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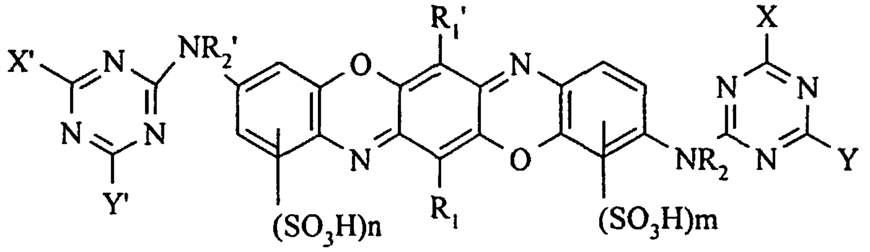
(54) Title: TRIPHENDIOXAZINE COMPOUNDS



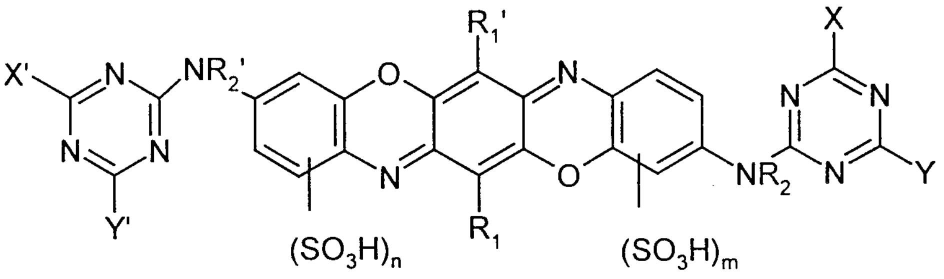
(I)

(57) **Abstract:** Compounds of formula (I) with the meanings of R_1, R_1', R_2, R_2', X, X', Y, Y', m and n as given in Claim 1 can be used as paper dyes or direct dyes or for the preparation of ink-jet inks.

Triphendioxazine Compounds

The invention relates to new triphendioxazine compounds, to a process for producing the new triphendioxazine compounds and to their use as direct dyestuffs.

According to the invention compounds of formula (I)



(I)

wherein

R_1 and R_1' independently from each other are hydrogen or halogen,

R_2 and R_2' independently from each other are hydrogen or C_{1-4}-alkyl,

X and X' independently from each other are optionally substituted aliphatic, aromatic, cycloaliphatic or heterocyclic amino or O-alkyl optionally substituted by a group selected from -OH, -COOH, $-NH_2$, -NHalkyl, $-N(alkyl)_2$, $-SO_3H$, -O-alkyl,

Y and Y' independently from each other and from X and X'have the same meaning as X and X',

m and n independently from each other have the value 1 or 2;

with the provisos that

(i) if Y = Y' is a β-sulfoethylamino radical then X = X' is neither β-sulfoethylamino nor amino nor morpholino nor 3-(β-sulfatoethyl-sulfonyl)-phenylamino nor 3-sulfo-phenylamino,

(ii) if Y = Y' is morpholino then X = X' is neither morpholino nor 4-sulfo-phenylamino,

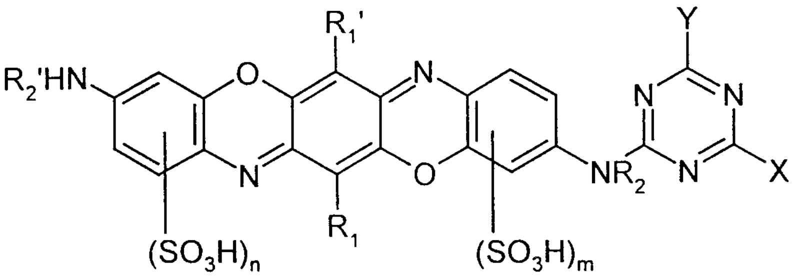
and salts thereof as well as mixtures of such compounds are provided.

In preferred compounds, mixtures and salts thereof R_1 and R_1' are halogen radicals, X, X', Y and Y' are optionally substituted aliphatic, aromatic, cycloaliphatic or heterocyclic amines and m and n have the value 1.

In most preferred compounds R_1 and R_1' are chlorine and R_2 and R_2' are hydrogen.

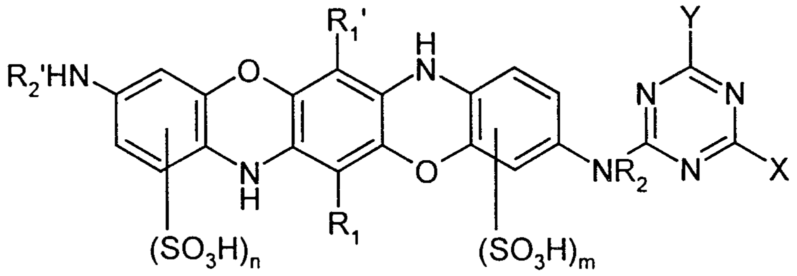
Examples for HX, HX', HY and HY' are monoethanolamine, diethanolamine, tetrahydro-1,4-oxazine, diethylaminopropylamine, 2-amino-propylamine, 1-amino-diethylaminoethane, 1-amino-dimethylaminopropane, N-(2-amino-ethyl)-tetrahydro-1,4-oxazine, N-(2-aminopropyl)-tetrahydro-1,4-oxazine, N,N-dibutylamino-propylamine, 3-methylamino-propylamine, 2-(3-aminopropyl)-aminoethanol, isopropylamino-ethylamine, N-(3-aminopropyl)-cyclohexylamine, N-(2-aminoethyl)-N-methylaniline, N,N-bis-(2-hydroxyethyl)-1,2-diaminopropane, N-(2-aminoethyl)-pyrrolidine, N-(3-aminopropyl)-pyrrolidine, 2-piperidino-ethylamine, N-(2-aminoethyl)-piperazine, N-phenyl-piperazine, N-methyl-ethanolamine 3-methoxypropylamine, 1-methylamino-ethyl-2-sulphonic acid, 1-aminobenzene-2-sulfonic acid, 1-amino-benzene-3-sulfonic acid, 1-amino-benzene-4-sulfonic acid, 2-amino-benzoic acid, 3-amino-benzoic acid, 4-amino-benzoic acid, 3-amino-6-methoxy-benzoic acid, 5-amino-isophthalic acid, 2-amino-naphthaline-6-sulfonic acid and 2-aminonaphthaline-1-sulfonic acid.

According to another aspect of the invention a process for producing compounds of formula (I) is provided which is characterized in that a compound of formula (II)

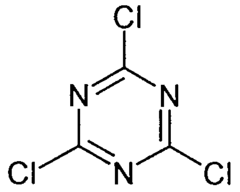


(II)

with the above-defined meanings of the symbols is reduced to the corresponding leuco form of formula (IIa)


(IIa)

with the same meanings for the substituents as defined above,
which is then reacted with one mole of the compound of formula (III)


(III)

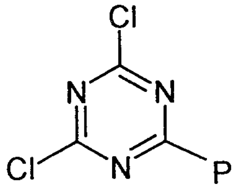
The remaining chlorine atoms of the triazine ring are replaced by X' and Y' by condensation and after oxidation a compound of formula (I) is obtained that can be isolated by known methods.

Depending on the meaning of X, X', Y and Y' the dioxazine compound can be symmetrically or asymmetrically substituted.

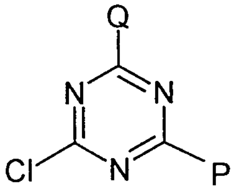
It is possible to prepare dioxazine compounds according to formula (I) with up to four different substituents attached to the triazine rings. In this way it is possible to design the compounds according to the desired needs. For example substituents with opposite ionogenicity may be introduced.

Alternatively, by replacement of all chlorine atoms with the same amino group, compounds with X = X' = Y = Y' may be obtained.

An alternative way to produce compounds according to formula (I) is to use triazine compounds according to formulae (IIIa) respectively (IIIb)



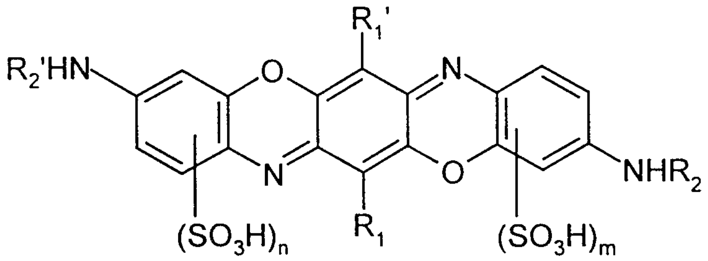
(IIIa) ;



(IIIb)

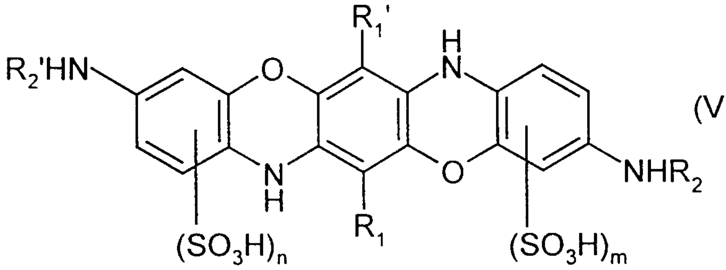
wherein P and Q signify X, X', Y or Y' as defined above.

Another procedure for producing the new dioxazine compounds is characterized in that first a compound of formula (IV)



(IV)

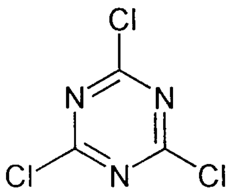
with the above defined meaning for R_1, R_1', R_2, R_2', m and n is reduced to the corresponding leuco form (V)



(V) .

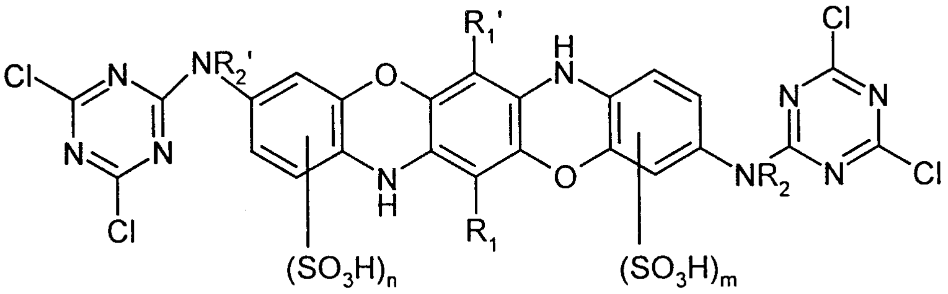
with the same definitions for substituents as defined above.

In the next step two moles of a compound of formula (III)



(III)

react with the compound of formula (V). The product of this reaction is a compound of formula (VI)



(VI)

with the above-defined meanings of the symbols.

In the next steps first of all two moles of a compound HX or HX' and two moles of a compound HY or HY' are reacted with the compound of formula (VI). A compound according to formula (I) is then obtained after oxidation.

Depending upon the methods of synthesis and purification, the new dyestuff can be obtained in free- or salt form. When the new dyestuff is obtained in salt form, the cation associated therewith is not critical and may be any one of those non-chromophoric cations conventional in the field of 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-, tri- and tetra-methylammonium, triethylammonium and mono-, di- and tri- ethanolammonium. The preferred cations are the alkali metal cations and ammonium, with sodium or lithium being the most preferred.

In the procedure of producing the new triphendioxazine compounds the starting compound of formula (II) can be synthesized by known processes. Preferably in a first step the cyanuric chloride is condensed to triphendioxazine backbone at a temperature of 0 - 10°C at a pH of 8 - 8.5. In a second step HX is condensed to the triazine ring at a temperature of 40 - 60°C at a pH of 5.5 - 6.5 and in a third step HY is condensed to the triazine ring at a temperature between 90 - 95°C at a pH of 8 - 8.5. As an alternative method mono- or bi-substituted cyanuric chlorides may be condensed to triphendioxazine backbone.

The reduction to the corresponding leuco form according to formula (IIa) respectively according to formula (V) can be done by known reducing agents under an inert gas atmosphere. Preferably powdery tin at room temperature is used at an acid pH value.

The condensation of the unsubstituted cyanuric chloride according to formula (III) with the corresponding leuco form according to formula (IIa) respectively according to formula (V) can be done under known conditions. Preferably at a pH between 5.5 - 6.5 and a temperature of 0 - 10°C under an inert gas atmosphere.
The condensation of the mono-substituted cyanuric chloride according to formula (IIIa) with the corresponding leuco form according to formula (IIa) respectively according to formula (V) can be done under known conditions. Preferably at a pH between 5.5 - 6.5 and a temperature of 40 - 60°C under an inert gas atmosphere.
The condensation of the bi-substituted cyanuric chloride according to formula (IIIb) with the corresponding leuco form according to formula (IIa) respectively according to formula (V) can be done under known conditions. Preferably at a pH between 5.5 - 8.5 and a temperature of 75 - 95°C under an inert gas atmosphere.

The oxidation of the triphendioxazine compound is done by known oxidizing agent under known conditions. Preferred oxidizing agent is oxygen.

The isolation is done under known conditions. Preferably it is done by precipitation with NaCl or ethanol.

In a new dyestuff according to the invention, the cations can be the same or different, e.g., they can also be a mixture of the above mentioned cations meaning that the dyestuff can be in a mixed salt form.

The compounds according to the invention, mixtures thereof or their salts may be used for dyeing cationic dyeable materials such as: homo- or mixed-polymers of acrylonitrile, acid modified polyester or polyamide; wool; leather including low affinity vegetable-tanned leather; cotton; bast fibers such as hemp, flax, sisal, jute, coir and straw; regenerated cellulose fibers, glass or glass products comprising glass fibers; and substrates comprising cellulose for example paper and cotton. They may also be used for printing fibers, filaments and textiles comprising any of the above mentioned materials in accordance with known methods. Printing may be effected by impregnation of the material to be printed with a suitable printing paste comprising one or more compounds of the present invention. The type of printing paste employed may vary depending on the material to be printed. Choice of a suitable commercially available printing paste or production of a suitable paste is routine for one skilled in the art. Alternatively the compounds of the present invention may be used in the preparation of inks suitable for example for jet printing, in accordance with conventional methods.

