

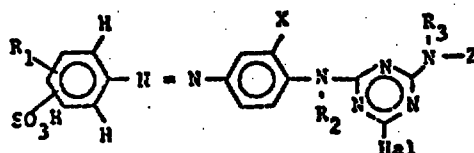
SPECIFICATION

Fibre-reactive monoazo compounds

The present invention relates to fibre-reactive monoazo compounds.

More particularly, the present invention provides monoazo dyestuff compounds having a sulphoaniline diazo component and an aniline coupling component, such components being free from substituents in ortho position to the azo group, the amine group of the coupling component bearing a 2,4,6-trihalo-1,3,5-triazinyl fibre-reactive group in which one halogen is replaced by an aromatic carbocyclic-substituted amino group which contains at least one water solubilizing group and mixtures of such dyestuff compounds which dyestuff compounds are in free acid or salt form.

Preferred compounds according to the invention are those of formula I,



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

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

each of R_2 and R_3 independently, is hydrogen or (C_{1-4}) alkyl, and

Hal is fluorine, chlorine or bromine, and

Z is an aromatic-carbocyclic group containing at least one water-solubilizing group, and mixtures thereof, which compounds and mixtures are in free acid or salt form.

Any halogen as R_1 is fluorine, chlorine or bromine. The preferred halogens are chlorine and bromine, especially chlorine. Preferred alkyl and alkoxy groups as R_1 contain 1 or 2 carbon atoms, with methyl and methoxy being most preferred.

Preferably R_1 is R'_1 , where R'_1 is hydrogen, methyl, methoxy or ethoxy. More preferably, R_1 is R''_1 , where R''_1 is hydrogen, methyl or methoxy. Most preferably R_1 is R'''_1 , where R'''_1 is hydrogen or methyl, especially hydrogen.

When R_1 is hydrogen the sulpho group is preferably in the 3-position to the azo group. When R_1 is a substituent such is preferably ortho to the sulpho group.

Any alkoxy as X is preferably methoxy or ethoxy, especially methoxy. Any alkyl is preferably methyl.

X is preferably X' , where X' is hydrogen, methyl, methoxy, ethoxy or carboxy. More preferably X is X'' , where X'' is hydrogen, methoxy or ethoxy. Most preferably X is X''' , where X''' is methoxy or ethoxy, with methoxy being especially preferred.

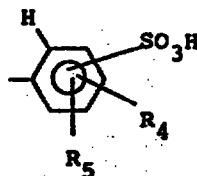
R_2 is preferably R'_2 , where R'_2 is hydrogen or methyl. Most preferably R_2 is hydrogen.

R_3 is preferably R'_3 , where R'_3 is hydrogen, methyl or ethyl. More preferably R_3 is hydrogen or methyl, with hydrogen being especially preferred.

Suitable water-solubilizing groups in the group Z are carboxy and sulpho. Z preferably contains at least one sulpho group.

Preferred aromatic groups as Z are phenyl groups which contain one or two substituents selected from carboxy and sulpho and are optionally further substituted by up to two substituents selected from the groups consisting of fluorine, chlorine, bromine, C_{1-4} (preferably C_{1-2})alkyl and C_{1-4} (preferably C_{1-2})alkoxy.

Preferably, Z is Z' , where Z' is a group of formula (a)



in which R_4 is hydrogen, sulpho or carboxy,

R_5 is hydrogen, chlorine, methyl, ethyl, methoxy or ethoxy.

More preferably Z is Z''' , where Z''' is a group of formula (a) wherein R_5 is hydrogen, methyl or methoxy. Yet even more preferably Z is Z'' , where Z'' is a group of formula (a) wherein R_5 is hydrogen or methyl. Most preferably Z is Z' , where Z' is a group of formula (a) wherein R_4 is sulpho or carboxy and R_5 is hydrogen or methyl, especially hydrogen, with disulphophenyl being especially preferred.

