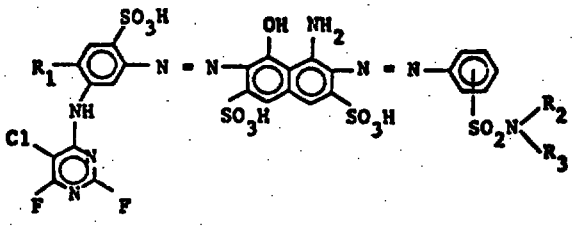
SPECIFICATION

Difluoro-chloropyrimidyl-group containing disazo compounds

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

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



I

in which

R_1 is hydrogen or methyl,

either,

R_2 is hydrogen; C_{1-6}alkyl; C_{1-4} alkyl monosubstituted by halogen or phenyl; C_{1-4}alkyl monosubstituted in the 2-, 3- or 4-position by hydroxy or C_{1-2}alkoxy; C_{5-7}cycloalkyl optionally substituted by up to three C_{1-4}alkyl radicals; phenyl optionally substituted by up to two substituents selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy; or $—CH_2CH_2SO_3H$, and

R_3 is hydrogen or C_{1-6}alkyl,

or,

R_2 and R_3, together with the nitrogen atom to which they are bound form a saturated 5- or 6-membered heterocyclic ring optionally containing a further hetero atom,

and mixtures thereof,

which compounds and mixtures are in free acid or salt form.

By halogen is meant fluorine, chlorine or bromine. Any unsubstituted alkyl radical as R_2 and/or R_3 is linear or branched and preferably contains 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, with methyl being especially preferred.

Any substituted alkyl as R_2 is preferably linear and the alkyl portion preferably contains 1 to 3 carbon atoms. The preferred halogen substituents are chlorine and bromine. The preferred substituents on such alkyl as R_2 are hydroxy, phenyl, chlorine, bromine, methoxy and ethoxy.

Any cycloalkyl as R_2 preferably contains 5 or 6 carbon atoms and is preferably cyclohexyl. Any substituted cycloalkyl is preferably cyclohexyl substituted by up to three methyl groups. Most preferably any cycloalkyl as R_2 is unsubstituted cyclohexyl.

Any halogen substituents on phenyl as R_2 are preferably chlorine and bromine. Any substituted phenyl as R_2 is preferably substituted by up to two substituents selected from the group consisting of chlorine, methyl, methoxy and ethoxy. Most preferably any phenyl as R_2 is unsubstituted.

When R_2 and R_3, together with the nitrogen atom to which they are bound, form a saturated heterocyclic ring they preferably form a pyrrolidine, piperidine or morpholine ring.

R_1 is preferably hydrogen.

Preferably R_2 is R_2', where R_2' is hydrogen; C_{1-4}alkyl, C_{1-3}alkyl monosubstituted by chlorine, bromine or phenyl; C_{1-3}alkyl monosubstituted in the 2- or 3-position by methoxy, ethoxy or hydroxy; phenyl; or $—CH_2CH_2SO_3H$. More preferably R_2 is R_2'', where R_2'' is hydrogen, methyl, ethyl, phenyl, benzyl or $—CH_2CH_2SO_3H$. Most preferably R_2 is R_2''', where R_2''' is hydrogen, methyl, ethyl or $—CH_2CH_2SO_3H$ with hydrogen being especially preferred.

R_3 is preferably R_3', where R_3' is hydrogen or C_{1-4}alkyl, more preferably R_3 is R_3'', where R_3'' is hydrogen, methyl or ethyl, with hydrogen being especially preferred.

The group $—SO_2NR_2R_3$ is preferably in the 4-position relative to the azo group.

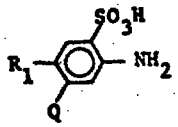
Preferred compounds of formula I are

(1) those in which R_2 is R_2' and R_3 is R_3' or R_2 and R_3, together with the nitrogen atom to which they are bound, form a pyrrolidine, piperidine or morpholine ring.
(2) those in which R_2 is R_2' and R_3 is R_3';
(3) those in which R_2 is R_2'' and R_3 is R_3'';
(4) those in which R_2 is R_2''' and R_3 is R_3'', especially hydrogen;
(5) those of (1) to (4) in which the $—SO_2NR_2R_3$ group is in the 4-position;
(6) those in which R_2 and R_3 are both hydrogen and the sulphonamide group is in the 4-position;
(7) those of (1) to (6) in which R_1 is hydrogen.