Most preferably, the dyestuffs are used for dyeing or printing of paper e.g., sized or unsized, wood-free or wood-containing paper or paper-based products such as cardboard. They may be used in continuous dyeing in the stock, dyeing in the size press, in a conventional dipping or surface coloring process. The dyeing and printing of paper is effected by known methods.

The dyeings and prints and particularly those obtained on paper, show good fastness properties.

The compounds of formula (I) may be converted into dyeing preparations. Processing into stable liquid, preferably aqueous, or solid (granulated or powder form) dyeing preparations may take place in a generally known manner. Advantageously suitable liquid dyeing preparations may be made by dissolving the dyestuff or its salt in suitable solvents such as formamide, dimethylformamide, urea, glycols and ethers thereof, dextrin or addition products of boric acid with sorbitol which may be used together with water, optionally adding an assistant, e.g. a stabilizer. Such preparations may be obtained, for example, as described in French patent specification No. 1,572,030.

The compounds of formula (I) (in the corresponding salt form) have good solubility especially in cold water. Owing to their high substantivity the compounds of the present invention exhaust practically quantitatively and show a good build-up power. They can be added to the stock directly, i.e. without previously dissolving, as either a dry powder or granulate, without reducing the brilliance or the yield of color. They can also be used in soft water without loss of yield. They do not mottle when applied on paper, are not inclined to give two-sided dyeing on paper and are practically insensitive to filler or pH variations. They operate over a broad pH range, in the range of from pH 3 to 10. When producing sized or unsized paper, the waste water is essentially colorless. This feature, which is extremely important from an environmental viewpoint, when compared with similar known dyes, shows a marked improvement. A sized paper dyeing when compared with the corresponding unsized paper dyeing does not show any decrease in strength.

The paper dyeings or printings made with the compounds, in particular the metal-free forms, according to the invention are clear and brilliant and have very good light fastness: On exposure to light for a long time, the shade of the dyeing fades tone in tone. They show very good wet fastness properties; being fast to water, milk, fruit juice, sweetened mineral water, tonic water, soap and sodium chloride solution, urine etc. Furthermore, they have good alcohol fastness properties. The wet fastness properties are improved compared to known dyes showing otherwise similar properties. They do not exhibit a tendency towards two-sidedness.

Paper dyed or printed with the compounds of the present invention can be bleached oxidatively, a feature that is important for the recycling of waste and old paper/paper products. This property, together with the improved backwater results and wet-fastness, shows a marked improvement over known dyes having otherwise similar properties.

The compounds of the present invention may also be used to dye paper containing wood-pulp where even dyeings, having good fastness properties are obtained. Furthermore, they may be used for the production of coated paper in accordance with known methods. Preferably when coating, a suitable filler, for example kaolin, is employed in order to give a one-side coated paper.

The compounds of the present invention are also suitable for the use as ink-jet inks.

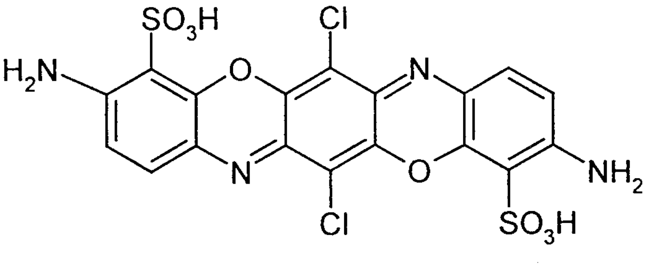
The compounds of the present invention are also suitable for dyeing in combination with other dyes for example other cationic or anionic dyes. The compatibility of the compounds of the present invention when used as a dye in mixtures with other commercially available dyes, may be determined according to conventional methods. The thus obtained dyeings have good fastness properties.

The invention further provides a substrate that has been dyed or printed with a compound of the present invention. The substrate may be selected from any of the above mentioned substrates. A preferred substrate is a substrate comprising cellulose such as cotton or paper or paper based product.

The following Examples further serve to illustrate the invention. In the Examples all parts and all percentages are by weight or volume, and the temperatures given are in degrees Celsius, unless indicated to the contrary.

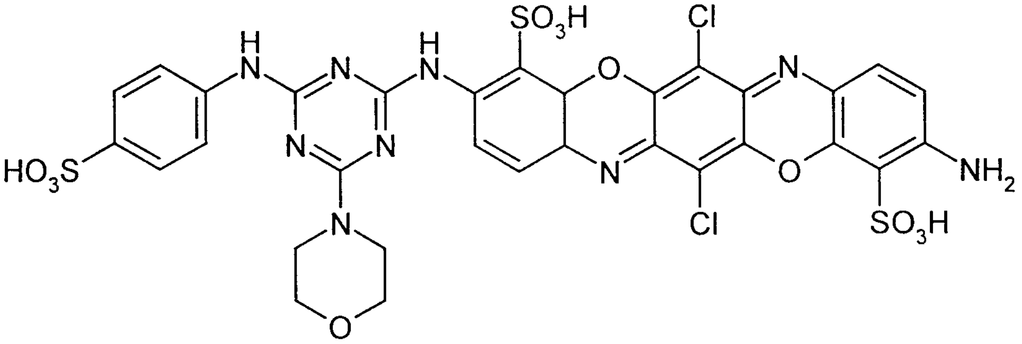
EXAMPLE 1

136.3 parts of compound A



(A)

are reacted with 55 parts of cyanuric chloride (compound III) at pH 8 - 8.5 and at a temperature of 0 - 10°C. Afterwards 50 parts of 4-aminobenzene sulfonic acid are added at a pH of 5.5 - 6.5 and a temperature of 50°C. 27 parts of tetrahydro-1,4-oxazine are added at a pH of 8 - 8.5 and a temperature of 90 - 95°C. The nascent hydrochloride acid is neutralized by a 4 N LiOH solution. Compound B

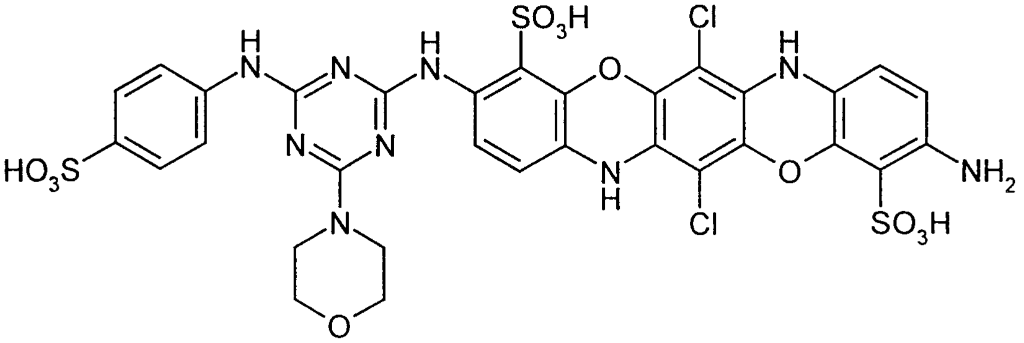


(B)

is obtained.

2500 parts of the compound B are suspended in 5 liter 5 M hydrochloride acid at room temperature under a nitrogen atmosphere. 50 parts of powdery tin are added to the suspension within 2 hours and the suspension is stirred until the color turns from blue-green to brown. Then the suspension is filtered and the filtrate is washed with 1 M hydrochloride acid.

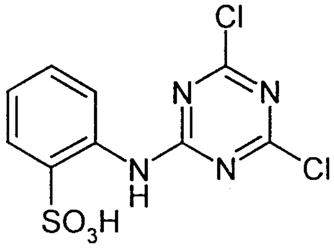
The moist presscake is kept under nitrogen. A compound of formula C



(C)

is obtained.

90 parts of compound D



(D)

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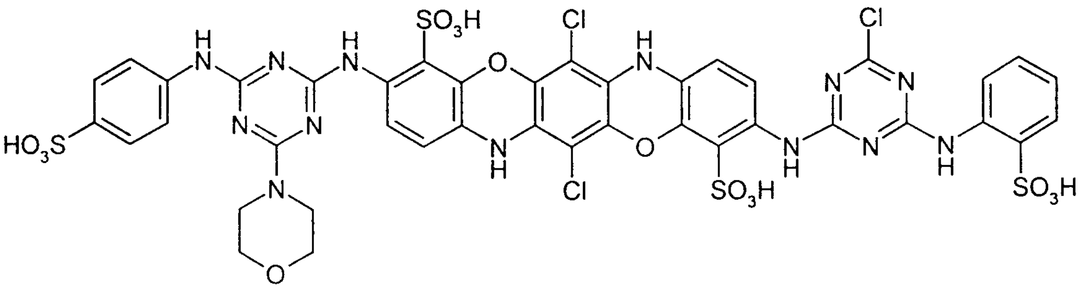
which is obtained by a condensation of compound (III) with 2-sulfophenylamino at a temperature of 0 - 10°C and at a pH of 6.5 - 7.5, are added at a pH of 5.5 - 6 and at a temperature of 45 - 50°C under a nitrogen atmosphere. The pH is adjusted by 4 N LiOH-solution.

3500 parts of a solution containing the compound E



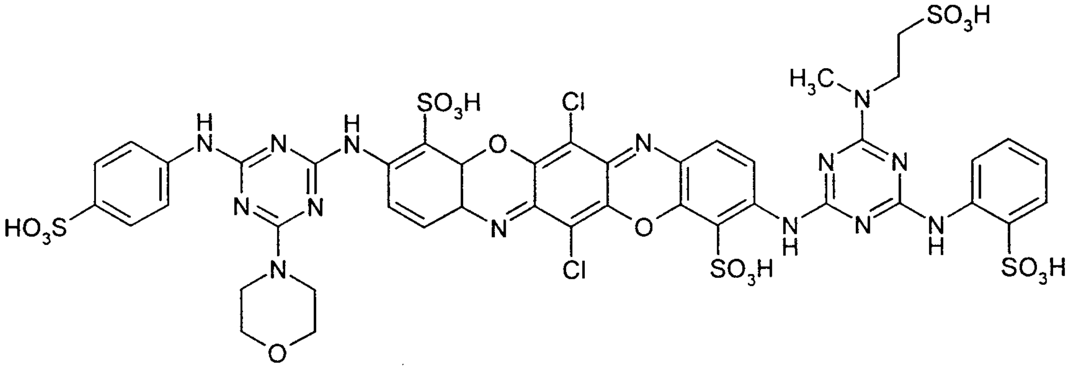
(E)

are obtained.

Afterwards the nitrogen atmosphere is removed and 50 parts of 1-methylamino-ethyl-2-sulfonic acid are added at a pH of 8 - 8.5 and a temperature of 90 - 95°C; the reoxidation occurs simultaneously. The pH value is adjusted by a 4 N LiOH solution.

The compound is precipitated by NaCl or ethanol and filtered and dried.

310 parts of a compound F

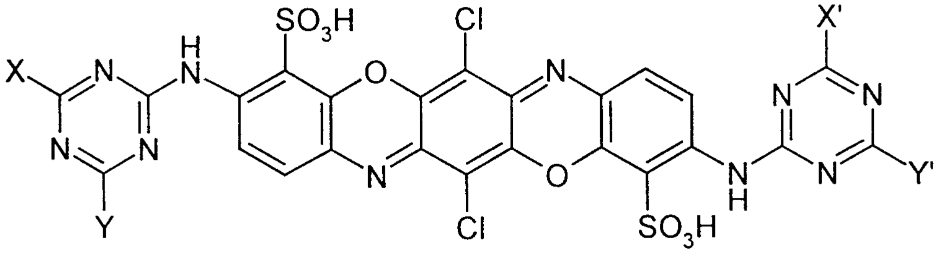


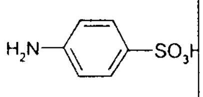
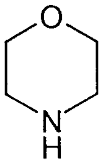
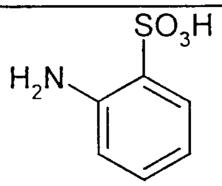
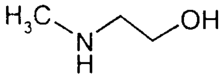
(F)

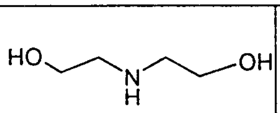
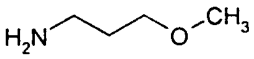
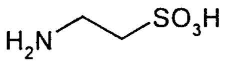
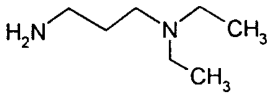
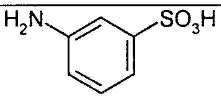
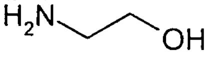
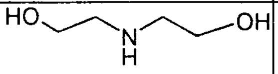
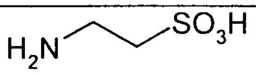
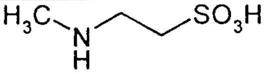
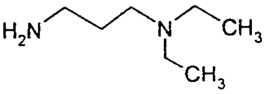
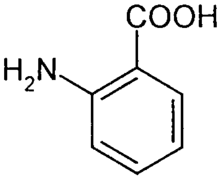
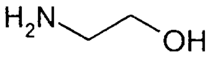
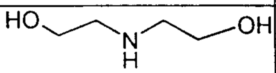
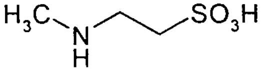
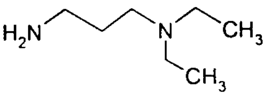
are obtained. The λ_{max} is 555.9 nm (in water and 1 % sodium acetate).

