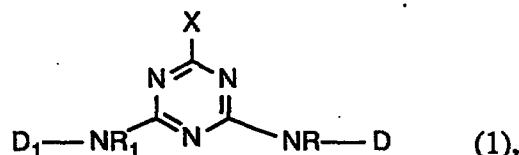


1-19560/A/19660

Fibre-reactive dyes and preparation and use thereof

The present invention relates to novel fibre-reactive dyes which are suitable for dyeing cellulose-containing fibre materials from an aqueous bath and for printing cellulose-containing fibre materials.

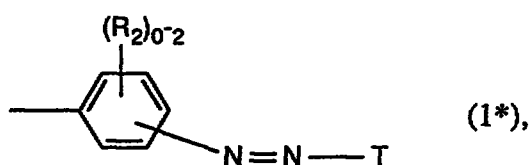
The present invention provides compounds of the formula



where

D is the radical of a monoazo, polyazo, metal complex azo, anthraquinone, triphendioxazine, phthalocyanine or formazan chromophore that contains at least one sulfo group,

D₁ is the radical of a monoazo chromophore of the formula



where (R₂)₀₋₂ represents 0 to 2 identical or different radicals R₂ selected from the group consisting of sulfo, sulfomethyl, hydroxyl, carboxyl, halogen, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C₂-C₄alkanoylamino, ureido, C₁-C₄alkyl, C₁-C₄alkoxy, or C₁-C₄alkoxy substituted by C₁-C₄alkoxy, hydroxyl or sulfato in the alkyl moiety, and T is the radical of a diazo component or coupling component of the benzene or naphthalene series or of the heterocyclic series, or is the radical of a polyazo, metal complex azo, anthraquinone, triphendioxazine, phthalocyanine or formazan chromophore, and at least one of the radicals D and D₁ contains a fibre-reactive radical -SO₂-Y, Y is vinyl or a radical -CH₂-CH₂-U and U is a leaving group,

X is fluorine, chlorine, bromine, 3-carboxy-1-pyridinyl or 3-carbamoyl-1-pyridinyl, and R and R₁ are each independently of the other hydrogen or unsubstituted or halogen-, hydroxyl-, cyano-, C₁-C₄alkoxy-, C₁-C₄alkoxycarbonyl-, carboxyl-, sulfo- or sulfato-substituted C₁-C₄alkyl,

with the proviso that the radical -NR- is not bonded to an NH₂-substituted phenylene radical when D is the radical of a monoazo or disazo chromophore.

Alkyl generally means methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl; C₁-C₄alkoxy generally encompasses methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy; halogen is generally for example fluorine, bromine or in particular chlorine; C₁-C₄alkoxycarbonyl generally means methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, isobutoxycarbonyl, sec-butoxycarbonyl or tert-butoxycarbonyl, preferably methoxycarbonyl or ethoxycarbonyl. Examples of C₁-C₄alkylsulfonyl include methylsulfonyl and ethylsulfonyl, examples of N-mono- or N,N-di-C₁-C₄alkylcarbamoyl include N-methylcarbamoyl, N-ethylcarbamoyl, N,N-dimethylcarbamoyl or N,N-diethylcarbamoyl, and examples of N-mono- or N,N-di-C₁-C₄alkylsulfamoyl include N-methylsulfamoyl, N-ethylsulfamoyl, N-propylsulfamoyl, N-isopropylsulfamoyl, N-butylsulfamoyl, N-β-hydroxyethylsulfamoyl, N,N-di-β-hydroxyethylsulfamoyl, N,N-dimethylsulfamoyl or N,N-diethylsulfamoyl. Examples of C₂-C₄alkanoylamino include acetylamino and propionylamino. Examples of C₁-C₄alkoxy substituted in the alkyl moiety include 2-hydroxyethoxy, 3-hydroxypropoxy, 2-sulfatoethoxy, 2-methoxyethoxy and 2-ethoxyethoxy.

Examples of suitable radicals R and R₁ include hydrogen, unsubstituted C₁-C₄alkyl, carboxymethyl, β-carboxyethyl, β-carboxypropyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, β-methoxyethyl, β-ethoxyethyl, β-methoxypropyl, β-chloroethyl, γ-bromopropyl, β-hydroxyethyl, β-hydroxybutyl, β-cyanoethyl, sulfomethyl, β-sulfoethyl and β-sulfatoethyl.

R and R₁ are each independently of the other preferably methyl, ethyl or in particular hydrogen.

X is preferably fluorine or in particular chlorine.

Suitable leaving groups U include for example halogen, e.g. chlorine, acyloxy, e.g.

acetoxo or phenoxy, phosphato, sulfato and thiosulfato.

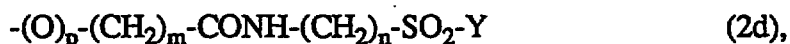
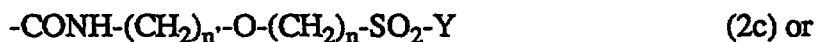
Examples of suitable radicals Y include accordingly vinyl, β -bromoethyl, β -chloroethyl, β -acetoxylethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl and β -thiosulfatoethyl. Y is preferably vinyl or β -sulfatoethyl.

The chromophore radicals D and D₁ may each contain independently of each other the customary organic dye substituents attached to their basic structure.

Examples of such further substituents on the chromophores include C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkoxy substituted for example by hydroxyl, C₁-C₄alkoxy or sulfato in the alkyl moiety, e.g. 2-hydroxyethoxy, 3-hydroxypropoxy, 2-sulfatoethoxy, 2-methoxyethoxy, 2-ethoxyethoxy, acylamino groups having 1 to 8 carbon atoms, in particular alkanoylamino groups and alkoxycarbonylamino groups, such as acetylamino, propionylamino, methoxycarbonylamino, ethoxycarbonylamino or benzoylamino, phenylamino, N,N-di- β -hydroxyethylamino, N,N-di- β -sulfatoethylamino, sulfobenzylamino, N,N-disulfobenzylamino, alkoxycarbonyl having 1 to 4 carbon atoms in the alkoxy radical, such as methoxycarbonyl or ethoxycarbonyl, alkylsulfonyl having 1 to 4 carbon atoms, such as methylsulfonyl or ethylsulfonyl, trifluoromethyl, nitro, cyano, halogen such as fluorine, chlorine or bromine, carbamoyl, N-alkylcarbamoyl having 1 to 4 carbon atoms in the alkyl radical such as N-methylcarbamoyl, or N-ethylcarbamoyl, sulfamoyl, N-alkylsulfamoyl having 1 to 4 carbon atoms such as N-methylsulfamoyl, N-ethylsulfamoyl, N-propylsulfamoyl, N-isopropylsulfamoyl or N-butylsulfamoyl, N-(β -hydroxyethyl)sulfamoyl, N,N-di(β -hydroxyethyl)sulfamoyl, N-phenylsulfamoyl, ureido, hydroxyl, carboxyl, sulfomethyl or sulfo. The reactive dyes contain at least one and preferably at least two sulfonic acid groups.

A fibre-reactive radical -SO₂-Z present in D or D₁ can be attached to the chromophore directly or via a bridge member.

Preferably D and/or D₁ contains as the fibre-reactive radical a radical of the formula



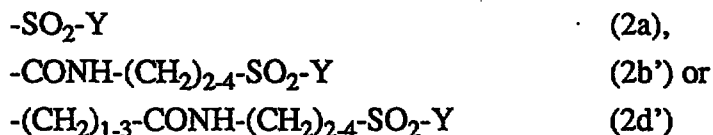
where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is as defined above.

n and n' are each preferably independently of the other 2, 3 or 4, particularly preferably 2 or 3, and very particularly preferably 2.

m is preferably 1, 2 or 3 and particularly preferably 1 or 2.

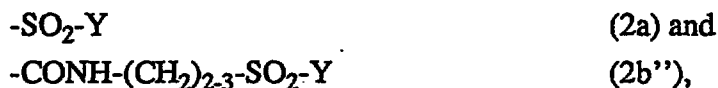
p is preferably 0.

Of particular interest are compounds of the formula (1) where D and/or D₁ contains one or more fibre-reactive radicals of the formula



where Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl.

Particularly preferably D and/or D₁ carry one or more fibre-reactive radicals of the formula

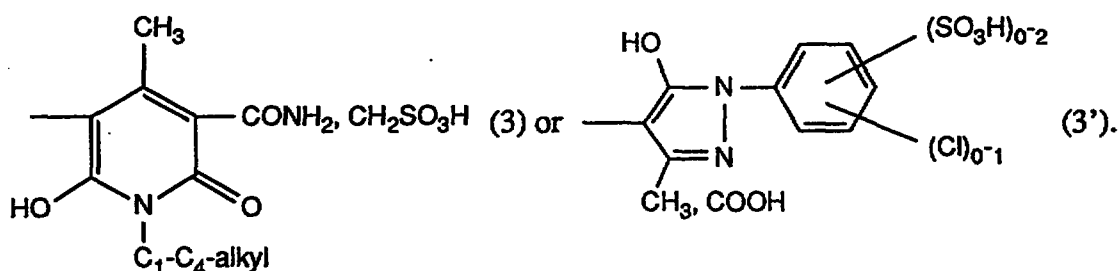


where Y is vinyl or β -sulfatoethyl. Here it is particularly preferable for only one of the radicals D and D₁ to contain a fibre-reactive radical and for this fibre-reactive radical to conform to the above-indicated formula (2a) or (2b'').

(R₂)₀₋₂ preferably represents 0 to 2 radicals R₂ selected from the group consisting of sulfo, C₂-C₄alkanoylamino, ureido, C₁-C₄alkyl, C₁-C₄alkoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, 2-methoxyethoxy and 2-ethoxyethoxy. Particularly preferably (R₂)₀₋₂ represents 0 to 2 radicals R₂ selected from the group consisting of sulfo, acetylamino, propionylamino,

ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy.

A radical T of a coupling component is for example a suitably substituted phenyl, naphthyl, 6-hydroxy-2-pyridone or 1-phenyl- or 1-naphthyl-5-pyrazolone radical. A coupling component radical T is unsubstituted or for example C₁-C₂alkyl-, C₁-C₂alkoxy-, halogen-, carboxyl-, sulfo-, hydroxyl-, amino-, N-mono-C₁-C₄alkylamino-, N,N-di-C₁-C₄alkylamino-, C₂-C₄alkanoylamino- or benzoylamino-substituted phenyl or naphthyl or a radical of the formula



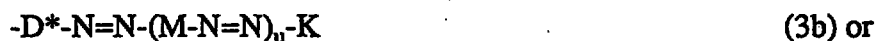
A radical T of a coupling component is particularly preferably an unsubstituted or methyl-, methoxy-, chlorine-, sulfo-, hydroxyl-, amino-, acetylamino- or benzoylamino-substituted phenyl or naphthyl radical or a radical of the above-indicated formula (3).

A radical T of a diazo component is for example an unsubstituted phenyl or naphthyl radical or a phenyl or naphthyl radical substituted for example by C₁-C₂alkyl, C₁-C₂alkoxy, carboxyl, sulfo, halogen or by a radical of the previously indicated formula (2a) to (2d). A radical T of a diazo component is preferably an unsubstituted phenyl or naphthyl radical or a phenyl or naphthyl radical substituted by sulfo, methyl, methoxy, chlorine or a radical of the formula (2a) or (2b'').