When the compounds of formula I are in the salt form, the cations of the sulpho groups are not critical and may be any of those non-chromophoric cations conventional in anionic reactive dyestuffs. Examples of suitable cations include alkali metals and substituted and unsubstituted ammonium cations such as lithium, sodium, potassium, ammonium, mono-, di-, tri- or tetramethylammonium,

triethylammonium and mono-, di- or triethanolammonium. Preferred cations are alkali metal and ammonium cations, with sodium being most preferred. Preferably the compounds of formula I are in salt form.

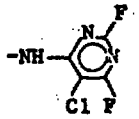
The present invention further provides a process for the production of compounds of formula I, or a mixture thereof, comprising coupling the diazotized amine of formula II



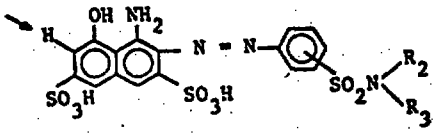
II

or a mixture thereof.

in which Q is a protected amino group or a radical of formula



with a compound of formula III,



III

or a mixture thereof,

in a weakly acid to weakly alkaline medium, and when Q is a protected amino group splitting off the same and condensing the free amino group with 2,4,6-trifluoro-5-chloropyrimidine.

Diazotization and coupling are effected in accordance with known methods. The preferred protecting group in Q is an acetyl group. The saponificiation of the protecting group is effected by known methods as is the condensation reaction with 2,4,6-trifluoro-5-chloropyrimidine.

The compounds of formula I may be isolated in accordance with known methods for example by salting out, filtering and drying in vacuo. In general owing to the process/isolation conditions the compounds of formula I are obtained in salt form or in a mixed salt form, however, the free acid form of the compounds of formula I may be obtained therefrom in accordance with known methods.

The amines of formula II are known. The compounds of formula III may be prepared in accordance with known methods for example, by coupling the diazotized sulphonamido-substituted aniline with 1-amino-8-hydroxynapthalene-3,6-disulphonic acid in an acid medium. The sulphonamido-substituted anilines are prepared in accordance with known methods for example, by reacting acetylaminobenzene sulphonylchloride with the amine HNR_2R_3 in weakly acid to weakly alkaline medium preferably at temperatures of from 20 to 80°C, followed by splitting off the protecting group.

The compounds of formula I and mixtures thereof are useful as reactive dyestuffs for dyeing and printing hydroxyl group- and/or amido group-containing organic substrates. Preferred substrates are textiles consisting of or comprising natural or synthetic polyamides such as wool, silk or nylon, and natural or regenerated cellulose such as cotton, viscose and spun rayon.

The compounds of formula I exhaust well and have good build-up power and are thus especially suitable for dyeing by the exhaust dyeing methods. Exhaust dyeing is carried out in accordance with conventional methods for reactive dyeings and especially deep dyeings are obtained with good fixation yields. Good dyeings are also obtained by the pad batch (short bath) process (up to 100°C) and by the continuous process.

The dyeings obtained have notable wet fastnesses such as wash-, water- and sweat fastness. Furthermore, the unbound dyestuff is easily removed from the substrate by washing.

The dyestuffs of the invention may also be employed for dyeing in combination with other dyestuffs.

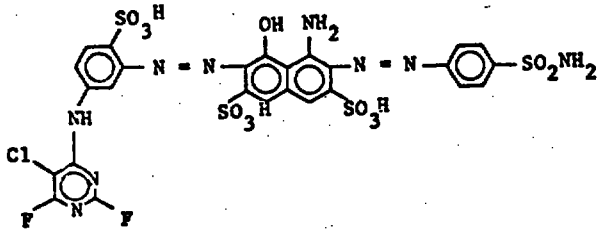
The following Examples further serve to illustrate the invention. In the Examples all parts are by weight and the temperatures are in degrees Centigrade.

