

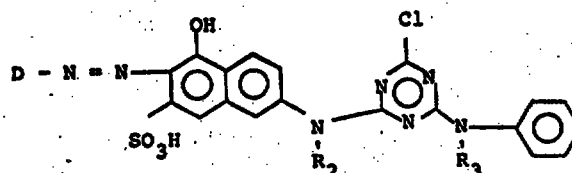
SPECIFICATION

Chloro triazinyl group-containing compounds

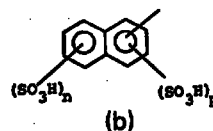
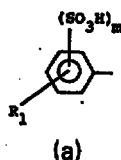
The present invention relates to azo compounds containing a fibre reactive group, their production and use as reactive dyestuffs.

5 More particularly, the present invention provides compounds of formula I,

5



in which D is a group of formula (a) or (b),



where

10 R_1 is hydrogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy,

10

m and n are 1 or 2, and

p is 0 or 1, with the proviso that

$n + p$ is 2 or 3,

R_2 is hydrogen or (C_{1-4}) alkyl and

15 R_3 is (C_{1-4}) alkyl,

15

or mixtures thereof, which compounds are in free acid or salt form.

Any alkyl groups as R_1 , R_2 and/or R_3 may be straight or branched, preferably straight chain. The preferred number of carbon atoms in such alkyl groups is 1 or 2. Any alkyl group as R_1 and/or R_2 is preferably methyl.

20 Any alkoxy group as R_1 is preferably straight chain and is preferably methoxy or ethoxy, especially methoxy.

20

R_1 is preferably R_1' where R_1' is hydrogen, methyl or methoxy. More preferably R_1 is R_1'' , where R_1'' is hydrogen or methyl.

R_2 is preferably R_2' where R_2' is hydrogen, methyl or ethyl. More preferably R_2 is R_2'' , where R_2'' is

25 hydrogen or methyl, especially hydrogen.

25

R_3 is preferably R_3' , where R_3' is methyl or ethyl.

m is preferably 2

n is preferably 2 and

p is preferably 1.

30 When the group (a) is monosubstituted, the sulfo group may be in any position; where R_1 has a significance other than hydrogen and m is 1 the two substituents are preferably in the 2,5-positions. When m is 2 and R_1 is hydrogen the two sulfo groups are preferably in the 2,4- or 2,5-positions. When m is 2 and R_1 is other than hydrogen, the positions 2- R_1 -4,6-disulpho or 4- R_1 -2,5-disulpho are preferred, especially the latter.

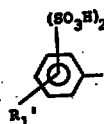
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35 When the group (b) bears 2 sulfo groups and the azo group is bound to the 1-position, the sulfo groups are preferably in the 3,6-; 3,8-; 4,6-; or 4,8-positions, and when the azo group is bound to the 2-position the sulfo groups are preferably in the 1,5-; 3,6-; 4,8-; 5,7- or 6,8-positions. When the radical (b) bears 3 sulfo groups they are preferably in the 3,6,8-positions with the azo group in the 1-position and in the 3,6,8- 4,6,8- or 1,5,7-positions with the azo group in the 2-position.

35

40 Preferably the group (a) is (a₁),

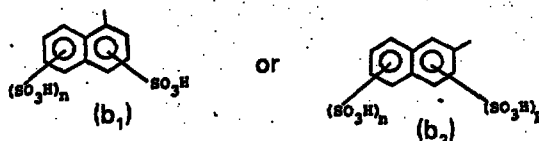
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(a₁)

with the above-given preferred positions for the substituents.

The group (b) is preferably (b₁) or (b₂),



with the above-given preferred positions for the substituents.

5 More preferably the group (b) is (b₃),

5



with the above-given preferred positions for the substituents. Most preferably (b) is (b₄),



in which the sulpho groups are in the 3,6,8- or 4,6,8-positions.