Preferred meanings of D concern:

a) Dye radicals of a 1:1 copper complex azo dye of the benzene or naphthalene series wherein the copper atom is bonded at each end to a metallizable group in the ortho position relative to the azo bridge.

b) Dye radicals of a monoazo or disazo dye, of the formula





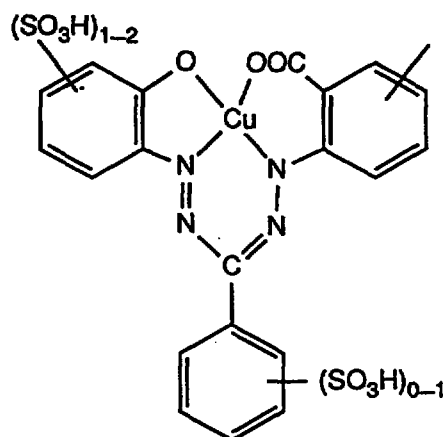
or of a metal complex derived therefrom; D^* is the radical of a diazo component of the benzene or naphthalene series, M is the radical of a middle component of the benzene or naphthalene series, and K is the radical of a coupling component of the benzene, naphthalene, pyrazolone, 6-hydroxy-2-pyridone or acetoacetarylamine series, and D^* , M and K can carry substituents customary in azo dyes, in particular hydroxyl, amino, methyl, ethyl, methoxy or ethoxy groups, 2-hydroxyethoxy, 2-methoxyethoxy or 2-sulfatoethoxy groups, substituted or unsubstituted alkanoylamino groups having 2 to 4 carbon atoms, substituted or unsubstituted benzoylamino groups, halogen atoms and also, in the case of D_1 , one or more fibre-reactive radicals of the previously indicated formula (2a), (2b), (2c) or (2d); u is 0 or 1; and D^* , M and K together contain at least two sulfo groups, preferably three or four sulfo groups.

c) Dye radicals of a disazo dye, of the formula

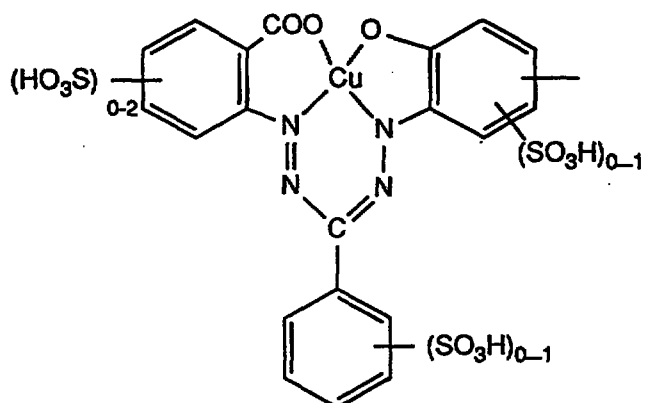


in which D^* and D_1^* are independently of each other the radical of a diazo component of the benzene or naphthalene series and K_1 is the radical of a coupling component of the naphthalene series, and D^* , D_1^* and K_1 can carry substituents customary in azo dyes, in particular hydroxyl, amino, methyl, ethyl, methoxy or ethoxy groups, substituted or unsubstituted alkanoylamino groups having 2 to 4 carbon atoms, 2-hydroxyethoxy, 2-methoxyethoxy or 2-sulfatoethoxy groups, substituted or unsubstituted benzoylamino groups, halogen atoms and also, in the case of D_1 , one or more fibre-reactive radicals of the previously indicated formula (2a), (2b), (2c) or (2d), and D^* , D_1^* and K_1 together contain at least two sulfo groups, preferably three or four sulfo groups.

d) Dye radicals of a formazan dye, of the formula

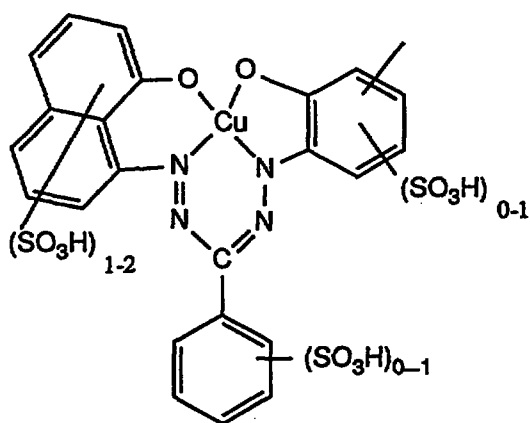


(5a)

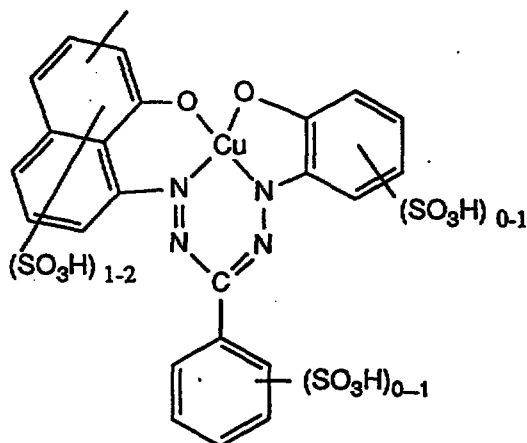


(5b)

or



(5c)

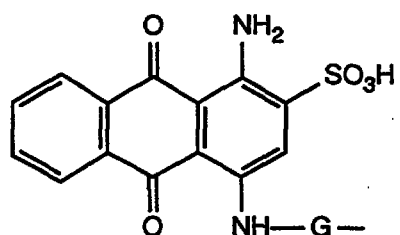


(5d),

or

in which the benzene nuclei may be further substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkylsulfonyl having 1 to 4 carbon atoms, halogen, carboxyl and also, in the case of D₁, by one or more fibre-reactive radicals of the previously indicated formula (2a), (2b), (2c) or (2d).

e) Dye radicals of an anthraquinone dye, of the formula



(6);

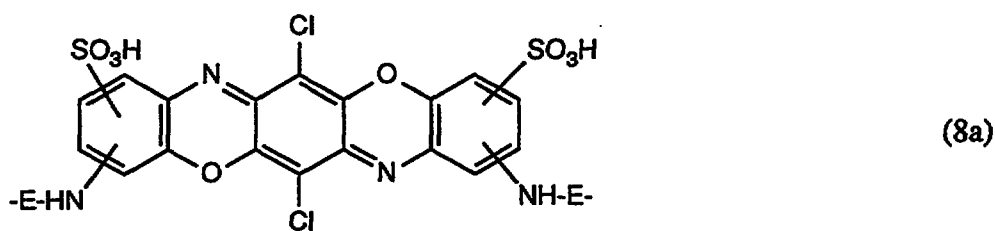
in which G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and the anthraquinone nucleus may be substituted by a further sulfo group, and G as phenyl radical may be substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo, and the dye preferably contains at least 2 sulfo groups.

f) Dye radicals of a phthalocyanine dye, of the formula

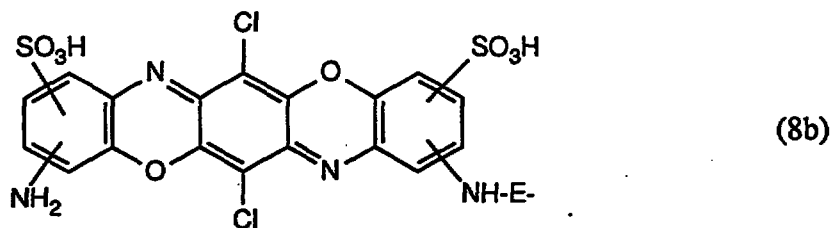


in which Pc is the radical of a copper or nickel phthalocyanine; W is -OH and/or -NR₄R₅; R₄ and R₅ are each independently of the other hydrogen or alkyl having 1 to 4 carbon atoms, which may be substituted by hydroxyl or sulfo; R₃ is hydrogen or alkyl having 1 to 4 carbon atoms; E is a phenylene radical which may be substituted by alkyl having 1 to 4 carbon atoms, halogen, carboxyl or sulfo; or is an alkylene radical having 2 to 6 carbon atoms, preferably a sulfophenylene or ethylene radical; and k is 1, 2 or 3.

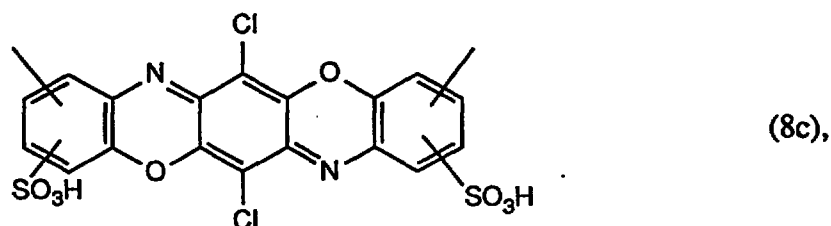
g) Dye radicals of a dioxazine dye, of the formula



or

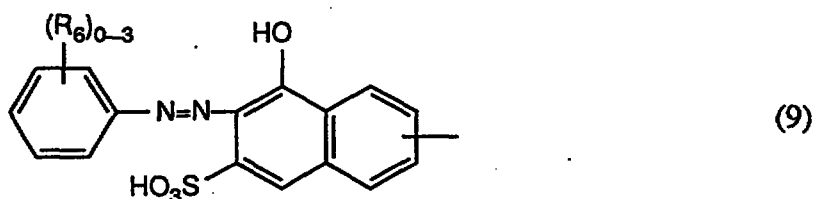


or

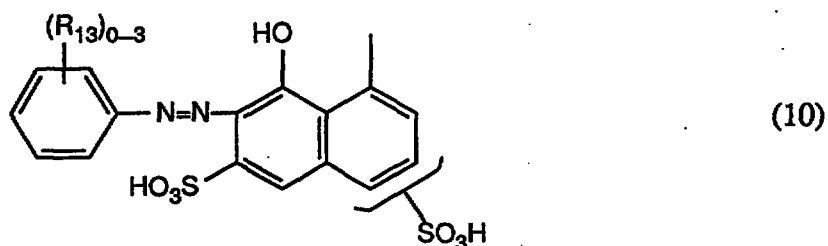


in which E is a phenylene radical which may be substituted by alkyl having 1 to 4 carbon atoms, halogen, carboxyl or sulfo; or is an alkylene radical having 2 to 6 carbon atoms; and the outer benzene rings in the formulae (8a), (8b) and (8c) may be further substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, acetylamino, nitro, halogen, carboxyl, sulfo and also, in the case of D₁ by one or more fibre-reactive radicals of the previously indicated formula (2a), (2b), (2c) or (2d).

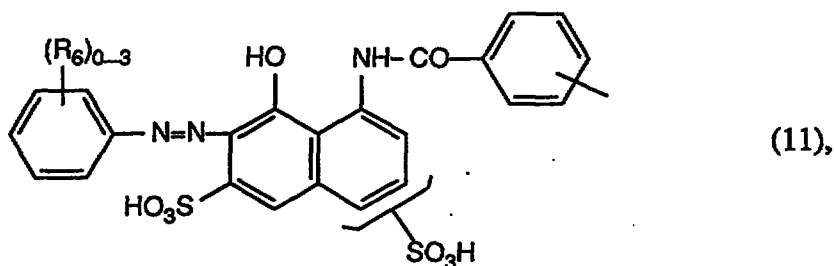
Particularly important dye radicals D for the reactive dyes of the formula (1) according to the invention are the chromophore radicals of the following formulae (9) to (20):



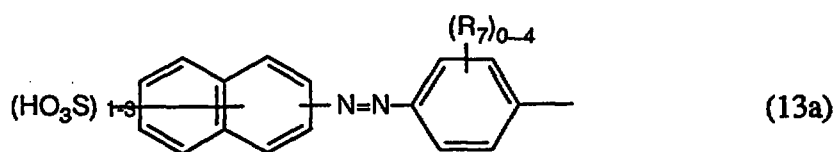
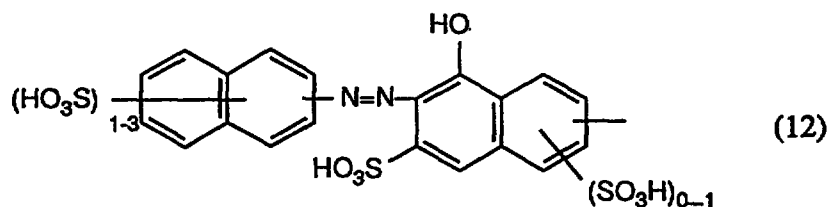
in which R₆ is C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl or sulfo.



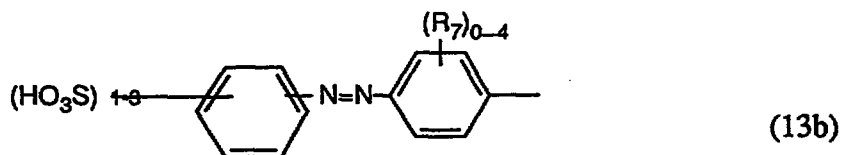
in which R₁₃ is C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl, sulfo or C₁-C₄alkoxyanilino.



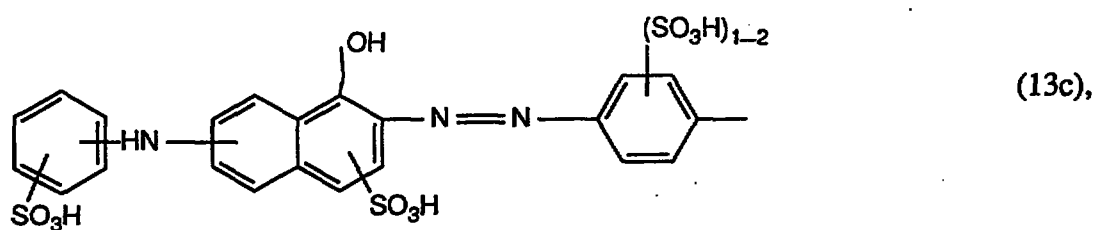
in which R_6 is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo.



