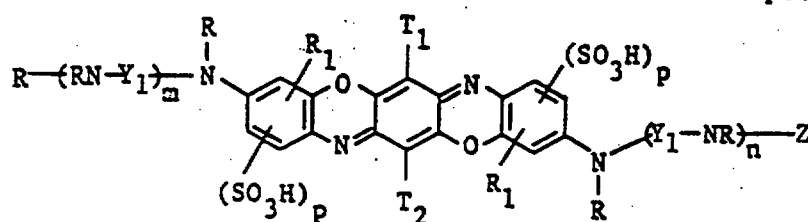


ANIONIC DIOXAZINE COMPOUNDS

This invention relates to sulfo group-containing dioxazine compounds having a triazinylamino bridge and their salts, a process for their production and processes for dyeing or printing hydroxy group- or nitrogen-containing organic substrates using these compounds, optionally combined with a special after-treatment of the dyeings or prints obtained, as well as dyeing preparations thereof.

More particularly, this invention provides compounds of formula I



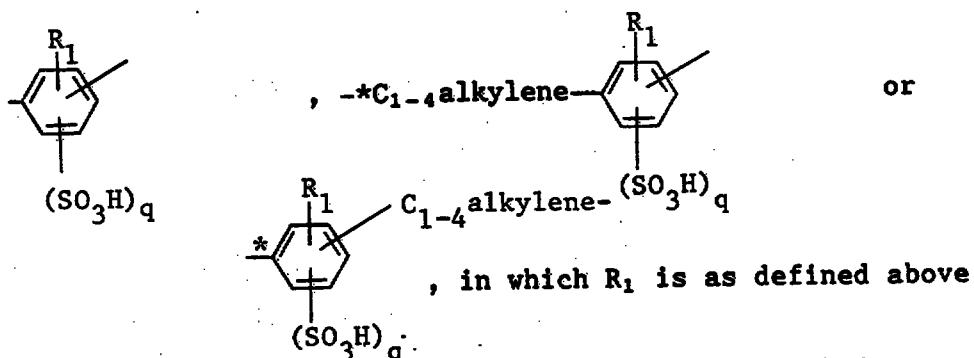
and salts thereof,
in which

each R, independently, is hydrogen, C₁₋₆alkyl or C₁₋₆alkyl monosubstituted by halogen, cyano, hydroxy, C₁₋₄alkoxy, -COOH, -SO₃H or -OSO₃H,

each R₁, independently, is hydrogen, halogen, C₁₋₄alkyl, C₁₋₄alkoxy or -COOH,

each T₁ and T₂, independently, is hydrogen, chlorine, bromine, unsubstituted C₁₋₄alkyl or C₁₋₄alkoxy, or C₁₋₄alkyl or C₁₋₄alkoxy monosubstituted by chlorine, methoxy, ethoxy or -OSO₃H, unsubstituted phenyl or phenoxy, or phenyl or phenoxy which are substituted by one or two substituents selected from chlorine, bromine, methyl, ethyl, methoxy and ethoxy,

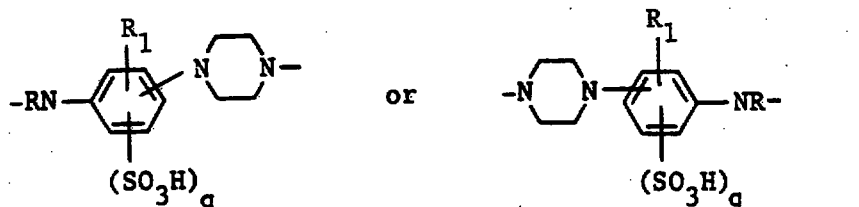
each Y_1 , independently, is $-C_{2-6}$ alkylene-, monohydroxy- or dihydroxy-substituted $-C_{3-6}$ alkylene-, $-C_{3-6}$ alkylene- which is interrupted by $-O-$, $-S-$ or $-NR-$, unsubstituted cyclohexylene or cyclohexylene which is substituted by up to three methyl groups,



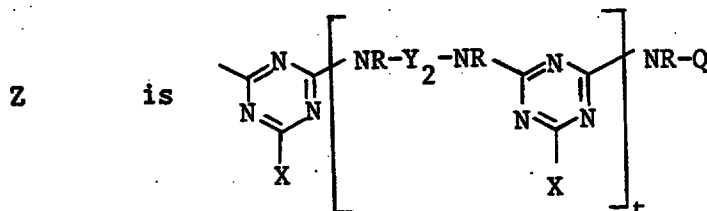
and each asterisk identifies the carbon atom which is attached to the amino group bound to the ring system, or

each $-NR-Y_1-NR-$, independently, is $-N$  $-N-$,

$-NR-C_{2-4}$ alkylene- N  $-N-$, $-N$  $-C_{2-4}$ alkylene- $NR-$,



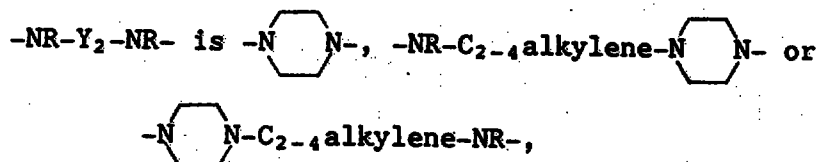
in which R and R_1 are as defined above,



each X , independently, is halogen or an unsubstituted or substituted amino group,

each R is as defined above,

Y₂ is a bridging group selected from a divalent aliphatic, cycloaliphatic, aromatic and aliphatic-aromatic group, where each such group is unsubstituted or substituted and where each aliphatic group is optionally interrupted by -O-, -S- or -NR-, or



Q is a chromophoric radical selected from the series of azo-, formazan-, anthraquinone-, phthalocyanine- and dioxazine- dyestuffs,

each m and n, independently, is 0 or 1,
 each p, independently, is 0, 1 or 2,
 each q, independently, is 0 or 1, and
 t is 0 or 1,

provided that in a compound of formula I at least one sulphonic acid group is present,
 and mixtures of compounds of formula I.

In the specification, any alkyl or alkylene group present is linear or branched unless indicated otherwise. In any hydroxy- or alkoxy-substituted alkyl or alkylene group which is attached to a nitrogen atom, the hydroxy or alkoxy group is preferably bound to a carbon atom which is not directly bound to this nitrogen atom. In any alkylene chain interrupted by -O-, -S- or -NR- which is bound to a nitrogen atom, preferably the -O-, -S- or -NR- is bound to a carbon atom which is not directly attached to this nitrogen atom.

Any halogen is preferably fluorine, chlorine or bromine; more preferably it is chlorine or bromine, and especially chlorine.

Any unsubstituted alkyl group as R preferably contains 1-4 carbon atoms and is more preferably methyl or ethyl. When R is a monosubstituted alkyl group it is preferably substituted by chlorine, cyano, hydroxy, methoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$.

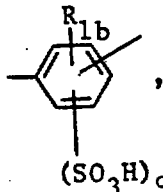
Each R is preferably R_a , where each R_a independently is hydrogen, C_{1-4} alkyl or C_{1-4} alkyl monosubstituted by chlorine, cyano, hydroxy, methoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$. More preferably it is R_b , where each R_b independently is hydrogen, methyl, ethyl or C_{2-3} alkyl monosubstituted by hydroxy or methoxy. Even more preferably it is R_c , where each R_c is independently hydrogen or methyl. Most preferably each R is hydrogen.

Any alkyl or alkoxy as R_1 preferably contains 1 or 2 carbon atoms.

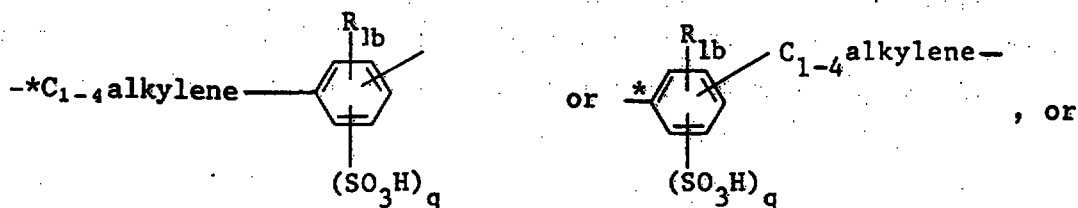
Each R_1 is preferably R_{1a} , where each R_{1a} independently is hydrogen, chlorine, methyl, ethyl, methoxy, ethoxy or $-COOH$. More preferably it is R_{1b} , where each R_{1b} is independently hydrogen, chlorine, methyl, methoxy or $-COOH$. Most preferably, each R_1 is hydrogen.

T_1 is preferably T_{1a} and T_2 is preferably T_{2a} , where each T_{1a} and T_{2a} independently is hydrogen, chlorine, bromine, methyl, ethyl, methoxy, ethoxy, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is substituted by one or two substituents selected from chlorine, bromine, methyl, ethyl, methoxy and ethoxy. It is particularly preferred that both T_1 and T_2 are chlorine.

Each Y_1 is preferably Y_{1a} , where each Y_{1a} independently is $-C_{2-6}$ alkylene-, monohydroxy-substituted $-C_{3-6}$ alkylene-, $-C_{3-6}$ alkylene-

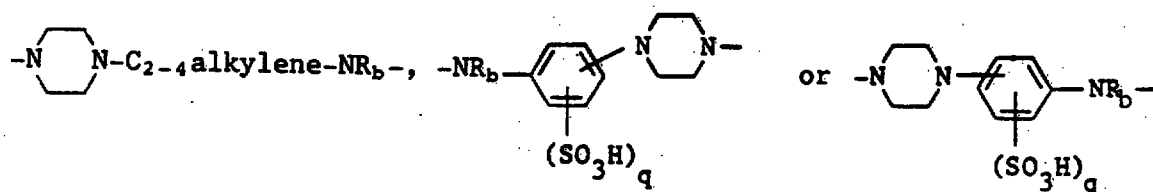
which is interrupted by $-O-$, $-S-$ or $-NR_b-$, cyclohexylene, ,

 $(SO_3H)_q$

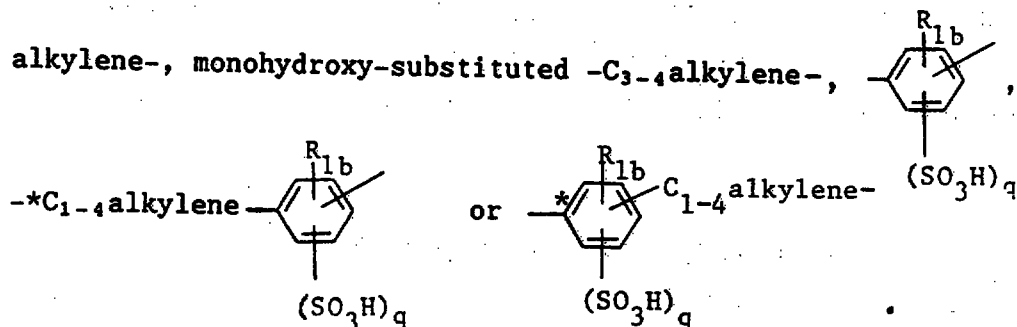


each $-\text{NR}-\text{Y}_1-\text{NR}-$ is preferably $-\text{NR}_b-\text{Y}_{1a}-\text{NR}_b-$, where each $-\text{NR}_b-\text{Y}_{1a}-\text{NR}_b-$

independently is $-\text{N}\text{C}_4\text{H}_8\text{N}-$, $-\text{NR}_b-\text{C}_{2-4}\text{alkylene}-\text{N}\text{C}_4\text{H}_8\text{N}-$,



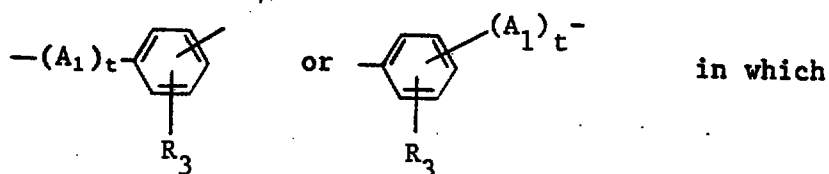
More preferably Y_1 is Y_{1b} , where each Y_{1b} independently is $-\text{C}_{2-4}$ -alkylene-, monohydroxy-substituted $-\text{C}_{3-4}$ alkylene-,



Any aliphatic bridging group as Y_2 is preferably $-\text{C}_{2-6}$ alkylene- which may be interrupted by $-\text{O}-$, $-\text{S}-$ or $-\text{NR}-$, or monohydroxy- or dihydroxy-substituted $-\text{C}_{3-6}$ alkylene-.

