from 17.3 parts of 1-aminobenzenesulphonic acid is added to the monoazo compound and the reaction continued to the end-point at pH 6 to 7 by dropping in aqueous sodium hydroxide solution. A solution of 10.9 parts of m-aminophenol, (1-amino-3-hydroxybenzene) in 30 parts of water and 25 parts of aqueous sodium hydroxide solution is added to the newly formed disazo compound so that coupling to the end-point takes place at pH 12. The resulting trisazo dye of formula Im is precipitated by charging 230 parts of 30% hydrochloric acid into the solution, separated by filtration and dried. It is obtained as a black powder which dissolves in water and gives deep blacks on leather.

WHAT WE CLAIM IS:—

1. A process for the production of compounds of formula I,



in which

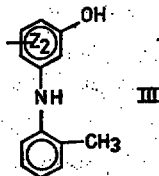
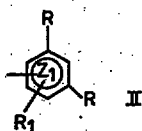
A signifies an unsubstituted phenyl radical or a phenyl radical which is substituted by lower alkyl, alkoxy, S-alkyl, —COOH, —SO₃H, —NO₂, hydroxyl, halogen, or an unsubstituted or substituted sulphonamide, carbonamide, alkylamino, arylamino or acylamino group,

X signifies a bridge member of formula —CS—NH—, —CO—NH—, —NHCS— or —NH—CO—,

m signifies the integer 1 or 2,

n signifies the integer 1 or 2 and

K signifies the radical of a coupling component of formula II or III,



in which

R in each instance signifies —NH₂ or —OH,

R₁ signifies hydrogen or —SO₃H,

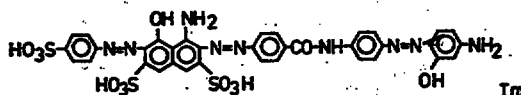
the aromatic rings B and/or D and/or Z₁ and/or Z₂ being otherwise unsubstituted or being further substituted once or twice and the aromatic rings Z₃ and Z₄ being otherwise unsubstituted, and water soluble salts thereof, which comprises,

a) coupling the diazo compound from an aminoazo compound of formula IV,



Example 41

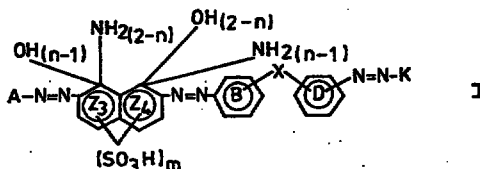
The dye of formula I m.



can be produced as follows. 22.7 Parts of 4,4'-diaminobenzanilide (4-aminobenzoyl-4'-aminoanilide) are tetrazotized with 60 parts of 30% hydrochloric acid, 30 parts of ice and 13.8 parts of sodium nitrite by the normal method. A neutral solution of 31.9 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid in 100 parts of water is added dropwise to the tetrazonium compound at 0-5° and unilateral coupling at pH 2 to 2.6 brought to completion by stirring sodium bicarbonate into the solution. On completion of the reaction the diazo compound from 17.3 parts of 1-aminobenzenesulphonic acid is added to the monoazo compound and the reaction continued to the end-point at pH 6 to 7 by dropping in aqueous sodium hydroxide solution. A solution of 10.9 parts of m-aminophenol, (1-amino-3-hydroxybenzene) in 30 parts of water and 25 parts of aqueous sodium hydroxide solution is added to the newly formed disazo compound so that coupling to the end-point takes place at pH 12. The resulting trisazo dye of formula Im is precipitated by charging 230 parts of 30% hydrochloric acid into the solution, separated by filtration and dried. It is obtained as a black powder which dissolves in water and gives deep blacks on leather.

WHAT WE CLAIM IS:—

1. A process for the production of compounds of formula I,



in which

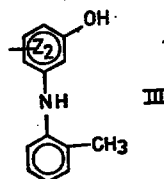
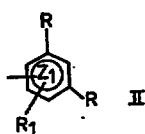
A signifies an unsubstituted phenyl radical or a phenyl radical which is substituted by lower alkyl, alkoxy, S-alkyl, —COOH, —SO₃H, —NO₂, hydroxyl, halogen, or an unsubstituted or substituted sulphonamide, carbonamide, alkylamino, arylamino or acylamino group,