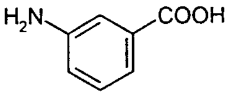
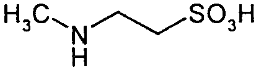
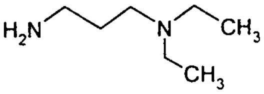
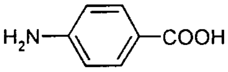
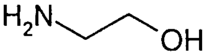
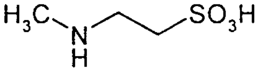
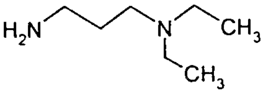
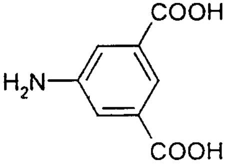
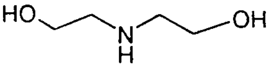
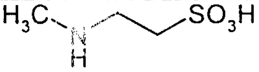
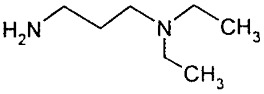
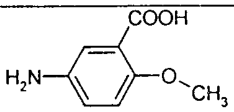
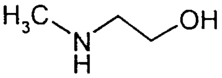
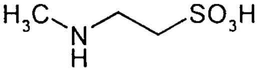
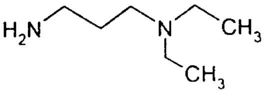
TABLE 1 Examples 2 - 67

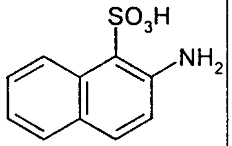
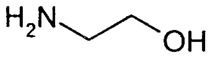
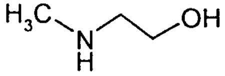
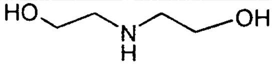
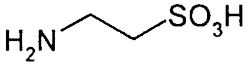
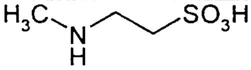
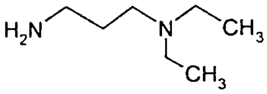
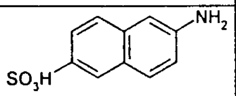
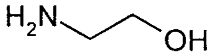
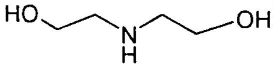
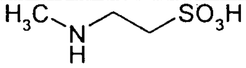
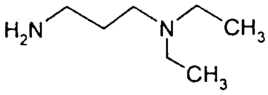
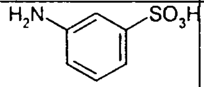
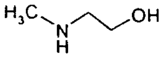
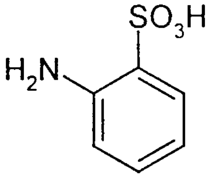
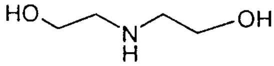
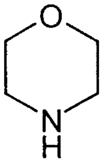
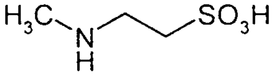
Analogously to Example 1 the following examples are obtained.

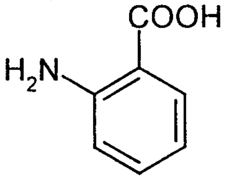
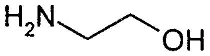
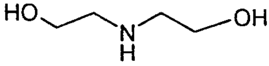
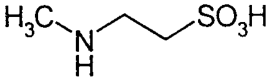
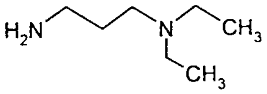
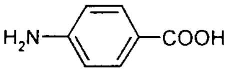
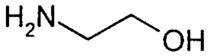
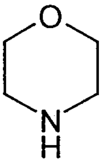
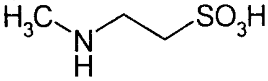
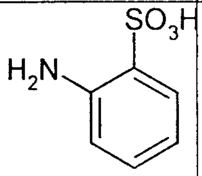
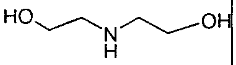
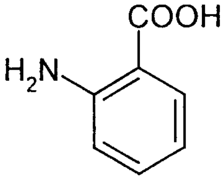
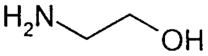
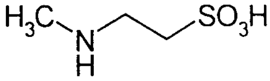
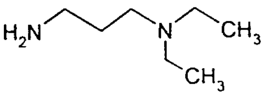
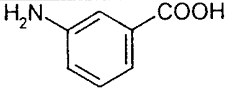
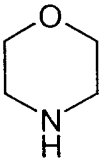
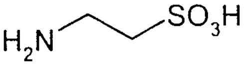


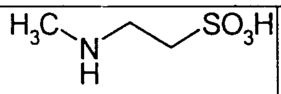
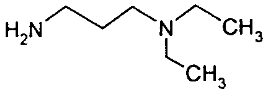
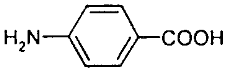
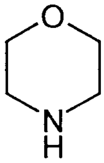
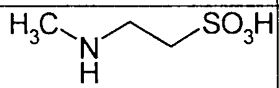
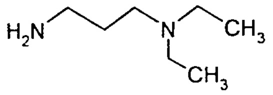
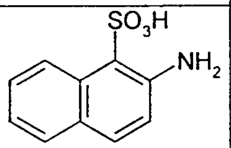
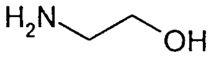
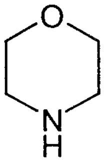
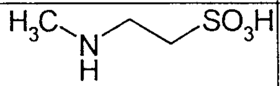
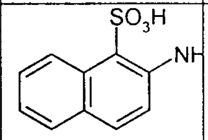
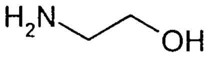
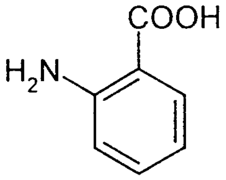
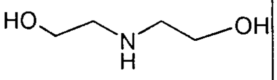
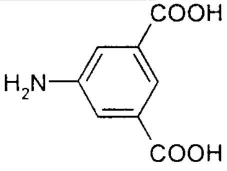
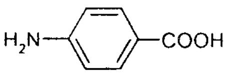
Ex.	X-H	Y-H	X'-H	Y'-H	λ_{max} 1)
2					550.2 nm

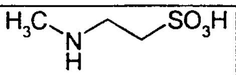
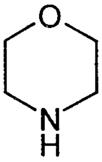
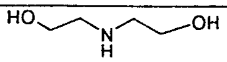
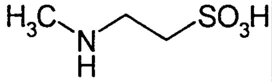
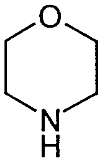
3	ditto	ditto	ditto		550.4 nm
4	ditto	ditto	ditto		549.9 nm
5	ditto	ditto	ditto		551.8 nm
6	ditto	ditto	ditto		552.1 nm
7	ditto	ditto			550.3 nm
8	ditto	ditto	ditto		550.0 nm
9	ditto	ditto	ditto		552.1 nm
10	ditto	ditto	ditto		552.4 nm
11	ditto	ditto	ditto		553.6 nm
12	ditto	ditto			551.7 nm
13	ditto	ditto	ditto		550.3 nm
14	ditto	ditto	ditto		554.2 nm
15	ditto	ditto	ditto		556.3 nm

16	ditto	ditto			550.1 nm
17	ditto	ditto	ditto		553.6 nm
18	ditto	ditto	ditto		554.3 nm
19	ditto	ditto			550.0 nm
20	ditto	ditto	ditto		552.3 nm
21	ditto	ditto	ditto		553.1 nm
22	ditto	ditto			549.8 nm
23	ditto	ditto	ditto		552.4 nm
24	ditto	ditto	ditto		553.7 nm
25	ditto	ditto			552.3 nm
26	ditto	ditto	ditto		554.6 nm
27	ditto	ditto	ditto		556.3 nm

28	ditto	ditto			560.1 nm
29	ditto	ditto	ditto		561.2 nm
30	ditto	ditto	ditto		560.4 nm
31	ditto	ditto	ditto		562.1 nm
32	ditto	ditto	ditto		562.7 nm
33	ditto	ditto	ditto		565.4 nm
34	ditto	ditto			549.7 nm
35	ditto	ditto	ditto		550.1 nm
36	ditto	ditto	ditto		552.1 nm
37	ditto	ditto	ditto		553.8 nm
38					551.0 nm
39	ditto	ditto	ditto		551.1 nm
40	ditto	ditto	ditto		554.3 nm

41	ditto	ditto			553.1 nm
42	ditto	ditto	ditto		552.5 nm
43	ditto	ditto	ditto		554.1 nm
44	ditto	ditto	ditto		557.0 nm
45	ditto	ditto			551.2 nm
46	ditto	ditto	ditto		550.1 nm
47	ditto	ditto	ditto		554.8 nm
48					553.0 nm
49	ditto	ditto	ditto		555.6 nm
50	ditto	ditto	ditto		557.3 nm
51	ditto	ditto			551.6 nm
52	ditto	ditto	ditto		554.3 nm

53	ditto	ditto	ditto		554.7 nm
54	ditto	ditto	ditto		555.1 nm
55	ditto	ditto			550.2 nm
56	ditto	ditto	ditto		553.4 nm
57	ditto	ditto	ditto		554.9 nm
58	ditto	ditto			561.3 nm
59	ditto	ditto	ditto		560.7 nm
60	ditto	ditto	ditto		563.2 nm
61					560.7 nm
62	ditto	ditto		ditto	558.3 nm
63	ditto	ditto		ditto	559.2 nm

64	ditto	ditto		ditto	561.1 nm
65	ditto	ditto	ditto		561.8 nm
66	ditto		ditto		563.2 nm
67	ditto	ditto	ditto		561.7 nm

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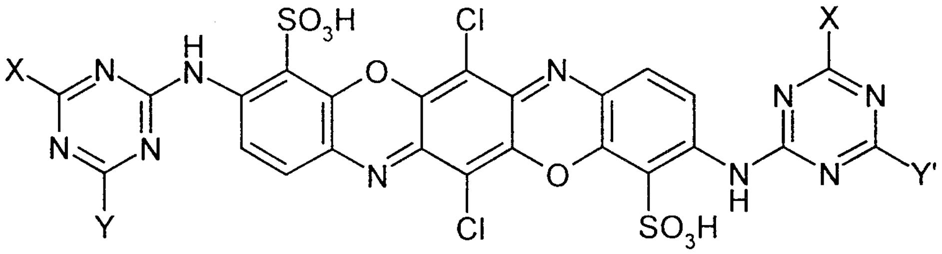
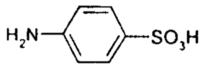
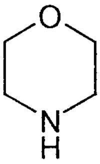
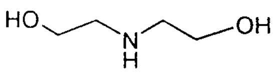
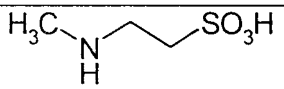
[1] all samples measured in water + 1% sodium acetate

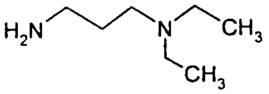
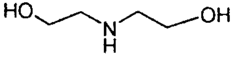
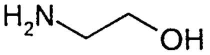
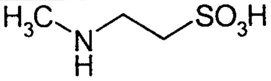
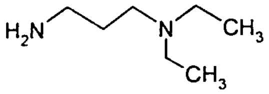
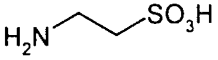
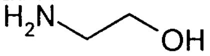
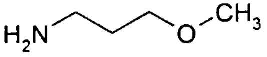
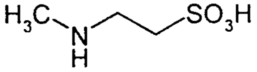
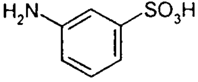
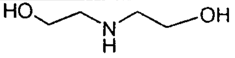
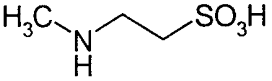
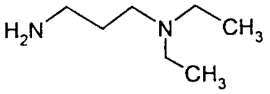
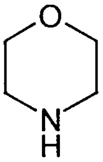
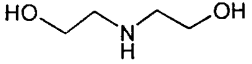
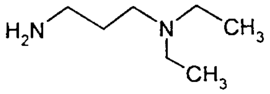
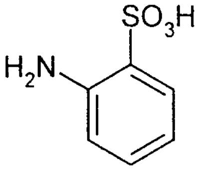
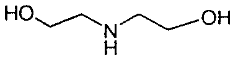
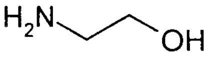
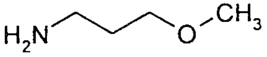
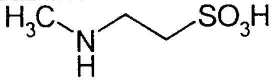
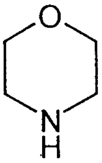
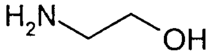
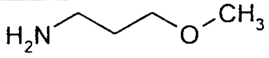
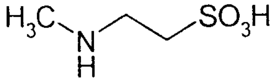
TABLE 2 Examples 68 - 112

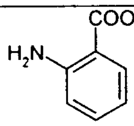
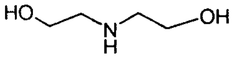
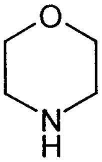
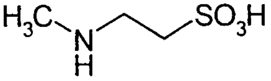
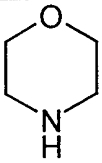
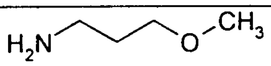
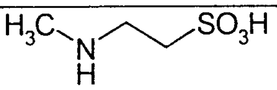
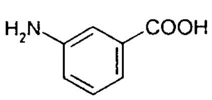
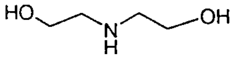
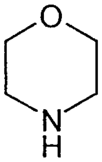
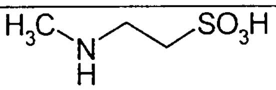
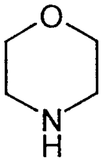
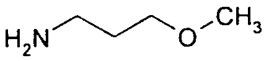
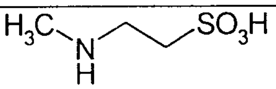
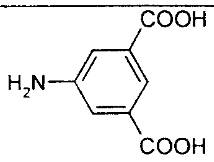
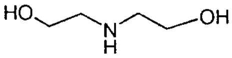
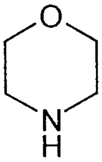
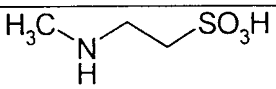
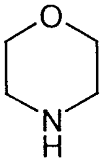
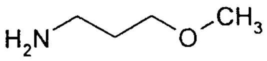
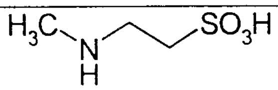
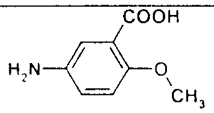
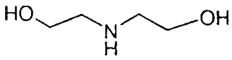
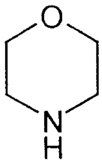
Analogously to Example 1 the Examples according to the following formula

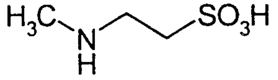
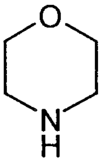
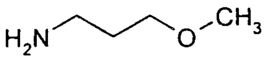
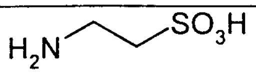
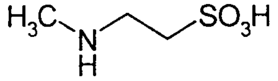
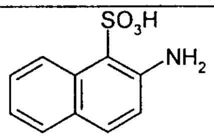
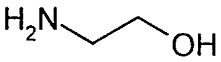
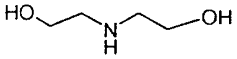
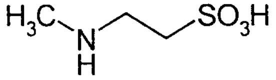
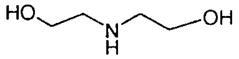
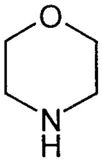
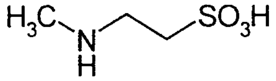
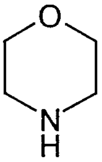
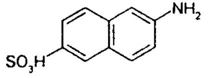
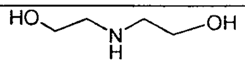
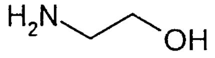
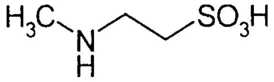
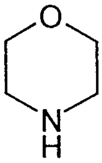
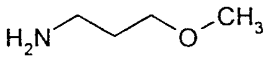
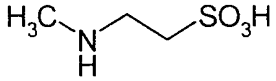


are obtainable.

