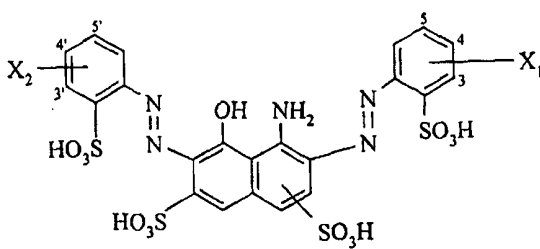




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09B 62/25, D06P 3/66	A1	(11) International Publication Number: WO 00/49092 (43) International Publication Date: 24 August 2000 (24.08.00)
(21) International Application Number: PCT/IB00/00169 (22) International Filing Date: 17 February 2000 (17.02.00) (30) Priority Data: 9903683.2 19 February 1999 (19.02.99) GB (71) Applicant (for all designated States except JP): CLARIANT FINANCE (BVI) LIMITED [-/-]; Citco Building, Wickhams Cay, P.O. Box 662, Road Town, Tortola (VG). (71) Applicant (for JP only): CLARIANT INTERNATIONAL LTD. [CH/CH]; Rothausstrasse 61, CH-4132 Muttenz (CH). (72) Inventor: GISLER, Markus; F.J. Dietschy-Weg 2, CH-4310 Rheinfelden (CH). (74) Agents: D'HAEMER, Jan et al.; Clariant International Ltd., Rothausstrasse 61, CH-4132 Muttenz (CH).		(81) Designated States: BR, CN, ID, JP, KR, MX, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: FIBER-REACTIVE DISAZO DYESTUFFS <div style="text-align: center;">  </div> (57) Abstract <p>The invention is concerned with compounds according to formula (I) and salts thereof, or a mixture of such compounds or salts. These compounds are useful as fiber-reactive dyestuffs in dyeing and printing hydroxy-group-containing and nitrogen-containing organic substrates.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

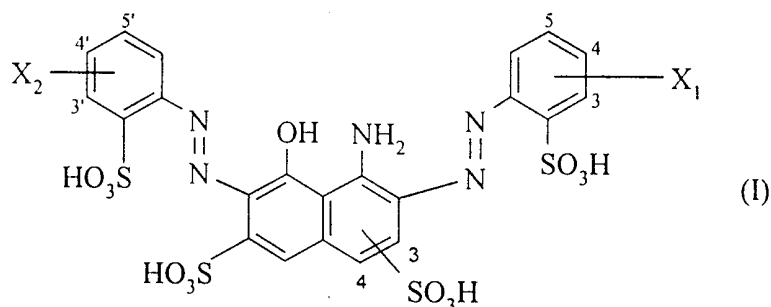
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FIBER-REACTIVE DISAZO DYESTUFFS

This invention relates to fiber-reactive disazo compounds and a process for their production. These compounds are suitable for use as fiber-reactive dyestuffs in any conventional dyeing or printing processes.

More particularly, the invention provides compounds of formula (I)



and salts thereof, or a mixture of such compounds or salts, in which

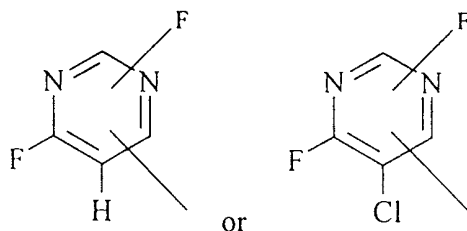
X_1 is $-\text{SO}_2\text{Z}$,

X_2 is $-\text{NRQ}$,

Z is a group $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{Y}$ in which Y is a group which can be split off under alkaline conditions,