When Z is a group of formula (a) and both R_4 and R_5 are hydrogen the sulpho group is preferably in the 3- or 4-position. When R_4 is carboxy and R_5 is hydrogen, the preferred positions are 2-carboxy-4- or 5-sulpho. When R_4 is sulpho and R_5 is hydrogen the sulpho groups are preferably in the 2,4- or 2,5-

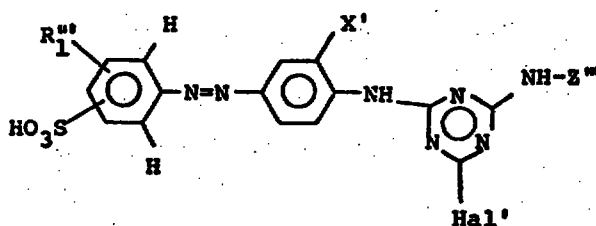
positions, especially the 2,5-positions. When R_4 is hydrogen and R_5 is other than hydrogen the preferred positions are 2- R_5 -4- or 5-sulpho especially 2- R_5 -4-sulpho. When R_4 is sulpho or carboxy and R_5 is other than hydrogen the three substituents are preferably in the 2,4,5-positions, most preferably with a carboxy or sulpho group in the 2-position.

- 5 Hal is preferably fluorine or chlorine, more preferably chlorine.
Preferred compounds of formula I are

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- (1) those where R_2 and R_3 are both hydrogen;
(2) those where Z is Z' ;
(3) those where Z is Z'' , especially Z''' ;
10 (4) those where Z is Z'' ;
(5) those of (1) where Z is Z' ;
(6) those of (2) where R_1 is R'_1 ; especially R''_1 ;
(7) those where X is X' ;
15 (8) those of (1) where Z is Z''' ;
(9) those of (1) where Z is Z'' ;
(10) those of (1) to (9) where Hal is fluorine or chlorine, especially those where Hal is chlorine;
(11) compounds of formula I,

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- 20 in which Hal' is fluorine or chlorine, especially chlorine, especially those where R''_1 is hydrogen and the sulphonyl group is in the 3-position and where R_1 is methyl the two groups are in ortho position to one another.

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- (12) those of (11) where R''_1 is hydrogen especially where the sulphonyl group is in the 3-position;
(13) those of (11) where X' is X'' ;
25 (14) those of (11) where X' is X''' , especially methoxy;
(15) those of (11) to (14) where Z''' is Z'' ; and
(16) those of (11) to (14) where Z''' is Z' , especially disulphophenyl.

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- 30 The salt form of the carboxy and sulphonyl groups in the compounds according to the present invention is not critical. The cation may be any one of the usual non-chromophoric cations for anionic dyestuffs. Examples of such cations are alkali metal cations and cations of the ammonium type e.g. sodium, lithium, potassium, ammonium, mono-, di-, tri- and tetramethylammonium, triethylammonium, mono-, di- and triethanolammonium and mono-, di and triisopropylammonium. The preferred cations are sodium, lithium, potassium and ammonium, with sodium being the most preferred.

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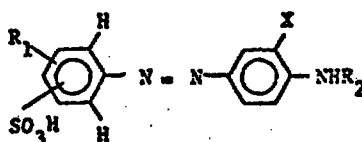
- 35 The present invention further provides a process for the preparation of monoazo dyestuff compounds having a sulphonyl aniline diazo component and an aniline coupling component, the ortho positions to the azo groups of such components being free from substituents and the amino group of said coupling component bearing a 1,6-trihalo-1,3,5-triazinyl fibre reactive group in which one halogen is replaced with an aromatic carbocyclic-substituted amino group which contains at least one water-solubilizing substituent comprising condensing cyanurotrihalogenide with a corresponding fibre-

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reactive group free monoazo dyestuff, or a mixture thereof,
and with an aromatic-substituted amine which contains at least one water solubilizing group, or a mixture thereof,

in any desired order, and optionally converting the product to a salt form.

- 5 Thus, the process for preparing the preferred dyes of formula I comprises
condensing cyanurotrihalogenide with a compound of formula II



and a compound of formula III, or a mixture thereof,



(III)

- 10 in any desired order, and optionally converting the product to the salt form. 10

The condensation reactions are carried out in accordance with known methods. The replacement of the halogen atoms of the cyanurotrihalogenide is preferably effected in a weakly acid to weakly alkaline medium. The replacement of the first halogen atom is suitably effected at temperatures from 0 to 5°C and the second at a higher temperature, preferably between room temperature and 65°C.

- 15 Suitably an acid binding agent such as sodium carbonate, sodium bicarbonate or sodium hydroxide is employed. The isolation of the compounds according to the invention is effected in accordance with known methods, for example by salting out, filtering and drying in vacuo. 15

The starting materials are either known or may be prepared by known methods from available starting materials.