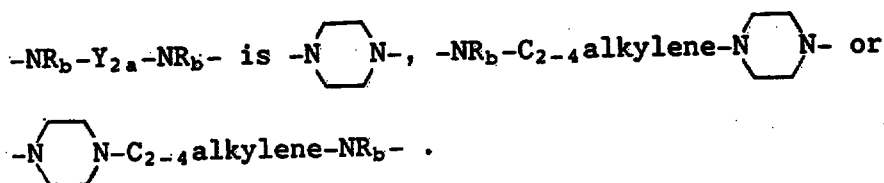
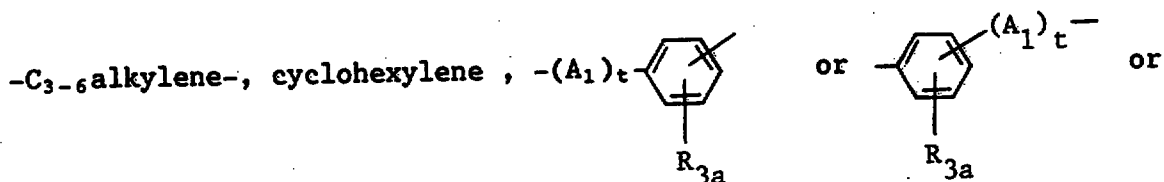
Any cycloaliphatic group as Y_2 is preferably cyclohexylene which is unsubstituted or substituted by up to three methyl groups.

Any aromatic or aliphatic-aromatic bridging group as Y_2 is preferably

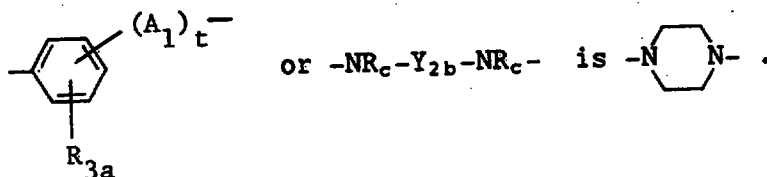
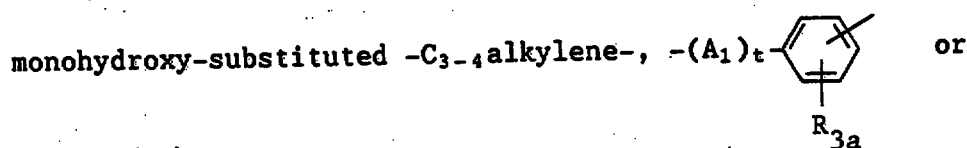


A_1 is $-C_{1-4}$ alkylene-, t is 0 or 1 and R_3 is hydrogen, chlorine, C_{1-4} -alkyl, C_{1-4} alkoxy, $-COOH$ or $-SO_3H$. More preferably R_3 is R_{3a} where R_{3a} is hydrogen, chlorine, methyl, methoxy, $-COOH$ or $-SO_3H$.

Y_2 is preferably Y_{2a} , where Y_{2a} is $-C_{2-6}$ alkylene-, $-C_{3-6}$ alkylene- which is interrupted by $-O-$, $-S-$ or $-NR_b-$, monohydroxy-substituted



More preferably Y_2 is Y_{2b} , where Y_{2b} is $-C_{2-4}$ alkylene-,



Any unsubstituted or substituted amino group as X is preferably $-NR_4R_5$ in which each R_4 and R_5 independently is hydrogen, C_{1-6} alkyl, C_{1-6} alkyl monosubstituted by hydroxy, halogen, cyano, C_{1-4} alkoxy, hydroxy-substituted C_{1-4} alkoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$, cyclohexyl, phenyl or phenyl(C_{1-4} alkyl) in which each phenyl ring is unsubstituted or substituted by one to three substituents selected from chlorine, C_{1-4} alkyl, C_{1-4} alkoxy, $-COOH$, $-SO_3H$ and $-NH_2$, or $-NR_4R_5$ forms a pyrrolidine, piperidine, morpholine or piperazine ring of which latter ring the second N-Atom is unsubstituted or substituted by methyl, ethyl, 2-hydroxyethyl or 2-aminoethyl.

R_4 and R_5 are preferably R_{4a} and R_{5a} , where each R_{4a} and R_{5a} independently is hydrogen, C_{1-4} alkyl, C_{1-4} alkyl monosubstituted by chlorine, hydroxy, methoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$, cyclohexyl, phenyl or benzyl in which each phenyl ring is unsubstituted or substituted by one or two substituents selected from chlorine, methyl, ethyl, methoxy, ethoxy, $-SO_3H$ and $-NH_2$, or

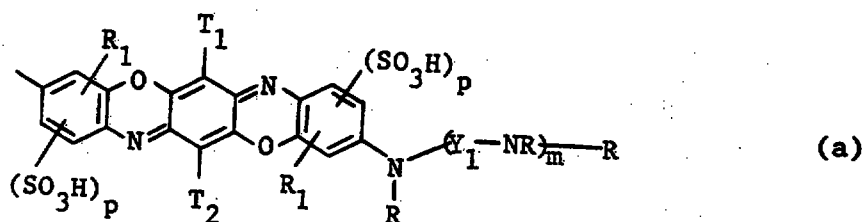
$-NR_{4a}R_{5a}$ forms a piperidine, morpholine, piperazine or N-methyl-piperazine ring.

More preferably R_4 and R_5 are R_{4b} and R_{5b} , where each R_{4b} and R_{5b} independently is hydrogen, methyl, ethyl, C_{2-3} alkyl monosubstituted by hydroxy or $-SO_3H$, cyclohexyl, phenyl or sulphophenyl or $-NR_{4b}R_{5b}$ forms a morpholine ring.

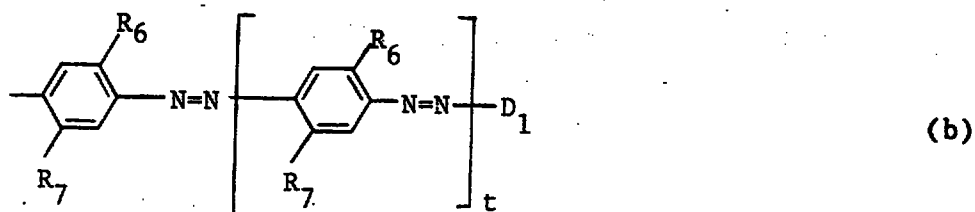
Each X is preferably X_a where each X_a independently is fluorine, chlorine or $-NR_4R_5$; more preferably X_b where each X_b is chlorine or $-NR_{4a}R_{5a}$; most preferably each X is X_c where each X_c independently is $-NR_{4b}R_{5b}$.

Q is preferably Q_a where Q_a is the radical of a metal-free or metallised monoazo or disazo dye or of a dioxazine dye, especially of a triphenendioxazine dye.

More preferably Q is Q_b where Q_b is one of the dyestuff radicals (a) to (e),



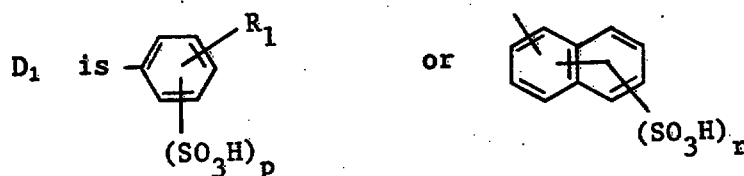
in which the symbols are as defined above,



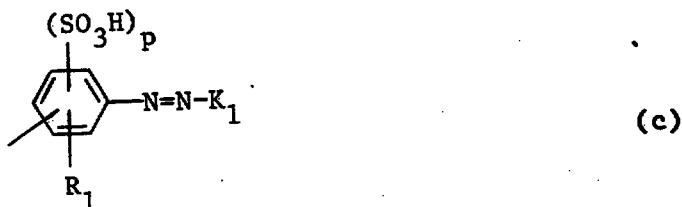
in which

each R_6 independently is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-NHCOC_{1-4}$ alkyl or $-NHCONH_2$,

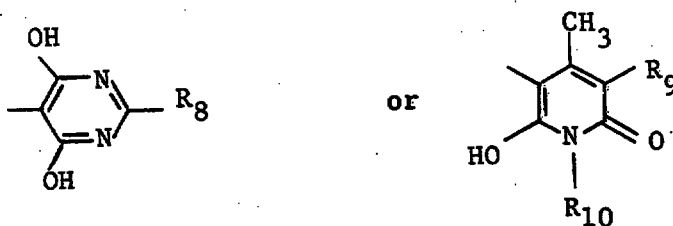
each R_7 independently is hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy, t is 0 or 1, and



in which R_1 and p are as defined above, and r is 1, 2 or 3;



in which R_1 and p are as defined above, and K_1 is the radical of a coupling component having the formula



in which

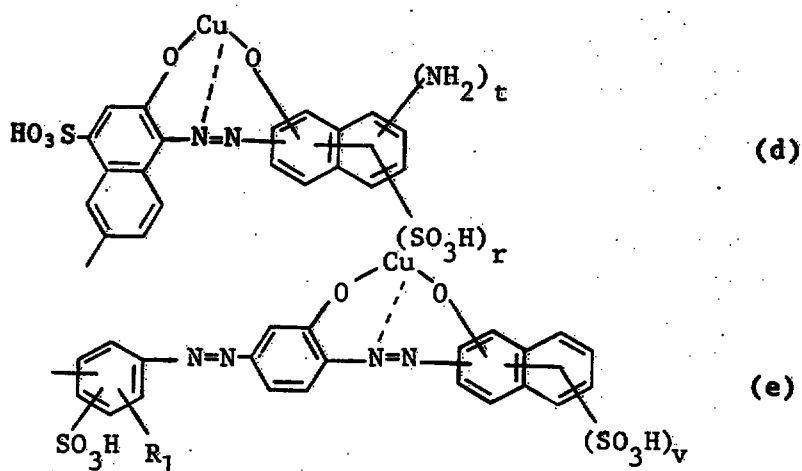
R_8 is OH or $-NHCN$,

R_9 is hydrogen, cyano, $-CONH_2$ or $-CH_2SO_3H$,

R_{10} is hydrogen, C_{1-4} alkyl or $-A_2-NR_4R_5$,

A_2 is $-C_{2-4}$ alkylene- or monohydroxy-substituted $-C_{3-4}$ alkylene-, and

R_4 and R_5 are as defined above;



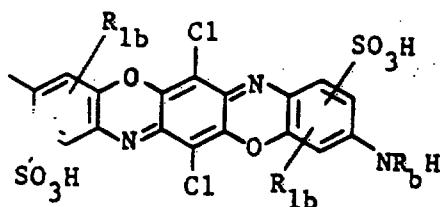
in which in the naphthyl ring of each radical (d) and (e),
 $-\text{N}=\text{N}-$ and $-\text{O}-$ are attached to carbon atoms which are ortho to each
 other in the 1,2- or 2,1-positions,

t is 0 or 1,

r is 1, 2 or 3, and

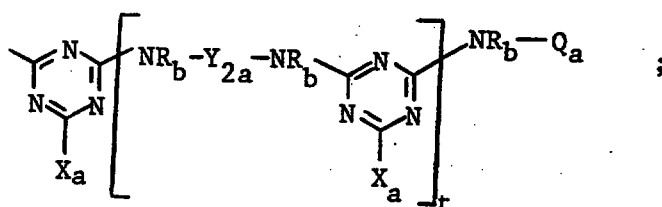
v is 2 or 3, and R_1 is as defined above.