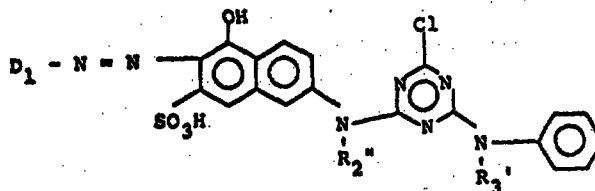
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10

Preferred compounds of formula I are:

- (i) those where D is a group of formula (a₁), (b₁) or (b₂)
- (ii) those wherein R₂ is R₂' and R₃ is R₃';
- (iii) those of (i), or (ii) where R₂ is R₂'' especially hydrogen;
- (iv) those of formula Ia,

15



15

in which D₁ is a group of formula (a₁) or (b₃);

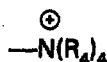
- (v) those of (iv) wherein D₁ is a group of formula (a₁) wherein R₁' is R₁'' or of formula (b₄) especially (b₄);
- (vi) those of (iv) wherein R₂'' is hydrogen; and

20 which preferred compounds of groups (i) to (vi) are in free acid or salt form.

20

The cation of the salt form of the compounds of the present invention is not critical and may be any non-chromophoric cation conventionally contained in anionic dyestuffs.

As examples of suitable such cations may be given alkali metal cations, or



25 in which each R₄ independently is hydrogen, (C₁₋₄)alkyl, 2-, 3- or 4-hydroxy (C₂₋₄)alkyl. It will be appreciated that cations which are known to cause steric or stability problems, for example tetraalkanolammonium cations, are excluded. Specific examples of suitable cations are lithium, sodium, potassium, ammonium, mono-, di- tri- or tetramethylammonium, triethylammonium, mono-, di- or triethanol ammonium and mon-, di- or trisopropanolammonium. Preferred cations are the alkali metal

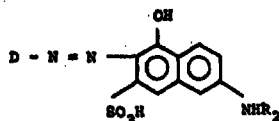
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30 cations and ammonium, with sodium being most preferred.

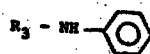
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The present invention further provides a process for the production of compounds of formula I, comprising

(a) reacting cyanuric chloride, with a compound of formula II,



or a mixture thereof, which compound(s) are in free acid or salt form, and a compound of formula III



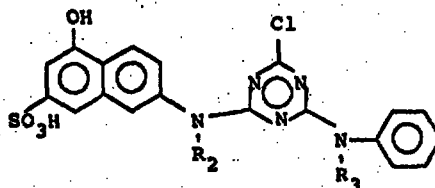
III

- 5 in any order or
5 (b) coupling the diazotized amine of formula IV,



IV

or a mixture thereof
with a compound of formula V,

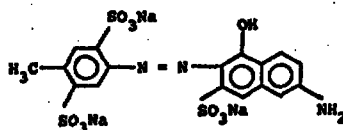


V

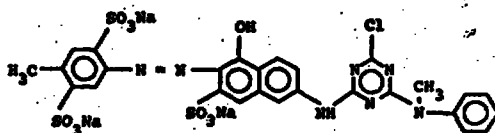
- 10 or a mixture thereof, which compound or mixture is in free acid or salt form. 10
The condensation reactions (a) may be carried out in accordance with known methods. Similarly coupling and diazotizing may be effected in accordance with known methods.
The compounds of formulae II, III and IV are known. The compounds of formula V may be prepared in analogy with known methods from available starting materials.
15 The compounds of formula I may be isolated in accordance with known methods, for example by salting out, filtering and drying in a vacuum. 15
The compounds of formula I and mixtures thereof are useful as dyestuffs for dyeing and printing hydroxy group-containing or amide group-containing organic substrates. Preferred substrates are leather and textiles consisting of or comprising natural or synthetic polyamides such as wool, silk or 20 nylon, natural or regenerated cellulose such as cotton, viscose or spun rayon. 20
Dyeing and printing may be carried out in accordance with conventional methods for reactive dyestuffs.
Those dyes in which $m = 1$ or $n + p = 2$ are especially suitable for dyeing by the exhaust method. The dyes wherein $m = 2$ or $n + p = 3$ are especially suitable for printing and are also suitable for use in 25 padding processes. 25
The compounds of formula I, and their mixtures give intense dyeings and exhibit notable build-up power and satisfactory fixation properties including a good fixation yield.
The dyeings and prints obtained exhibit notable light and wetfastness such as, fastness to washing, sweat, chlorine, chlorine bleaching agents and are stable to the action of reducing agents.
30 In the case of the prints the contours are sharp, also to be mentioned are the easy removal by washing of non-bound dyestuff and the stability of the printing pastes. In the case of padding, the solubility of the dyes of the invention and stability of the padding liquor containing the same is notable and the easy removal of non-bound dyestuff is a distinct advantage. 30
The following examples further serve to illustrate the present invention. In the Examples all parts are by weight and temperatures are in degrees Centigrade. 35