Ex.	X-H	Y-H	Y'-H	λ_{max}[1]
68				549.4 nm
69	ditto	ditto		555.9 nm

70	ditto	ditto		546.9 nm
71	ditto			550.1 nm
72	ditto	ditto		552.7 nm
73	itto	ditto		553.0 nm
74	ditto			552.3 nm
75	ditto	ditto		552.8 nm
76	ditto		ditto	552.5 nm
77				552.7 nm
78	ditto	ditto		554.3 nm
79	ditto			550.1 nm
80	ditto	ditto		554.2 nm
81				549.8 nm
82	ditto	ditto		550.2 nm
83	ditto	ditto		552.1 nm
84	ditto			550.1 nm
85	ditto	ditto		550.3 nm
86	ditto	ditto		552.3 nm

87				550.4 nm
88	ditto	ditto		555.0 nm
89	ditto			551.0 nm
90	ditto	ditto		554.3 nm
91				554.2 nm
92	ditto	ditto		557.0 nm
93	ditto			551.2 nm
94	ditto	ditto		556.9 nm
95				551.4 nm
96	ditto	ditto		554.6 nm
97	ditto			550.3 nm
98	ditto	ditto		553.9 nm
99				552.7 nm

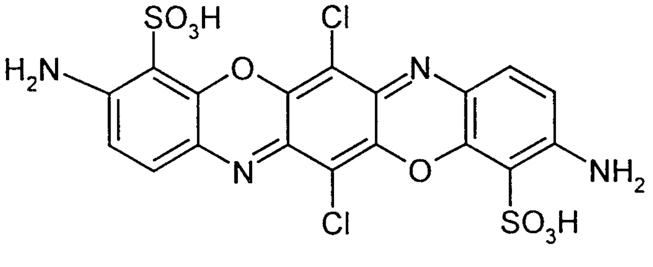
100	ditto	ditto		555.7 nm
101	ditto			551.4 nm
102	ditto	ditto		556.1 nm
103	ditto	ditto		556.4 nm
104				557.2 nm
105	ditto	ditto		560.3 nm
106	ditto			558.1 nm
107	ditto	ditto		561.2 nm
108	ditto		ditto	560.9 nm
109				550.7 nm
110	ditto	ditto		552.3 nm
111	ditto			550.0 nm
112	ditto	ditto		553.1 nm

[1] all samples measured in water + 1% sodium acetate

EXAMPLE 113

1. Preparation of Intermediate G

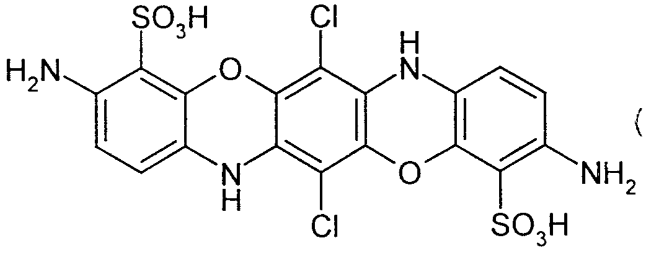
136.3 parts of compound A



(A)

are suspended in 5 liter 5 M hydrochloride acid at room temperature under a nitrogen atmosphere. 50 parts of powdery tin are added to the suspension within 2 hours and the suspension is stirred until the color turns from blue-green to brown. Then the suspension is filtered and the filtrate is washed with 1 M hydrochloride acid.

The moist filtrate is kept under nitrogen. 440 parts of this moist filtrate of formula G are obtained.

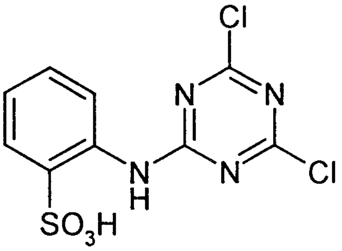


(G)

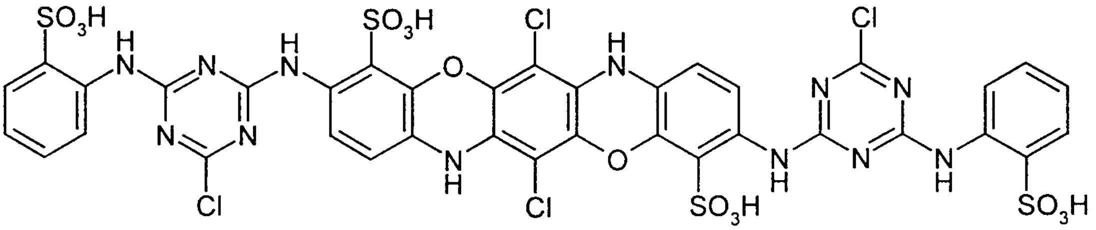
2. Preparation of Intermediate J

440 parts of the moist filtrate of the compound of formula G are suspended in 2500 parts of water under a nitrogen atmosphere at room temperature. The pH-value is adjusted at 6 with a 4 N LiOH-solution.

200 parts of compound H

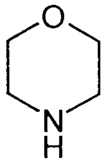

(H)

are added to suspension and the suspension is stirred at a temperature of 45 - 50°C and a pH of 5.5 - 6 until all educts have reacted. A compound of formula J is obtained.


(J)

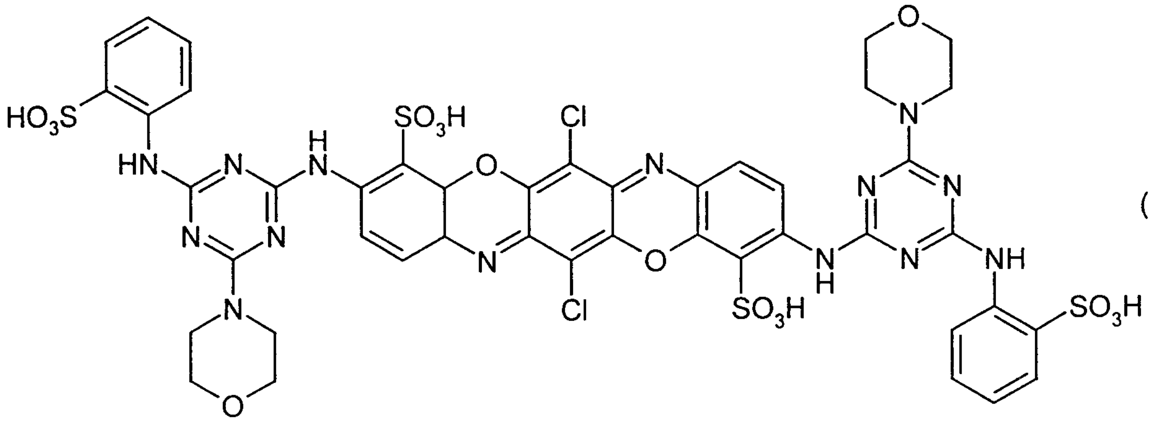
3. Preparation of Example 113:

65 parts of a compound with the formula E


(K)

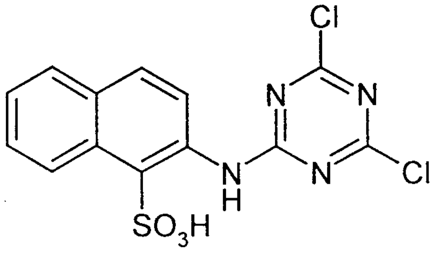
are added to 5300 parts of a solution with 0.25 mol of the compound J at 50°C and the solution is heated up to 90 - 95°C. The pH is kept at 8 - 8.5 with a 4 N LiOH-solution.

A dyestuff of formula L is obtained after an oxidation and a precipitation with NaCl or ethanol. Its λ_{max} is 550.2 nm (in water and 1 % sodium acetate).

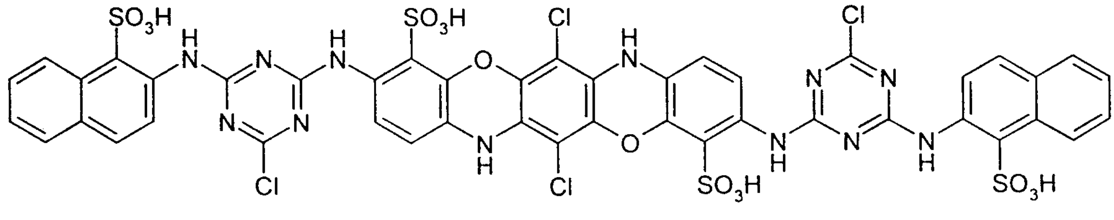

(L)

EXAMPLE 114

Analogously to Example 113 440 parts of the moist filtrate of formula M are added to 230 parts of compound G

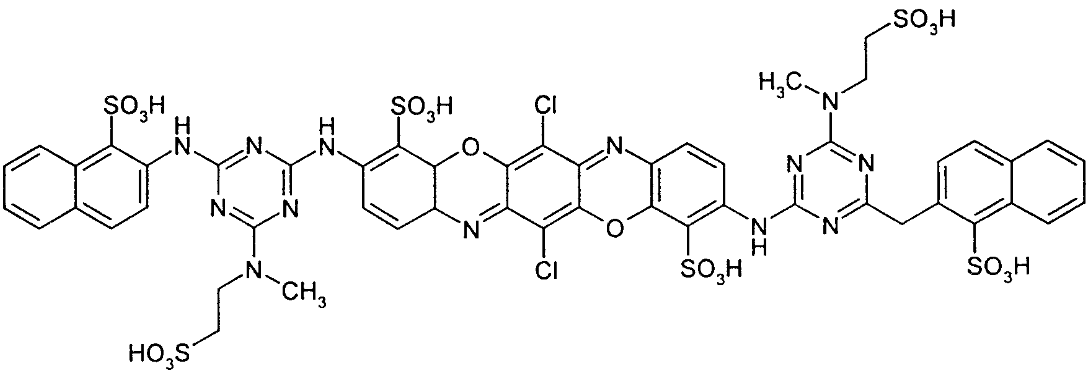

(M)

and the solution is stirred under a nitrogen atmosphere at pH 5.5 - 6 and a temperature of 45 - 50°C. A compound of formula N is obtained.


(N)

5300 parts of an aqueous solution containing 0.25 mol of the compound M are mixed with 100 parts of 1-methylamino-ethyl-2-sulfonic acid at 50°C. The solution is heated up to 90 - 95°C and the pH is kept at 8 - 8.5 by a 4 N LiOH-solution. After the oxidation and filtration 6000 parts of the solution are ultrafiltered by a suitable membrane such as e.g. G10, G20 or

G50. The solution is now concentrated to 4000 parts. This obtained liquid dyestuff formulation of the compound of formula O contains only traces of inorganic salts and shows an excellent storing property.

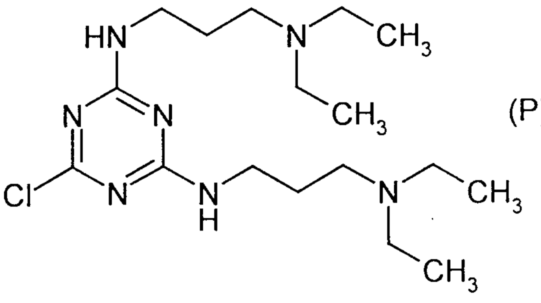


(O)

The λ_{max} of this formulation is 556.7 nm (in water and 1 % sodium acetate).

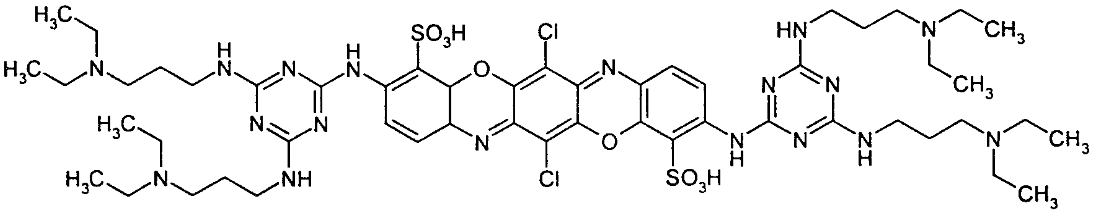
EXAMPLE 115

Analogously to Example 113 440 parts of the moist filtrate of formula G are mixed to 233 parts of the compound P



(P)

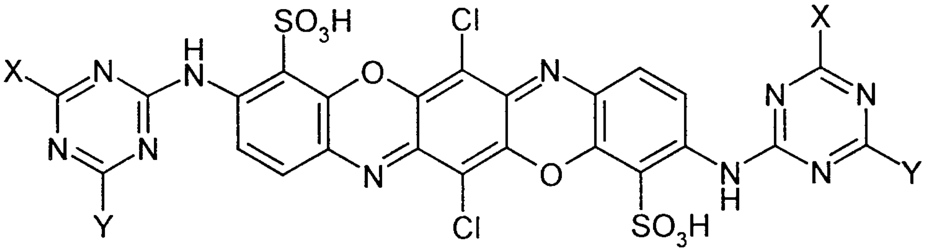
The solution is heated up to 95°C and stirred at a pH of 5.5 - 6 under a nitrogen atmosphere. Afterwards the leuco form is oxidized by oxygen. The dyestuff of formula R is filtered and washed by water. 300 parts of the dyestuff are obtained. This dyestuff is soluble in common organic acids such as e.g. lactic acid, formic acid or acetic acid and stable liquid dyestuff formulations are obtained. The λ_{max} value of this formulation is 656.6 nm (in DIF and 1 % glacial acetic acid).