Most preferably Q is Q_c where Q_c is

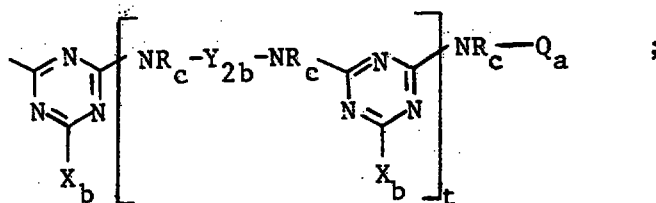


in which R_b and each R_{1b} are as defined above.

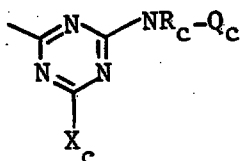
Z is preferably Z_a where Z_a is



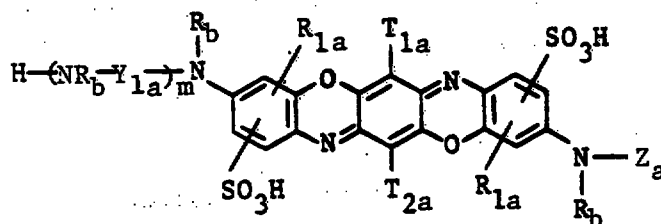
more preferably Z_b , where Z_b is



even more preferably Z_c , where Z_c is Z_b in which t is 0 and Q_a is Q_b . Most preferably Z is Z_d , where Z_d is



Preferred compounds of formula I correspond to formula Ia



Ia

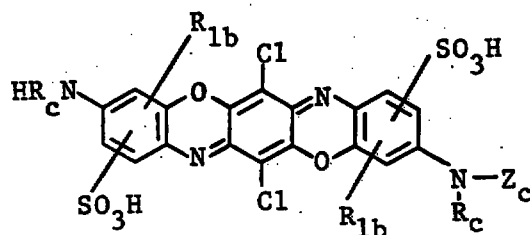
and salts thereof.

More preferred are compounds of formula Ia in which

- (1) each T_{1a} and T_{2a} is chlorine;
- (2) Y_{1a} is Y_{1b} ;
- (3) each R_b independently is R_c ;
- (4) Z_a is Z_b ;
- (5) m is 0.

Even more preferred compounds of formula I correspond to formula

Ib



Ib

and salts thereof.

Most preferred are compounds of formula Ib in which

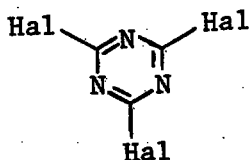
- (1) each R_c is hydrogen;
- (2) each R_{1b} is hydrogen;
- (3) Z_c is Z_d .

In the compounds of formula I, Ia and Ib, any floating sulpho group on each terminal phenyl ring of the condensed ring system is preferably bound to a carbon atom which is in an ortho-position to the carbon atom to which the external amino group is attached.

The compounds of formula I are in free acid or salt form (including mixed salt forms). Preferably, each cation of a salt is independently a non-chromophoric cation. Such salt forms include salts of alkali metals, such as lithium, sodium or potassium, or unsubstituted or substituted ammonium salts, or mixed salts thereof. Substituted ammonium salts may be those in which the ammonium cation is derived from a primary, secondary or tertiary amine, and the following amines may be suitable for example: mono-, di- or trimethyl-, -ethyl-, -propyl- or -butyl-amine; mono-, di- or tri-ethanol-, -propanol- or isopropanol-amine; N-methyl-N-hydroxyethylamine, N-methyl-N,N-di-(hydroxyethyl)amine, N-ethyl-N-hydroxyethoxyethylamine, morpholine, piperidine, piperazine, N-hydroxyethylmorpholine, N-hydroxyethylpiperazine, N-aminoethylpiperazine; ethylenediamine, hexamethylenediamine; dimethylaminopropylamine, diethylamino-propylamine, diethylene glycol amine, diglycol amine and 3-methoxypropylamine. Also suitable as amines are polyglycol amines which may be obtained for example by reacting ammonia, alkyl- or hydroxyalkylamine with alkylene oxides.

The substituted ammonium ion may also be a quaternary ammonium ion which is derived from ammonium compounds which preferably contain one or two quaternary ammonium ions; examples which may be mentioned are: tetramethyl-, tetraethyl-, trimethylethyl-, dimethyl-di(2-hydroxypropyl)-, trimethylhydroxyethyl-, tetra-hydroxyethyl- and trimethylbenzyl-ammonium hydroxide.

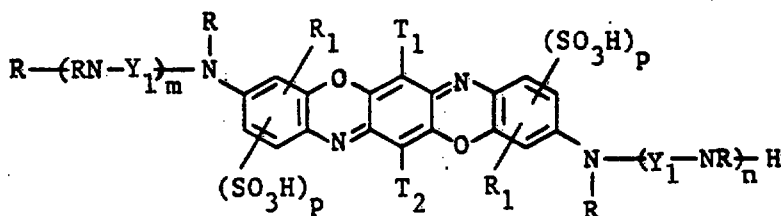
The present invention further provides a process for the preparation of compounds of formula I and mixtures thereof comprising reacting one mole of a compound of formula II



II

in which Hal is halogen,
with

- one mole of a compound of formula III



III

in which the symbols are as defined above,
and

- one mole of a compound of formula IV



IV

in which R and Q are as defined above,
and optionally

- one mole of a compound of formula V

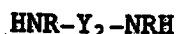


V

in which X' is an unsubstituted or substituted amino group,

in any desired order to obtain a compound of formula I in which for the group Z t is 0.

Compounds of formula I in which for the group Z t is 1 may be prepared in an analogous manner as described above but adding a further reaction step to introduce the group -NR-Y₂-NR- by reacting one mole of a cyanuric halide or one or two different appropriate mono- or dicondensation products thereof with 1/2 mole of a compound of formula VI



VI

in which R and Y₂ are as defined above.

The separate condensation reactions for the stepwise exchange of the halogen atoms on the triazine ring may be effected in accordance with known methods and take place under conditions which are conventional for the exchange of the first, second and third halogen atom on the triazine ring.

Preferably, introducing of a group X' is carried out as the last step in the reaction sequence.

The compounds of formulae III, IV, V and VI used as starting material are either known or may be prepared in accordance with known methods using known starting compounds.

The compounds of formula I may be isolated in accordance with known methods, for example by precipitating the compound of formula I from the reaction solution, for example with ethanol, filtering off and drying. Furthermore, a resultant compound of formula I may be used per se in the form of the solution obtained, or the solution can also be converted into a solid form by spray-drying.

When a compound of formula I is in salt form, the cation associated with the sulpho groups is not critical and may be any one of those non-chromophoric cations mentioned above but can be influenced in various manner depending on the process used in accordance with conventional methods. In particular, mixed salts may be produced.

The compounds according to the invention in form of their water-soluble salts may be used for dyeing or printing hydroxy group- or nitrogen-containing organic substrates. They may be used for example for dyeing or printing fibres, filaments or textiles produced therefrom, which consist of or contain natural or synthetic polyamides or natural or regenerated cellulose material, e.g. cotton, in accordance with known methods; cotton is preferably dyed by the exhaust process,

for example from a long or short liquor and at room temperature to boiling temperature.

Printing is effected by impregnation with a printing paste which is prepared by known methods.

The new compounds can also be employed for dyeing or printing leather, preferably chrome-tanned types of leather, by known methods. In addition, they may be used in the production of inks according to known methods.

The compounds of formula I are especially suitable for dyeing or printing paper, e.g. for the production of mass-dyed, sized or unsized paper. They can also be used for dyeing paper by the dipping process or in the sizing press. Dyeing and printing take place by known methods. The dyeings and prints obtained (especially those on paper) have good fastness to use properties.

The compounds of formula I may also be used in the form of dyeing preparations. This form of application is preferred in particular when dyeing paper. The processing into stable, liquid, preferably aqueous, concentrated dyeing preparations may take place in accordance with known methods, advantageously by dissolving in suitable solvents, optionally in the presence of an adjuvant, e.g. a hydrotropic compound or a stabiliser. Of particular advantage is the possibility of producing such stable, aqueous-concentrated preparations in the course of dyestuff synthesis itself, without intermediate isolation of the dye.

Suitable hydrotropic assistants are for example low molecular weight amides, lactones, alcohols, glycols or polyols, low molecular weight ethers or oxyalkylation products, as well as nitriles or esters. Preferred assistants are methanol, ethanol, propanol; ethylene-, propylene-, diethylene-, thiodiethylene- and dipropylene-glycol; butanediol; β -hydroxy-propionitrile, pentamethylene-glycol, ethylene-glycol-monoethyl- and -propyl-ether, ethylene-diglycol-monoethylether, triethylene-glycol-monobutylether, butyl-polyglycol, formamide, dimethyl-formamide, pyrrolidone, N-methyl-pyrrolidone, glycol acetate, butyrolactone, urea and ϵ -caprolactam.

Due to the presence of a hydrotropic compound, the stability in storage of the dyestuff preparation and the solubility of the dyestuff used can be further improved.

A suitable composition of a liquid preparation is as follows (parts are by weight):

100 parts of a compound of formula I as a water-soluble salt,
1-100, preferably 1-10 parts of an inorganic salt,
100-800 parts of water,
0-500 parts of one of the above-listed hydrotropic compounds.

Depending on the salt form, the liquid preparations may be suspensions or preferably true solutions. The preparations are stable and can be stored for a long period of time.

Similarly, the compounds of formula I can be processed in accordance with known manner into solid, preferably granulated dyeing preparations, advantageously by granulating, as described in British Patent Specification No. 1.241.053 A.

A suitable solid composition is as follows (parts are by weight):

100 parts of a compound of formula I as a water-soluble salt,
1-100, preferably 1-10 parts of an inorganic salt,
0-800 parts of a standardising agent (preferably non-ionic,
such as starch, dextrin, sugar, grape sugar or urea).

The solid preparation may contain up to 10% residual moisture.

The compounds of formula I have good solubility properties dependent on the cation or cation mixture associated with the sulpho groups, and are especially notable for their solubility in cold water. Furthermore, when producing sized or unsized paper, they hardly colour the waste water at all or only slightly. They do not mottle on paper, are substantially insensitive to filler and pH variations and have

minimal inclination towards two-sided effects on paper.

The dyeings on paper have good light fastness; after a long-term exposure to light, the shade alters tone-in-tone. The dyed papers have good wet fastness properties to water, milk, fruit juices, sweetened mineral water and tonic water, and in addition have good alcohol fastness. The dyes have high substantivity, i.e. they are absorbed practically quantitatively, and thus show good build-up. They can be added to the paper pulp directly, i.e. without previously dissolving, as a dry powder or as granules, without any reduction in brilliance or colour yield. However, true solutions of the dyestuffs as given above are advantageously employed. They are stable, of low viscosity and can therefore be dosed well.