R is hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl

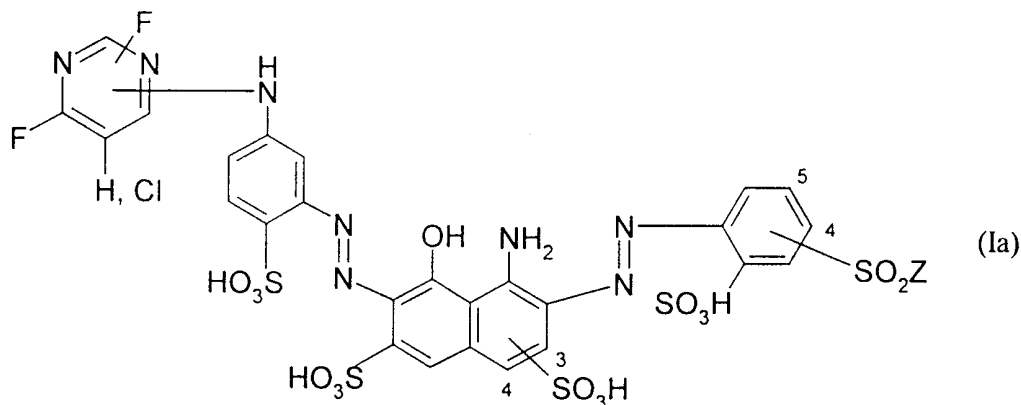
Q is



Preferred meanings of Y are $-\text{OSO}_3\text{H}$, $-\text{Cl}$ and $-\text{SSO}_3\text{H}$, especially preferred is $-\text{OSO}_3\text{H}$.

Preferably, R is hydrogen.

More preferred compounds of formula (I) correspond to formula (Ia)



and salts thereof.

Preferably, the $-\text{SO}_3\text{H}$ group is in 3 position.

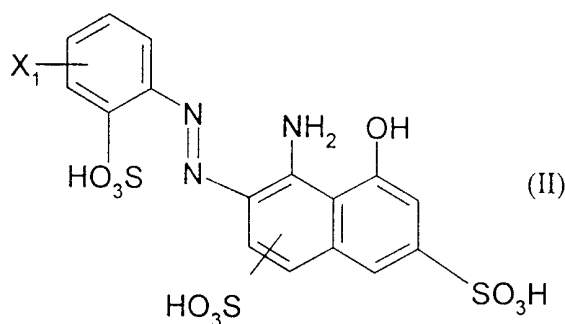
Preferably, the $-\text{SO}_2\text{Z}$ group is in 4 position.

When a compound of formula (I) is in salt form, the cation associated with the sulpho groups and any carboxy group is not critical and may be any one of those non-chromophoric cations conventional in the field of fiber-reactive dyes provided that the corresponding salts are water-soluble. Examples of such cations are alkali metal cations and unsubstituted and substituted ammonium cations, *e.g.*, lithium, sodium, potassium, ammonium, mono-, di- and tri-ethanolammonium.

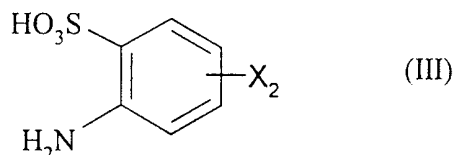
The preferred cations are the alkali metal cations and ammonium, with sodium and potassium being the most preferred.

In a compound of formula (I) the cations of the sulpho groups can be the same or different, *e.g.*, they can also be a mixture of the above mentioned cations meaning that the compound of formula (I) can be in a mixed salt form.

The invention further provides a process for the preparation of compounds of formula (I) or mixtures thereof which is characterized by coupling a compound of formula (II)



with a diazotized amine of formula (III)



wherein X_1 is the rest $-SO_2Z$ and X_2 is $-NRQ$, and optionally compounds with the rest $-SO_2CH_2CH_2Y$ are converted to compounds with the rest $-SO_2CH=CH_2$.

Compounds of formula (II) are obtained by diazotisation and coupling of appropriate amines with an 1-amino-8-hydroxynaphthalene disulfonic acid.

Compounds of formula (III) carrying the rest $-NRQ$ are obtained by condensation of the appropriate starting material with 2,4,6-trifluoro- or 5-chloro-2,4,6-trifluoropyrimidine.

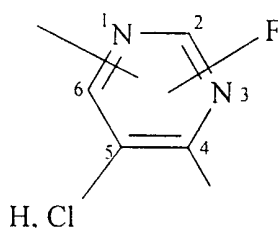
The condensation reaction of the amino compound with 2,4,6-trifluoropyrimidine or 5-chloro-2,4,6-trifluoropyrimidine is carried out in a manner known per se, preferably at 0° to 50°C , more preferably at 10° to 20°C , and at a pH of about 5 - 7.

The diazotisation and coupling reactions are effected in accordance with conventional methods; coupling is preferably carried out at 5° to 30°C , the first coupling to a compound of formula (II) in an acidic medium at a pH of 0 to 4, the second coupling to a compound of formula (I) in a weakly acidic to weakly basic reaction medium at a pH of 4 to 9.