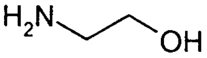
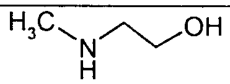
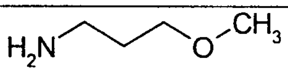
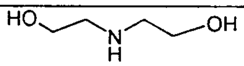
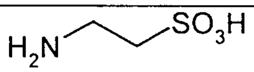
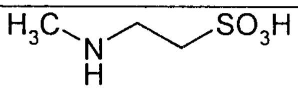
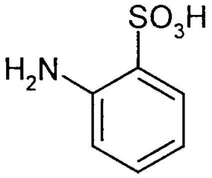
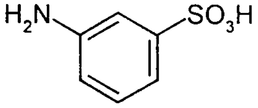
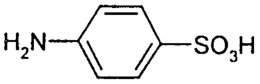
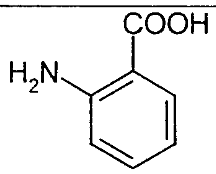
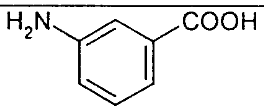
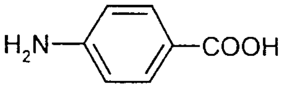
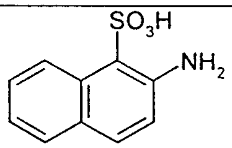
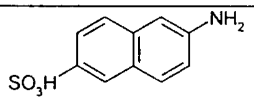
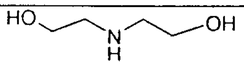
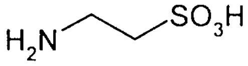
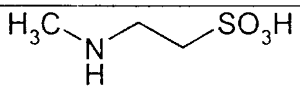


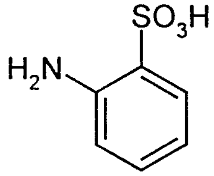
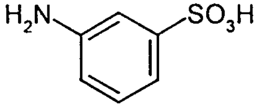
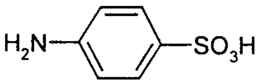
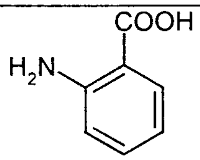
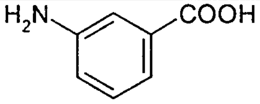
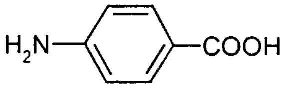
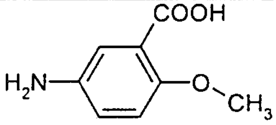
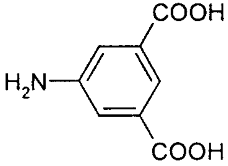
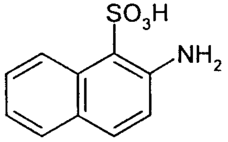
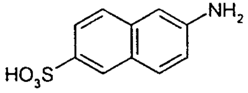
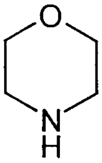
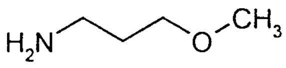
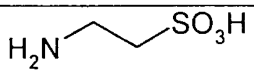
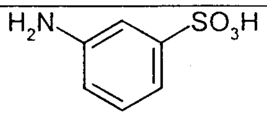
(R)

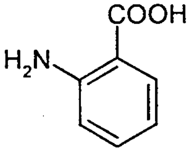
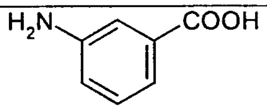
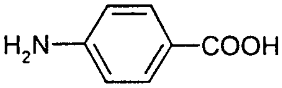
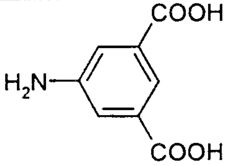
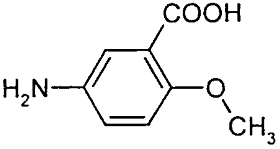
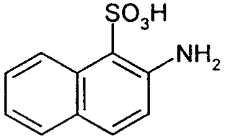
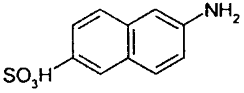
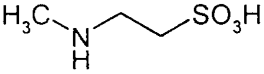
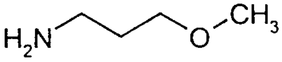
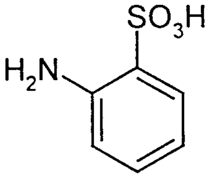
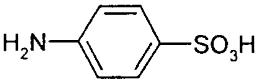
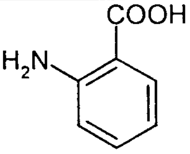
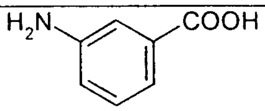
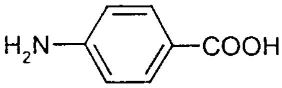
TABLE 3 Examples 116 - 194

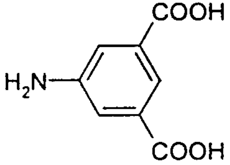
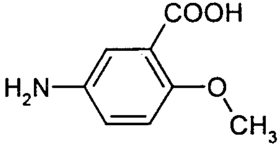
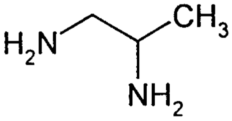
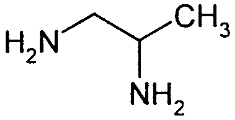
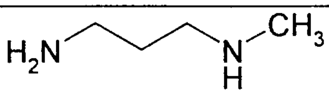
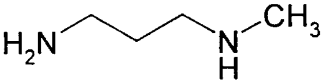
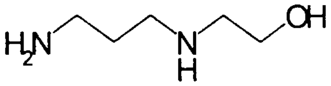
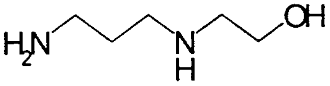
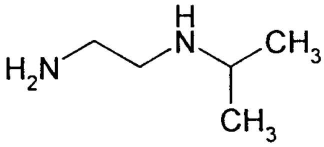
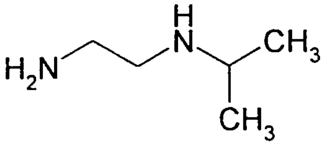
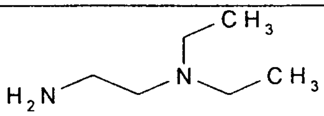
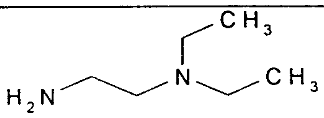
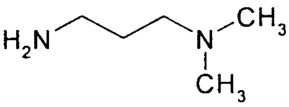
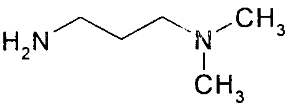
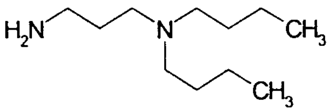
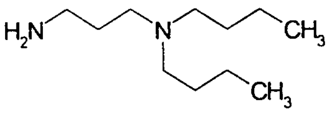
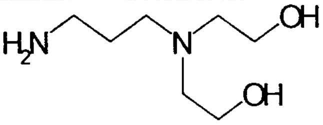
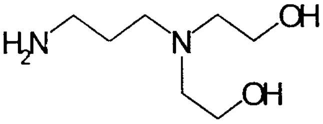
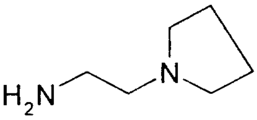
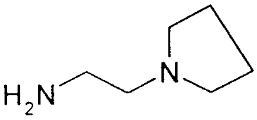
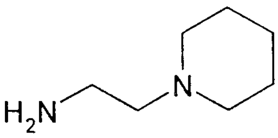
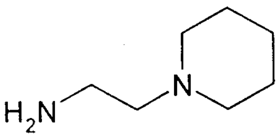
Analogously to the examples 113 - 115 the following compounds are obtainable.

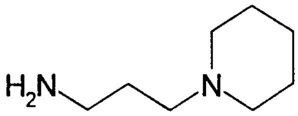
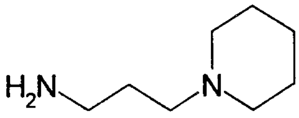
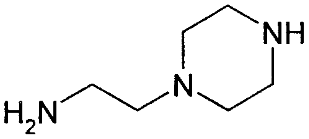
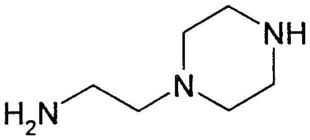
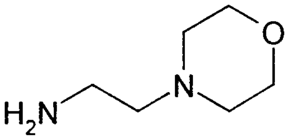
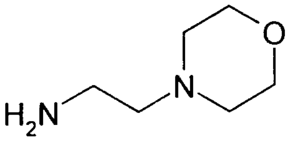
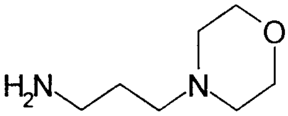
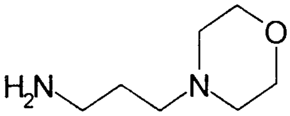
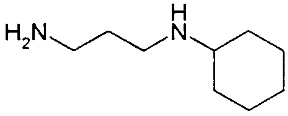
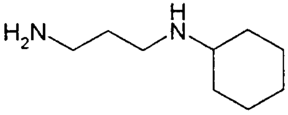
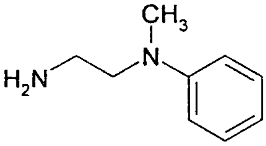
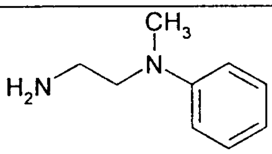
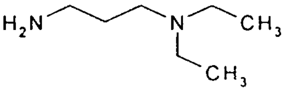
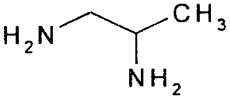
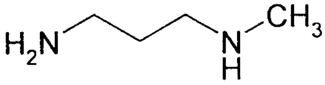
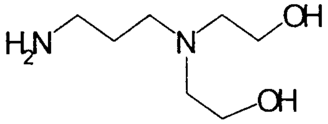
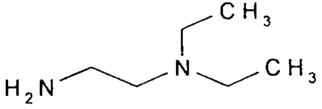
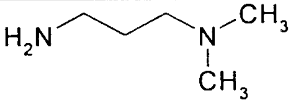
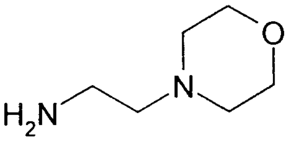
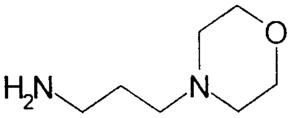


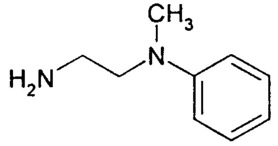
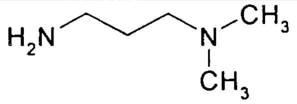
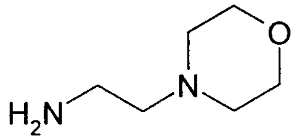
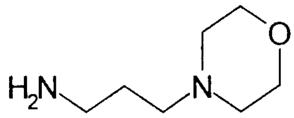
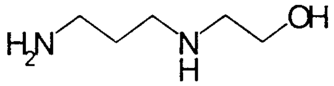
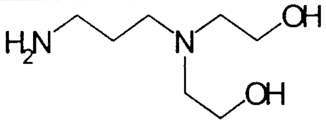
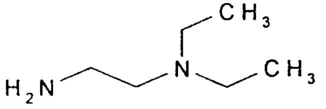
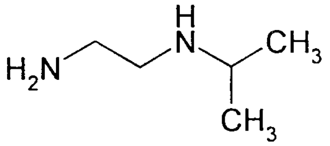
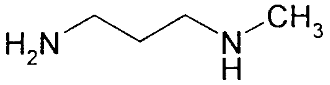
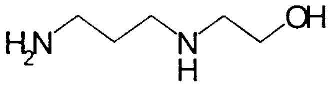
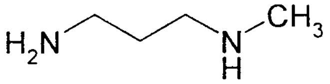
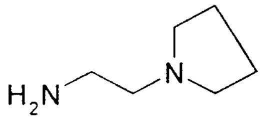
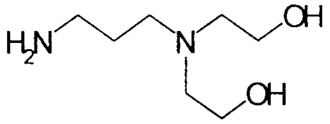
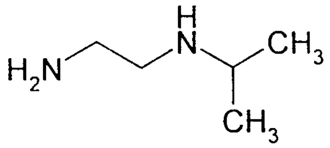
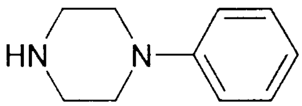
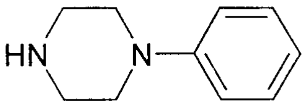
Ex.	X-H	Y-H	λ_{max}1)
116			554.3 nm
117	ditto		546.1 nm
118	ditto		544.2 nm
119	ditto		547.0 nm
120	ditto		547.3 nm
121	ditto		549.6 nm
122	ditto		549.9 nm
123	ditto		549.1 nm
124	ditto		554.4 nm
125	ditto		557.2 nm
126	ditto		557.4 nm
127	ditto		560.1 nm
128	ditto		549.6 nm
129			548.1 nm
130	ditto		549.6 nm

131	ditto		550.4 nm
132	ditto		550.7 nm
133	ditto		549.2 nm
134	ditto		550.3 nm
135	ditto		551.9 nm
136	ditto		553.5 nm
137	ditto		554.2 nm
138	ditto		553.9 nm
139	ditto		557.3 nm
140	ditto		546.9 nm
141			546.0 nm
142	ditto		548.0 nm
143	ditto		550.1 nm

144	ditto		551.0 nm
145	ditto		552.9 nm
146	ditto		559.7 nm
147	ditto		553.4 nm
148	ditto		569.9 nm
149	ditto		543.9 nm
150	ditto		548.2 nm
151			548.3 nm
152	ditto		552.4 nm
153	ditto		551.4 nm
154	ditto		556.1 nm
155	ditto		557.5 nm
156	ditto		565.2 nm

157	ditto		583.0 nm
158	ditto		556.8 nm
159	ditto		560.1 nm
160		ditto	558.8 nm
161			557.4 nm
162			563.6 nm
163			558.2 nm
164			559.8 nm
165			560.1 nm
166			559.7 nm
167			569.0 nm
168			561.3 nm
169			564.2 nm

170			563.1 nm
171			562.2 nm
172			563.7 nm
173			559.4 nm
174			558.7 nm
175			568.2 nm
176			561.0 nm
177	ditto		560.4 nm
178	ditto		562.1 nm
179	ditto		559.7 nm
180	ditto		562.4 nm
181	ditto		565.8 nm
182	ditto		562.3 nm

183	ditto		566.7 nm
184		ditto	565.9 nm
185	ditto		561.0 nm
186	ditto		560.0 nm
187	ditto		561.7 nm
188	ditto		562.1 nm
189			558.7 nm
190	ditto		559.5 nm
191			561.0 nm
192			563.1 nm
193	ditto		559.1 nm
194			552.1 nm

[1] all samples measured in water + 1 % sodium acetate, except sample 160, which is measured in DIF + 1 % glacial acetic acid and samples 162-194, which are measured in water + 1 % EE

APPLICATION EXAMPLE A

70 parts of chemically bleached sulphite cellulose of pinewood and 30 parts of chemically bleached sulphite cellulose of birchwood are ground in a Holländer in 2000 parts of water. 0.2 parts of the dyestuff of Example 1 are sprinkled into this pulp. After mixing for 20 minutes, paper is produced therefrom. The absorbent paper obtained in this way is dyed (reddish) blue. The waste water is practically colorless.