The dyed papers can be bleached perfectly both by oxidation and by reduction, which is important for the re-use of waste paper.

Production of the paper dyeings using the described dyes can also be effected in soft water. In addition, fibrous materials containing mechanical wood pulp can be dyed in good quality.

Furthermore, the dyeings and prints obtained on textile material, and particularly those on textiles containing or consisting of cellulose, exhibit good light and wet fastness properties.

The wet fastness properties of these dyeings or prints obtained with compounds of formula I and especially with those in which for a group Z t is 1, may be notably improved by a special resin after-treatment with selected auxiliaries. Particularly, this treatment gives improved wash fastness properties, allowing repeated washing at high temperatures.

Suitable for applying to the dyed or printed substrate is a fixing agent comprising a precondensate or mixture of either

(A) the product of reacting a mono- or polyfunctional primary or secondary amine with cyanamide, dicyandiamide, guanidine or biguanide; or ammonia with cyanamide or dicyandiamide, said product (A) contain-

ing reactive hydrogen atoms bound to nitrogen,
or

(B) a quaternary polyalkylene polyamine
with

(C) an N-methylol derivative of a urea, melamine, guanamine,
triazinone, urone, carbamate or acid amide, optionally together with

(D) a catalyst for the crosslinking of N-methylol compounds of the
type (C) above.

Details concerning the fixing agent as a combination of (A), (C)
and (D) and its use are described in British Patent Application No.
2.070.006 A; details concerning the combination (B), (C) and (D) are
described in British Patent Application No. 2.084.597 A.

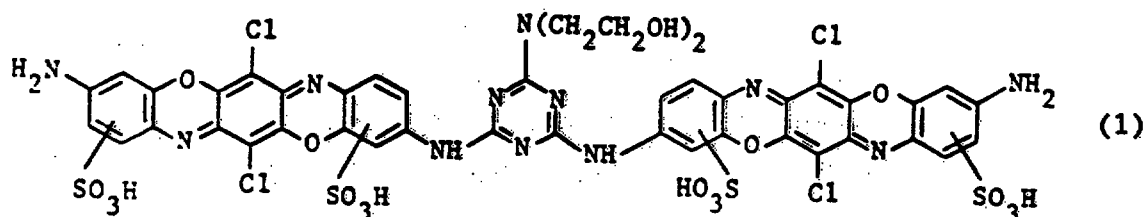
The following examples illustrate the invention. All parts and
percentages are by weight and all temperatures are given in degrees
celsius, unless indicated to the contrary.

Example 1

10 Parts of cyanuric chloride are stirred well into 100 parts of
water and 100 parts of ice. To the suspension thus obtained 27 parts
of 2,9-diamino-6,13-dichloro-triphenedioxazine disulphonic acid are
added dropwise which have been dissolved in 200 parts of water and
adjusted to pH 7 by the addition of sodium hydroxide solution. During
the condensation, the pH is maintained at 6-7 by adding sodium hydrox-
ide solution and stirring is effected for at least three hours at
15-18°. After this time, the monocondensation is completed. It is
evident from thin layer chromatogram which does not show a red zone
that the starting compound has only been monoacylated.

In a second step, a further 27 parts of 2,9-diamino-6,13-dichloro-
triphenedioxazine disulphonic acid which have been dissolved in 200
parts of water and adjusted to pH 7 are added. The temperature is
raised to 80° and the pH is maintained at 6-7 with sodium hydroxide
solution. After four hours, the dicondensation is completed. 50 Parts
of diethanolamine are subsequently added and the temperature is ele-

vated to 98°. After one further hour, from thin layer chromatogram it can be seen that the reaction has been completed. The blue dyestuff solution thus produced is cooled to 40-50° and the dyestuff precipitates by adding 1000 parts of ethanol. It is filtered off by suction and dried. The dyestuff thus obtained having the formula

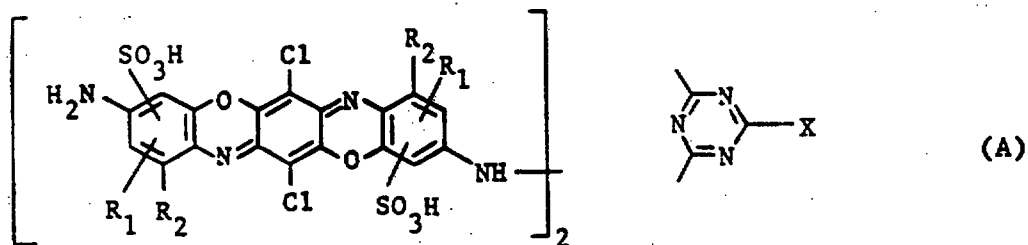


is a blue powder which is well soluble in water and dyes paper a brilliant blue shade. The properties of these paper dyeings with respect to wet fastnesses and backwater colouration are good, their light fastness is notably good.

In formula (1) each floating $-SO_3H$ group is preferably in one of the ortho positions relative to the carbon atom of the phenyl ring to which the external amino group is attached.

Examples 2-24

By analogy with the method described in Example 1, using appropriate starting compounds, further compounds of formula I may be prepared. They correspond to formula (A)



in which the symbols are as defined in the following Table 1.

In case where in formula (A) R_1 is hydrogen, the floating $-SO_3H$ group on each terminal phenyl ring may be in one of the ortho positions relative to the carbon atom to which the external amino group is attached. Similarly, in case where R_1 is other than hydrogen, R_1 and SO_3H , respectively, can be attached to each of these ortho positions. This is due to the directions possible for the ring closure reaction.

The paper dyeings obtained with the dyestuffs listed in Table 1 are all brilliant blue. They show good properties with respect to backwater colouration and light- and wet-fastnesses.

Table 1 / Compounds of formula (A)

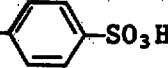
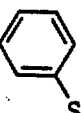
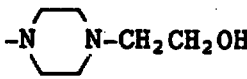
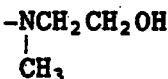
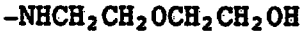
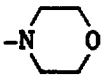
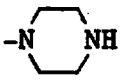
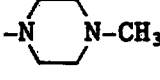
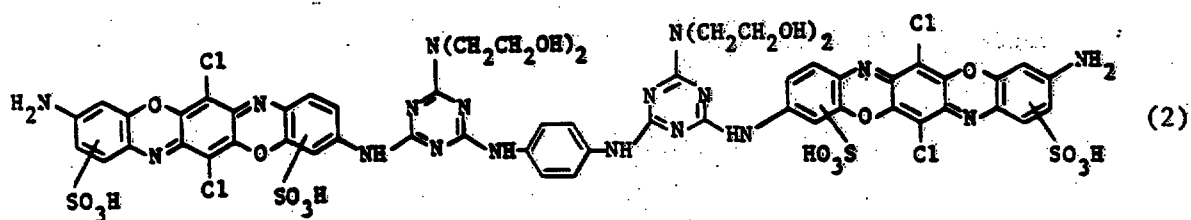
Ex.No.	R_1	R_2	X
2	H	OCH ₃	$-N(CH_2CH_2OH)_2$
3	H	COOH	do.
4	CH ₃	H	do.
5	Cl	H	do.
6	H	H	$-NHCH_2CH_2OH$
7	H	H	Cl
8	H	H	$-NHCH_2CH_2SO_3H$
9	H	H	$-NH_2$
10	H	H	$-NH-$ 
11	Cl	H	$-N-$ 
12	H	H	$-NH-$ 
13	H	H	$-NH-$ 
14	H	H	$-NHCH_2CHCH_3$ OH
15	H	OCH ₃	$-NHCH_2CH_2OH$

Table 1 (continued)

Ex.No.	R ₁	R ₂	X
16	H	H	
17	H	H	
18	H	H	
19	H	H	
20	H	H	
21	H	H	
22	H	COOH	do.
23	H	H	
24	H	H	

Example 25

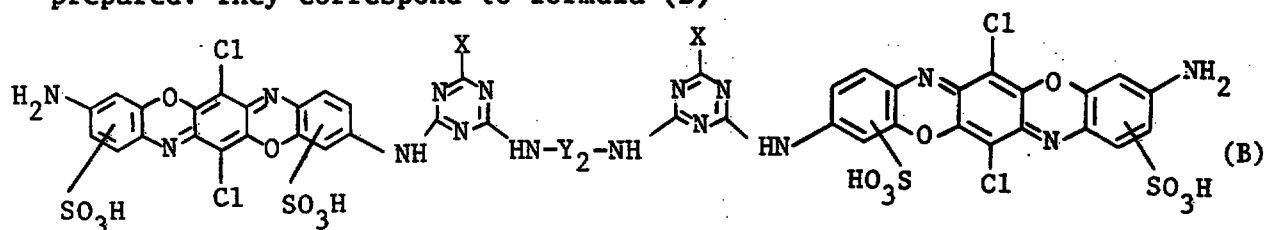
10 Parts of cyanuric chloride are reacted with 27 parts of 2,9-diamino-6,13-dichlorotriphenyldioxazine disulphonic acid in accordance with the method described in Example 1 to form a monocondensate. Subsequently, 2.9 parts of 1,4-diaminobenzene are added and the temperature is raised to 50-60°. The pH is kept at 7-8 by the addition of sodium carbonate. After approximately four hours the reaction is completed. 50 Parts of diethanolamine are then added. The temperature is elevated to 95° and the mixture is stirred for one further hour. The resultant blue dyestuff solution is then cooled to ca. 30-40° to which 1000 parts of acetone are added. The dyestuff precipitates and is filtered off and dried; it corresponds, in free acid form, to the formula



and is well soluble in water. This dyestuff dyes paper or cotton a brilliant blue shade. The fastness properties of these dyeings with respect to backwater colouration and wet fastnesses are perfect, their light fastness is excellent.

Examples 26 to 40

By analogy with the method described in Example 25, using appropriate starting compounds, further compounds of formula I may be prepared. They correspond to formula (B)

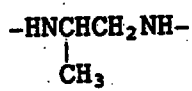
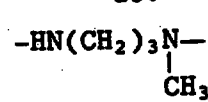
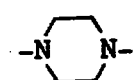


in which the symbols are as defined in the following Table 2.

The paper or cotton dyeings obtained with the dyestuffs listed in Table 2 are all brilliant blue and show perfect fastness properties.

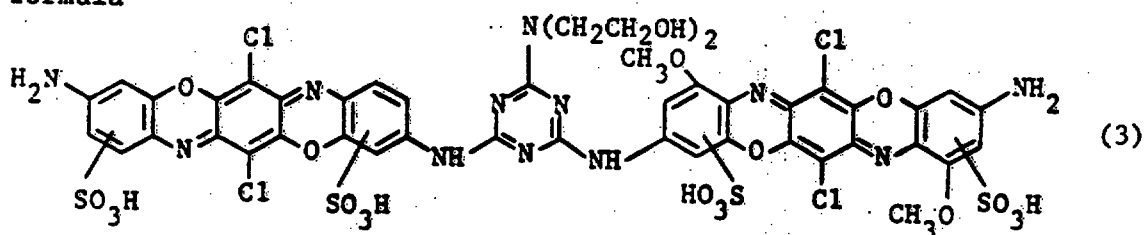
In a compound of formula (2) as well as in a compound of formula (B), each floating $-SO_3H$ group is preferably in an ortho position relative to the carbon atom of the phenyl ring to which the external amino group is attached.