The compounds of formula (I) may be isolated in accordance with known methods, for example, by conventional salting out with an alkali metal salt, filtering and drying optionally in vacuum and at slightly elevated temperatures.

Depending on the reaction and isolation conditions, a compound of formula (I) is obtained in free acid or preferably salt form or even mixed salt form containing, for example, one or more of the above mentioned cations. It may be converted from free acid to a salt form or mixture of salt forms or vice versa or from one salt form to another by conventional means.

It should be noted that any group Q which is a pyrimidinyl radical with a floating fluoro substituent according to the formula



can occur in two isomeric forms where the floating fluoro substituent is bound either to the 2- or to the 6-position.

In general, it is preferred to use this mixture as it is without resorting to the isolation of a single isomer for use, but should this be desired it can be readily achieved by conventional methods.

The compounds of formula (I) and mixtures thereof are useful as fiber-reactive dyestuffs for dyeing or printing hydroxy group- or nitrogen-containing organic substrates. Preferred substrates are leather and fiber material comprising natural or synthetic polyamides and, particularly, natural or regenerated cellulose such as cotton, viscose, lyocell fibers and spun rayon. The most preferred substrate is textile material comprising cotton.

Dyeing or printing is effected in accordance with known methods conventional in the fiber-reactive dyestuff field. Preferably, for the compounds of formula (I) the exhaust dyeing method is

used at temperatures within the range of 30° to 100°C, particularly at 40° - 80°C, respectively, whereby a liquor to goods ratio of 6:1 to 30:1 is used and more preferably of 10:1 to 20:1.

The compounds of this invention have good compatibility with known fiber-reactive dyes; they may be applied alone or in combination with appropriate fiber-reactive dyestuffs of the same class having analogous dyeing properties such as common fastness properties and the extent of ability to exhaust from the dyebath onto fiber. The dyeings obtained with such combination mixtures have good fastness properties and are comparable to those obtained with a single dyestuff.

The compounds of formula (I) give good exhaust and fixation yields when used as dyestuffs. Moreover, any unfixed compound is easily washed off the substrate. The dyeings and prints derived from the compounds of formula (I) exhibit good light fastness and good wet fastness properties such as wash, water, seawater and sweat fastness. They also exhibit good resistance to oxidation agents such as chlorinated water, hydrochloride bleach, peroxide bleach and perborate-containing washing detergents.

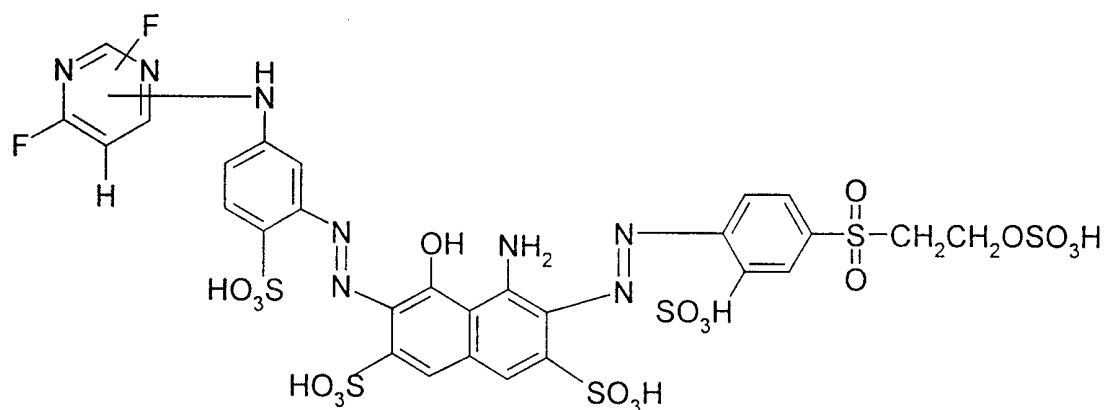
The new dyestuffs can also be used in the preparation of printing inks which are suitable for the ink jet process.

The following examples illustrate the invention. In the examples all parts and percentages are by weight unless indicated to the contrary, and all temperatures are given in degrees Centigrade.

EXAMPLE 1

497 parts 2-amino-5-(2'-sulfatoethylsulfonyl)benzene sulfonic acid are put into 1500 parts water under stirring and the violet suspension is cooled to about 0° to 5°C by addition of about 600 parts ice. At this temperature about 190 parts of a 40% sodium nitrite solution are added dropwise and at the same time 319 parts 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid are suspended in 1000 parts water. This suspension is combined with the first diazo suspension and the pH value is raised to 3 to 4 by addition of about 1250 parts of a 15% sodium carbonate solution.