EXAMPLE 1

- 132 Parts of 1-amino-4-methyl-benzene-2,5-disulphonic acid are stirred in 350 parts water and are adjusted to a pH value of 0.9 with 120 parts of a 30% sodium hydroxide solution; the temperature of the solution rises to 47°C. 103 Parts of the sodium salt of naphthalene-2-sulphonic acid are added 40 thereto, the solution is cooled with ice and subsequently diazotized at 0—5° with 143 parts of a 4N sodiumnitrite solution. 136.7 Parts 6-N-acetylamino-1-hydroxy-naphthalene-3-sulphonic acid dissolved in 450 parts water are added to the diazonium solution, coupling is carried out at pH 6—7 in the presence of 62 parts sodiumcarbonate. After the coupling is complete the dyestuff suspension is treated with 213 parts of a 30% sodium hydroxide solution for 1 to 2 hours at 90—95° in order to split 45 off the acetyl group. After adding 184 parts 30% hydrochloric acid, the dyestuff is salted out from the cooled reaction mixture by adding 250 parts sodium chloride. The dyestuff obtained of formula



- is dissolved in 1000 parts water. To the solution 85.5 parts cyanuric chloride suspended in 700 parts ice water are added, a temperature of 0—5° is maintained and the pH is kept at 3.0 by adding 20.6 parts sodium carbonate. After 1½ to 2 hours condensation is complete, 52.3 parts N-methylaniline are added to the dyestuff, the temperature is raised to 55—60° and the pH adjusted to 7.0—7.5 by adding 60 parts sodium carbonate. The reaction is complete in 2½ hours and the resulting dye is separated by adding 17 parts 30% hydrochloric acid and 390 parts sodium chloride. The dye of formula



dissolves in water to give a orange-red solution and dyes cotton in pure orange shades. The dyeings and prints exhibit good light- and wet-fastnesses.

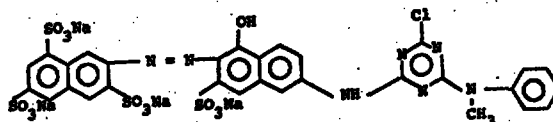
10 EXAMPLE 2

A diazo solution is prepared by dissolving 38.3 parts 2-aminonaphthalene-3,6,8-trisulphonic acid in 400 parts water and treating the same with 25 parts of a 30% hydrochloric acid and diazotizing for 10 minutes at 0—5° with 6.9 parts sodium nitrite dissolved in 24 parts water. Coupling is effected by adding this diazonium solution to 27.3 parts 6-N-acetylamino-1-hydroxynaphthalene-3-sulphonic acid in 90 parts water. During the coupling reaction the pH was set at 5—6 with sodium carbonate and the temperature was held at 8—12°. After coupling the product was deacetylated and separated in analogy with the procedure described in Example 1.

The paste is dissolved in 500 parts water and the pH value is set at 6 with hydrochloric acid.