Table 2 / Compounds of formula (B)

Ex.No.	-NH-Y ₂ -NH-	each X
26		Cl
27	do.	-NHCH ₂ CH ₂ OH
28		do.
29	do.	Cl
30	do.	-N(CH ₂ CH ₂ OH) ₂
31	-HNCH ₂ CH ₂ NH-	do.
32	do.	Cl
33		Cl
34	do.	-NHCH ₂ CH ₂ OH
35		Cl
36	do.	-N(CH ₂ CH ₂ OH) ₂
37		Cl
38	do.	-N(CH ₂ CH ₂ OH) ₂
39		do.
40	do.	Cl

Example 41

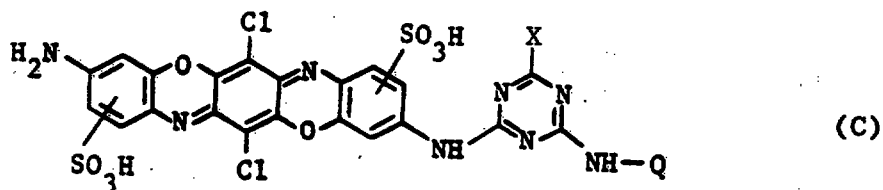
By analogy with the method described in Example 1 but using, after the monocondensation has been completed, 28 parts of 2,9-diamino-4,11-dimethoxy-6,13-dichlorotriphenyldioxazine disulphonic acid instead of 27 parts of 2,9-diamino-6,13-dichlorotriphenyldioxazine disulphonic acid and replacing the last chloro substituent of the triazine with the corresponding amount of diethanolamine, the dyestuff of the formula



is obtained which dyes paper a brilliant blue shade. These paper dyeings show good properties with respect to backwater colouration and wet fastnesses and have very good light fastness properties.

Examples 42 to 61

By analogy with the method described in Example 41, using appropriate starting compounds, further compounds of formula I may be prepared containing different chromophoric parts. They correspond to formula (C)



in which the symbols are as defined in the following Table 3. In the last column of Table 3 the shade on paper is given. The paper dyeings thus obtained show notably good light fastness and their properties with respect to backwater colouration and wet fastnesses are good.

In a compound of formula (3) and in a compound of formula (C) listed in Table 3, each floating $-SO_3H$ group is preferably in an ortho position relative to the carbon atom of the phenyl ring to which the external amino group is attached.

Table 3 / Compounds of formula (C)

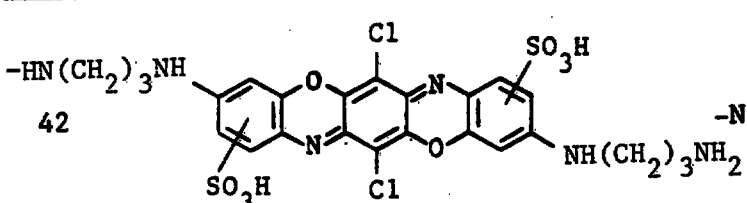
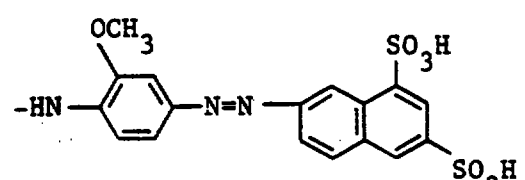
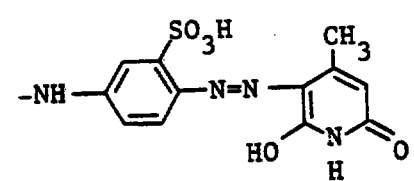
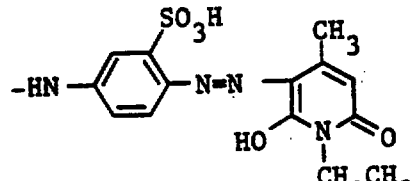
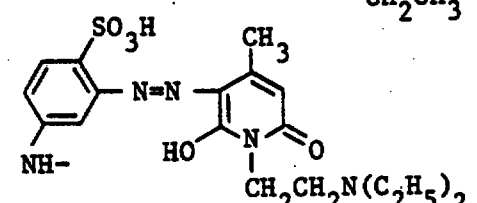
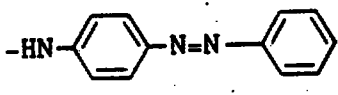
Ex.No.	-NH-Q	X	shade on paper
42		$-N(CH_2CH_2OH)_2$	blue
43	do.	$-NHCH_2CH_2OH$	do.
44	do.	$-NH_2$	do.
45		$-N(CH_2CH_2OH)_2$	greenish olive
46		do.	do.
47		do.	do.
48		$-NHCH_2CH_2OH$	do.

Table 3 (continued)

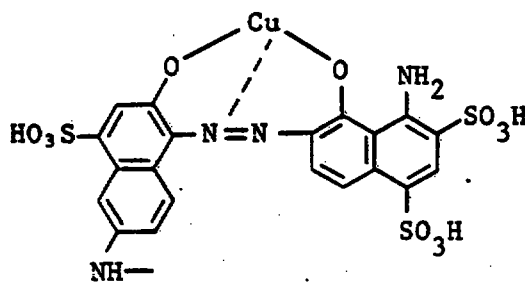
Ex.No.	-NH-Q	X	shade on paper
49		-NHCH ₂ CH ₂ OH	bluish olive
50	do.	-N(CH ₂ CH ₂ OH) ₂	do.
51		do.	do.
52	do.	Cl	do.
53	do.	-NHCH ₂ CH ₂ SO ₃ H	do.
54	do.		do.
55		do.	do.
56			do.
57		-NHCH ₂ CH ₂ OH	do.

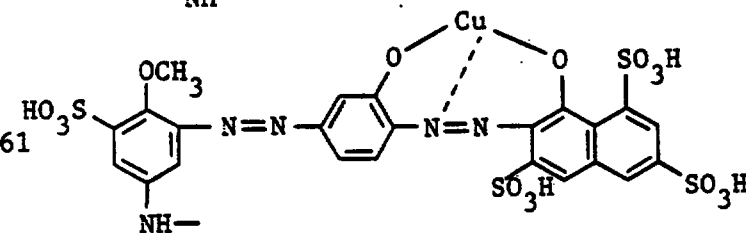
Table 3 (continued)

Ex.No.	-NH-Q	X	shade on paper
--------	-------	---	----------------

58		$-N(CH_2CH_2OH)_2$	bluish olive
----	---	--------------------	--------------

59	do.		do.
----	-----	--	-----

60		$-N(CH_2CH_2OH)_2$	blue
----	---	--------------------	------

61		do.	do.
----	---	-----	-----

In accordance with the preparation method as described in Example 1 or 25 the compounds of Examples 1 to 61 are obtained in sodium salt form or, depending on the amine used for replacing the last chloro substituent on the triazine ring to introduce X, in mixed sodium / mono- or di-ethanolammonium salt form. They may, depending on the reaction and isolation conditions or by reacting the sodium salts or mixed sodium/ammonium salts in accordance with known methods, also be obtained in free acid form or in other salt forms, for example those salt forms containing one or more cations indicated in the description above.

Each compound of Examples 1 to 61 is obtained as a mixture of isomers with respect to the position of the sulpho groups and any R_1 relative to the sulpho group of the condensed ring system. Such a mixture normally has not to be separated into individual isomers due to the fact that the position of the sulpho group whether it is in one

ortho position or in the other does not affect the dyeing properties of each compound; but separation into individual isomers could be done if necessary by conventional means, for example by thin layer chromatography.

In the following examples some liquid-aqueous dyeing preparations of the compounds as exemplified are illustrated.

Example 62

35 Parts of the dyestuff prepared according to Example 1 as a moist presscake are stirred into 1400 parts of water, and 375 parts of urea are added. A solution is produced by heating to 40°. This solution is stable in storage for a long period of time, i.e. there is no precipitation either in the cold or in the heat.

Example 63

Using the method of Example 1, but treating the reaction solution with hydrochloric acid to make it strongly acid, instead of treating it with ethanol following the third condensation step, the dyestuff of formula (1) precipitates in free acid form. The resultant presscake is dissolved in 300 parts of water and 100 parts of diethanolamine. A stable solution of the dyestuff of Example 1, which is ready for use, is formed in the form of the diethanolamine salt.

Example 64

By using 20 parts of lithium monohydrate, instead of the diethanolamine in Example 63, a stable concentrated solution of the dyestuff in form of the lithium salt is similarly obtained.

Analogously to the method described in Examples 62 to 64, the dyestuffs of Examples 2-61 can be used in place of that of Example 1, to form the appropriate salt forms and produce liquid-aqueous dyeing preparations having high stability in storage.

In the following examples the application of the compounds according to the invention and their liquid-aqueous dyeing preparations are illustrated. Percentage figures for components of a dyebath or treatment bath are based on the dry weight of substrate.

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 Hollander in 2000 parts of water. 0.2 Parts of the dyestuff of Example 1 are sprinkled into this mass, or 1.0 part of the liquid dyestuff preparation according to Example 62 or 63 is added. After mixing for 20 minutes, paper is produced therefrom. The absorbent paper thus obtained is dyed brilliant blue. The waste water is practically colourless.

Application Example B

0.6 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 Hollander in 2000 parts of water. After thorough mixing for 15 minutes, sizing takes place in the usual way with rosin size and aluminium sulphate. Paper which is produced from this material has a brilliant blue shade and possesses good properties with respect to waste water colouration and wet fastnesses, as well as notably 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°:

- 0.6 parts of the dyestuff of Example 1
- 0.4 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 brilliant blue.

Similarly, the dyestuffs of Examples 2 to 61 or a liquid-aqueous dyeing preparation thereof may be used to dye paper in accordance with the method described in Application Examples A to C. The paper dyeings thus obtained have a blue to olive shade and show good general fastness properties.

Application Example D

50 Parts of bleached sulphite cellulose of pinewood and 50 parts of bleached beech cellulose [grinding degree 30°SR*)] are mixed together with 0.6 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 intensively brilliant blue shade. A dyeing at pH 7 on the other hand shows no variation in depth or shade.

The exhaustion rate reaches 100% and the waste water is colourless.

*) °SR = Schopper-Riegler degree

Application Example E

100 Parts of intermediately-dried chrome suede leather are drummed for one hour at 50° in a vat containing a bath of 400 parts of water, 2 parts of 25% ammonium hydroxide solution and 0.2 parts of a commercial wetting agent. The bath is subsequently drained. 400 parts of water of 60° and 1 part of 25% ammonium hydroxide solution are added to the drummed, still moist chrome suede leather. After adding 5 parts of the dyestuff of Example 1, dissolved in 200 parts of water, dyeing is effected for 90 minutes at 60°. 50 Parts of a 8% formic acid are then slowly added so as to make the pH acidic. Treatment is effected for a further 30 minutes. Finally, the leather is rinsed, dried and finished in the usual way. The blue leather dyeing thus obtained is evenly dyed.

The dyestuffs of Examples 2-61 may also be used for dyeing leather analogously to the method described in Application Example E.

Application Example F

100 Parts of pre-moistened cotton fabric are added at 30° to a dye-bath consisting of 3000 parts of demineralised water, 2 parts of sodium carbonate and 1 part of the dyestuff of Example 1. After adding 10 parts of Glauber's salt, the bath is heated to boiling temperature over the course of 30 minutes, whereby during this heating process, a further 10 parts of Glauber's salt is added respectively at the temperature stage 50° and again at 70°. Dyeing then continues for a further 15 minutes at boiling temperature, and 10 parts of Glauber's salt are finally added. The dyebath is then allowed to cool. At 50°, the dyed fabric is removed from the liquor, rinsed with water and dried at 60°. A blue cotton dyeing with good fastness properties is obtained.