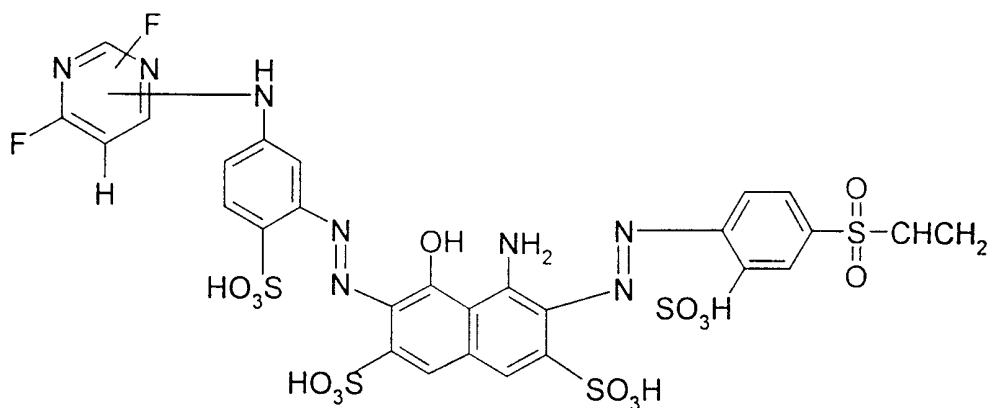
Independently, 332 parts of a condensation product obtained from 2,4-diaminobenzene sulfonic acid and 2,4,6-trifluoropyrimidine are diazotized and this second diazo suspension added to the suspension of the monoazo dyestuff. The pH value is raised further to 6 to 8 by addition of about 75 parts of the 15% sodium carbonate solution and the obtained solution spray dried. About 2000 parts of a bluish black salt containing powder are obtained which dyes cellulose fibers in deep navy shades. The dyestuff corresponds to the formula



and the dyeings have excellent fastnesses whereby the unfixed dyestuff can easily be washed out, even from deep dyeings.

EXAMPLE 2

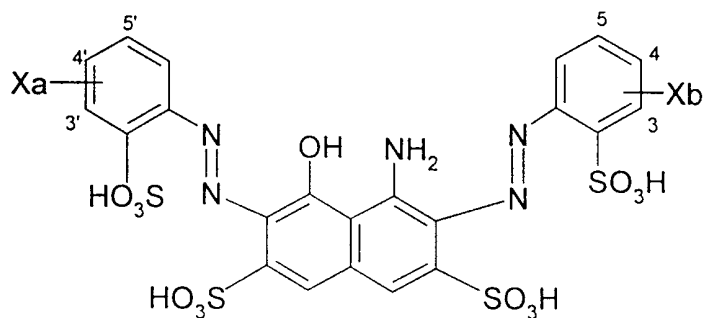
If the solution of the dyestuff obtained in Example 1 is treated at pH 10 with 400 parts of a 10% sodium hydroxide solution, the dyestuff in its vinylsulfonic form is obtained which corresponds to the formula



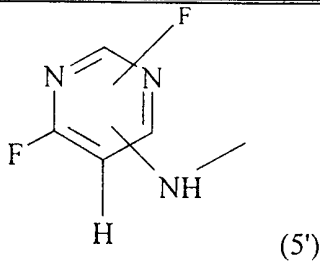
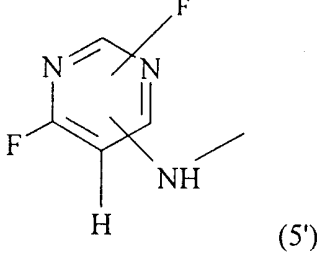
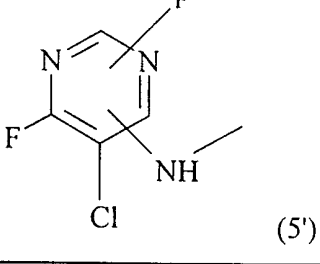
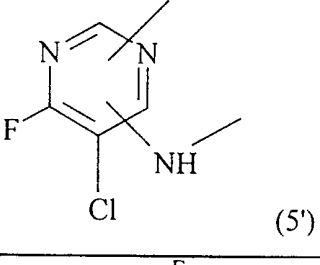
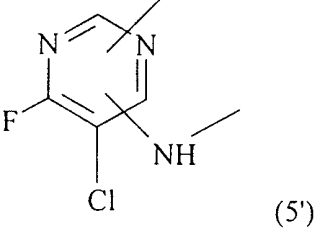
After neutralization of the solution with hydrochloric acid and spray drying of this solution, about 2100 parts of a bluish black salt containing powder are obtained which dyes cellulose fibers in deep navy shades. The fastnesses and the ability to be washed out correspond to the dyeings obtained in Example 1.