14.75 Parts cyanuric chloride are added portionwise at 15—20° and the mixture is stirred for 3 hours.

- 20 The pH value is adjusted to 5—6 by the addition of a dilute sodium carbonate solution. After completion of the condensation the reaction mixture is diluted with 400 parts water. Subsequently, 8.6 parts N-methylaniline are added thereto and the mixture is heated to 35—40° and stirred for 40 minutes, the pH value being maintained at a value of 6.5 to 7 by the addition of a dilute sodium carbonate solution. The dye which is subsequently isolated by adding sodium chloride is of the formula



and is obtained as a dark red powder which dissolves in water to give a red solution and dyes and prints cotton in scarlet shades, the dyeings and prints having good light- and wet-fastnesses.

In analogy with the procedure described in Examples 1 and 2, further dyes as given in the following Table, may be prepared. The dyes when prepared in analogy with the procedure of Examples 1 and 2 are obtained in the sodium salt form. However, in accordance with conventional methods they may be isolated in the free acid form or in another salt form. The dyes give prints and dyeings on cellulose fibres which are of the following shades:

yellow-orange	— dyes of Examples 3 to 6, 13 to 17, 38 and 39;
orange	— dyes of Examples 7 to 12, 24, and 34 to 37; and
scarlet	— dyes of Examples 18 to 23 and 25 to 33.

TABLE

Example No.	D	R ₂	Hal	Amino Component III
3	1-aminobenzene-2,5-disulphonic acid	H	Cl	N-methylaniline
4	do.	H	Cl	N-ethylaniline
5	1-amino-4-methylbenzene-2,5-disulphonic acid	H	Cl	do.
6	do.	CH ₃	Cl	N-methylaniline
7	1-amino-4-ethylbenzene-2,5-disulphonic acid	H	Cl	do.
8	do.	H	Cl	N-ethylaniline
9	1-aminobenzene-2,4-disulphonic acid	H	Cl	do.
10	do.	H	Cl	N-methylaniline
11	do.	CH ₃	Cl	do.
12	1-amino-2-methylbenzene-4,6-disulphonic acid	H	Cl	do.
13	do.	H	Cl	N-ethylaniline
14	2-aminonaphthalene-3,6,8-trisulphonic acid	H	Cl	do.
15	do.	CH ₃	Cl	N-methylaniline
16	2-aminonaphthalene-4,6,8-trisulphonic acid	H	Cl	do.
17	do.	H	Cl	N-ethylaniline
18	2-aminonaphthalene-1,5,7-trisulphonic acid	H	Cl	do.
19	1-aminonaphthalene-3,6,8-trisulphonic acid	H	Cl	N-methylaniline
20	2-aminonaphthalene-3,6-disulphonic acid	H	Cl	do.
21	do.	CH ₃	Cl	do.
22	2-aminonaphthalene-4,8-disulphonic acid	H	Cl	do.
23	do.	CH ₃	Cl	do.

TABLE (Continued)

Example No.	D	R ₂	Hal	Amino Component III
24	2-aminonaphthalene-5,7-disulphonic acid	H	Cl	N-methylaniline
25	do.	CH ₃	Cl	do.
26	do.	H	Cl	N-ethylaniline
27	1-aminonaphthalene-3,6-disulphonic acid	H	Cl	N-methylaniline
28	1-aminonaphthalene-4,6-disulphonic acid	H	Cl	do.
29	do.	CH ₃	Cl	do.
30	1-aminonaphthalene-4,8-disulphonic acid	H	Cl	do.
31	1-aminobenzene-2-sulphonic acid	H	Cl	do.
32	do.	CH ₃	Cl	do.

APPLICATION EXAMPLE A

1 Part of the product of Example 31 is dissolved in 300 parts of water. 10 Parts of cotton are immersed in the solution and the temperature is raised to 80° over a period of 10 minutes. 15 Parts of Glauber's salt are then added, followed 30 minutes later by 3 parts of sodium carbonate. Dyeing is continued for 1 hour at 80°.