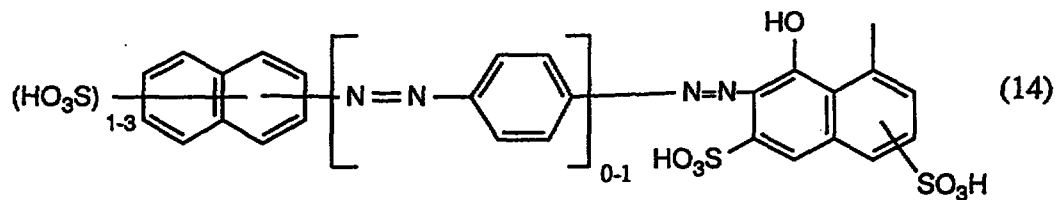
or

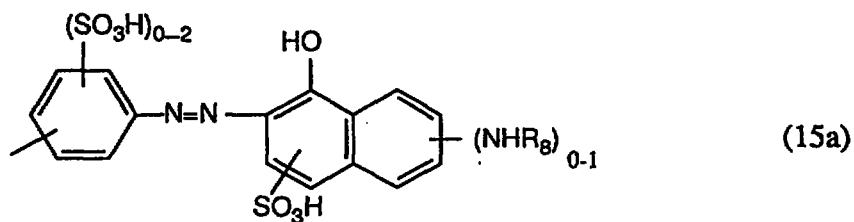


or

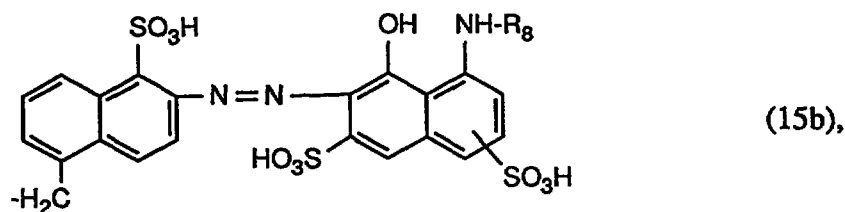


in which R_7 is halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, acetylamino, ureido, hydroxyl, carboxyl, sulfomethyl or sulfo.

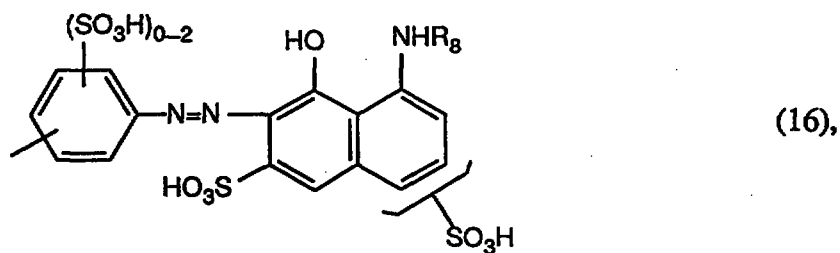




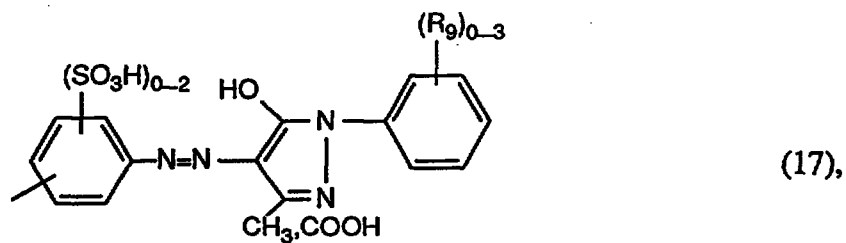
or



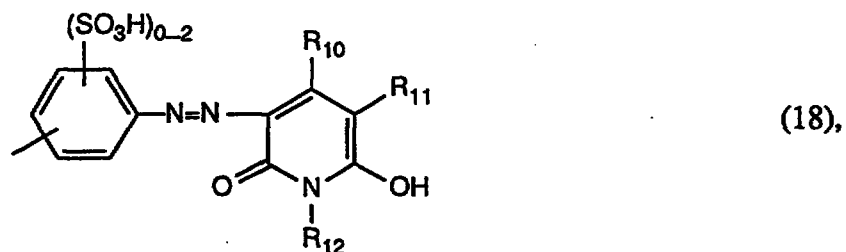
in which R_8 is C_1 - C_4 alkanoyl or benzoyl.



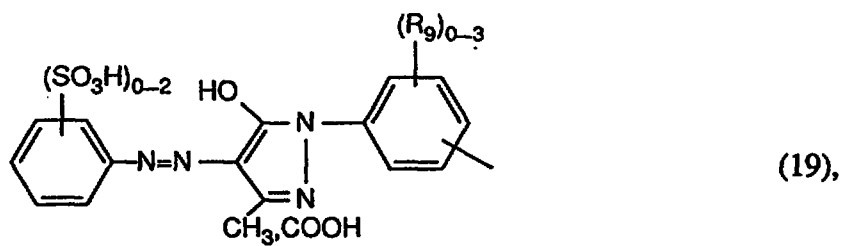
in which R_8 is C_1 - C_4 alkanoyl or benzoyl.



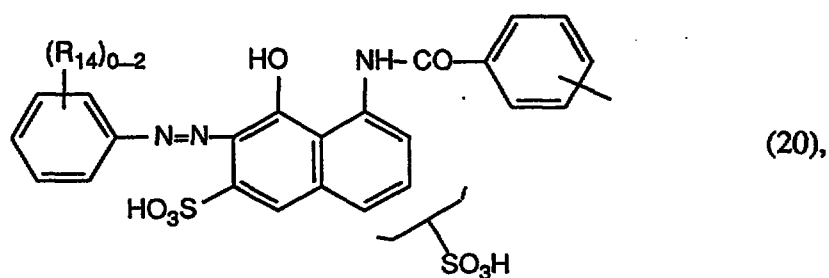
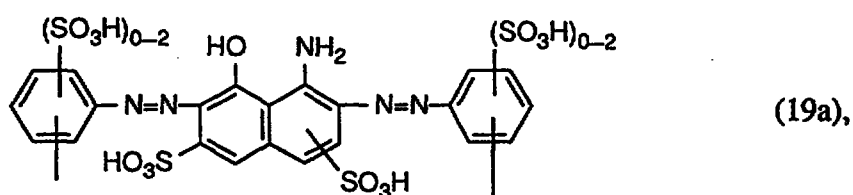
in which R_9 is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo.



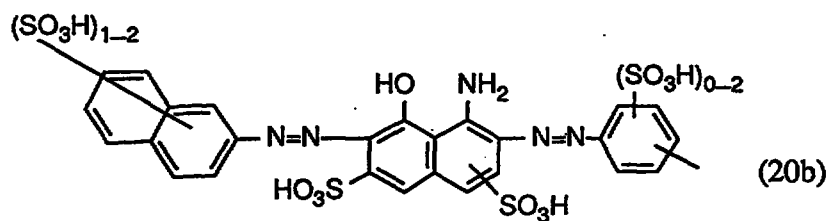
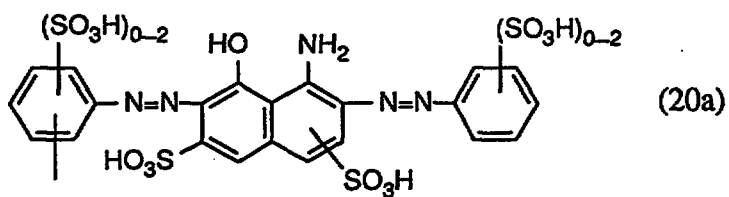
in which R_{12} and R_{10} are independently of each other hydrogen, C_1 - C_4 alkyl or phenyl, and R_{11} is hydrogen, cyano, carbamoyl or sulfomethyl.

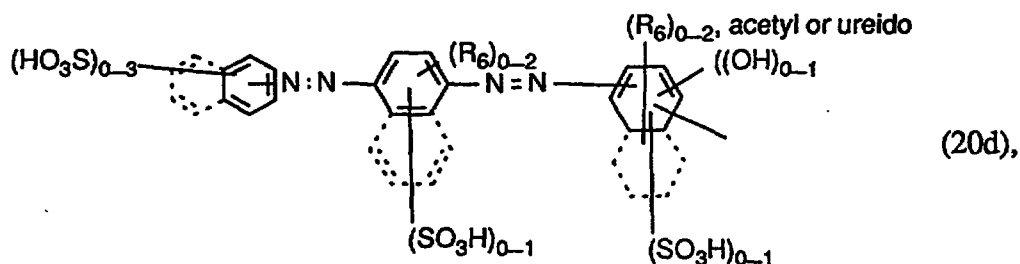
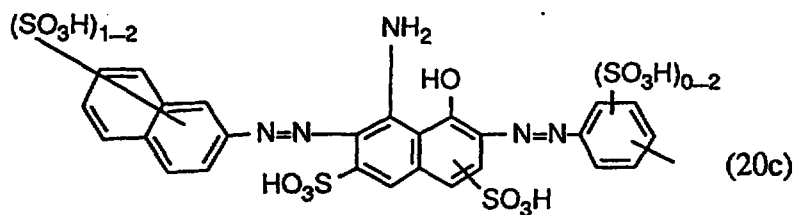


in which R_9 is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo.

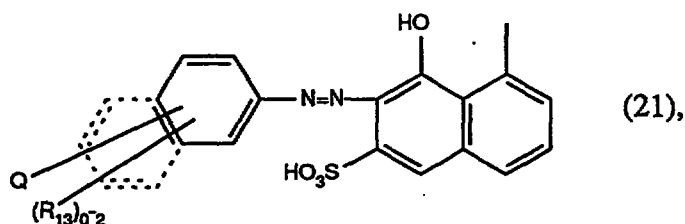


in which R_{14} is C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo.

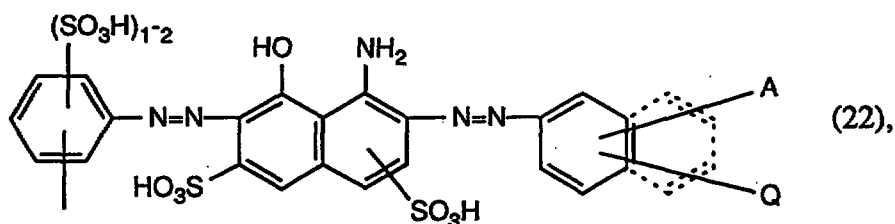




in which R_6 is as defined under formula (11).