EXAMPLE 1

A solution of 13.8 parts sodiumnitrite in 150 parts water is added dropwise, at a temperature not exceeding 7°, over a period of 20 minutes to a solution of 34.7 parts sulphanilamide in 300 parts water and 60 parts 30% hydrochloric acid, subsequently the reaction mixture is stirred for 30 minutes at the same temperature. A solution of 63.8 parts 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and 100 parts urea in 300 parts water, adjusted to pH 5.6 with 30% aqueous sodium hydroxide is added over 30 minutes to the resulting diazonium-salt suspension. Coupling is complete in 90 minutes. The

reaction mixture is adjusted from pH 1.2—1.5 to pH 6.0—6.5 with 30% aqueous sodium hydroxide whereby the monoazo dyestuff formed goes into solution.

68.9 Parts 30% hydrochloric acid are added with vigorous stirring to a suspension of 67.3 parts 1-amino-3-(5'-chloro-2',6'-difluoropyrimidyl-4')-aminobenzene-6-sulphonic acid in 400 parts water. At a temperature not exceeding 12° a solution of 13.8 sodium nitrite in 50 parts water are added dropwise thereto over 40 minutes and the whole is then stirred for a further 30 minutes. The resulting diazonium-salt suspension is poured onto the solution of the monoazo compound obtained as described above. The pH of the reaction mixture is adjusted to a value of 6.0 to 6.5 by the addition of 20% aqueous sodium carbonate solution and is kept at this value. Coupling is complete in 30 minutes and 405 parts sodium chloride are added (portionwise) thereto. The mixture is stirred for 30 minutes and the precipitated dyestuff is isolated and dried at 80—100° in vacuo. The dyestuff obtained is, in the free acid form, of formula



and dyes cotton navy blue by the exhaust dyeing method with good fixation yield when the amount of dyestuff is chosen so as to give a standard depth dyeing.

In analogy with the procedure described in Example 1, the compounds of formula I with R_1 =H given in the following Table may be prepared. The position of the $—SO_2NR_2R_3$ is with respect to the azo group. Taking the amount of each dyestuff which is required to give a standard depth dyeing, the dyestuffs of the Table give navy blue dyeings on cotton.

TABLE

Example No.	R_2	R_3	position $-SO_2NR_2R_3$
2	H	H	2
3	H	H	3
4	CH_3	H	4
5	do.	CH_3	4
6	do.	do.	3
7	C_2H_5	H	4
8	do.	C_2H_5	4
9	CH_3	H	3
10	do.	H	2
11	n-C_4H_9	H	3
12	do.	H	4
13	C_2H_9	H	2
14	$-CH_2CH_2SO_3Na$	H	4
15	do.	H	3
16	do.	H	2
17	do.	CH_3	2
18	do	do.	3
19	do.	do.	4
20	Isopropyl	H	3
21	$-CH_2CH_2OH$	H	3
22	do.	H	4
23	do.	CH_3	4
24	$-CH_2CH_2CH_2OH$	H	3
25	do.	H	4
26	Benzyl	H	4
27	do.	CH_3	4
28	do	H	2
29	Cyclohexyl	H	4
30	do.	CH_3	4

TABLE (Continued)

Example No.	R_2	R_3	position $-SO_2NR_2R_3$
31	Phenyl	H	4
32	R_2 und R_3 zusammen mit dem N-Atom: Morpholinyl		4
33	*p.* tolyl	H	4

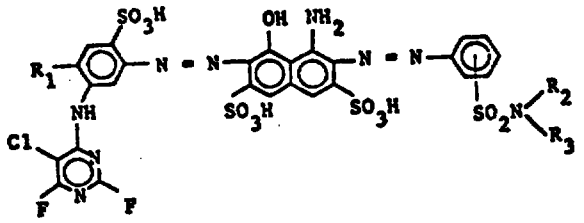
The dyestuffs of Examples 1 to 33 may be obtained in forms other than the sodium salt form in accordance with known methods by choosing the appropriate reaction/isolation conditions.

APPLICATION EXAMPLE

0.6 Parts of the dyestuff of Example 1 are dissolved in 200 parts water. 10 parts cotton are put in the dyebath and the temperature is raised to 40° within 10 minutes. 10 parts Glauber's salts are then added followed 30 minutes later by 4 parts soda. Dyeing is continued for a further 60 minutes. Then the dyed substrate is rinsed cold and then hot. The dyeing is soaped at the boil for 20 minutes in 500 parts water containing 0.25 parts sodiumalkylsulphonate detergent. After rinsing, a deep dyeing of a navy blue shade is obtained.