The dyed cotton is removed from the dyebath, rinsed in cold water followed by hot rinsing, and soaped for 20 minutes in a boiling solution containing 500 parts of water and 0.5 parts of sodium alkylsulphonate. After rinsing a scarlet dyeing with good fastnesses is obtained.

10 APPLICATION EXAMPLE B

2 Parts of the dye of Example 1, are dissolved in 100 parts warm (c. 40°) water to which 10 parts of urea have been added. 30 Parts of a 30% sodium carbonate and 0.5 parts 1-nitrobenzene-3-sulphonic acid sodium salts are added thereto. Spun rayon fabric is impregnated with this solution to a 75% weight increase. After drying, the fabric is treated for 5 to 10 minutes with wet steam at 102°, rinsed and soaped in a boiling solution for 15 minutes. After drying, an orange dyeing having good light- and wet-fastnesses is obtained.

APPLICATION EXAMPLE C

2 Parts of the dye of Example 3 and 20 parts of urea are dissolved in 50 parts of water at 20°. After the addition of 15 parts of 10% aqueous sodium carbonate solution, the volume of the solution is made up to 100 parts.

The solution is padded onto 20 parts of cotton fabric to an uptake of 80% of its dry weight, and the padded fabric is first dried and then steamed at 103° for 10 minutes. Finally the dyeing is rinsed, soaped in a boiling solution, rinsed again and dried to give a yellow-orange dyeing having good fastnesses.

25 APPLICATION EXAMPLE D

A printing paste consisting of

25 parts dyestuff of Example 1 or 2

100 parts urea

440 parts water

400 parts 4% sodium alginate thickener and

10 parts sodium salt of 1-nitrobenzene-3-sulphonic acid

25 parts sodium bicarbonate

5

1000 parts

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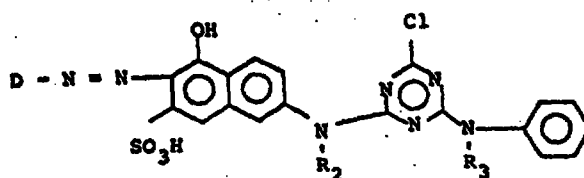
was applied to cotton fabric in accordance with a conventional printing method.

The printed material is dried and fixed in steam at 102—104° for 4 to 8 minutes. The fabric is then rinsed in hot water, soaped in a boiling solution and dried. An orange respectively scarlet print with good light- and wet fastnesses is obtained.

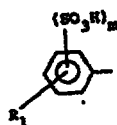
10 CLAIMS

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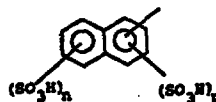
1. A compound of formula I,



in which D is a group of formula (a) or (b)



(a)



(b)

15 where

15

R_1 is hydrogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy,

m and n are 1 or 2, and

p is 0 or 1, with the proviso that

$n + p$ is 2 or 3

20

R_2 is hydrogen or (C_{1-4}) alkyl and

20

R_3 is (C_{1-4}) alkyl,

or a mixture thereof,

which compound is in free acid or salt form.

2. A compound according to Claim 1, in which R_1 is R_1' , where R_1' is hydrogen, methyl or methoxy.

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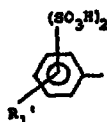
3. A compound according to Claim 1 or Claim 2, in which R_2 is R_2' , where R_2' is hydrogen, methyl or ethyl.

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4. A compound according to any one of Claims 1 to 3, in which R_3 is methyl or ethyl.