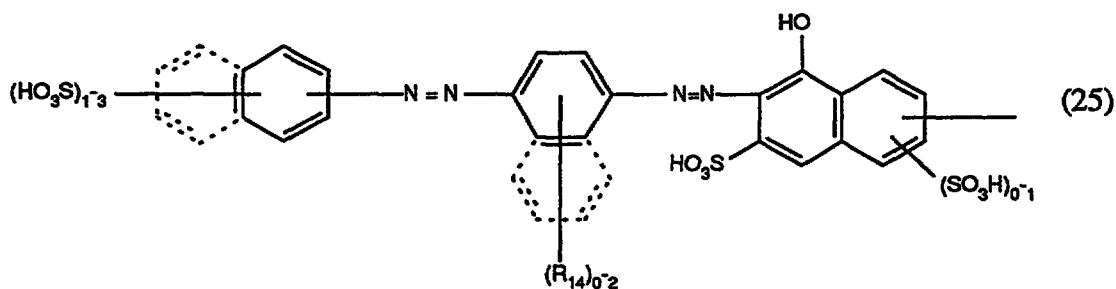
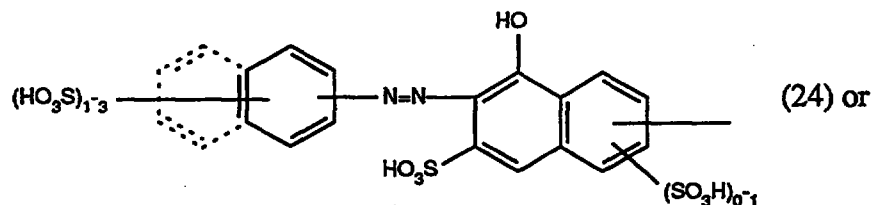
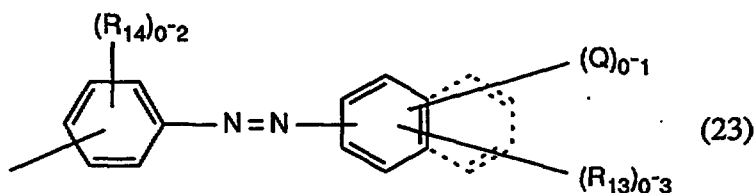
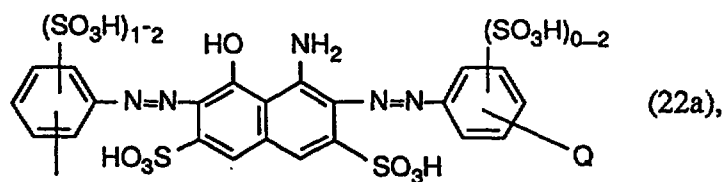
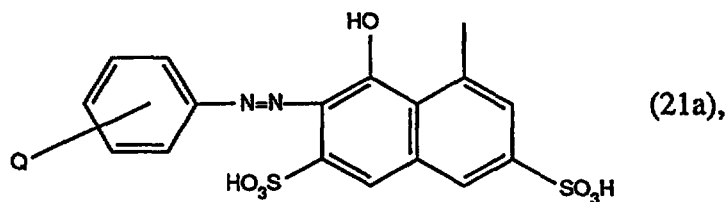


in which Q is a radical of the previously indicated formula (2a), (2b') or (2d') and $(R_{13})_{0-2}$ represents 0 to 2 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo.



in which A is hydrogen, halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di- C_1 - C_4 alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di- C_1 - C_4 alkylsulfamoyl, C_1 - C_4 alkylsulfonyl or C_1 - C_4 alkoxycarbonyl and Q is a radical of the formula (2a), (2b), (2c) or (2d).

The radicals D which are particularly preferred according to the invention conform to the previously indicated formula (5a), (5b) or (6) or to the formula

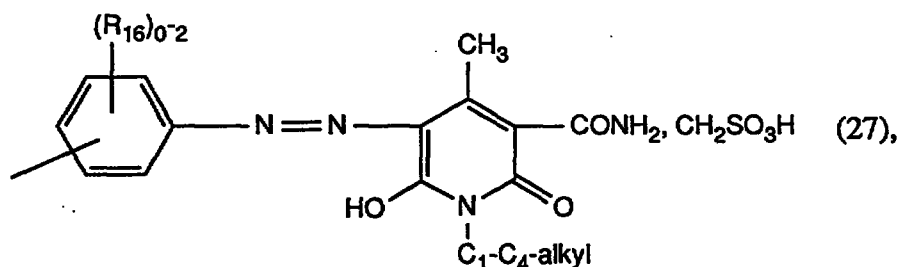
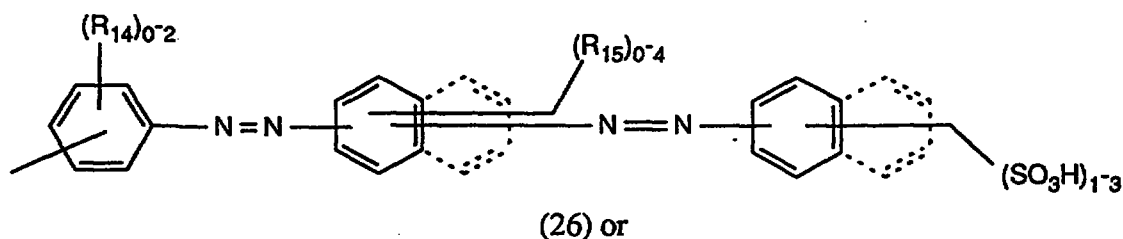


in which $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetilamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, and Q is a radical of the previously indicated formula (2a) or (2b'').

A radical D_1 of a polyazo, metal complex azo, anthraquinone, triphendioxazine, phthalocyanine or formazan chromophore is subject to the meanings and preferences previously indicated for D.

A radical D_1 of a monoazo chromophore is preferably a radical of the previously indicated formula (1*) in which the variables present therein have the stated meanings and preferences.

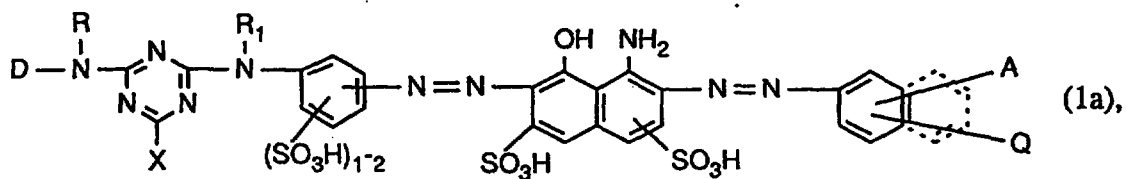
Particularly preferably D_1 is a radical of the above-indicated formula (5a), (5b), (6), (22), (22a) or (23) or a radical of the formula



in which $(R_{14})_{0-2}$ has the previously indicated meaning, $(R_{15})_{0-4}$ represents 0 to 4 identical or different radicals selected from the group consisting of sulfo, hydroxyl, amino, methoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, methyl, acetylamino, benzoylamino, propionylamino and ureido, and $(R_{16})_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, methyl, methoxy and chlorine.

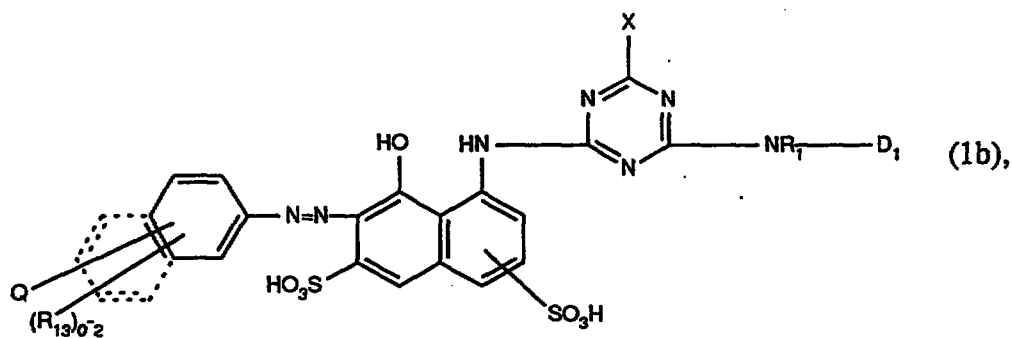
The radicals D and D_1 can be identical or preferably different.

A preferred embodiment of the present invention concerns compounds of the formula



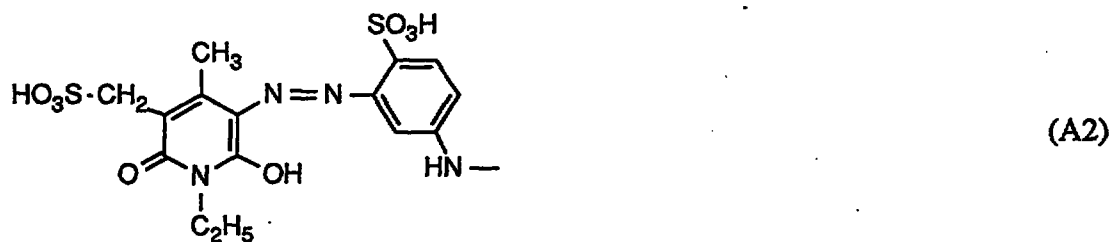
in which A, D, Q, R, R₁ and X are each subject to the aforementioned meanings and preferences.

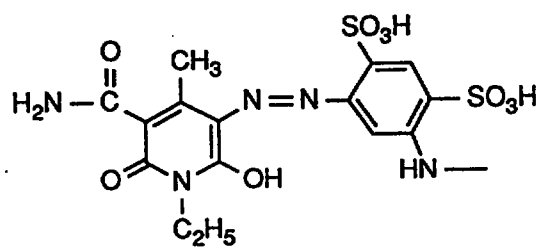
A further preferred embodiment of the present invention concerns compounds of the formula



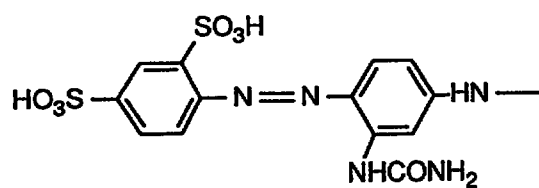
in which D₁, Q, (R₁₃)₀₋₂ and X are each subject to the aforementioned meanings and preferences.

Examples of suitable radicals D or D₁ are:

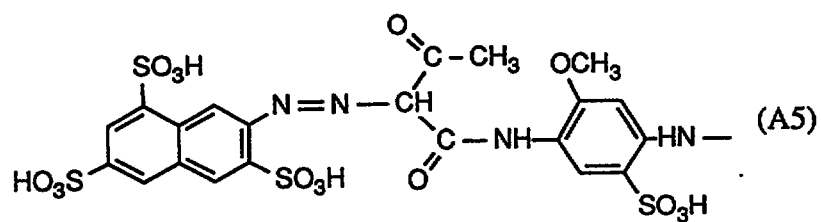




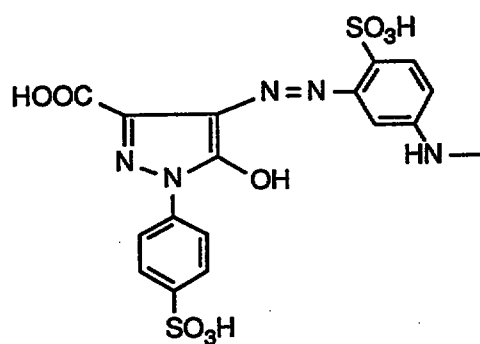
(A3)



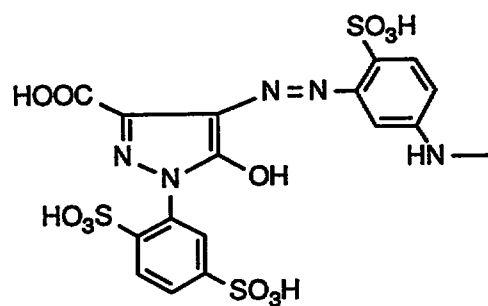
(A4)



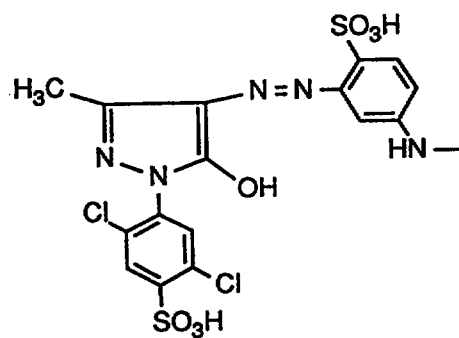
(A5)



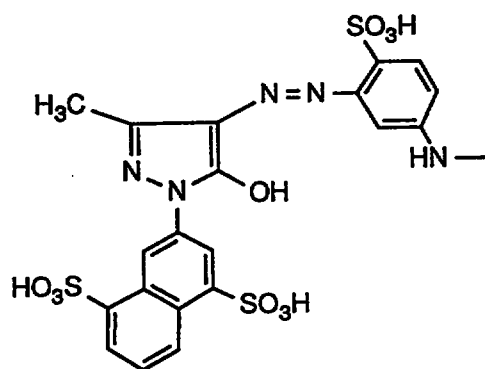
(A6)



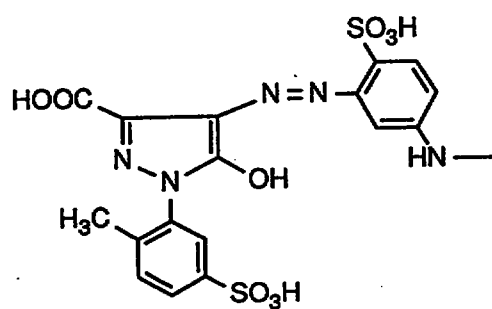
(A7)



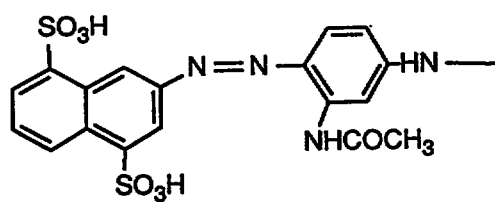
(A8)