- 20 The compounds according to the present invention and mixtures thereof in free acid or salt form are useful as reactive dyestuffs for dyeing or printing hydroxyl-group or amino-group-containing organic substrates. Preferred substrates are leather and textiles for example those comprising or consisting of neutral or synthetic polyamides such as wool, silk and nylon and especially those comprising or consisting of natural or regenerated cellulose such as cotton, viscose and spun rayon. The dyestuffs according to the invention give deep dyeings and have a good fixation yield as well as a short fixation time. 25

Dyeing and printing with the dyes of the invention may be carried out in accordance with known methods.

- 30 The dyeings and prints obtained exhibit notable light-fastness in conjunction with good general fastness properties such as wet-fastness, wash-fastness (especially repeated washing at the boil), sweat-fastness, and fastness to chlorine and hypochlorine bleach. 30

The dyestuffs and mixtures of the invention are suitable for combination dyeings employing dyestuffs of the same class and such combination dyeings do not exhibit catalytic fading.

- 35 The dyestuffs and mixtures of the invention form notably stable padding liquors and printing pastes and unbound dyestuff is easily washed off the substrate. 35

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

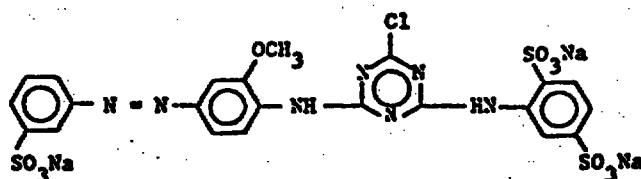
EXAMPLE 1

- 40 92.3 Parts of finely-powdered 2,4,6-trichloro-1,3,5-triazine are stirred to homogeneity in 500 parts ice water. With ice cooling, a solution of 126.5 parts 1-aminobenzene-2,5-disulphonic acid in 500 parts water and the necessary amount of a sodium hydroxide solution are added over a period of approximately 5 minutes and the whole is subsequently stirred for ca. 3 hours at 0—5°C. The pH is maintained at approximately 6 by the addition of a 3N sodium carbonate solution whereupon the condensation product goes into solution. 40

- 45 153.5 Parts of 4-amino-3-methoxy-1,1'-azobenzene-3'-sulphonic acid (prepared by coupling diazotized 1-aminobenzene-3-sulphonic acid with 1-amino-2-methoxybenzene-N-ω-methanesulphonic acid and splitting off the ω-methanesulphonic acid group) are stirred in 1000 parts water and the pH is adjusted to 7 by the addition of aqueous sodium hydroxide. Approximately 75 parts sodium bicarbonate are added thereto and the mixture is added over the course of 15 minutes to the solution of the condensation product obtained as described above. The temperature is raised over an hour to approximately 35—40° and the whole is stirred for 3—4 hours until the reaction is complete. 50

The dyestuff is salted out by the addition of sodium chloride, filtered and dried in vacuo at 100°.

The dyestuff which corresponds to the formula

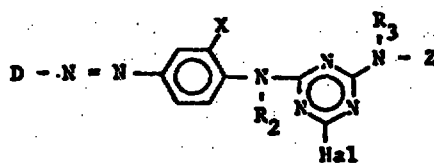


gives wool and regenerated cellulose dyeings of a slightly greenish yellow shade having good light- and wash-fastness.

5 In the following Table further dyestuffs are given which are prepared in analogy with the procedure described in Example 1 and owing to the isolation step are obtained in the sodium salt form. However, they may also be isolated in the free acid form employing conventional methods. In the table the symbol y denotes the dyeshade on cotton where a is yellow and b is reddish yellow. The dyestuffs correspond to the general formula