5. A compound according to any one of the preceding claims, in which D is a group of formula (a₁), (b₁) or (b₂)

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(a₁)

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440 parts water

400 parts 4% sodium alginate thickener and

10 parts sodium salt of 1-nitrobenzene-3-sulphonic acid

25 parts sodium bicarbonate

5

1000 parts

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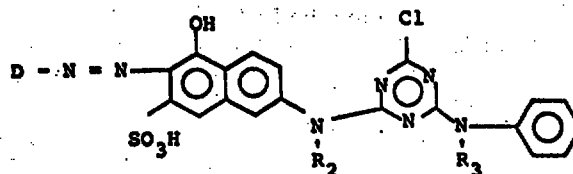
was applied to cotton fabric in accordance with a conventional printing method.

The printed material is dried and fixed in steam at 102—104° for 4 to 8 minutes. The fabric is then rinsed in hot water, soaped in a boiling solution and dried. An orange respectively scarlet print with good light- and wet fastnesses is obtained.

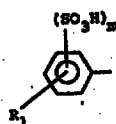
10 CLAIMS

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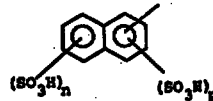
1. A compound of formula I,



in which D is a group of formula (a) or (b)



(a)



(b)

15 where

15

R₁ is hydrogen, (C₁₋₄)alkyl or (C₁₋₄)alkoxy,

m and n are 1 or 2, and

p is 0 or 1, with the proviso that

n + p is 2 or 3

20

R₂ is hydrogen or (C₁₋₄)alkyl and

20

R₃ is (C₁₋₄)alkyl,

or a mixture thereof,

which compound is in free acid or salt form.

25

2. A compound according to Claim 1, in which R₁ is R₁', where R₁' is hydrogen, methyl or methoxy.

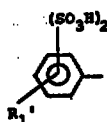
3. A compound according to Claim 1 or Claim 2, in which R₂ is R₂', where R₂' is hydrogen, methyl or ethyl.

25

4. A compound according to any one of Claims 1 to 3, in which R₃ is methyl or ethyl.

5. A compound according to any one of the preceding claims, in which D is a group of formula (a₁), (b₁) or (b₂)

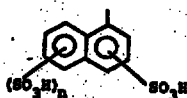
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(a₁)

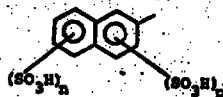
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in which when R_1' is hydrogen the two sulpho groups are in the 2,4- or 2,5-positions and where R_1' is other than hydrogen, the substituents are 2- R_1' -4,6-disulpho or 4- R_1' -2,5-disulpho, and R_1' is hydrogen, methyl or methoxy,

(b₁)

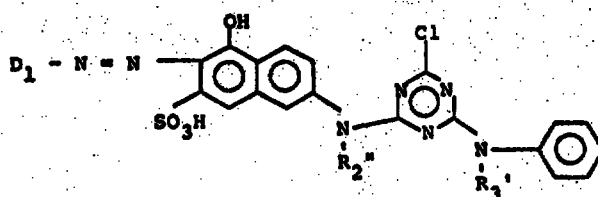
- 5 in which the sulpho groups where n is 1 are in the 3,6-, 3,8-, 4,6- or 4,8-positions and where n is 2 are in the 3,6,8-positions

(b₂)

- 10 in which the sulpho groups, where n is 1 and p is 1 are in the 1,5-, 3,6- or 4,8-positions; where n is 2 and p is 0, are in the 5,7- or 6,8-positions and where n is 2 and p is 1 are in the 3,6,8-, 4,6,8- or 1,5,7-positions.

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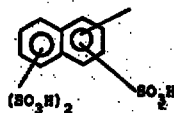
6. A compound according to Claim 5, in which R_2 is R_2'' where R_2'' is hydrogen or methyl.
7. A compound according to Claim 5 or Claim 6, in which R_2 is hydrogen.
8. A compound according to Claim 5, of formula Ia,



Ia

- 15 in which D_1 is a group of formula (a₁) as defined in Claim 5, or a group (b₃)

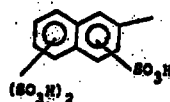
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(b₃)

- 20 in which the sulpho groups are in the 3,6,8-position when the azo group is in the 1-position and in the 3,6,8-, 4,6,8- or 1,5,7-positions when the azo group is in the 2-position, R_2'' is hydrogen or methyl, and R_3'' is methyl or ethyl.