APPLICATION EXAMPLE B

0.5 parts of the dyestuff powder of Example 1 are dissolved in 100 parts of hot water and cooled to room temperature. The solution is added to 100 parts of chemically bleached sulphite cellulose, which have been ground in a Holländer with 2000 parts of water. After thorough mixing for 15 minutes, sizing takes place in the usual way with rosin size and aluminum sulfate. Paper that is produced from this material has a (reddish) blue shade, and has good waste-water and wet fastness, as well as good light fastness.

APPLICATION EXAMPLE C

An absorbent length of unsized paper is drawn through a dyestuff solution of the following composition at 40 - 50°C:

0.5	parts	of the dyestuff of Example 1
0.5	parts	of starch and
99.0	parts	of water.

The excess dyestuff solution is squeezed out through two rollers. The dried length of paper is dyed (reddish) blue.

Dyeing may also take place in a similar manner to that of examples A to C using the dyestuffs of Examples 2 to 194 or respectively a dye preparation thereof. The paper dyeings obtained are red and have a high level of fastness.

APPLICATION EXAMPLE D

50 parts of bleached pinewood sulphite cellulose and 50 parts of bleached beech cellulose (degree of beating 30 SR*) are mixed with 0.5 parts of the dyestuff of Example 1 in water (pH 4, water hardness 10 dH). After 16 minutes, sheet formation takes place. The paper is dyed in an intense reddish-yellow shade. In contrast, a dyeing made at pH 7 shows no variation in depth or shade. The rate of exhaustion reaches 100 % and the waste water is colorless.

*) SR = Schopper Riegler degree

In a similar manner as described in Application Example D the dyestuffs according to Examples 2 - 194 may be used for dyeing bleached beech cellulose.

APPLICATION EXAMPLE E

100 parts of intermediate-dried chrome velours leather are drummed for one hour at 50 in a drum containing a bath of 400 parts of water, 2 parts of 25 % ammonium hydroxide solution and 0.1 parts of a commercial wetting agent. The bath is subsequently drained. 400 parts of water of 60°C and 1 part of 25 % ammonium hydroxide solution are added to the drummed chrome velours leather that is still moist. After adding 5 parts of the dyestuff of Example 1, dissolved in 200 parts of water, dyeing is effected for 90 minutes at 60°C. Then 50 parts of 8 % formic acid are slowly added in order to acidify the pH. The treatment is then continued for a further 30 minutes. Finally, the leather is rinsed, dried and finished in the usual way. The red leather dyeing obtained is level.

In a similar manner as described in Application Example E the dyestuffs according to Examples 2 - 194 may be used for dyeing intermediate-dried chrome velours.

APPLICATION EXAMPLE F

1.1 parts of the dyestuff of Example 1 are dissolved at 60°C in 100 parts of demineralized water and subsequently diluted with 900 parts of cold, demineralized water. Then, 100 parts of cotton tricot (bleached) are added to the dye bath. After 5 minutes, 10 parts of calcined sodium sulphate and 2 parts of ammonium sulphate are added. During 70 minutes, the temperature of the dye bath is continuously raised to 98°C. This temperature is maintained for 20 minutes and the dye bath is then cooled to 70°C over the course of 30 minutes. The dyed material is rinsed for 2 minutes firstly with cold, demineralized water, and subsequently for 2 minutes with cold tap water, then centrifuged and dried. The cotton dyeing obtained is red.
In a similar manner as described in Application Example F the dyestuffs according to Examples 2 - 194 may be used for dyeing cotton tricot.

APPLICATION EXAMPLE G

100 parts of cotton tricot, which have been dyed with the dyestuff of Example 1 analogously to the method of Application Example F in ca. 1/1 standard depth, are mixed without intermediate drying in 1000 parts of tap water at 25°C with 5 parts of sodium chloride and 4 parts of an after-treatment agent obtained from the reaction of diethylenetriamine with dicyandiamide. The pH value of the dye bath is set at 6.5 - 7. The bath is heated to 60°C over the course of 20 minutes, and this temperature is maintained for a further 20 minutes. Afterwards, the material is rinsed with cold tap water. The red cotton dyeing which has been after-treated in this way has perfect washing fastness and very good light fastness.
In a similar manner as described in Application Example G the dyestuffs according to Examples 2 - 194 may be used for dyeing cotton tricot.

APPLICATION EXAMPLE H

A cotton dyeing produced with the dyestuff of Example 1 analogously to the method of Application Example F in 1/1 standard depth, is impregnated on a padder with a solution, which contains 100 g/l of an after-treatment agent obtained by reacting the after-treatment

agent of Application Example G with dimethyloldihydroxyethyleneurea and a hardening catalyst, and it is squeezed out to a pick-up of ca. 80 %. It is subsequently shock-dried for 45 seconds on a stenter at a temperature of 175 - 180°C. The yellow cotton dyeing thus obtained is notable for its perfect washing fastness. At the same time, there is a considerable improvement in the creasing fastness, and reduced swelling value of the cellulosic fibres.
In a similar manner as described in Application Example H the dyestuffs according to Examples 2 - 194 may be used for dyeing cotton.

APPLICATION EXAMPLE I

A printing paste having the components

40	parts	of the dyestuff of Example 1
100	parts	of urea
330	parts	of water
500	parts	of a 4% sodium alginate thickener
10	parts	of the sodium salt of 1-nitrobenzene-3-sulphonic acid
20	parts	of soda
1000	parts	in all

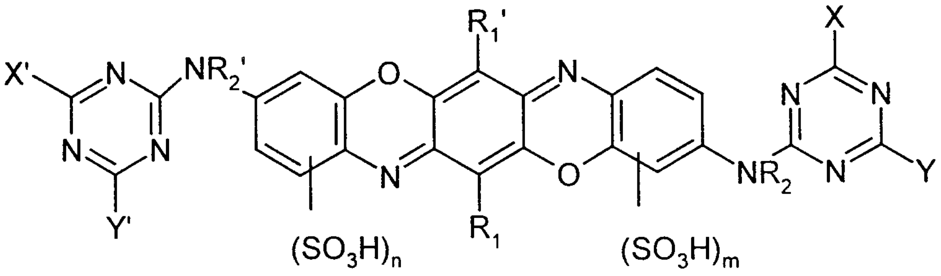
is applied to cotton material by conventional printing processes.
The printed and dried material is steamed for 4 - 8 minutes at 102 - 105°C and then given a cold and a hot rinse. The fixed cotton material is subsequently washed at the boil.
In a similar manner as described in Application Example I the dyestuffs according to Examples 2 - 194 may be used for dyeing cotton.

APPLICATION EXAMPLE J

12.6 parts dyestuff solution of Example 114 are added dropwise at room temperature to a stirred mixture of 20.0 parts diethyleneglycole and 67.4 parts of demineralized water. The resulting ink exhibits good light- and waterfastness properties.
In a similar manner as described in Application Example J all the Examples of Table 1 and Table 2 and Table 3 may be used.

Claims

1. Compounds of formula (I)



(I)

wherein

R₁ and R₁' independently from each other are hydrogen or halogen,

R_2 and R_2' independently from each other are hydrogen or C_{1-4}-alkyl,

X and X' independently from each other are optionally substituted aliphatic, aromatic, cycloaliphatic or heterocyclic amino or O-alkyl optionally substituted by a group selected from -OH, -COOH, $-NH_2$, -NHalkyl, $-N(alkyl)_2$, $-SO_3H$, -O-alkyl,

Y and Y' independently from each other and from X and X' have the same meaning as X and X',

m and n independently from each other have the value 1 or 2;

with the provisos that

(i) if Y = Y' is a β-sulfoethylamino radical then X = X' is neither β-sulfoethylamino nor amino nor morpholino nor 3-(β-sulfatoethyl-sulfonyl)-phenylamino nor 3-sulfophenylamino,

(ii) if Y = Y' is morpholino radical then X = X' is neither morpholino nor 4-sulfophenylamino,

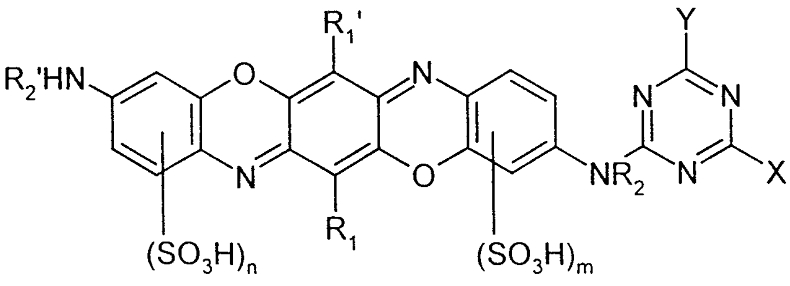
and salts thereof as well as mixtures of such compounds.

2. Compounds according to Claim 1 wherein R_1 and R_1' are halogen radicals and X, X', Y, Y' are substituted or unsubstituted aliphatic, aromatic, cycloaliphatic or heterocyclic amines and m and n are 1 and salts thereof as well as mixtures of such compounds.

3. Compounds according to any one of Claims 1 and 2 wherein R_1 and R_1' are chlorine radicals and R_2 and R_2' are hydrogen and salts thereof as well as mixtures of such compounds.

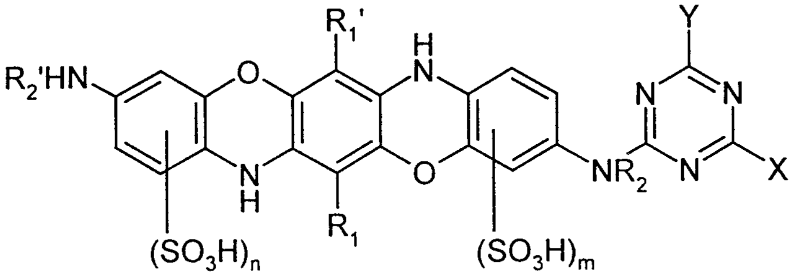
4. Compound according to any one of Claims 1 to 3 wherein X, X', Y and Y' independently are the rest of an amine of the group monoethanolamine, diethanolamine, tetrahydro-1,4-oxazine, diethylaminopropylamine, 2-amino-propylamine, 1-amino-diethylaminoethane, 1-amino-dimethylaminopropane, N-(2-amino-ethyl)-tetrahydro-1,4-oxazine, N-(2-aminopropyl)-tetrahydro-1,4-oxazine, N,N-dibutylamino-propylamine, 3-methylamino-propylamine, 2-(3-aminopropyl)-aminoethanol, isopropylamino-ethylamine, N-(3-aminopropyl)-cyclohexyl-amine, N-(2-aminoethyl)-N-methylaniline, N,N-bis-(2-hydroxyethyl)-1,2-diaminopropane, N-(2-aminoethyl)-pyrrolidine, N-(3-aminopropyl)-pyrrolidine, 2-piperidino-ethylamine, N-(2-aminoethyl)-piperazine, N-phenyl-piperazine, N-methyl-ethanolamine 3-methoxypropyl-amine, 1-methylamino-ethyl-2-sulphonic acid, 1-aminobenzene-2-sulfonic acid, 1-amino-benzene-3-sulfonic acid, 1-amino-benzene-4-sulfonic acid, 2-amino-benzoic acid, 3-amino-benzoic acid, 4-amino-benzoic acid, 3-amino-6-methoxy-benzoic acid, 5-amino-isophthalic acid, 2-amino-naphthaline-6-sulfonic acid and 2-aminonaphthaline-1-sulfonic acid.

5. A process for producing compounds of formula (I) according to Claim 1 characterized in that a compound of formula (II)



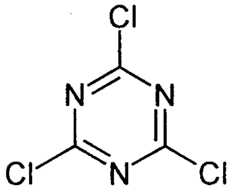
(II)

with the meanings of the symbols as defined in Claim 1 is reduced to the corresponding leuco form (IIa)



(IIa)

with the same meanings of the substituents as defined in Claim 1,
which is then reacted with one mole of the compound of formula (III)

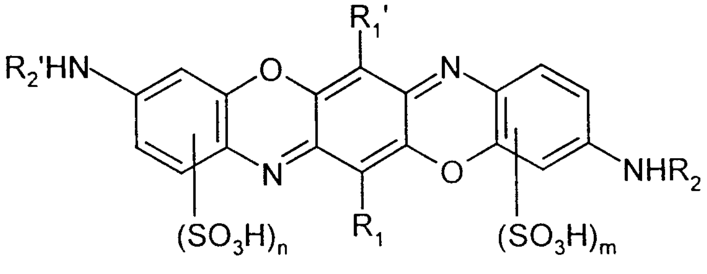


(III)

and the remaining chlorine atoms of the triazine ring are replaced by X' and Y' by condensation and the compound is oxidized to a compound according to formula (I).