CLAIMS

1. A compound of formula I



I

in which

R_1 is hydrogen or methyl,

either,

R_2 is hydrogen; C_{1-6}alkyl; C_{1-4}alkyl monosubstituted by halogen or phenyl; C_{1-4}alkyl monosubstituted in the 2-, 3- or 4-position by hydroxy or C_{1-2}alkoxy; C_{5-7}cycloalkyl optionally substituted by up to three C_{1-4}alkyl radicals; phenyl optionally substituted by up to two substituents selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy; or $—CH_2CH_2SO_3H$, and

R_3 is hydrogen or C_{1-6}alkyl,

or,

R_2 and R_3, together with the nitrogen atom to which they are bound form a saturated 5- or 6-membered heterocyclic ring optionally containing a further hetero atom, and mixtures thereof, which compound and mixture is in free acid or salt form.

2. A compound according to Claim 1, in which any substituted alkyl as R_2 contains 1 to 3 carbon atoms and is monosubstituted by hydroxy, phenyl, chlorine, bromine, methoxy or ethoxy.

3. A compound according to Claim 1 or Claim 2, in which any unsubstituted or substituted cycloalkyl as R_2 is cyclohexyl or cyclohexyl substituted by up to three methyl groups.

4. A compound according to any one of Claims 1 or 3, in which any substituted phenyl as R_2 is phenyl substituted by up to two substituents selected from chlorine, methyl, methoxy and ethoxy.

5. A compound according to Claim 1 or Claim 2, in which any cycloalkyl as R_2 is unsubstituted cyclohexyl and any phenyl as R_2 is unsubstituted phenyl.

6. A compound according to any one of the preceding claims, in which R_2 is R_2', where R_2' is hydrogen; C_{1-4}alkyl, C_{1-3}alkyl monosubstituted by chlorine, bromine or phenyl; C_{1-3}alkyl monosubstituted in the 2- or 3-position by methoxy, ethoxy or hydroxy; phenyl; or $—CH_2CH_2SO_3H$; and R_3 is R_3', where R_3' is hydrogen or C_{1-4}alkyl; or R_2 and R_3 together with the nitrogen atom form a pyrrolidine, piperidine or morpholine ring.

7. A compound according to Claim 6, in which R_2 is R_2' and R_3 is R_3'.

8. A compound according to any one of the preceding claims, in which R_2 is R_2'', where R_2'' is hydrogen, methyl, ethyl, phenyl, benzyl or $—CH_2CH_2SO_3H$.

TABLE (Continued)

Example No.	R_2	R_3	position $-SO_2NR_2R_3$
31	Phenyl	H	4
32	R_2 und R_3 zusammen mit dem N-Atom: Morpholinyl		4
33	*p.* tolyl	H	4

The dyestuffs of Examples 1 to 33 may be obtained in forms other than the sodium salt form in accordance with known methods by choosing the appropriate reaction/isolation conditions.

APPLICATION EXAMPLE

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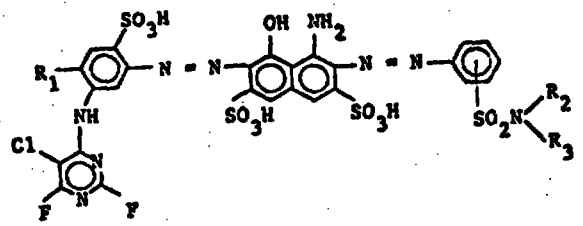
CLAIMS

1. A compound of formula I



I

in which

R_1 is hydrogen or methyl,

either,

R_2 is hydrogen; C_{1-6}alkyl; C_{1-4}alkyl monosubstituted by halogen or phenyl; C_{1-4}alkyl monosubstituted in the 2-, 3- or 4-position by hydroxy or C_{1-2}alkoxy; C_{5-7}cycloalkyl optionally substituted by up to three C_{1-4}alkyl radicals; phenyl optionally substituted by up to two substituents selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy; or $—CH_2CH_2SO_3H$, and

R_3 is hydrogen or C_{1-6}alkyl,

or,

R_2 and R_3, together with the nitrogen atom to which they are bound form a saturated 5- or 6-membered heterocyclic ring optionally containing a further hetero atom, and mixtures thereof, which compound and mixture is in free acid or salt form.

2. A compound according to Claim 1, in which any substituted alkyl as R_2 contains 1 to 3 carbon atoms and is monosubstituted by hydroxy, phenyl, chlorine, bromine, methoxy or ethoxy.