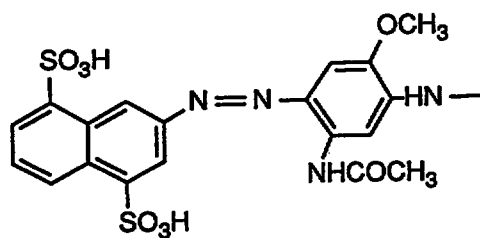
(A9)



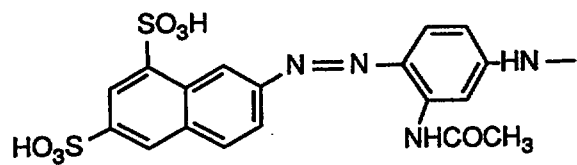
(A10)



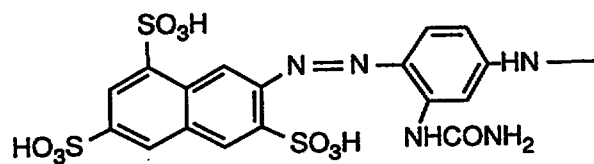
(A11)



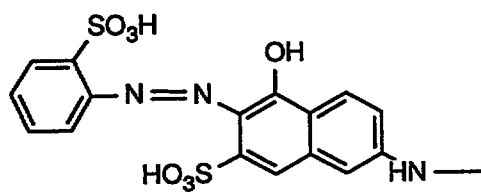
(A12)



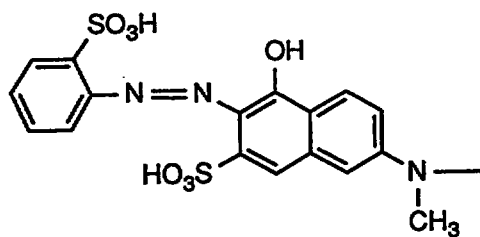
(A13)



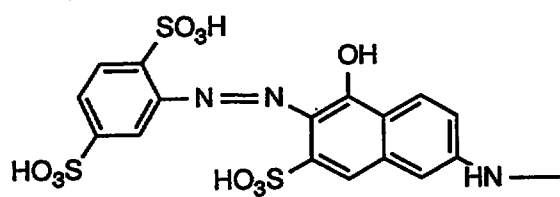
(A14)



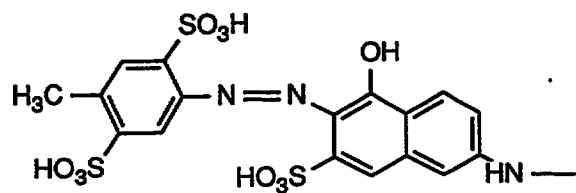
(A15)



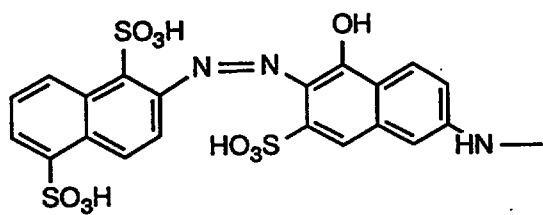
(A16)



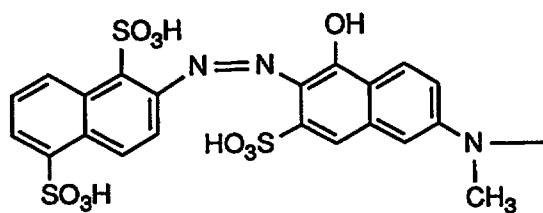
(A17)



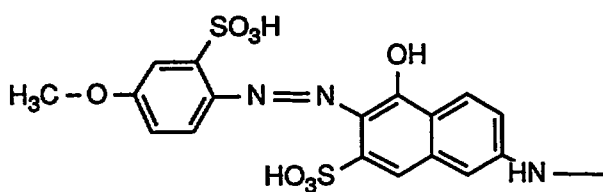
(A18)



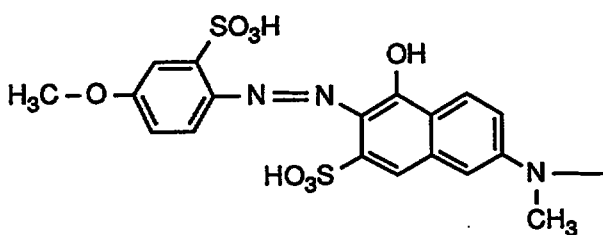
(A19)



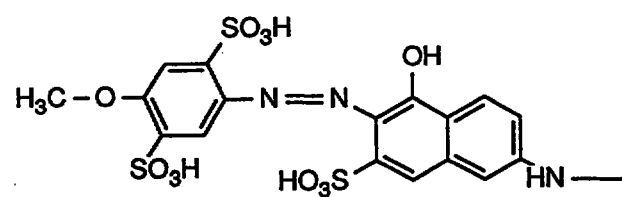
(A20)



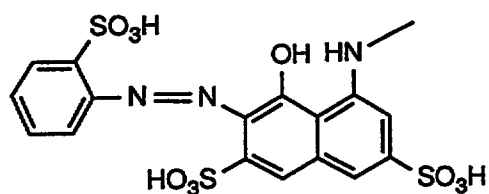
(A21)



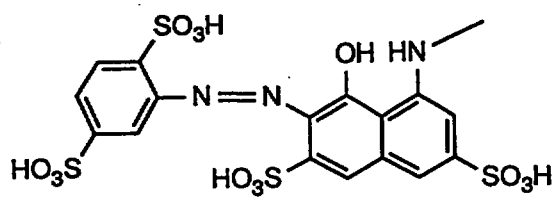
(A22)



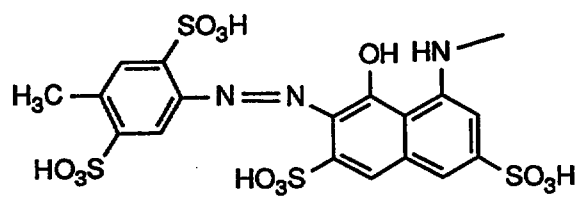
(A23)



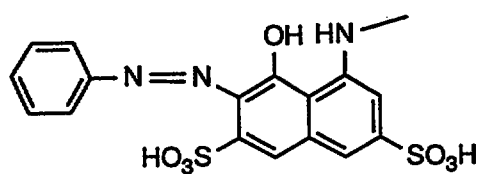
(A24)



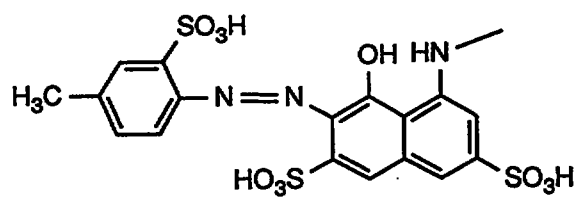
(A25)



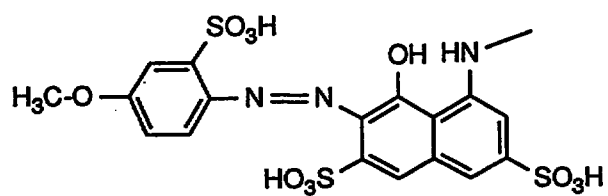
(A26)



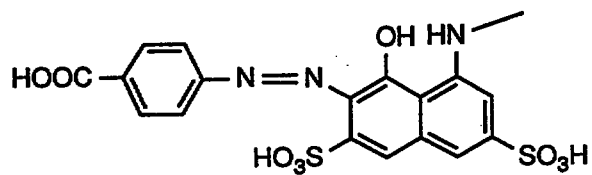
(A27)



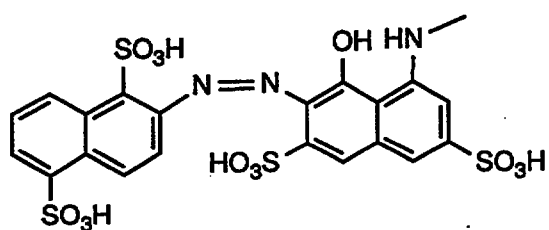
(A28)



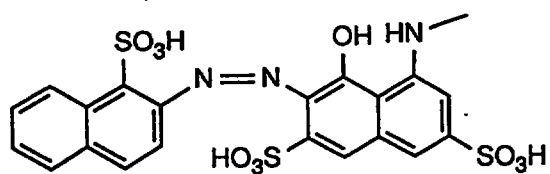
(A29)



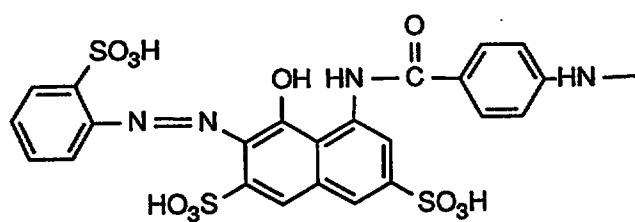
(A30)



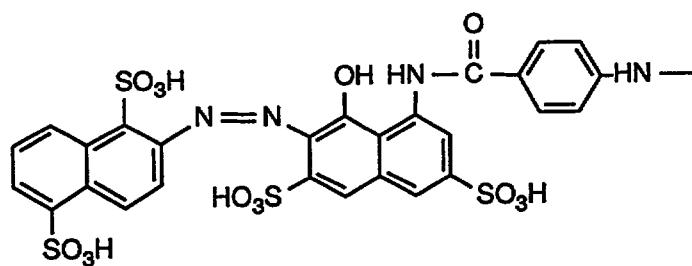
(A31)



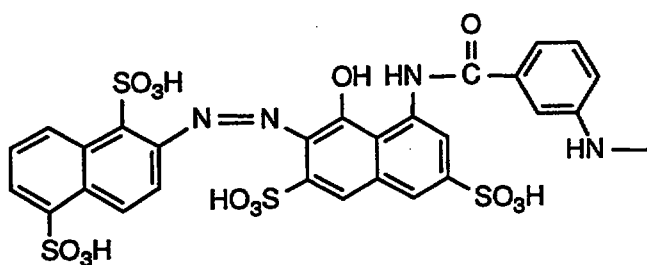
(A32)



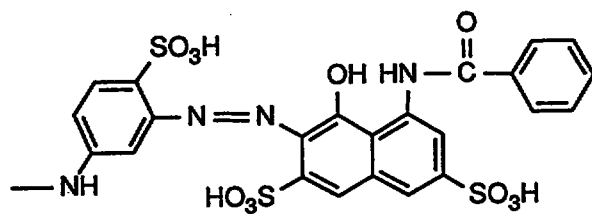
(A33)



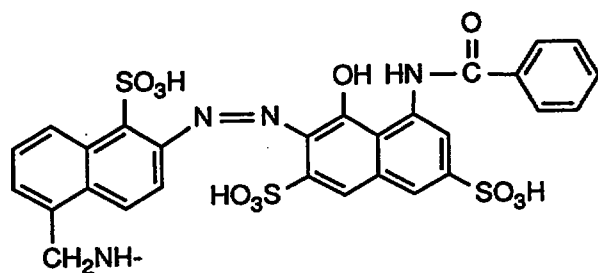
(A34)



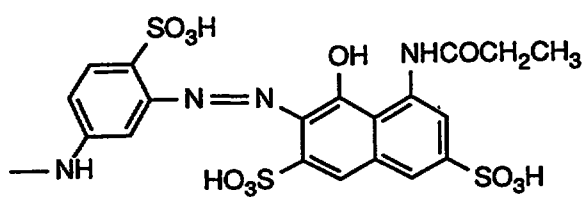
(A35)



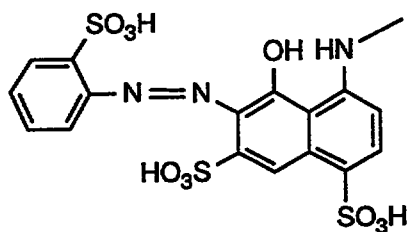
(A36)



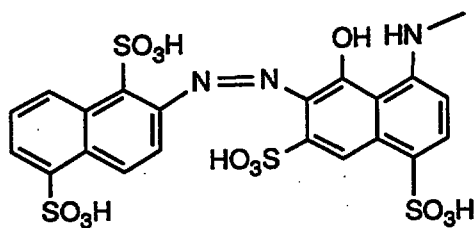
(A37)



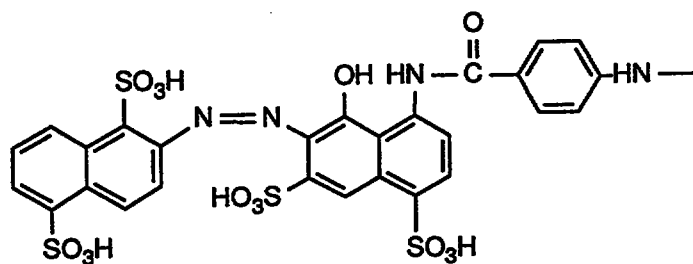
(A38)