Similarly, the dyestuffs of Examples 2-61 may be used for dyeing cotton analogously to the method described in Application Example F.

Application Example G

0.1 Part of the dyestuff of Example 26 is dissolved in 200 parts of water at 60°. 10 Parts of cotton, 16 parts of Glauber's salt and 4 parts of sodium carbonate are subsequently added to the dyebath. The temperature is raised to 98° over the course of 45 minutes.

Dyeing is continued for one hour at 98°. During dyeing, the water that evaporates is continuously replaced. The dyed fabric is then removed from the liquor and is rinsed with running cold and then hot water. The cotton dyeing is washed at the boil for 20 minutes in 500 parts of demineralised water in the presence of 0.5 parts of Marseilles soap. After being rinsed, a brilliant blue cotton dyeing is obtained showing good properties with respect to light fastness, wet fastnesses and fastness to chlorine.

Application Example H

0.1 Part of the dyestuff of Example 25 is dissolved in 200 parts of demineralised water. The dyebath is heated to 40-50°, then 10 parts of cotton cretonne (bleached) are added. Within 30 minutes the temperature is elevated to 98°. At this temperature 1 part and after 10 minutes further 2 parts of Glauber's salt (calcined) are added, and the dyeing temperature is kept at 98° for 35 minutes. Finally, the dyebath is cooled to 80° within 15 minutes. Water that evaporates during the dyeing process is continuously replaced by demineralised water at 98°. The dyed fabric is rinsed with running cold water for 5 minutes, centrifuged and dried at 80°. The resultant cotton dyeing is brilliant blue and shows notably good light- and wet-fastness properties.

Application Example I

A blue standard depth dyeing on cotton fabric obtained with the dyestuff of Example 25 in accordance with the method described in Application Example H, is padded with an aqueous solution containing 100g/l of a fixing agent which is a mixture given below, and is squeezed out to give a pick-up of about 80%. The fabric is then shock-dried on a tension frame at 175-180° in such a way that the cross-linking time of the dry fabric is 30-45 seconds at this temperature.

The fixing agent is a reaction product (at 70° during three hours) of

(A) 68.5 parts of a spray-dried solution at pH 7.5 which has been obtained by condensation of 103 parts of diethylene triamine with 84 parts of dicyandiamide at 110° (raised to 160°) and subsequent stepwise neutralisation with a 44.6% sulphuric acid with the addition of ice, and

(C) 457 parts of a 50% solution of dimethyloldihydroxyethylene urea heated to 70°,
to which 23 parts of dicyandiamide are added to use as a stabilising agent. This product may be employed as such or together with a catalyst to increase the cross-linking, e.g., magnesium chloride.

The brilliant blue cotton dyeing fixed in such a way exhibits excellent wash fastness and withstands repeated washing at 60° and even a washing at the boil.

Application Example K

Instead of the fixing agent used in Application Example I it is also possible to employ the water-soluble pre-condensate which is obtained reacting

(B) 100 parts of a 50% aqueous solution of the reaction product of epichlorohydrin and dimethylamine with

(C) 150 parts of a 50% aqueous solution of dimethyloldihydroxyethylene urea in the presence of

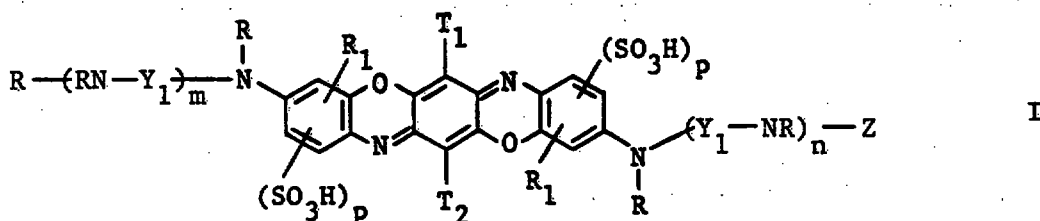
(D) 20 parts of magnesium chloride · hexahydrate at 70° during 30 minutes.

The resultant brilliant blue cotton dyeing after-treated in such a way shows excellent wash-fastness. At the same time a significant improvement of crease-resistance is obtained.



CLAIMS:

1. A compound of formula I



and salts thereof,

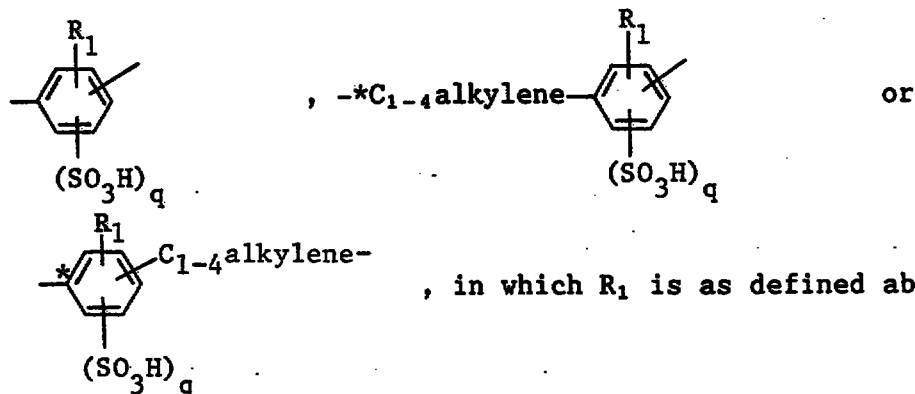
in which

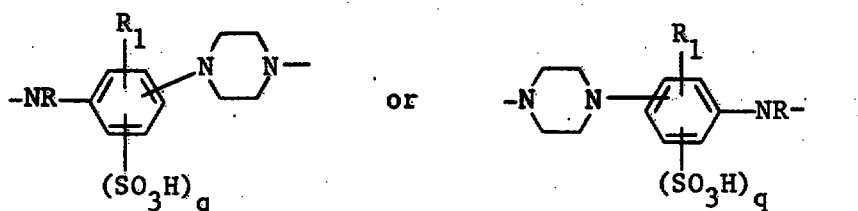
each R, independently, is hydrogen, C₁₋₆alkyl or C₁₋₆alkyl monosubstituted by halogen, cyano, hydroxy, C₁₋₄alkoxy, -COOH, -SO₃H or -OSO₃H,

each R₁, independently, is hydrogen, halogen, C₁₋₄alkyl, C₁₋₄alkoxy or -COOH,

each T₁ and T₂, independently, is hydrogen, chlorine, bromine, unsubstituted C₁₋₄alkyl or C₁₋₄alkoxy, or C₁₋₄alkyl or C₁₋₄alkoxy monosubstituted by chlorine, methoxy, ethoxy or -OSO₃H, unsubstituted phenyl or phenoxy, or phenyl or phenoxy which are substituted by one or two substituents selected from chlorine, bromine, methyl, ethyl, methoxy and ethoxy,

each Y₁, independently, is -C₂₋₆alkylene-, monohydroxy- or dihydroxy-substituted -C₃₋₆alkylene-, -C₃₋₆alkylene- which is interrupted by -O-, -S- or -NR-, unsubstituted cyclohexylene or cyclohexylene which is substituted by up to three methyl groups,

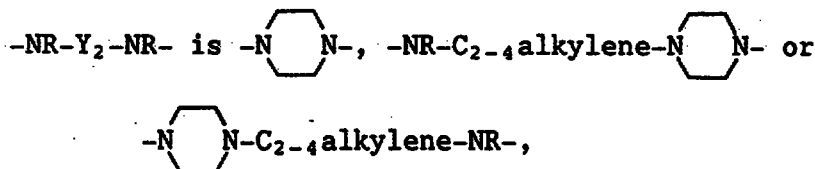



$$-\text{NR}-\text{C}_{2-4}\text{alkylene}-\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{N} \begin{array}{c} \diagdown \\ \diagup \end{array} \text{N}-\text{C}_{2-4}\text{alkylene}-\text{NR}-,$$


Z is

$$\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{X} \end{array} \right] \text{NR}-\text{Y}_2\text{NR}-\left[\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{X} \end{array} \right] \text{NR}-\text{Q}$$

Y₂ is a bridging group selected from a divalent aliphatic, cycloaliphatic, aromatic and aliphatic-aromatic group, where each such group is unsubstituted or substituted and where each aliphatic group is optionally interrupted by -O-, -S- or -NR-, or





Q is a chromophoric radical selected from the series of
azo-, formazan-, anthraquinone-, phthalocyanine- and
dioxazine- dyestuffs,

each m and n, independently, is 0 or 1,
each p, independently, is 0, 1 or 2,
each q, independently, is 0 or 1, and
t is 0 or 1,

provided that in a compound of formula I at least one sulphonic
acid group is present,
and a mixture of compounds of formula I.

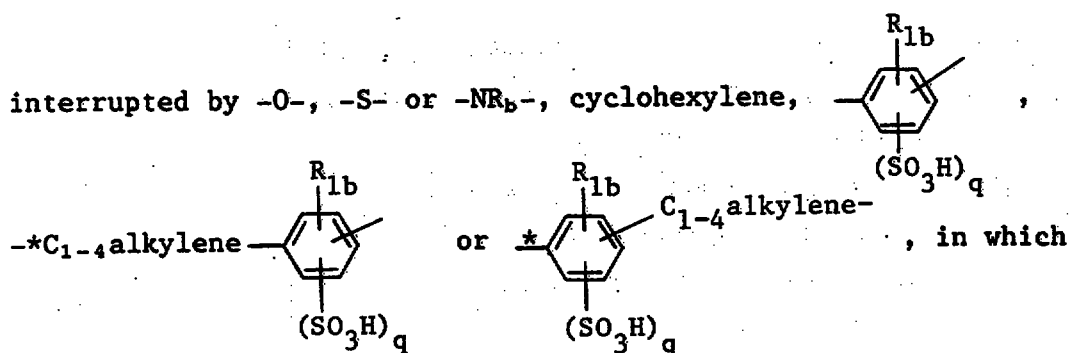
2. A compound according to Claim 1, in which any floating sulpho
group on each terminal phenyl ring of the condensed ring system is
bound to a carbon atom which is in an ortho-position relative to the
carbon atom to which the external amino group is attached.

3. A compound according to Claim 1 or 2, in which each R is R_a
where each R_a independently is hydrogen, unsubstituted C₁₋₄alkyl or
C₁₋₄alkyl monosubstituted by chlorine, cyano, hydroxy, methoxy, -COOH,
-SO₃H or -OSO₃H.

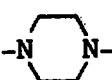
4. A compound according to any one of Claims 1 to 3, in which
each R₁ is R_{1a} where each R_{1a} independently is hydrogen, chlorine,
methyl, ethyl, methoxy, ethoxy or -COOH.

5. A compound according to any one of Claims 1 to 4, in which T₁
is T_{1a} and T₂ is T_{2a}, where each T_{1a} and T_{2a} independently is
hydrogen, chlorine, bromine, methyl, ethyl, methoxy, ethoxy, unsub-
stituted phenyl or phenoxy or phenyl or phenoxy which is substituted
by one or two substituents selected from chlorine, bromine, methyl,
ethyl, methoxy and ethoxy.