X signifies a bridge member of formula —CS—NH—, —CO—NH—, —NHCS— or —NH—CO—,

m signifies the integer 1 or 2,

n signifies the integer 1 or 2 and

K signifies the radical of a coupling component of formula II or III,



in which

R in each instance signifies —NH₂ or —OH,

R₁ signifies hydrogen or —SO₃H,

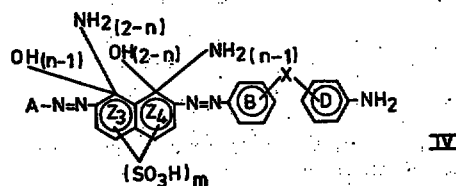
the aromatic rings B and/or D and/or Z₁ and/or Z₂ being otherwise unsubstituted or being further substituted once or twice and the aromatic rings Z₃ and Z₄ being otherwise unsubstituted, and water soluble salts thereof, which comprises,

a) coupling the diazo compound from an aminoazo compound of formula IV,

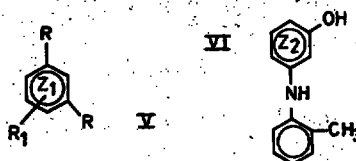


1,419,312

11



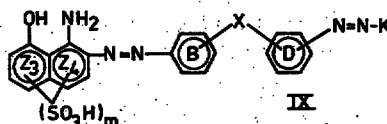
in which A, X, n, m, B, D, Z₃ and Z₄ are as defined above, with one of the coupling components of formulae V or VI,



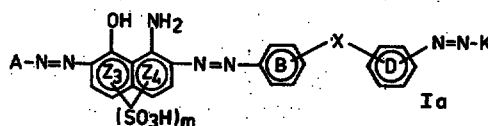
- 5 in which R, R₁, Z₁ and Z₂ are as defined above,
b) coupling the diazo compound from an amine of formula VIII,



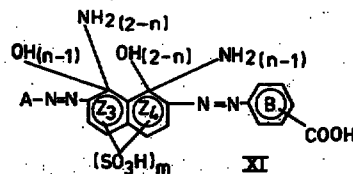
in which A is as defined above, with an azo compound of formula IX,



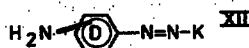
- 10 in which m, X, K, Z₃, Z₄, B and D are as defined above, to form a compound of formula Ia,



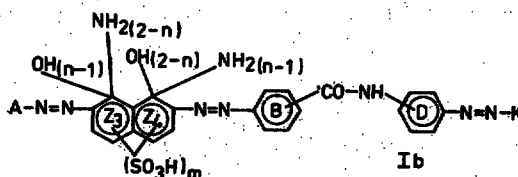
- 15 in which A, K, X, m, Z₃, Z₄, B and D are as defined above,
c) reacting a carboxylic acid or a functional derivative of a carboxylic acid of formula XI,



in which A, n, m, Z₃, Z₄ and B are as defined above, with an aminoazo compound of formula XII,



- 20 in which K and D are as defined above, to form a compound of formula Ib,



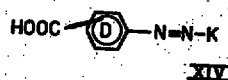
in which A, K, m, n, Z₃, Z₄, B and D are as defined above,



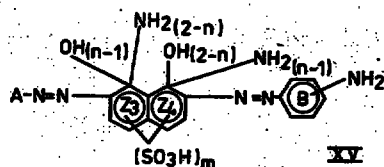
12

1,419,312

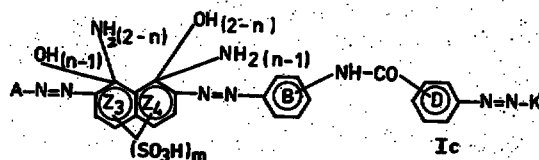
d) reacting a carboxylic acid of formula XIV,



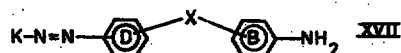
in which D and K are as defined above, or a functional derivative thereof, with an aminoazo compound of formula XV,



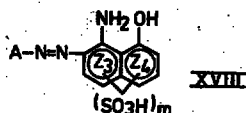
in which A, n, m, B, Z₃ and Z₄ are as defined above, to form a compound of formula Ic,



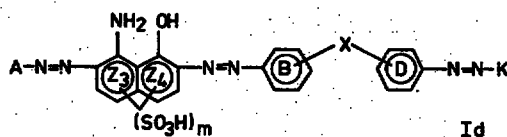
in which A, m, n, K, Z₃, Z₄, B and D are as defined above,
e) coupling the diazo compound from an amine of formula XVII,



in which K, D, X and B are as defined above, with an azo compound of formula XVIII,



in which A, m, Z₃ and Z₄ are as defined above, to form a compound of formula Id,



in which A, m, Z₃, Z₄, B, X, D and K are as defined above.