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TABLE 1

Ex.	D	X	R ₂	Hal	R ₃	Z	y
2	3-sulphophenyl	OCH ₃	H	F	H	2,5-disulphophenyl	a
3	do.	H	H	Cl	H	do.	a
4	do.	OC ₂ H ₅	H	Cl	H	do.	a
5	do.	CH ₃	H	Cl	H	do.	a
6	4-sulphophenyl	OCH ₃	H	Cl	H	do.	a
7	do.	do.	H	F	H	do.	b
8	do.	H	H	Cl	H	do.	b
9	do.	OC ₂ H ₅	H	Cl	H	do.	b
10	3-sulphophenyl	OCH ₃	H	Cl	H	2,5-disulpho-4-methylphenyl	a
11	do.	OC ₂ H ₅	H	Cl	H	do.	a
12	4-sulphophenyl	OCH ₃	H	Cl	H	do.	b
13	do.	do.	H	Cl	H	4-sulphophenyl	b
14	3-sulphophenyl	do.	H	Cl	H	2-carboxy-4-sulphophenyl	a
15	do.	do.	CH ₃	Cl	H	2,5-disulphophenyl	a
16	4-methoxy-3-sulphophenyl	H	H	Cl	H	do.	b
17	4-ethoxy-3-sulphophenyl	H	H	Cl	H	2,5-disulphophenyl	b
18	3-methyl-4-sulphophenyl	OCH ₃	H	Cl	H	do.	b
19	do.	OC ₂ H ₅	H	Cl	H	do.	b
20	3-methoxy-4-sulphophenyl	H	H	Cl	H	do.	b
21	do.	OCH ₃	H	Cl	H	do.	b
22	4-sulphophenyl	COONa	H	Cl	H	4-sulphophenyl	b
23	do.	do.	H	F	H	do.	b
24	do.	do.	H	Cl	H	3-sulphophenyl	b
25	do.	do.	H	Cl	H	2-methyl-4-sulphophenyl	b
26	3-sulphophenyl	do.	H	Cl	H	do.	a
27	do.	do.	H	Cl	H	2-carboxy-4-sulphophenyl	a

TABLE 1 (Continued)

Ex.	D	X	R ₂	Hal	R ₃	Z	y
28	4-sulphophenyl	COONa	H	Cl	H	2-carboxy-4-sulphophenyl	b
29	do.	do.	H	Cl	H	2-carboxy-5-sulphophenyl	b
30	do.	do.	H	Cl	H	2,5-disulphophenyl	b
31	3-sulphophenyl	do.	H	Cl	H	do.	a
32	do.	do.	H	F	H	do.	a

EXAMPLE A

- 5 2 Parts of the dye of Example 1 are dissolved in 100 parts warm water (ca. 40°) to which 10 parts urea have been added. 30 Parts 10% sodium hydroxide and 0.5 parts sodium salt of 1-nitrobenzene-3-sulphonic acid are added thereto. Spun rayon fabric is impregnated with this solution (take-up 75% of dry weight). After drying, the fabric is steamed for 5 to 10 minutes at 102°, rinsed and soaped at the boil for 15 minutes. After drying, a neutral yellow dyeing with good light- and wet-fastness is obtained. 5

EXAMPLE B

- 10 2 Parts of the dyestuff of Example 6 are dissolved in 50 parts water and 20 parts urea at 20°. After the addition of 15 parts 10% sodium carbonate the solution is made up to 100 parts by volume. The solution is padded onto 20 parts cotton fabric (take-up 80% of the dry weight). After intermediate drying the fabric is steamed at 103° for 10 minutes, rinsed, soaped at the boil, rinsed again and dried. A reddish-yellow dyeing with good fastnesses is obtained. 10

EXAMPLE C

- 15 Mercerised cotton satin is printed in accordance with known methods with a printing paste containing:— 15

25 parts dye of Example 1

100 parts urea

440 parts water

- 20 400 parts 4% sodium alginate 20

10 parts sodium salt of 1-nitrobenzene-3-sulphonate

25 parts sodium bicarbonate.

- 25 The printed textile is steamed for 4—8 minutes at 102—104°C and then cold- and hot- rinsed. After hot-soaping followed by rinsing and drying, a neutral yellow print with good light- and wet-fastness is obtained. 25

The dyestuffs of Example 2 to 5 and 7 to 32 may be employed for dyeing or printing in analogy with the procedure described in the above Examples A to C.

CLAIMS

- 30 1. A monoazo dyestuff compound having a sulphoaniline diazo component and an aniline coupling component, such components being free from substituents in ortho position to the azo group, the amine group of the coupling component bearing a 2,4,6-trihalo-1,3,5-triazinyl fibre-reactive group in which one halogen is replaced by an aromatic carbocyclic-substituted amino group which contains at least one water solubilizing group, or a mixture thereof which compound or mixture is in free acid or salt form. 30

TABLE 1 (Continued)