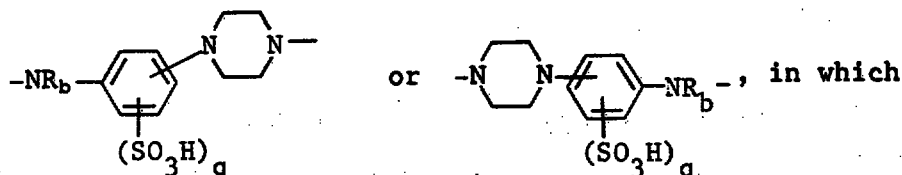
6. A compound according to any one of Claims 1 to 5, in which
each Y₁ is Y_{1a} where each Y_{1a} independently is -C₂₋₆alkylene-,
monohydroxy-substituted -C₃₋₆alkylene-, -C₃₋₆alkylene- which is



R_b is hydrogen, methyl, ethyl or C₂₋₃alkyl monosubstituted by hydroxy or methoxy,
 R_{1b} is hydrogen, chlorine, methyl, methoxy or -COOH,
 q is 0 or 1, and
 each asterisk identifies the carbon atom which is attached to the amino group bound to the ring system, or
 each -NR-Y₁-NR- is -NR_b-Y_{1a}-NR_b-, where each -NR_b-Y_{1a}-NR_b-

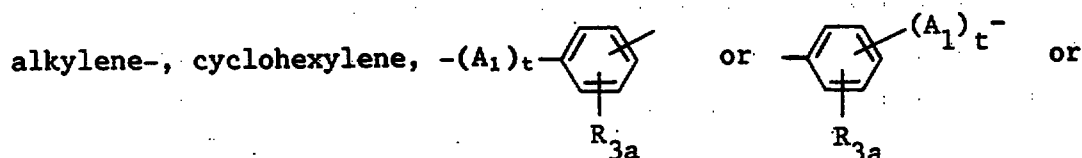
independently is ,

-NR_b-C₂₋₄alkylene-, -C₂₋₄alkylene-NR_b-,



R_b and q are as defined above.

7. A compound according to any one of Claims 1 to 6, in which Y₂ is Y_{2a}, where Y_{2a} is -C₂₋₆alkylene-, -C₃₋₆alkylene- which is interrupted by -O-, -S- or -NR_b, monohydroxy-substituted -C₃₋₆-



-NR-Y₂-NR- is -NR_b-Y_{2a}-NR_b- where -NR_b-Y_{2a}-NR_b- is ,

-NR_b-C₂₋₄alkylene- or -C₂₋₄alkylene-NR_b-,



in which

each R_b independently is hydrogen, methyl, ethyl or C_{2-3} alkyl monosubstituted by hydroxy or methoxy,

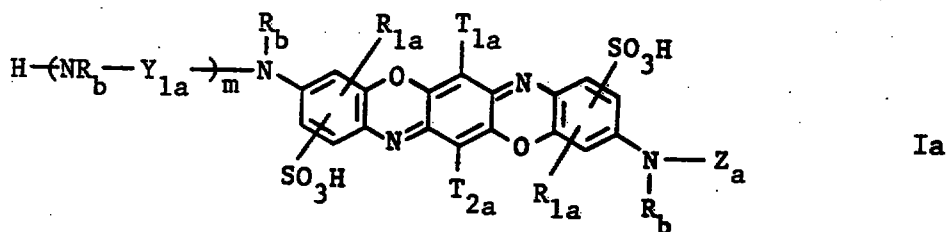
A_1 is $-C_{1-4}$ alkylene-,

t is 0 or 1, and

R_{3a} is hydrogen, chlorine, methyl, methoxy, $-COOH$ or $-SO_3H$.

8. A compound according to Claim 7, in which each X is X_a where each X_a independently is fluorine, chlorine or $-NR_4R_5$, in which each R_4 and R_5 independently is hydrogen, C_{1-6} alkyl, C_{1-6} alkyl monosubstituted by hydroxy, halogen, cyano, C_{1-4} alkoxy, hydroxy-substituted C_{1-4} alkoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$, cyclohexyl, phenyl or phenyl(C_{1-4} alkyl) in which each phenyl ring is unsubstituted or substituted by one to three substituents selected from chlorine, C_{1-4} alkyl, C_{1-4} alkoxy, $-COOH$, $-SO_3H$ and $-NH_2$, or $-NR_4R_5$ forms a pyrrolidine, piperidine, morpholine or piperazine ring of which latter ring the second N-Atom is unsubstituted or substituted by methyl, ethyl, 2-hydroxyethyl or 2-aminoethyl.

9. A compound according to Claim 1 or 2, which corresponds to formula Ia



and salts thereof, in which

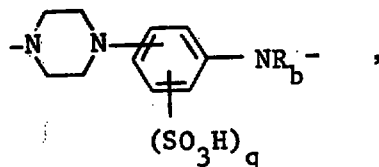
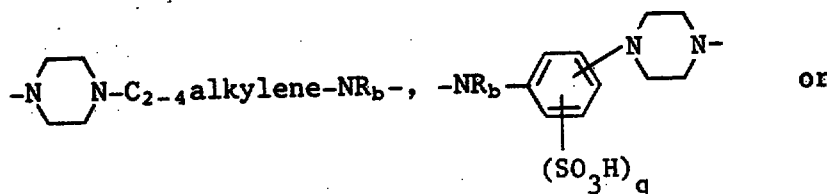
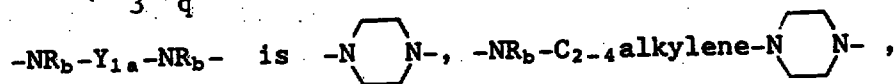
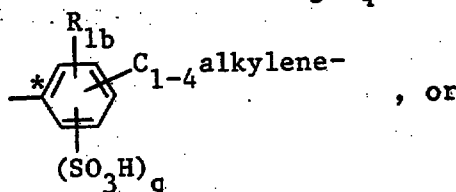
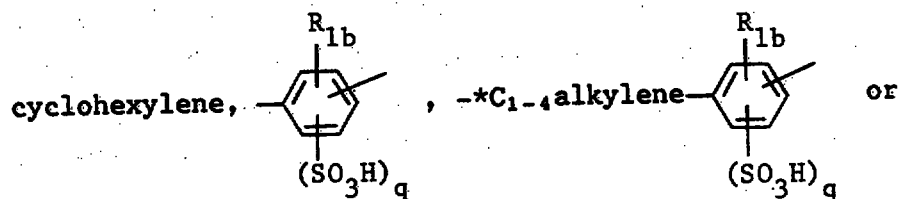
each R_b independently is hydrogen, methyl, ethyl or C_{2-3} alkyl monosubstituted by hydroxy or methoxy,

each R_{1a} independently is hydrogen, chlorine, methyl, ethyl, methoxy, ethoxy or $-COOH$,



each T_{1a} and T_{2a} independently is hydrogen, chlorine, bromine, methyl, ethyl, methoxy, ethoxy, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is substituted by one or two substituents selected from chlorine, bromine, methyl, ethyl, methoxy and ethoxy,

Y_{1a} is $-C_{2-6}$ alkylene-, monohydroxy-substituted $-C_{3-6}$ alkylene-, $-C_{3-6}$ alkylene- which is interrupted by $-O-$, $-S-$ or $-NR_b-$,



in which

R_b is as defined above,

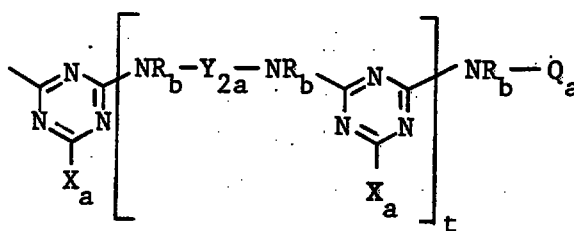
R_{1b} is hydrogen, chlorine, methyl, methoxy or $-COOH$,

q is 0 or 1 and

each asterisk identifies the carbon atom which is attached to the amino group bound to the ring system,

m is 0 or 1, and

Z_a is



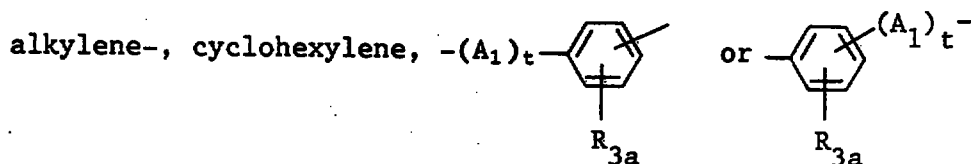
in which

R_b is as defined above,

t is 0 or 1,

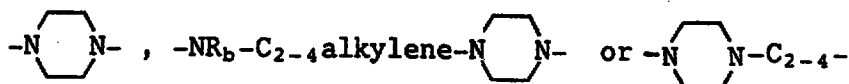
each X_a independently is fluorine, chlorine or $-\text{NR}_4\text{R}_5$, in which each R_4 and R_5 independently is hydrogen, C_{1-6} alkyl, C_{1-6} alkyl monosubstituted by hydroxy, halogen, cyano, C_{1-4} alkoxy, hydroxy-substituted C_{1-4} alkoxy, $-\text{COOH}$, $-\text{SO}_3\text{H}$ or $-\text{OSO}_3\text{H}$, cyclohexyl, phenyl or phenyl(C_{1-4} alkyl) in which each phenyl ring is unsubstituted or substituted by one to three substituents selected from chlorine, C_{1-4} alkyl, C_{1-4} alkoxy, $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{NH}_2$, or $-\text{NR}_4\text{R}_5$ forms a pyrrolidine, piperidine, morpholine or piperazine ring of which latter ring the second N-Atom is unsubstituted or substituted by methyl, ethyl, 2-hydroxyethyl or 2-aminoethyl,

Y_{2a} is $-\text{C}_{2-6}$ alkylene-, $-\text{C}_{3-6}$ alkylene- which is interrupted by $-\text{O}-$, $-\text{S}-$ or $-\text{NR}_b-$, monohydroxy-substituted $-\text{C}_{3-6}-$



or

$-\text{NR}-\text{Y}_2-\text{NR}-$ is $-\text{NR}_b-\text{Y}_{2a}-\text{NR}_b-$ where $-\text{NR}_b-\text{Y}_{2a}-\text{NR}_b-$ is



alkylene- NR_b- ,

in which R_b is as defined above,

A_1 is $-\text{C}_{1-4}$ alkylene-,

t is 0 or 1, and



R_{3a} is hydrogen, chlorine, methyl, methoxy, $-COOH$ or $-SO_3H$,

and

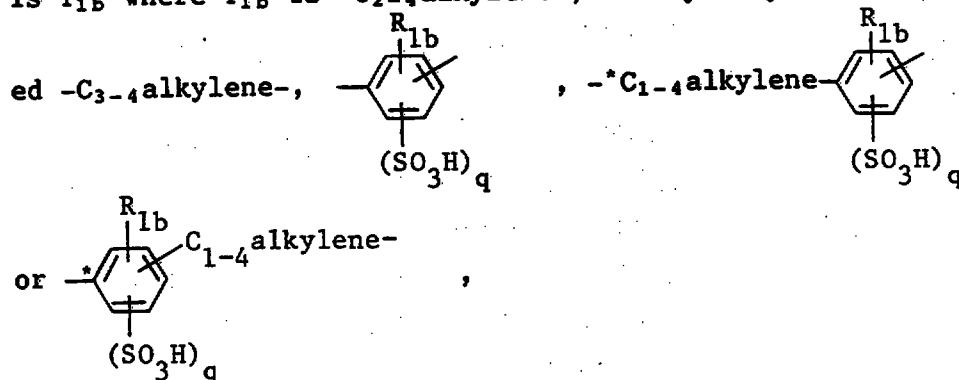
Q_a is the radical of a metal-free or metallised monoazo or disazo dye or of a dioxazine dye.