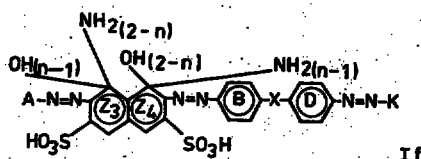
2. A process according to Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 23 or 41.

3. A process according to Claim 1, substantially as hereinbefore described with reference to any one of Examples 24 to 40.

4. A compound of formula I and water soluble salts thereof, whenever prepared by a process according to any one of Claims 1 to 3.

5. A compound of formula I, as defined in Claim 1, and water soluble salts thereof.

6. A compound according to Claim 5, of the formula If,



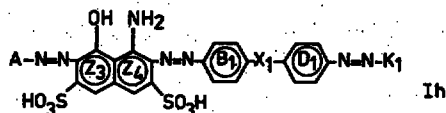


1,419,312

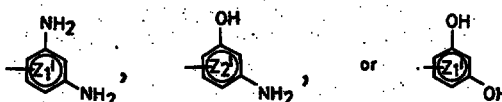
13

in which A, n, X, K, Z₃, Z₄, B and D are as defined in Claim 1, and water soluble salts thereof.

7. A compound according to Claim 5, of the formula Ih,



5 in which A, Z₃ and Z₄ are as defined in Claim 1, and
X₁ signifies a group of formula —CO—NH— or —NH—CO—
K₁ signifies the radical of a coupling component of formula



10 and the aromatic rings B₁, D₁, Z₁ and Z₁' bear no further substituents, and water soluble salts thereof.

8. A compound according to Claim 5, in which A signifies an unsubstituted phenyl radical or a phenyl radical substituted once or twice by groups selected from —COOH, —SO₃H, —NO₂, —SO₂NH₂, methyl, methoxy, chlorine, m
15 signifies 2, X signifies —NHCO— or —CONH— and the aromatic rings B and D are otherwise unsubstituted, and water soluble salts thereof.

9. A compound according to any one of Claims 5 to 8, in which X signifies —CO—NH—.

10. A compound according to any one of Claims 5 to 8, in which X signifies —NH—CO—.

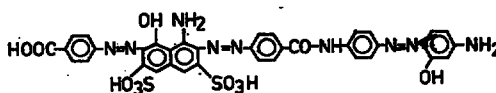
20 11. A compound according to Claim 9, in which A signifies *para*-sulphophenyl.

12. A compound according to any one of Examples 7, 8, 10, 12, 14, 16, 19, 21 or 23 and water soluble salts thereof.

25 13. A compound according to any one of Examples 9, 11, 13, 15, 17, 20 or 22 and water soluble salts thereof.

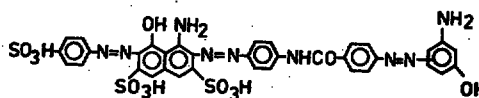
14. A compound according to any one of Examples 24, 25 and 27 to 40 and water soluble salts thereof.

15. A compound of formula



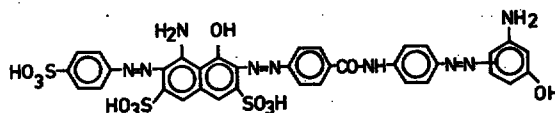
30 and water soluble salts thereof.

16. A compound of formula



and water soluble salts thereof.

17. A compound of formula



and water soluble salts thereof.

26



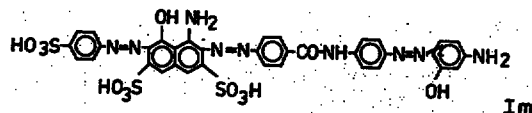
* C L M S *

14

1,419,312

18. A compound according to claim 4, of the formula

Im,



and water soluble salts thereof.

19. A method of dyeing or printing substrates consisting of or comprising animal vegetable or synthetic fibres which comprises applying to the substrate a compound, or water soluble salt, according to any one of Claims 4 to 18.

20. A method according to Claim 19, in which the substrate is leather.

21. A method of dyeing or printing substrate consisting of or comprising animal vegetable or synthetic fibres substantially as hereinbefore described with reference to any one of Example A to D.

22. Dyed or printed substrates whenever obtained by a method according to any one of Claims 19 to 21.

B. A. YORKE & CO.,
Chartered Patent Agents,
98 The Centre,
Feltham,
Middlesex, TW13 4EP.

Reference has been directed, in pursuance of Section 8 of the Patents Act 1949, to Specifications Nos. 1,327,914 and 1,327,915.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.