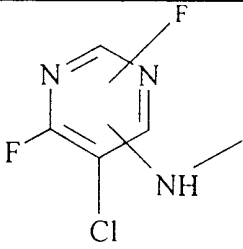
When using an analogous process and varying the amines to be diazotized, optionally also changing the sequence of coupling reactions, dyestuffs as illustrated in Table 1 can be obtained.

TABLE 1



EXAMPLES 3 - 8

Ex. No.	Xa (Pos.)	Xb (Pos.)
3	 (5')	-SO ₂ CH ₂ CH ₂ OSO ₃ H (4)
4	 (5')	-SO ₂ CH=CH ₂ (4)
5	 (5')	-SO ₂ CH ₂ CH ₂ OSO ₃ H (4)
6	 (5')	-SO ₂ CH=CH ₂ (4)
7	 (5')	-SO ₂ CH ₂ CH ₂ OSO ₃ H (5)

8	 (5')	-SO ₂ CH=CH ₂ (5)
---	---	---

APPLICATION EXAMPLE A

0.3 Part of the dyestuff of Example 1 is dissolved in 100 parts of demineralized water and 3g Glauber's salt (calcined) is added. The dyebath is heated to 50°C, then 10 parts of cotton fabric (bleached) are added. After 30 minutes at 50°C, 0.4 part of sodium carbonate (calcined) is added to the bath. During the addition of sodium carbonate the temperature is kept at 50°C. Subsequently, the dyebath is heated to 60°C, and dyeing is effected for a further one hour at 60°C.

The dyed fabric is then rinsed with running cold water for 3 minutes and afterwards with running hot water for a further 3 minutes. The dyeing is washed at the boil for 15 minutes in 500 parts of demineralized water in the presence of 0.25 part of Marseille soaps. After being rinsed with running hot water (for 3 minutes) and centrifuged, the dyeing is dried in a cabinet drier at about 70°C. A navy cotton dyeing is obtained showing good fastness properties, and particularly high wet fastness properties, which is stable towards oxidative influences.

APPLICATION EXAMPLE B

To a dyebath containing in 100 parts of demineralized water and 3g Glauber's salt (calcined) 10 parts of cotton fabric (bleached) are added. The bath is heated to 50°C within 10 minutes, and 0.5 part of the dyestuff of Example 1 is added. After a further 30 minutes at 50°C, 1 part of sodium carbonate (calcined) is added. The dyebath is then heated to 60°C and dyeing is continued at 60°C for a further 45 minutes.

The dyed fabric is rinsed with running cold and then hot water and washed at the boil according to the method of application Example A. After rinsing and drying a navy cotton dyeing is obtained which had the same good fastness properties as indicated in Application Example A.

Similarly, the dyestuffs of Examples 2 - 8 or mixtures of the exemplified dyestuffs are employed to dye cotton in accordance with the method described in Application Example A or B. The cotton dyeings thus obtained are navy and show good fastness properties.

APPLICATION EXAMPLE C

A printing paste consisting of

40	parts of the dyestuff of Example 1
100	parts of urea
350	parts of water
500	parts of a 4% sodium alginate thickener and
10	parts of sodium bicarbonate
<hr/>	
1000	parts in all

is applied to cotton fabric in accordance with conventional printing methods.

The printed fabric is dried and fixed in steam at 102 - 104°C for 4 - 8 minutes. It is rinsed in cold and then hot water, washed at the boil (according to the method described in Application Example A) and dried. An navy print is obtained which has good general fastness properties.

Similarly, the dyestuffs of Examples 2 to 8 or mixtures of the exemplified dyestuffs are employed to print cotton in accordance with the method given in Application Example C. All prints obtained are navy and show good fastness properties.