Ex.	D	X	R ₁	Hal	R ₂	Z	y
28	4-sulphophenyl	COONa	H	Cl	H	2-carboxy-4-sulphophenyl	b
29	do.	do.	H	Cl	H	2-carboxy-5-sulphophenyl	b
30	do.	do.	H	Cl	H	2,5-disulphophenyl	b
31	3-sulphophenyl	do.	H	Cl	H	do.	a
32	do.	do.	H	F	H	do.	a

EXAMPLE A

5 2 Parts of the dye of Example 1 are dissolved in 100 parts warm water (ca. 40°) to which 10 parts urea have been added. 30 Parts 10% sodium hydroxide and 0.5 parts sodium salt of 1-nitrobenzene-3-sulphonic acid are added thereto. Spun rayon fabric is impregnated with this solution (take-up 75% of dry weight). After drying, the fabric is steamed for 5 to 10 minutes at 102°, rinsed and soaped at the boil for 15 minutes. After drying, a neutral yellow dyeing with good light- and wet-fastness is obtained. 5

EXAMPLE B

10 2 Parts of the dyestuff of Example 6 are dissolved in 50 parts water and 20 parts urea at 20°. After the addition of 15 parts 10% sodium carbonate the solution is made up to 100 parts by volume. The solution is padded onto 20 parts cotton fabric (take-up 80% of the dry weight). After intermediate drying the fabric is steamed at 103° for 10 minutes, rinsed, soaped at the boil, rinsed again and dried. A reddish-yellow dyeing with good fastnesses is obtained. 10

EXAMPLE C

15 Mercerised cotton satin is printed in accordance with known methods with a printing paste containing:— 15

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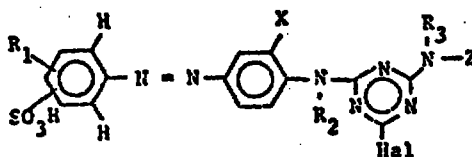
The dyestuffs of Example 2 to 5 and 7 to 32 may be employed for dyeing or printing in analogy with the procedure described in the above Examples A to C.

CLAIMS

30 1. A monoazo dyestuff compound having a sulphoaniline diazo component and an aniline coupling component, such components being free from substituents in ortho position to the azo group, the amine group of the coupling component bearing a 2,4,6-trihalo-1,3,5-triazinyl fibre-reactive group in which one halogen is replaced by an aromatic carbocyclic-substituted amino group which contains at least one water solubilizing group, or a mixture thereof which compound or mixture is in free acid or salt form. 30



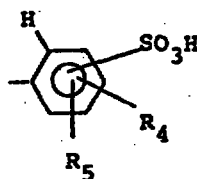
2. A compound or mixture of formula I,



in which R_1 is hydrogen, halogen, (C_{1-4}) alkyl or (C_{1-4}) alkoxy, X is hydrogen, (C_{1-4}) alkyl, (C_{1-4}) alkoxy or carboxy, each of R_2 and R_3 independently, is hydrogen or (C_{1-4}) alkyl, and Hal is fluorine, chlorine or bromine, and

Z is an aromatic-carbocyclic group containing at least one water-solubilizing group,

3. A compound or mixture according to Claim 2, in which Z is Z' , where Z' is a group of formula (a)



in which R_4 is hydrogen, sulpho or carboxy,

R_5 is hydrogen, chlorine, methyl, ethyl, methoxy or ethoxy.

4. A compound or mixture according to Claim 2 or Claim 3, in which R_1 is R'_1 , where R'_1 is hydrogen, methyl, methoxy or ethoxy.

5. A compound or mixture according to Claim 4, in which R_1 is R'_1 , where R'_1 is hydrogen, methyl or methoxy.

6. A compound or mixture according to Claim 5, in which R_1 is R''_1 , where R''_1 is hydrogen or methyl.

7. A compound or mixture according to any one of Claims 2 to 6, in which R_2 and R_3 are both hydrogen.

8. A compound or mixture according to any one of Claims 2 to 7, in which Z is Z''' , where Z''' is a group of formula (a) wherein R_5 is hydrogen, methyl or methoxy.

9. A compound or mixture according to any one of Claims 2 to 8, in which X is X' , where X' is hydrogen, methyl, methoxy, ethoxy or carboxy.