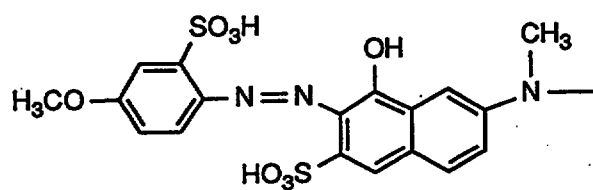
(A39)



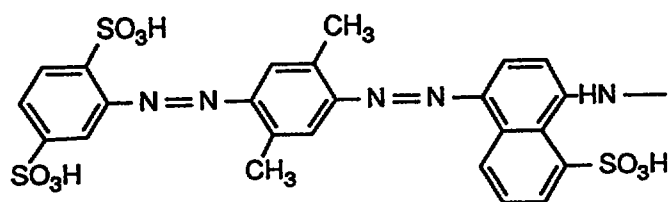
(A40)



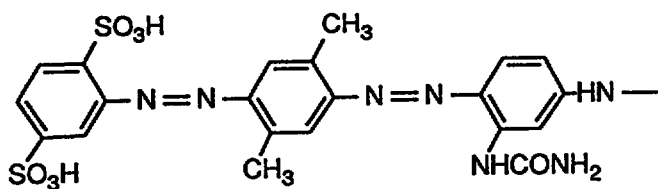
(A41)



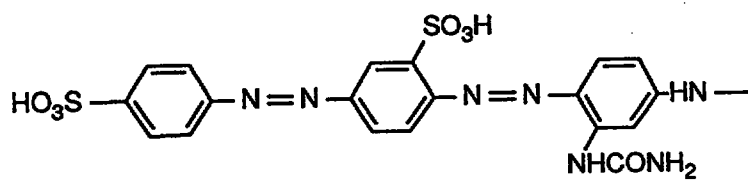
(A42)



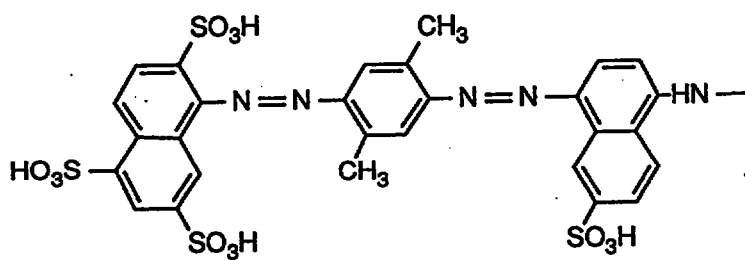
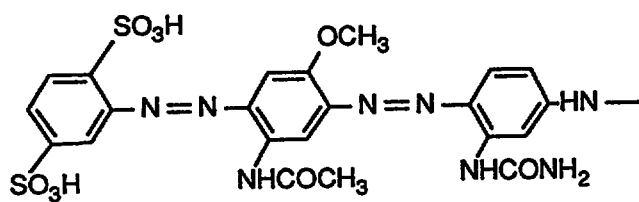
(A43)



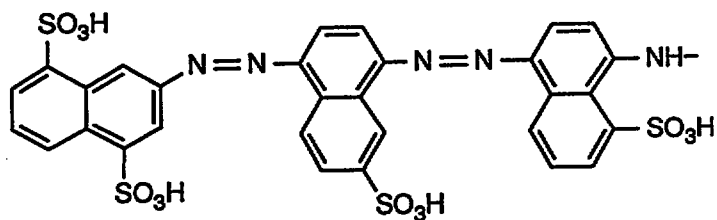
(A44)



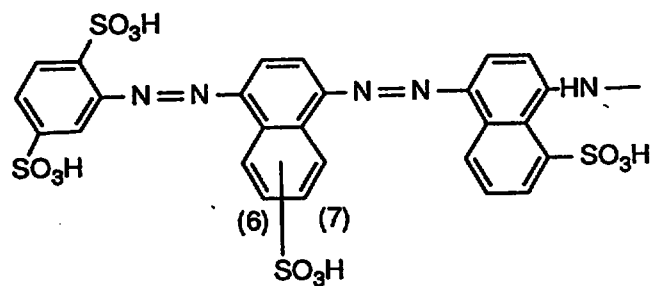
(A44a)



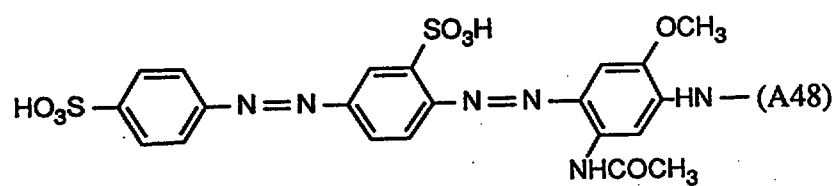
(A45)



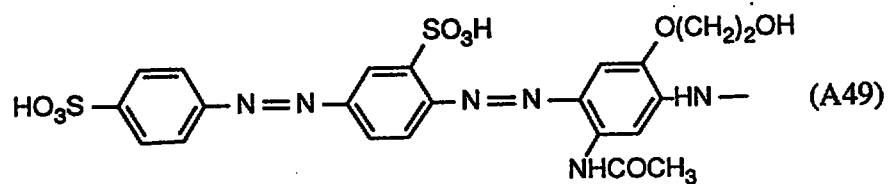
(A46)



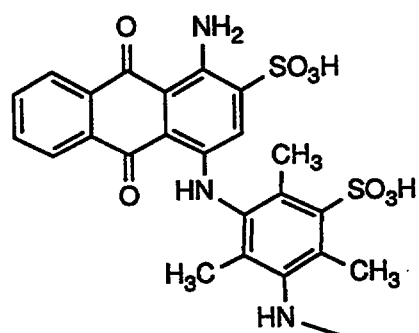
(A47)



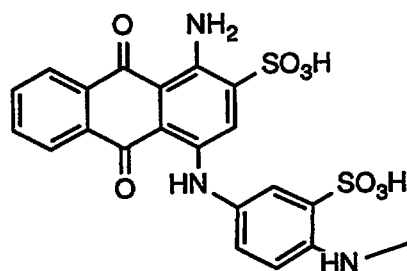
(A48)



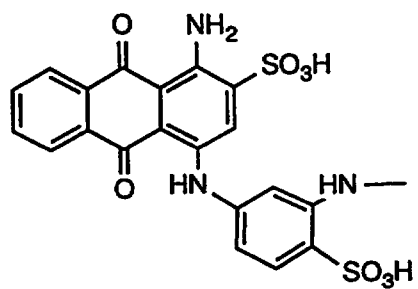
(A49)



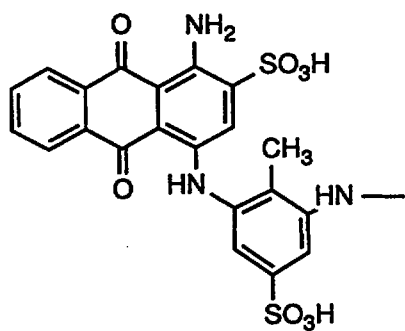
(A50)



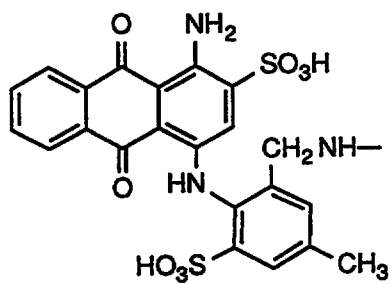
(A51)



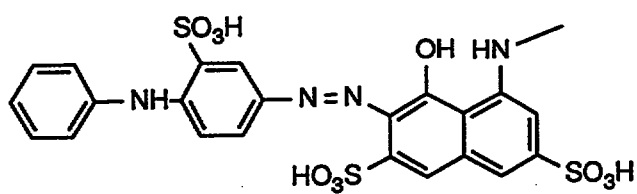
(A52)



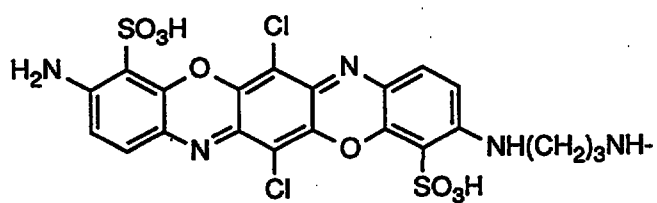
(A53)



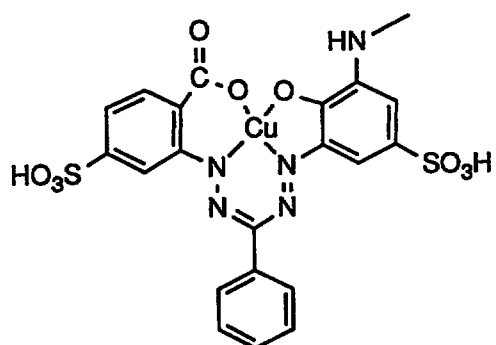
(A54)



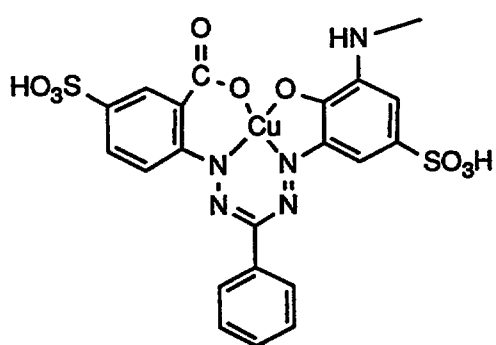
(A55)



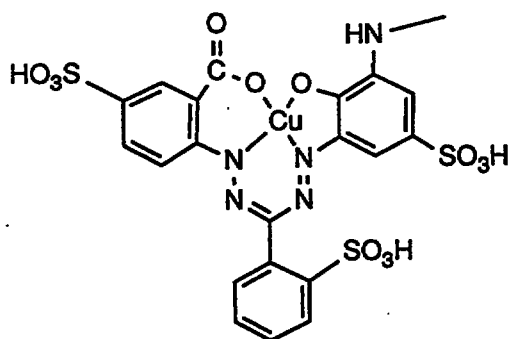
(A56)



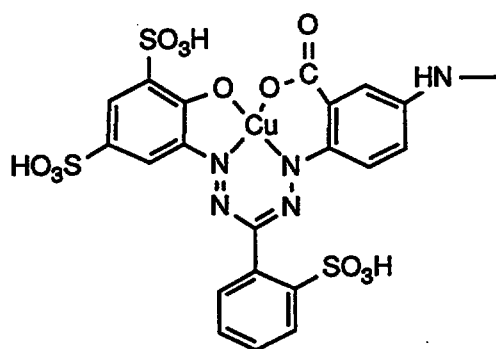
(A57)



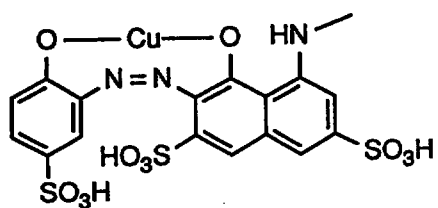
(A58)



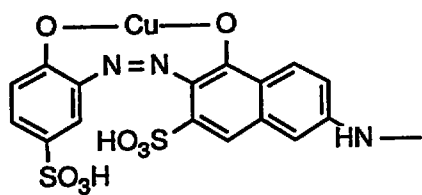
(A59)



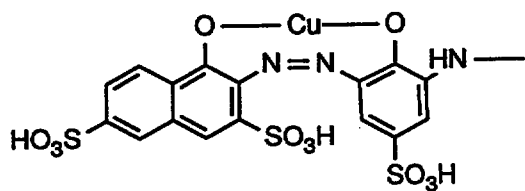
(A60)



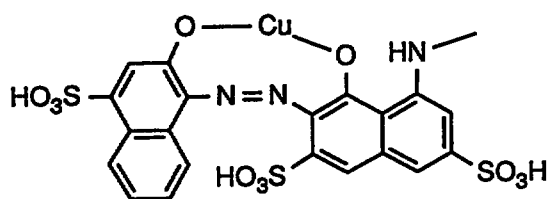
(A61)