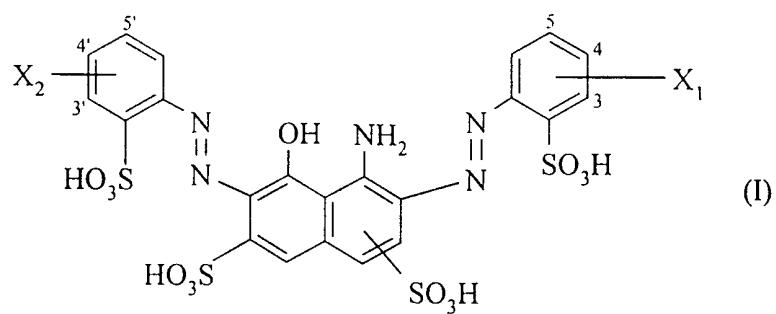
APPLICATION EXAMPLE D

2.5 parts of the dyestuff obtained in Example 1 are dissolved with stirring at 25°C in a mixture of 20 parts diethyleneglycol and 77.5 parts water to obtain a printing ink suitable for ink jet printing.

The dyestuffs of Examples 2 to 8 or dyestuff mixtures of Examples 1 to 8 can also be used in a manner analogous to that described in Application Examples D.

CLAIMS

1. Compounds of formula (I)



and salts thereof, or a mixture of such compounds or salts, in which

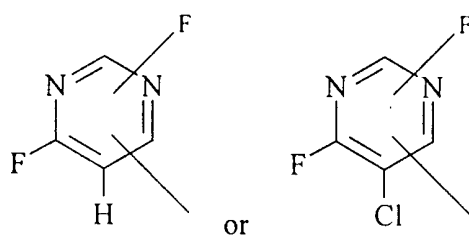
X_1 is $-\text{SO}_2\text{Z}$,

X_2 is $-\text{NRQ}$,

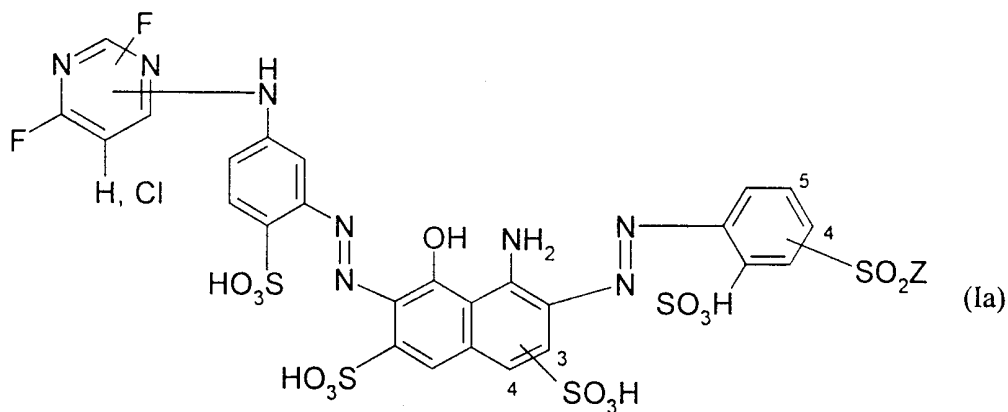
Z is a group $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{Y}$ in which Y is a group which can be split off under alkaline conditions,

each R is independently hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl and

Q is

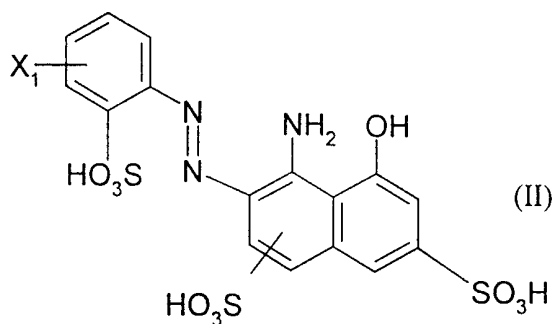


2. Compounds according to claim 1 which correspond to formula (Ia)

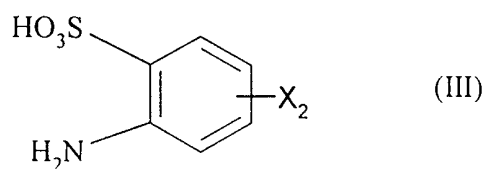


and salts thereof.