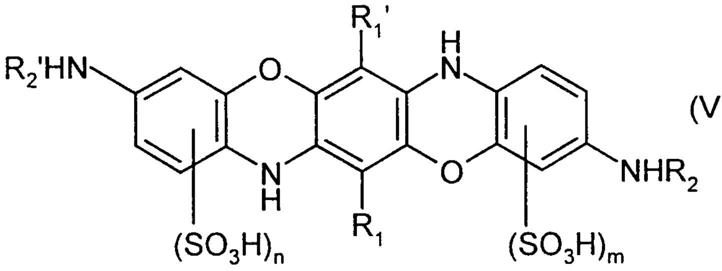
6. A process for producing compounds of formula (I) according to Claim 1 characterized in that

a compound of formula (IV)



(IV)

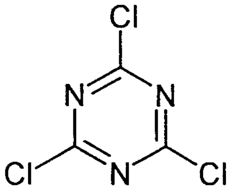
with the same meaning for R_1, R_1', R_2, R_2', m and n as defined in Claim 1 is reduced to the corresponding leuco form (V)



(V)

with the same definitions for substituents as defined in Claim1

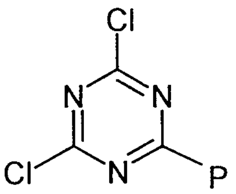
and two moles a compound of formula (III)



(III)

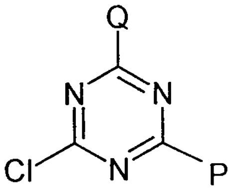
react with the compound of formula (V); two moles of a compound HX or HX' and two moles of a compound HY or HY' are condensed to the triazine rings of triphendioxazine backbone and the compound is oxidized.

7. A process according to Claims 5 and 6 characterized in that mono-and/or di-substituted cyanuric chloride compounds according to formula (IIIa) respectively according to formula (IIIb)



(IIIa)

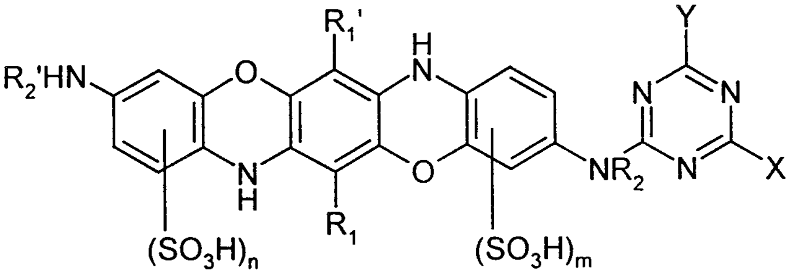
;



(IIIb)

wherein P and Q signify X, X', Y and Y' as defined in Claim 1,

are condensed to the triphendioxazine backbone according to formula (IIa)


(IIa)

with the same meanings for the substituents as defined above, respectively according to formula (V).

8. Use of compounds of formula (I) or mixtures thereof according to any one of Claims 1 to 4 for dyeing or printing organic substrates containing hydroxy groups, thiol groups or nitrogen, in particular as paper dyes or direct dyes, or for preparing ink-jet inks.

9. Process for dyeing or printing organic substrates containing hydroxy groups, thiol groups or nitrogen atoms, comprising the application of a compound of formula (I) or mixtures thereof according to any one of Claims 1 to 4 to such substrates.

10. Process according to Claim 9 for dyeing or printing cellulosic textile materials or paper.

11. Organic substrates dyed or printed by the process of Claim 9.

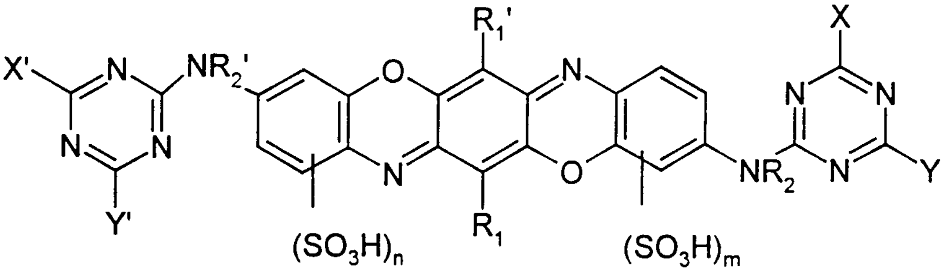
12. Process for the preparation of ink-jet inks, characterized in that a compound of formula (I) or mixtures thereof according to Claims 1 to 4 is used.

13. Ink-jet inks prepared by the process of Claim 12.

AMENDED CLAIMS

[received by the International Bureau on 20 September 2000 (20.09.00);
original claims 1-13 replaced by new claims 1-12 (8 pages)]

1. Compounds of formula (I)



(I)

wherein

R_1 and R_1' independently from each other are hydrogen or halogen,

R_2 and R_2' independently from each other are hydrogen or C_{1-4}-alkyl,

X and X' independently from each other are the rest of an amine of the group monoethanolamine, diethanolamine, tetrahydro-1,4-oxazine, diethylaminopropylamine, 2-amino-propylamine, 1-amino-diethylaminoethane, 1-amino-dimethylaminopropane, N-(2-amino-ethyl)-tetrahydro-1,4-oxazine, N-(2-aminopropyl)-tetrahydro-1,4-oxazine, N,N-dibutylamino-propylamine, 3-methylamino-propylamine, 2-(3-aminopropyl)-aminoethanol, isopropylamino-ethylamine, N-(3-aminopropyl)-cyclohexyl-amine, N-(2-aminoethyl)-N-methylaniline, N,N-bis-(2-hydroxyethyl)-1,3-diaminopropane, N-(2-aminoethyl)-pyrrolidine, N-(3-aminopropyl)-pyrrolidine, 2-piperidino-ethylamine, N-(2-aminoethyl)-piperazine, N-phenyl-piperazine, N-methyl-ethanolamine 3-methoxypropyl-amine, 1-methylamino-ethyl-2-sulphonic acid, 1-aminobenzene-2-sulfonic acid, 1-amino-benzene-3-sulfonic acid, 1-amino-benzene-4-sulfonic acid, 2-amino-benzoic acid, 3-amino-benzoic acid, 4-amino-benzoic acid, 3-amino-6-methoxy-benzoic acid, 5-amino-isophthalic acid, 2-amino-naphthaline-6-sulfonic acid and 2-aminonaphthaline-1-sulfonic acid,

Y and Y' independently from each other and from X and X' have the same meaning as X and X', m and n independently from each other have the value 1 or 2;

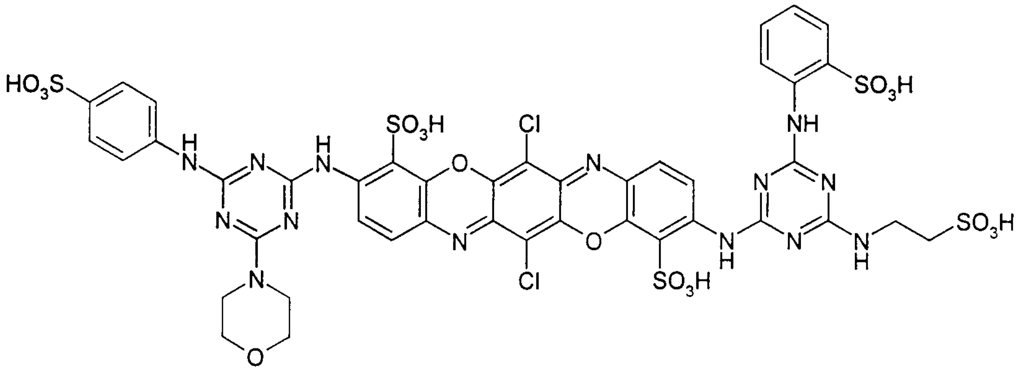
with the provisos that

(i) if Y = Y' is morpholino radical then X = X' is neither morpholino nor 4-sulfophenylamino,

and salts thereof as well as mixtures of such compounds.

2. Compounds according to Claim 1 wherein R_1 and R_1' are chlorine radicals and R_2 and R_2' are hydrogen and salts thereof as well as mixtures of such compounds.

3. Compounds according to the following formulae



(a)

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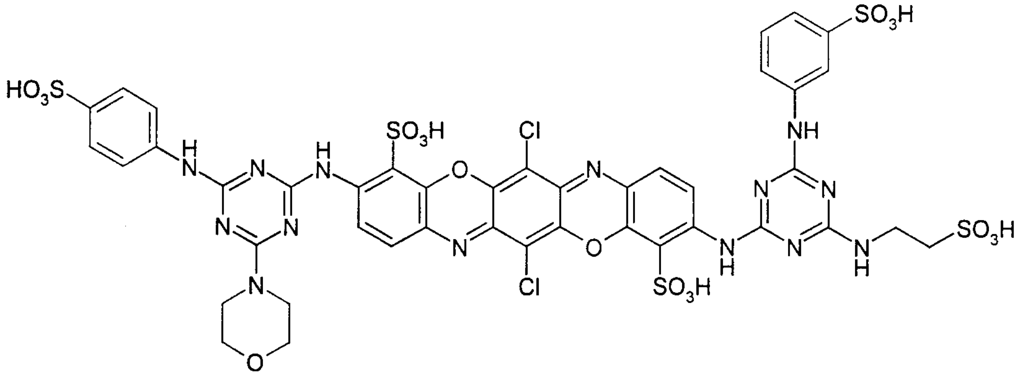

(b)

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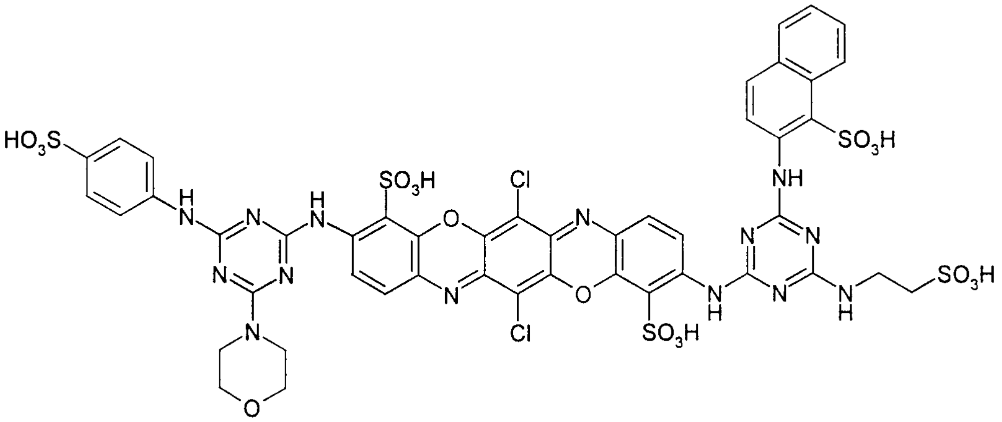

(c)

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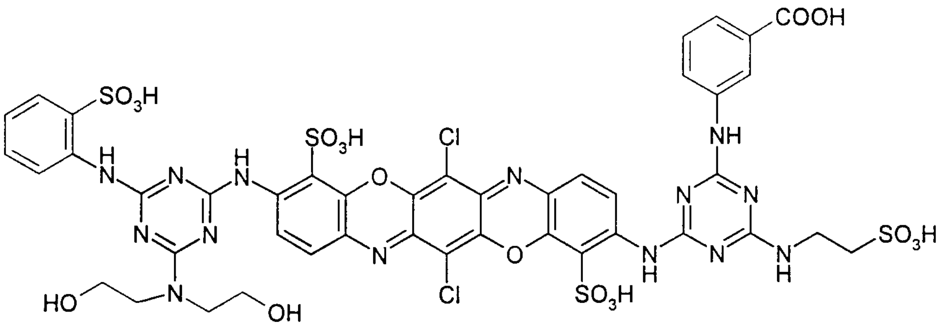

(d)

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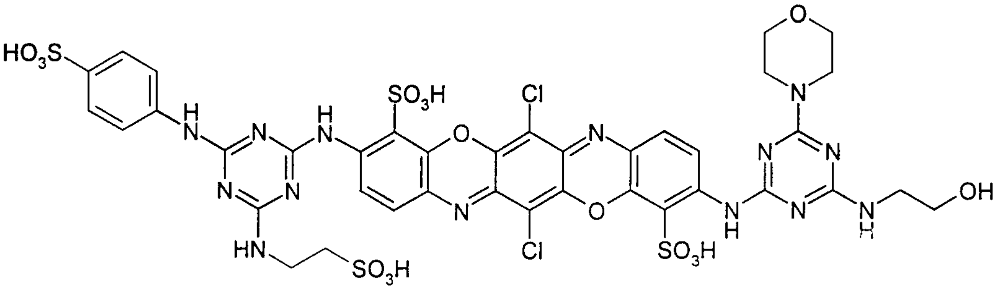

(e)

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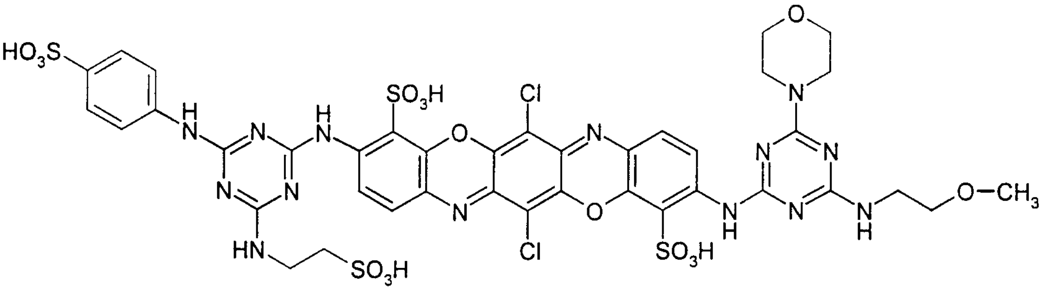