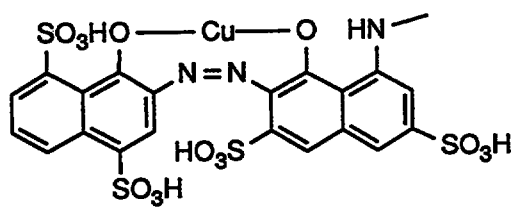
(A62)



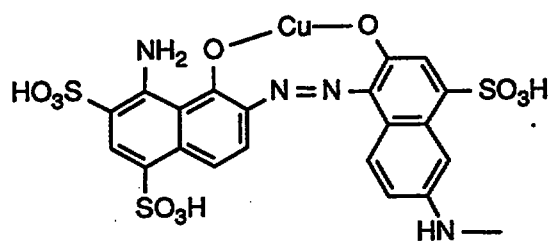
(A63)



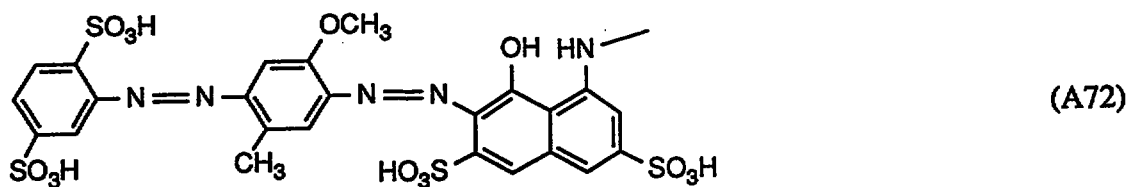
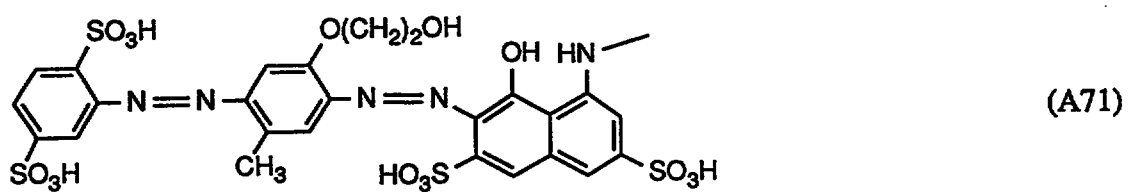
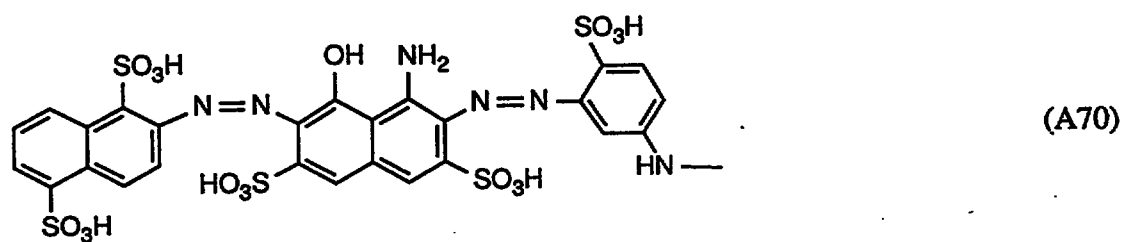
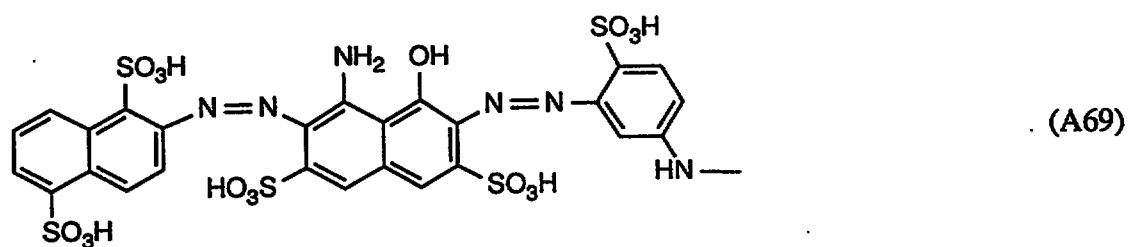
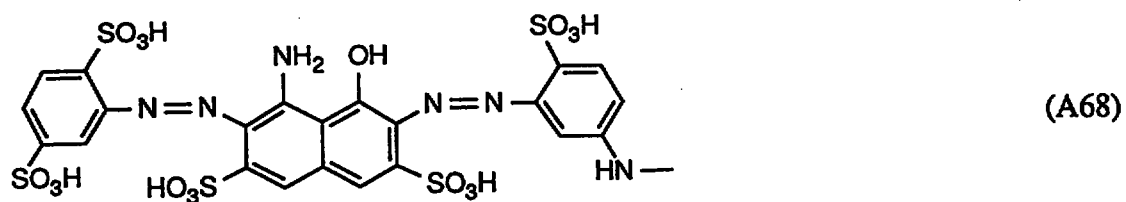
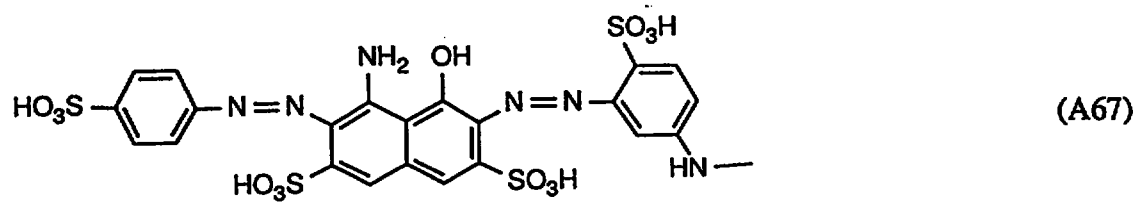
(A64)

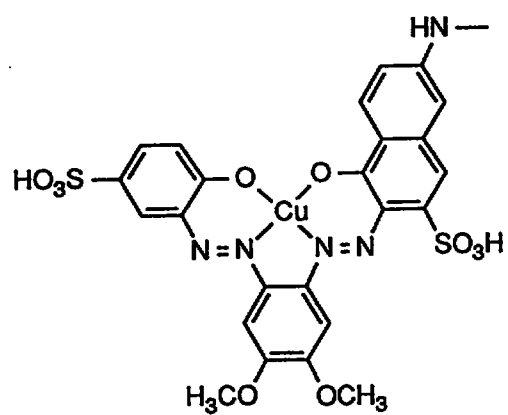


(A65)

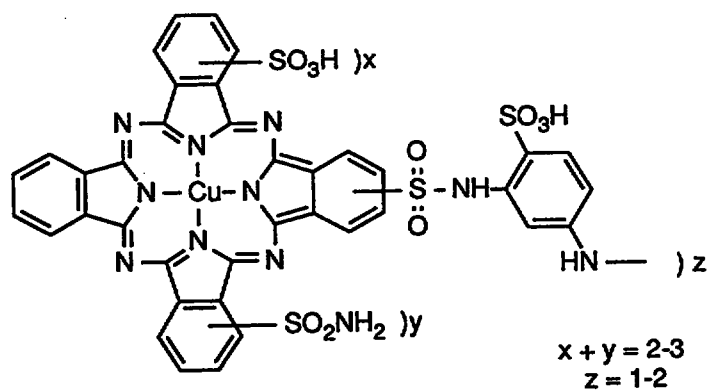


(A66)

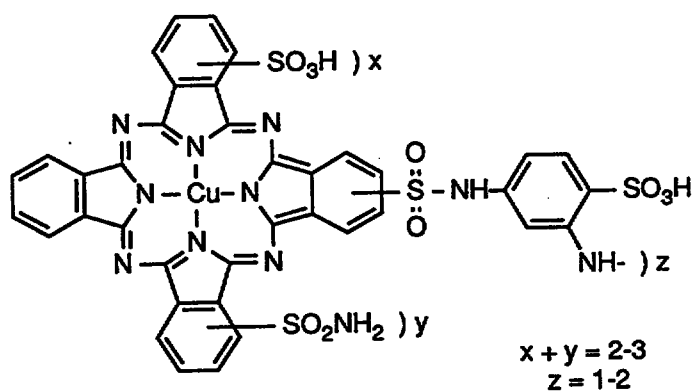




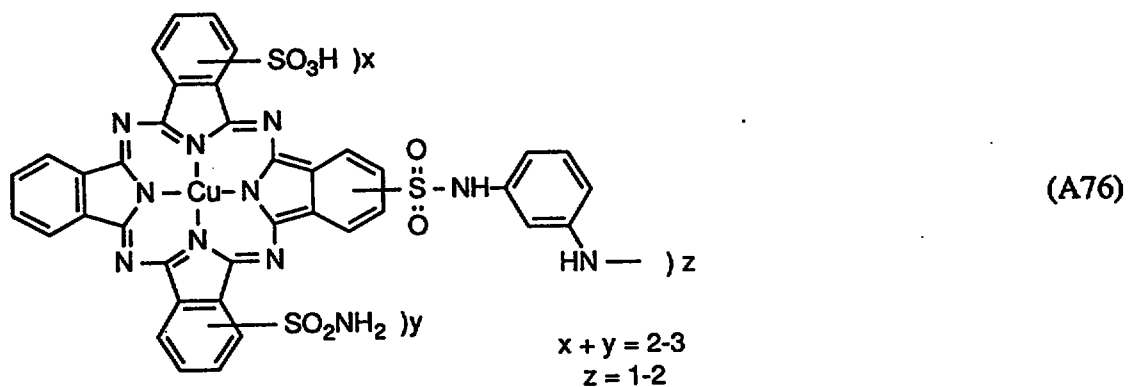
(A73)



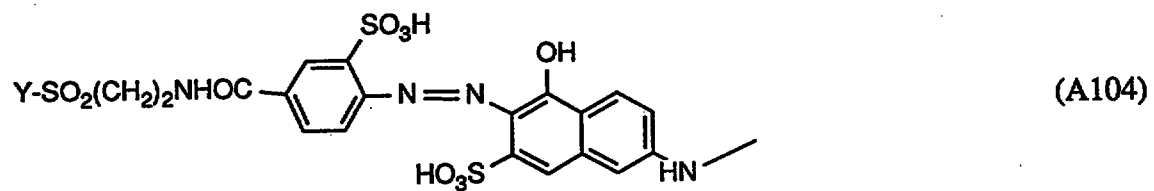
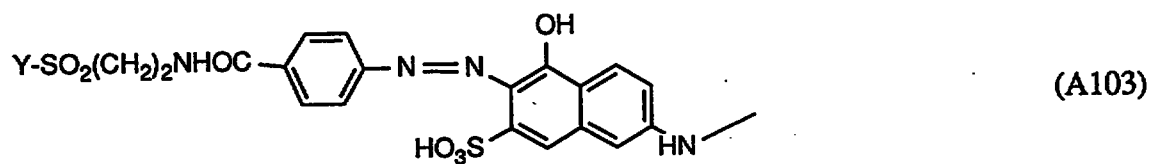
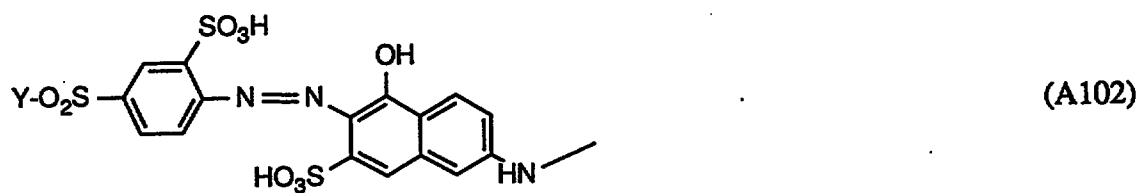
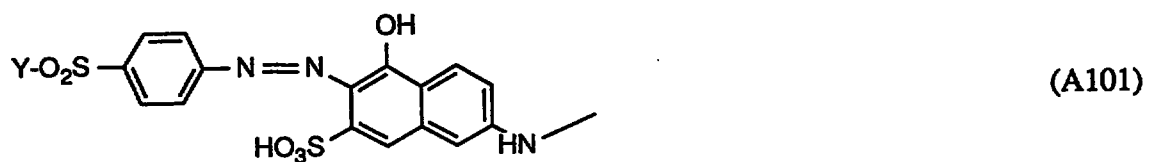
(A74)