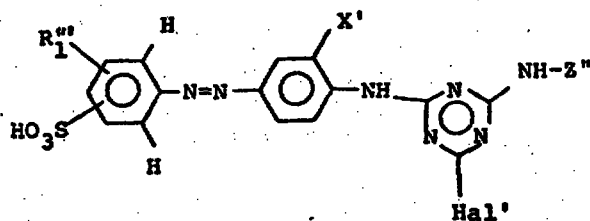
10. A compound or mixture according to any one of Claims 2 to 9, in which Z is Z^{iv} , where Z^{iv} is a group of formula (a) wherein R_5 is hydrogen or methyl.

11. A compound or mixture according to any one of Claims 2 to 10, in which Z is Z^v , where Z^v is a group of formula (a) wherein R_4 is sulpho or carboxy and R_5 is hydrogen or methyl.

12. A compound or mixture according to claim 2, in which any water solubilizing group in Z is sulpho or carboxy.

13. A compound or mixture according to any one of Claims 2 to 12, in which Hal is Hal' where Hal' is fluorine or chlorine.

14. A compound or mixture according to any one of Claims 2 to 13, of formula I_a,



and where R''_1 is hydrogen the sulpho group is in the 3-position and where R''_1 is methyl, the two groups are in ortho position to one another.

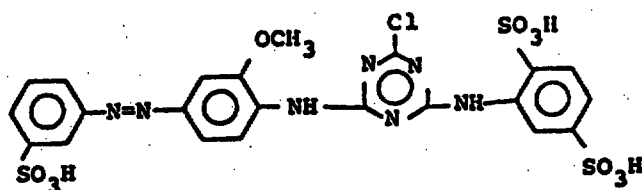
15. A compound or mixture according to any one of Claims 2 to 14, in which X is X'' , where X'' is hydrogen, methoxy or ethoxy.

16. A compound or mixture according to any one of Claims 2 to 15, in which X is X''' , where X''' is methoxy or ethoxy.

17. A compound or mixture according to any one of Claims 2 to 16, in which Z is disulphophenyl.

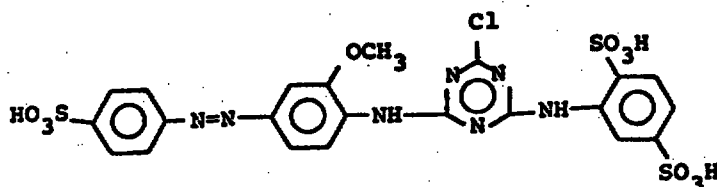


18. A compound of formula



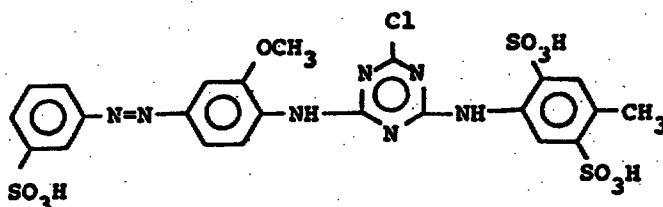
or a salt thereof.

19. A compound of formula



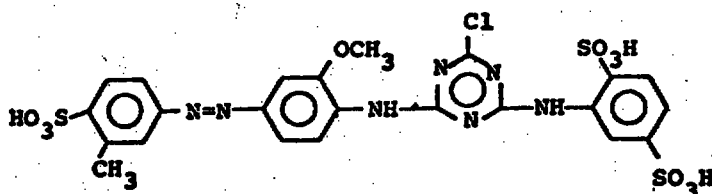
or a salt thereof.

20. A compound of formula



or a salt thereof.

21. A compound of formula



or a salt thereof.

22. A process for the production of a monoazo dyestuff compound as claimed in Claim 1, or a mixture thereof, comprising condensing cyanurotrihalogenide with a corresponding fibre-reactive free-containing monoazo dyestuff, or a mixture thereof, and with an aromatic-substituted amine which contains at least one water solubilizing group or a mixture thereof, in any desired order, and optionally converting the product to a salt form.

23. A process for the production of a monoazo dye as claimed in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 32.

24. A monoazo dye or mixture thereof, whenever prepared by a process according to Claim 22 or Claim 23.

25. A process for dyeing or printing hydroxyl-group or amino-group containing organic substrates comprising applying a compound or mixture according to any one of Claims 1 to 21 or 24, thereto.

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

27. A process for dyeing or printing hydroxyl-group or amino-group containing organic substrates substantially as hereinbefore described with reference to any one of Examples A to C.

28. Dyed or printed substrates whenever obtained by a process according to any one of Claims 25 to 27.