3. A process for the preparation of compounds of formula (I) or mixtures thereof which is characterized by coupling a compound of formula (II)



with a diazotized amine of formula (III)



in which formulae X_1 is the rest $-SO_2Z$ and X_2 is $-NRQ$, and optionally compounds with the rest $-SO_2CH_2CH_2Y$ converting to compounds with the rest $-SO_2CH=CH_2$.

4. A process for the preparation of printing inks comprising the use of a dyestuff or a mixture of dyestuffs according to claim 1.
5. A process of dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates wherein the dyeing or printing is performed with compounds according to formula (I), their salts or mixtures thereof.
6. Hydroxy-group-containing or nitrogen-containing organic substrates dyed or printed with compounds as defined in claim 1, their salts or mixtures thereof.
7. Textile material according to claim 6 consisting of or containing cotton dyed or printed with compounds in claim 1, their salts or mixtures thereof.
8. Compounds as hereinabove described with reference to any of the Examples 1 to 8.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 00/00169

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B62/25 D06P3/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 134 193 A (CIBA-GEIGY AG) 13 March 1985 (1985-03-13) claims 1-9; example 8 ---	1-8
Y	EP 0 167 490 A (CIBA-GEIGY AG) 8 January 1986 (1986-01-08) claims 1-14; examples 49,60 ---	1-8
Y	EP 0 455 054 A (BAYER AG) 6 November 1991 (1991-11-06) claims 1-8 ---	1-8
Y	EP 0 309 405 A (CIBA-GEIGY AG) 29 March 1989 (1989-03-29) claims 1-21; examples 17,18 ---	1-8
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 May 2000

Date of mailing of the international search report

11/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Herz, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 00/00169

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 262 533 A (SANDOZ LTD.) 23 June 1993 (1993-06-23) claims 1-17 ---	1-8
P,Y	EP 0 972 810 A (DYSTAR TEXTILFARBEN GMBH & CO. DEUTSCHLAND KG) 19 January 2000 (2000-01-19) claims 1-13 ---	1-8
Y	DE 41 25 754 A (BAYER AG) 4 February 1993 (1993-02-04) claims 1-7 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 00/00169

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 134193	A	13-03-1985	DE 3465104 D	03-09-1987
			DE 3468694 D	18-02-1988
			DE 3480794 D	25-01-1990
			EP 0133843 A	06-03-1985
			EP 0208331 A	14-01-1987
			JP 1596353 C	27-12-1990
			JP 2018706 B	26-04-1990
			JP 60069162 A	19-04-1985
			JP 1026619 B	24-05-1989
			JP 1545974 C	28-02-1990
			JP 60058470 A	04-04-1985
			JP 2132160 A	21-05-1990
			JP 5079262 B	01-11-1993
			JP 2175764 A	09-07-1990
			JP 5079263 B	01-11-1993
			US 4935501 A	19-06-1990
			US 4996304 A	26-02-1991
			US 4746732 A	24-05-1988
EP 167490	A	08-01-1986	JP 61062566 A	31-03-1986
EP 455054	A	06-11-1991	DE 4013986 A	07-11-1991
			DE 59103317 D	01-12-1994
			JP 4227767 A	17-08-1992
			US 5166325 A	24-11-1992
EP 309405	A	29-03-1989	AU 2241788 A	23-03-1989
			CA 1313188 A	26-01-1993
			DE 3889828 D	07-07-1994
			ES 2053804 T	01-08-1994
			JP 1097282 A	14-04-1989
			JP 2672346 B	05-11-1997
			KR 9616212 B	06-12-1996
			NZ 226248 A	26-10-1990
			US 4917705 A	17-04-1990
			US 4990599 A	05-02-1991
GB 2262533	A	23-06-1993	BR 9205067 A	29-06-1993
			CH 684482 A	30-09-1994
			CN 1074229 A,B	14-07-1993
			DE 4241924 A	24-06-1993
			ES 2062929 A	16-12-1994
			FR 2685342 A	25-06-1993
			JP 6220347 A	09-08-1994
			MX 9207425 A	01-07-1993
			PT 101146 A,B	31-03-1994
			TR 28458 A	04-07-1996
EP 972810	A	19-01-2000	DE 19832220 A	20-01-2000
			JP 2000072978 A	07-03-2000
DE 4125754	A	04-02-1993	DE 59209083 D	05-02-1998
			EP 0526792 A	10-02-1993
			JP 5247365 A	24-09-1993
			US 5538518 A	23-07-1996
			US 5436324 A	25-07-1995