(f)

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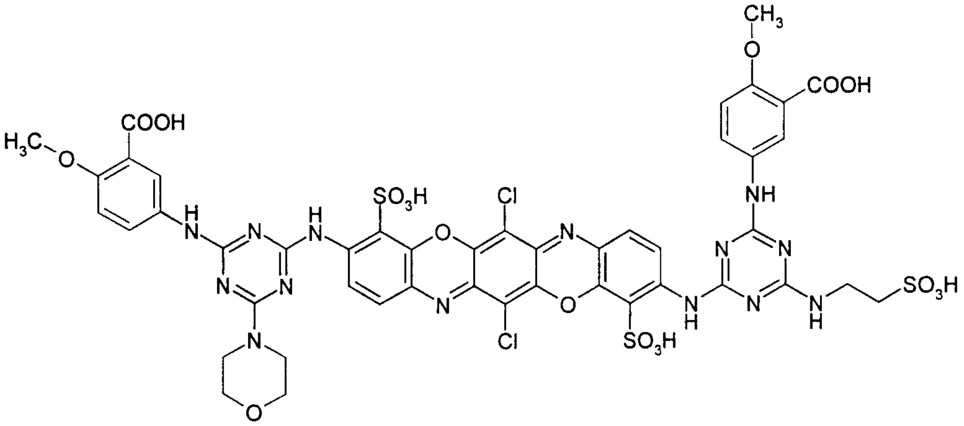

(g)

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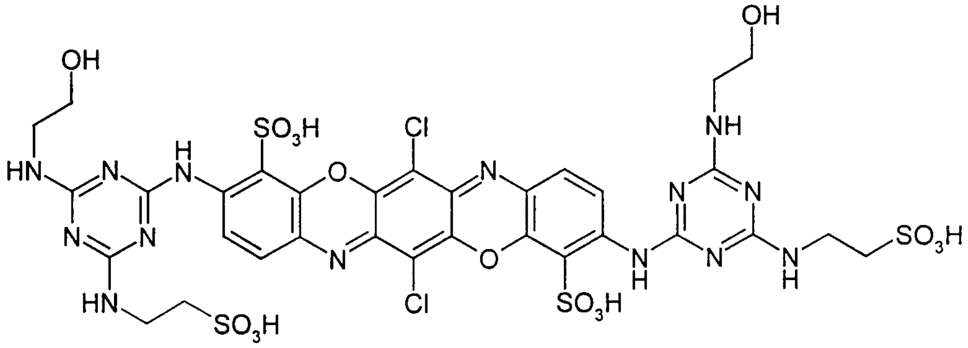

(h)

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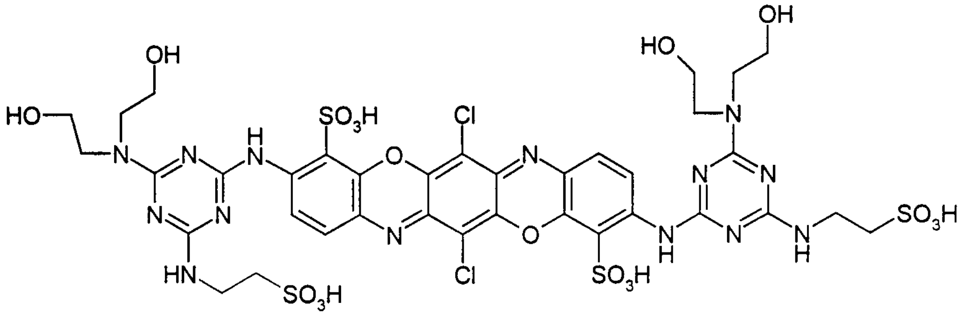
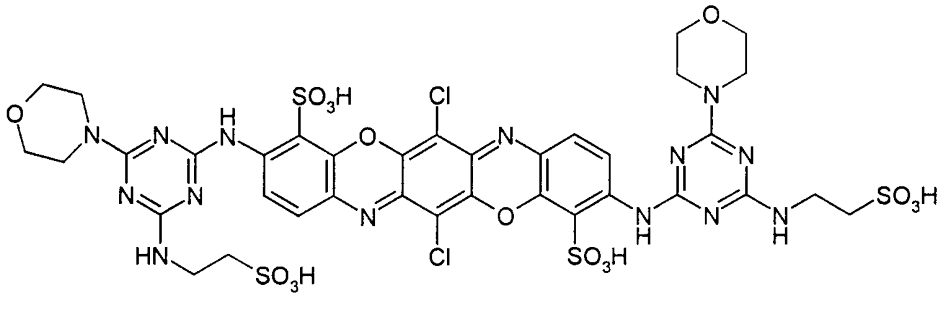


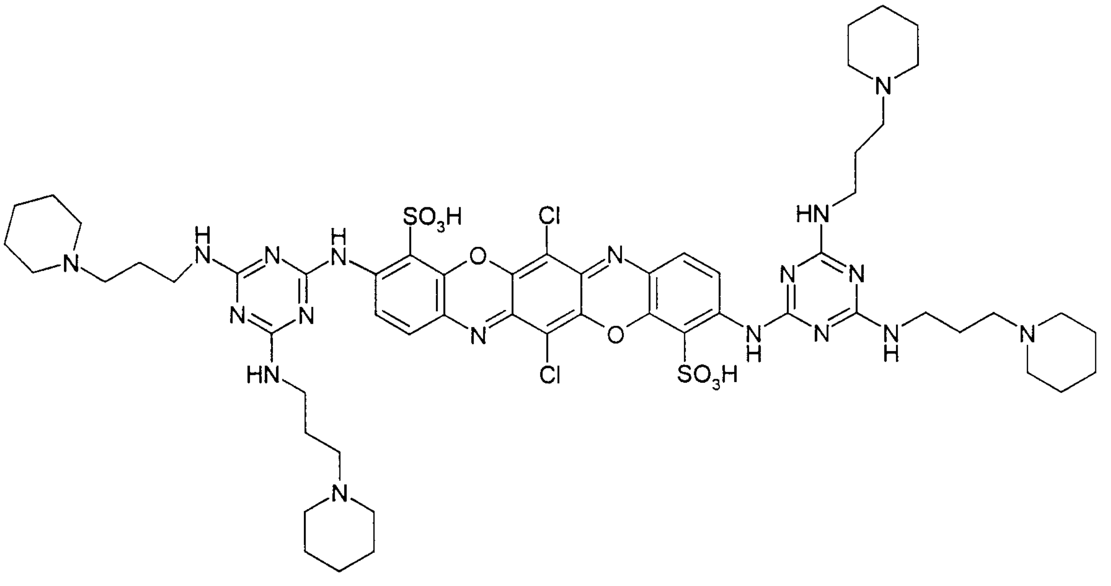
(i)

,



(j)

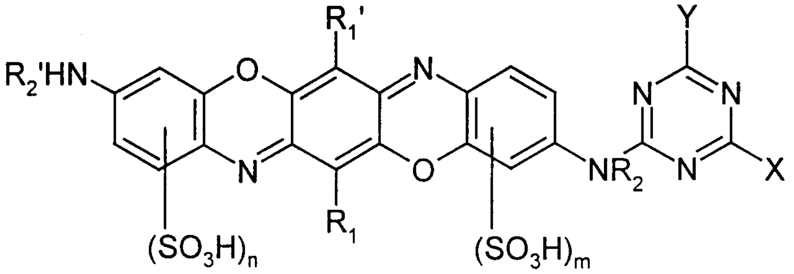
and



(k)

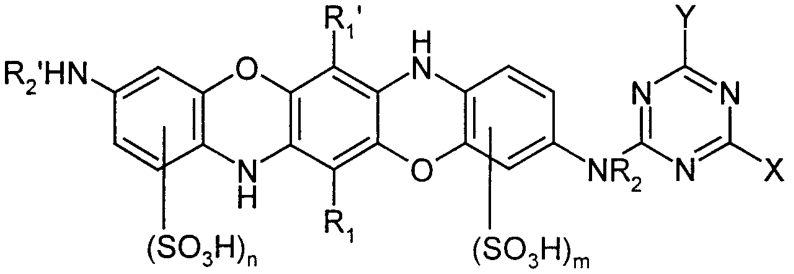
and salts thereof as well as mixtures of such compounds.

4. A process for producing compounds of formula (I) according to Claim 1 and formulae (a) - (k) according to Claim 3 characterized in that a compound of formula (II)



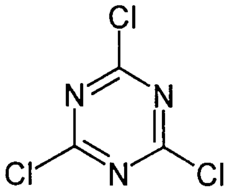
(II)

with the meanings of the symbols as defined in Claim 1 is reduced to the corresponding leuco form (IIa)



(IIa)

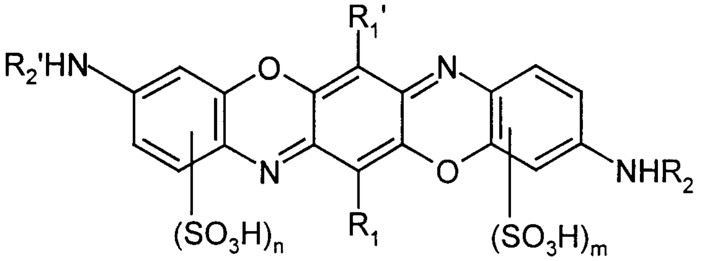
with the same meanings of the substituents as defined in Claim 1,
which is then reacted with one mole of the compound of formula (III)



(III)

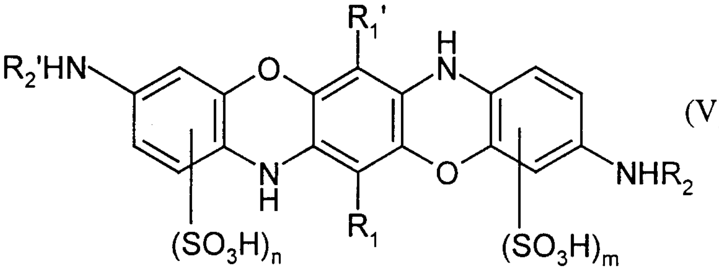
and the remaining chlorine atoms of the triazine ring are replaced by X' and Y' by condensation and the compound is oxidized to a compound according to formula (I).

5. A process for producing compounds of formula (I) according to Claim 1 and formulae (a) - (k) according to Claim 3 characterized in that a compound of formula (IV)



(IV)

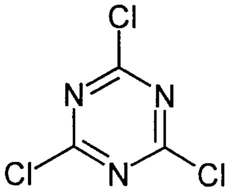
with the same meaning for R_1, R_1', R_2, R_2', m and n as defined in Claim 1 is reduced to the corresponding leuco form (V)



(V)

with the same definitions for substituents as defined in Claim1

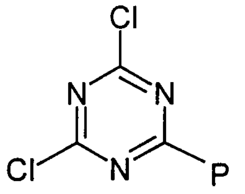
and two moles a compound of formula (III)



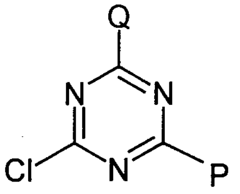
(III)

react with the compound of formula (V); two moles of a compound HX or HX' and two moles of a compound HY or HY' are condensed to the triazine rings of triphendioxazine backbone and the compound is oxidized.

6. A process according to Claims 4 and 5 characterized in that mono-and/or di-substituted cyanuric chloride compounds according to formula (IIIa) respectively according to formula (IIIb)

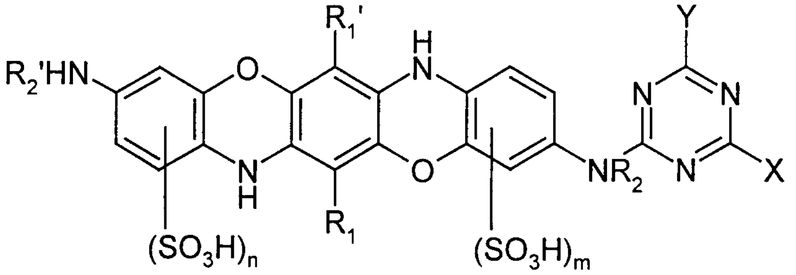


(IIIa) ;



(IIIb)

wherein P and Q signify X, X', Y and Y' as defined in Claim 1,
are condensed to the triphendioxazine backbone according to formula (IIa)



(IIa)

with the same meanings for the substituents as defined above, respectively according to formula (V).

7. Use of compounds of formula (I) or mixtures thereof according to any one of Claims 1 to 3 for dyeing or printing organic substrates containing hydroxy groups, thiol groups or nitrogen, in particular as paper dyes or direct dyes, or for preparing ink-jet inks.

8. Process for dyeing or printing organic substrates containing hydroxy groups, thiol groups or nitrogen atoms, comprising the application of a compound of formula (I) or mixtures thereof according to any one of Claims 1 to 3 to such substrates.

9. Process according to Claim 8 for dyeing or printing cellulosic textile materials or paper.

10. Organic substrates dyed or printed by the process of Claim 8.

11. Process for the preparation of ink-jet inks, characterized in that a compound of formula (I) or of formulae (a) - (k) or mixtures thereof according to Claims 1 to 3 is used.

12. Ink-jet inks prepared by the process of Claim 11.

INTERNATIONAL SEARCH REPORT

I ational Application No
PCT/IB 00/00670

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D498/04 C09B62/503 C09B62/04 C09B62/002 C09B19/02
C09D11/00 C09D11/02 //(C07D498/04,265:00,265:00)

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 C07D C09B C09D

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)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 385 120 A (SUMITOMO CHEMICAL CO., LTD.) 5 September 1990 (1990-09-05) page 59, line 20 -page 63, line 45; claims 1,14,15 ---	1-4,8-10
X	DE 33 41 886 A (BAYER AG) 30 May 1985 (1985-05-30) claims; example 46 ---	1-4,6,8,11
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 7, 31 July 1996 (1996-07-31) & JP 08 073789 A (ORIENT CHEM IND LTD), 19 March 1996 (1996-03-19) abstract --- -/--	1-3,8

☒ 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

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