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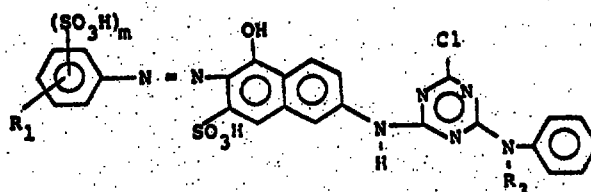
9. a compound according to Claim 8, in which D_1 is a radical of formula (a₁) wherein R_1' is hydrogen or methyl or D_1 is a radical of formula (b₄),

(b₄)

- 25 in which the sulpho groups are in the 3,6,8- or 4,6,8-positions.

25

10. a compound according to Claim 8 or Claim 9, in which R_2'' is hydrogen.
11. A compound of formula



in which

R_1 is hydrogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy,

R_3 is (C_{1-4}) alkyl and

m is 1 or 2,

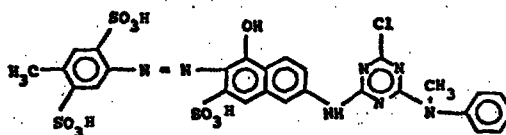
5 in free acid or salt form or a mixture of such compounds.

12. A compound according to any one of the preceding claims in alkali metal or ammonium salt form.

13. A mixture of compounds according to any one of claims 2 to 12.

14. A compound of formula

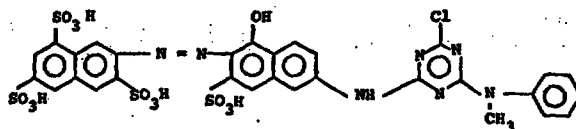
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in free acid or salt form.

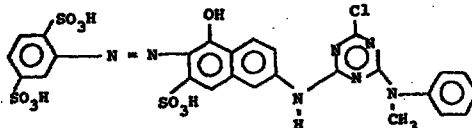
15. A compound of formula



in free acid or salt form.

15 16. A compound of formula

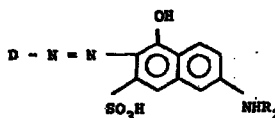
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in free acid or salt form.

17. A process for the production of a compound of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting chloride, with a compound of formula II

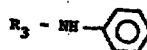
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20

II

or a mixture thereof, which compound or mixture is in the free acid or salt form, and a compound of formula III

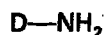


III

in any order.

25 18. A process for the production of a compound of formula I, as defined in Claim 1, or a mixture thereof, comprising coupling the diazotized amine of formula IV,

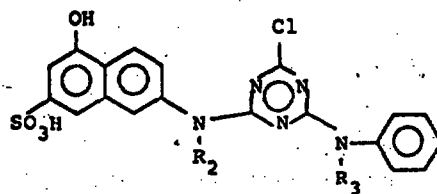
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IV

or a mixture thereof
with a compound of formula V,





V

or a mixture thereof, which compound or mixture is in free acid or salt form.

19. A process for the production of a compound of formula I, as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 32.

5 20. A compound of formula I, as defined in Claim 1, whenever obtained by a process according to any one of Claims 17 to 19.

21. A process for dyeing or printing amido or hydroxy group-containing organic substrates comprising applying a compound or mixture according to any one of Claims 1 to 16 or 20, thereto.

10 22. A process according to Claim 25, in which the substrate is leather or consists of or comprises natural or synthetic polyamides or natural or regenerated cellulose.

23. A process for dyeing or printing amido or hydroxy group-containing organic substituents substantially as hereinbefore described with reference to any one of Examples A to E.

24. Dyed or printed substrates whenever obtained by a process according to any one of Claims 21 to 23.

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