10. A compound according to Claim 9, in which each T_{1a} and T_{2a} is chlorine.

11. A compound according to Claim 9 or 10, in which

each R_b is R_c , where each R_c independently is hydrogen or methyl, and

Y_{1a} is Y_{1b} where Y_{1b} is $-C_{2-4}$ alkylene-, monohydroxy-substituted $-C_{3-4}$ alkylene-,



in which

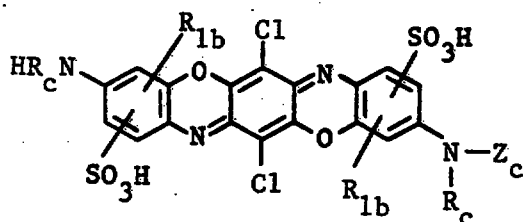
each asterisk identifies the carbon atom which is attached to the amino group bound to the ring system,

R_{1b} is hydrogen, chlorine, methyl, methoxy or $-COOH$, and

q is 0 or 1.

12. A compound according to Claim 9 or 10, in which m is 0.

13. A compound according to Claim 1 which corresponds to formula Ib



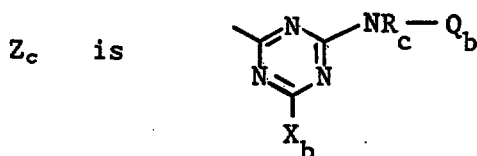
Ib

and salts thereof,

in which

each R_c independently is hydrogen or methyl,

each R_{1b} independently is hydrogen, chlorine, methyl, methoxy or $-COOH$, and



, in which

R_c is as defined above,

X_b is chlorine or $-NR_{4a}R_{5a}$ wherein

each R_{4a} and R_{5a} independently is hydrogen, C_{1-4} alkyl,

C_{1-4} alkyl monosubstituted by chlorine, hydroxy, methoxy,

$-COOH$, $-SO_3H$ or $-OSO_3H$, cyclohexyl, phenyl or benzyl in which

each phenyl ring is unsubstituted or substituted by one or

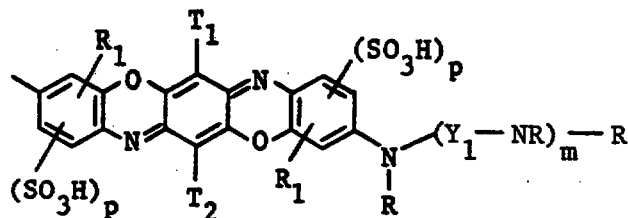
two substituents selected from chlorine, methyl, ethyl,

methoxy, ethoxy, $-SO_3H$ and $-NH_2$, or

$-NR_{4a}R_{5a}$ forms a piperidine, morpholine, piperazine or

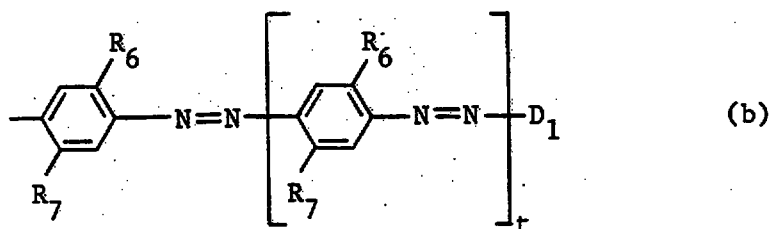
N-methyl-piperazine ring, and

Q_b is one of the dyestuff radicals (a) to (e),



(a)

in which the symbols are as defined in Claim 1,



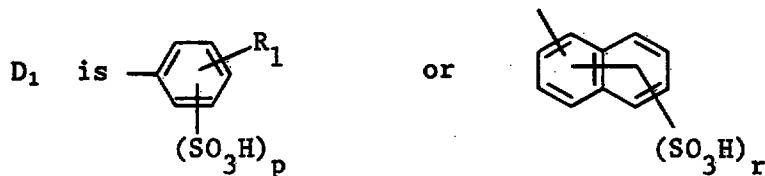
in which

each R_6 independently is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy,

$\text{---} \text{NHCOC}_{1-4}\text{alkyl}$ or $\text{---} \text{NHCONH}_2$,

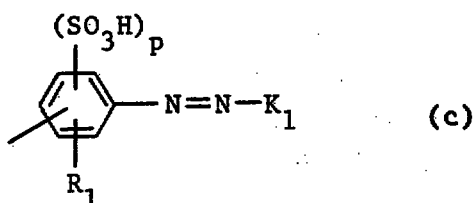
each R_7 independently is hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy,

t is 0 or 1, and

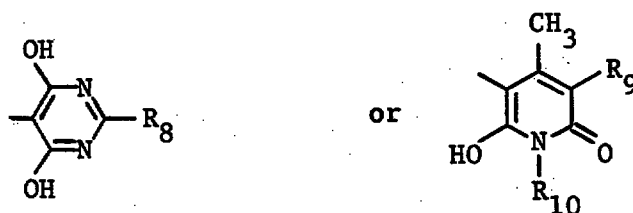


in which R_1 and p are as defined above, and

r is 1, 2 or 3;



in which R_1 and p are as defined above, and K_1 is the radical of a coupling component having the formula



in which

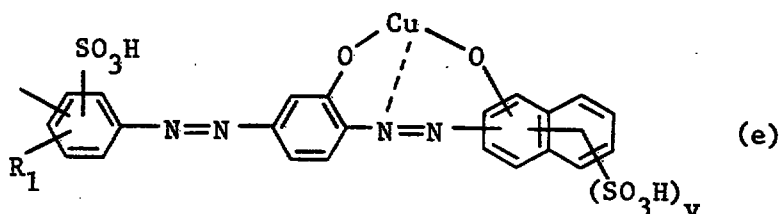
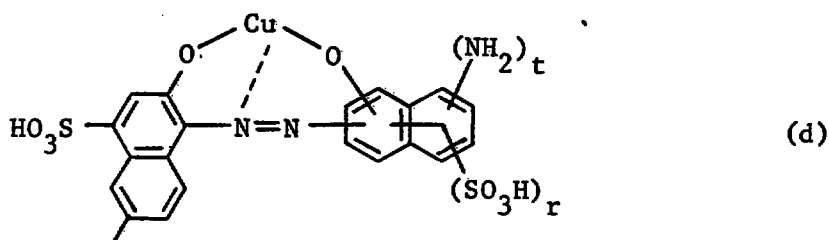
R_8 is OH or $\text{---} \text{NHCN}$,

R_9 is hydrogen, cyano, $\text{---} \text{CONH}_2$ or $\text{---} \text{CH}_2\text{SO}_3\text{H}$,

R_{10} is hydrogen, C_{1-4} alkyl or $\text{---} \text{A}_2\text{---} \text{NR}_4\text{R}_5$,



A_2 is $-C_{2-4}$ alkylene- or monohydroxy-substituted $-C_{3-4}$ alkylene-, and each R_4 and R_5 independently is hydrogen, C_{1-6} alkyl, C_{1-6} alkyl monosubstituted by hydroxy, halogen, cyano, C_{1-4} alkoxy, hydroxy-substituted C_{1-4} alkoxy, $-COOH$, $-SO_3H$ or $-OSO_3H$, cyclohexyl, phenyl or phenyl (C_{1-4} alkyl) in which each phenyl ring is unsubstituted or substituted by one to three substituents selected from chlorine, C_{1-4} alkyl, C_{1-4} alkoxy, $-COOH$, $-SO_3H$ and $-NH_2$, or $-NR_4R_5$ forms a pyrrolidine, piperidine, morpholine or piperazine ring of which latter ring the second N-Atom is unsubstituted or substituted by methyl, ethyl, 2-hydroxyethyl or 2-aminoethyl;



in which in the naphthyl ring of each radical (d) and (e), $-N=N-$ and $-O-$ are attached to carbon atoms which are ortho to each other in the 1,2- or 2,1-positions,

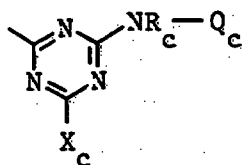
t is 0 or 1,

r is 1, 2 or 3, and

v is 2 or 3, and R_1 is as defined above.

14. A compound according to Claim 13, in which each R_c and each R_{1b} are hydrogen.

15. A compound according to Claim 13 or 14, in which Z_c is Z_d where Z_d is



in which

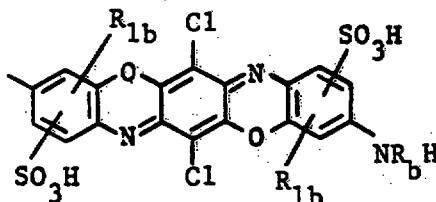
X_c is $-NR_{4b}R_{5b}$, where

each R_{4b} and R_{5b} independently is hydrogen, methyl, ethyl, C_{2-3} alkyl monosubstituted by hydroxy or $-SO_3H$, cyclohexyl, phenyl or sulphophenyl or

$-NR_{4b}R_{5b}$ forms a morpholine ring,

R_c is hydrogen or methyl, and

Q_c is



wherein

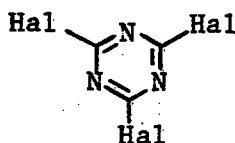
R_b is hydrogen, methyl, ethyl or C_{2-3} alkyl monosubstituted by hydroxy or methoxy, and

each R_{1b} independently is hydrogen, chlorine, methyl, methoxy or $-COOH$.

16. A liquid-aqueous dyeing preparation stable in storage, containing a compound of formula I as defined in Claim 1, in water-soluble salt form.

17. A compound or composition according to Claim 1 or Claim 16 substantially as herein described with reference to any one of Examples 1 to 64.

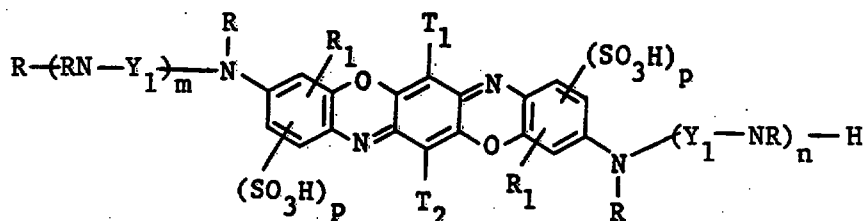
18. A process for the preparation of a compound of formula I and a mixture thereof comprising reacting one mole of a compound of formula II



II

in which Hal is halogen,
with

- one mole of a compound of formula III



III

in which the symbols are as defined in Claim 1,
and

- one mole of a compound of formula IV



in which R and Q are as defined in Claim 1,
and optionally

- one mole of a compound of formula V



in which X' is an unsubstituted or substituted amino group,

in any desired order to obtain a compound of formula I in which for the group Z t is 0.

19. A process according to Claim 18 for the preparation of a compound of formula I in which for Z t is 1, comprising adding to the process according to Claim 18 a further reaction step to introduce the group -NR-Y₂-NR- by reacting one mole of a cyanuric halide or one or to different appropriate mono- or dicondensation products thereof with 1/2 mole of a compound of formula VI



in which R and Y₂ are as defined in Claim 1.



20. A process for dyeing or printing a hydroxy group- or nitrogen-containing organic substrate comprising applying to the substrate a compound according to any one of the preceding Claims 1 to 15 or 17 or a mixture thereof, or a liquid-aqueous dyeing preparation according to Claim 16.

21. A process according to Claim 20, wherein the substrate is paper or cotton.

22. A process for dyeing or printing substantially as herein described with reference to any one of Application Examples A to H.

23. A process for dyeing or printing hydroxy group- or nitrogen-containing organic textile fibres comprising dyeing or printing the fibres with a compound according to any one of Claims 1 to 15 or 17 or a mixture thereof, and subsequently after-treating the dyed or printed substrate with a polymer polybasic amino compound.

24. A process for dyeing and after-treating of textile fibres as herein described with reference to Application Example I or K.