3. A compound according to Claim 1 or Claim 2, in which any unsubstituted or substituted cycloalkyl as R_2 is cyclohexyl or cyclohexyl substituted by up to three methyl groups.

4. A compound according to any one of Claims 1 or 3, in which any substituted phenyl as R_2 is phenyl substituted by up to two substituents selected from chlorine, methyl, methoxy and ethoxy.

5. A compound according to Claim 1 or Claim 2, in which any cycloalkyl as R_2 is unsubstituted cyclohexyl and any phenyl as R_2 is unsubstituted phenyl.

6. A compound according to any one of the preceding claims, in which R_2 is R_2', where R_2' is hydrogen; C_{1-4}alkyl, C_{1-3}alkyl monosubstituted by chlorine, bromine or phenyl; C_{1-3}alkyl monosubstituted in the 2- or 3-position by methoxy, ethoxy or hydroxy; phenyl; or $—CH_2CH_2SO_3H$; and R_3 is R_3', where R_3' is hydrogen or C_{1-4}alkyl; or R_2 and R_3 together with the nitrogen atom form a pyrrolidine, piperidine or morpholine ring.

7. A compound according to Claim 6, in which R_2 is R_2' and R_3 is R_3'.

8. A compound according to any one of the preceding claims, in which R_2 is R_2'', where R_2'' is hydrogen, methyl, ethyl, phenyl, benzyl or $—CH_2CH_2SO_3H$.

9. A compound according to any one of the preceding claims, in which R_3 is R_3'', where R_3'' is hydrogen, methyl or ethyl.

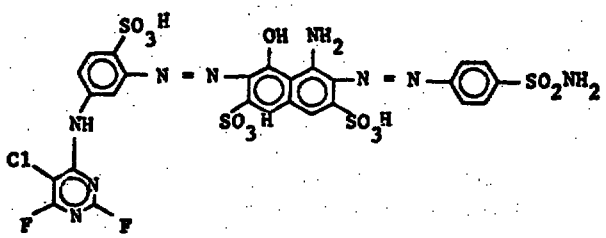
10. A compound according to Claim 9, in which R_3 is hydrogen.

11. A compound according to any one of the preceding claims in which R_2 is hydrogen.

12. A compound according to any one of the preceding claims, in which R_1 is hydrogen.

13. A compound according to any one of the preceding claims, in which the group $—SO_2N_2R_3$ is in the 4-position with respect to the azo group.

14. The compound of formula

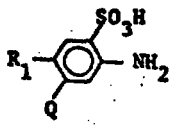


in free acid or salt form.

15. The compound according to Claim 14, in sodium salt form.

16. A compound according to any one of Examples 1 to 33.

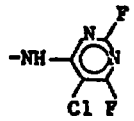
17. A process for the production of a compound of formula I, as defined in Claim 1, or a mixture thereof, comprising coupling the diazotized amine of formula II



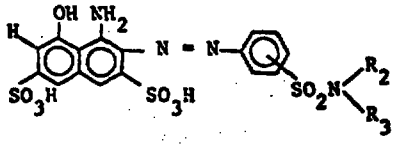
II

or a mixture thereof.

in which Q is a protected amino group or a radical of formula



with a compound of formula III,



III

or a mixture thereof,

in a weakly acid to weakly alkaline medium, and when Q is a protected amino group splitting off the same and condensing the free amino group with 2,4,6-trifluoro-5-chloropyrimidine.

18. 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 33.

19. A compound of formula I, whenever obtained by a process according to Claim 17 or Claim 18.

20. A process for dyeing or printing hydroxy- or amido-group-containing organic substrates comprising employing a compound or mixture according to any one of Claims 1 to 16 or 19, as dyeing or printing agent.

21. A process according to Claim 20, in which the substrate is a textile consisting of or comprising natural or synthetic polyamide or natural regenerated cellulose.

22. A process according to Claim 21, in which the substrate consists of wool, silk, nylon, cotton, viscose or spun rayon.

23. A process according to any one of Claims 20 to 22 in which dyeing is effected by the exhaust dyeing method.

24. A process for dyeing hydroxy-group- or amido-group-containing organic substrates substantially as hereinbefore described with reference to the Application Example.

25. Dyed or printed substrates whenever obtained by a process according to any one of Claims 20 to 24.

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