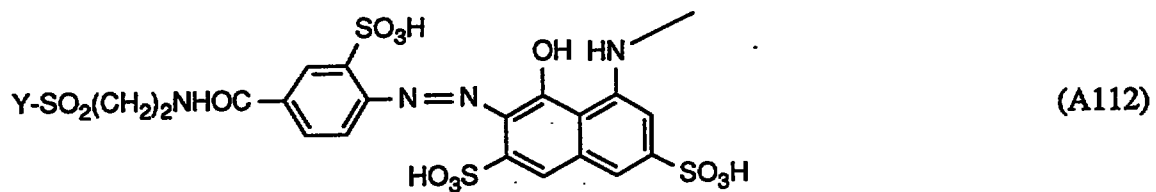
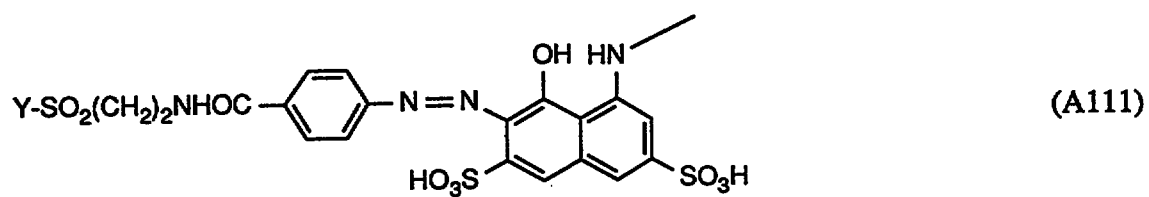
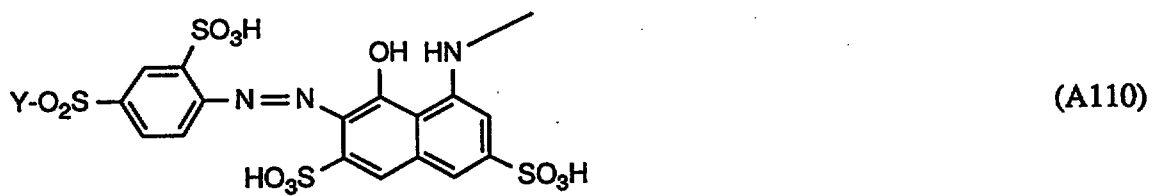
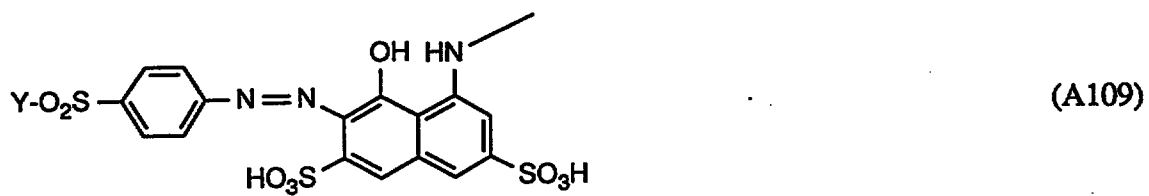
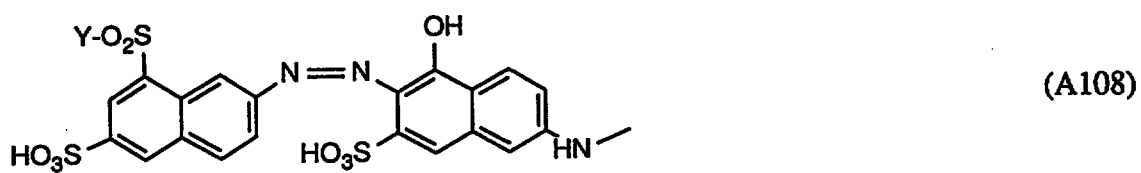
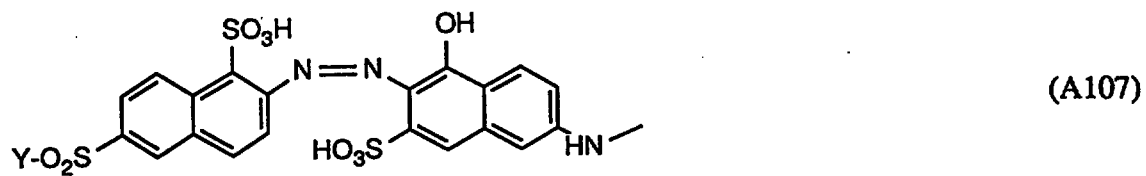
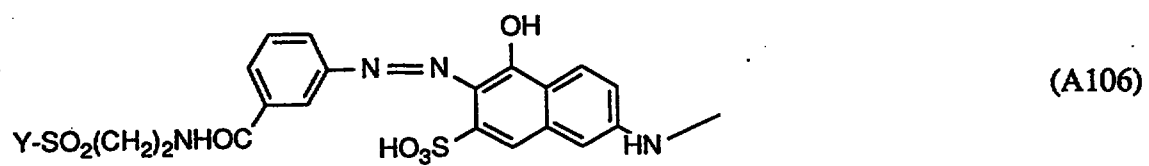


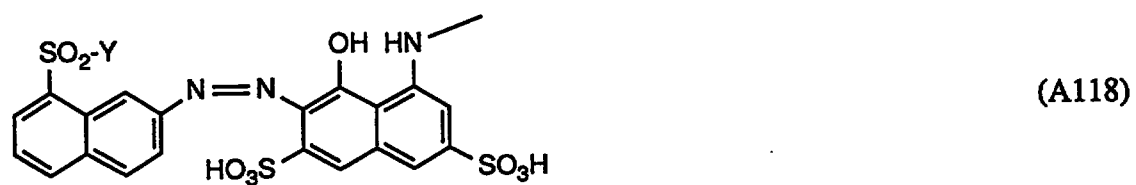
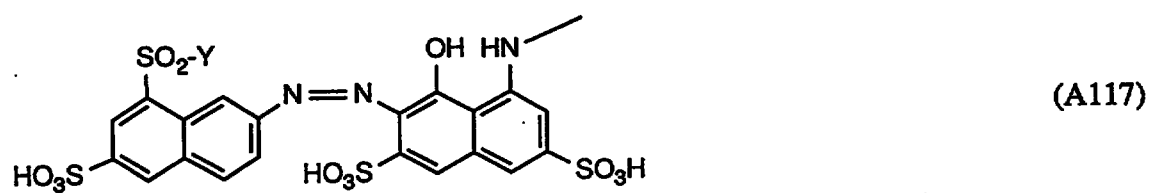
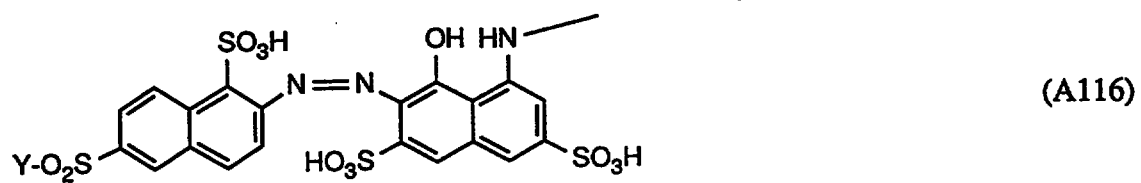
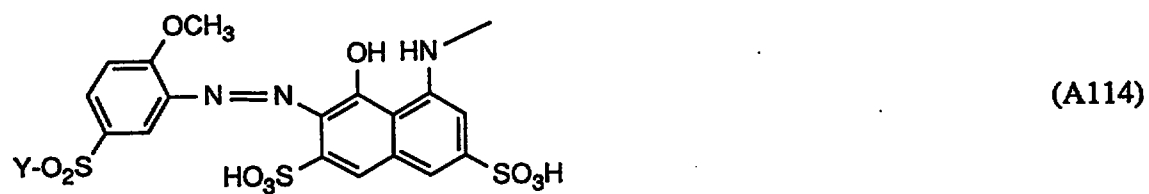
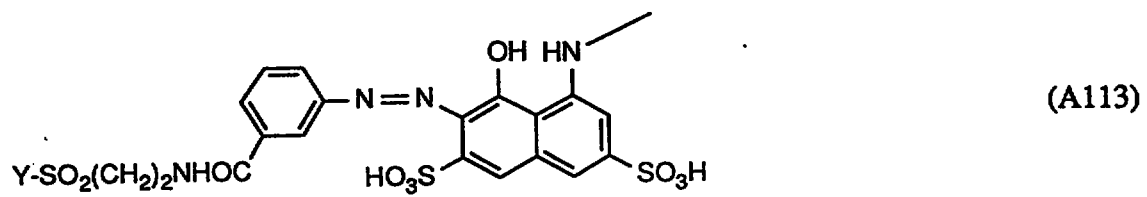
(A75)

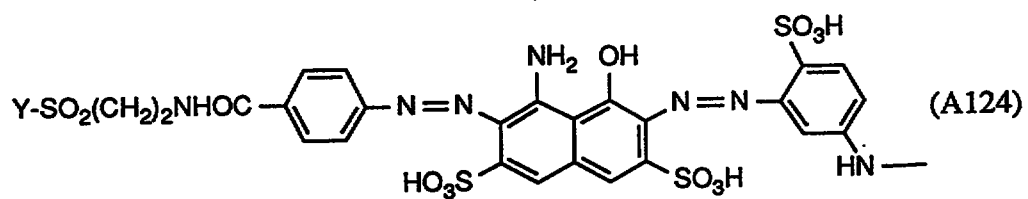
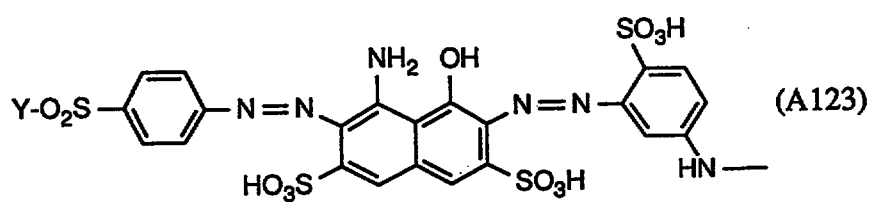
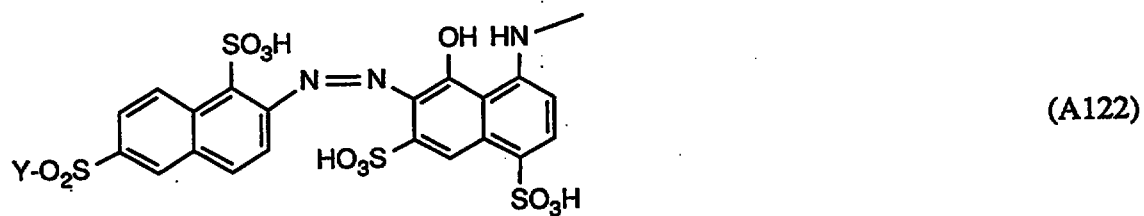
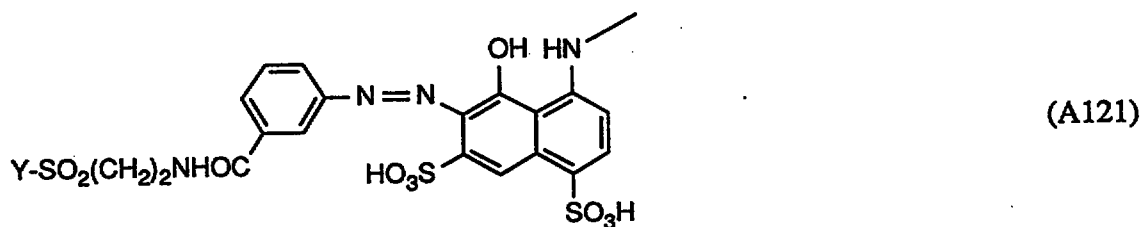
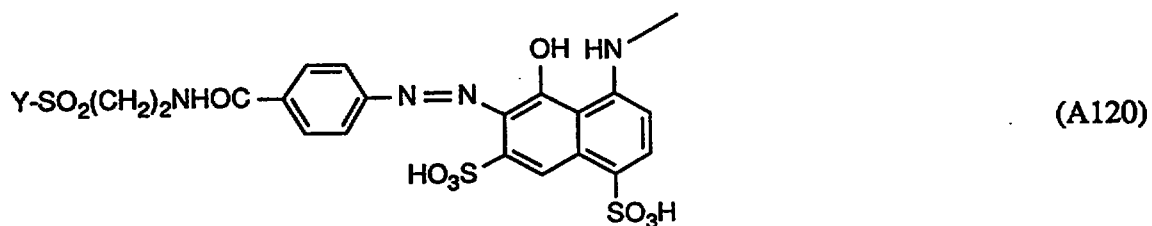
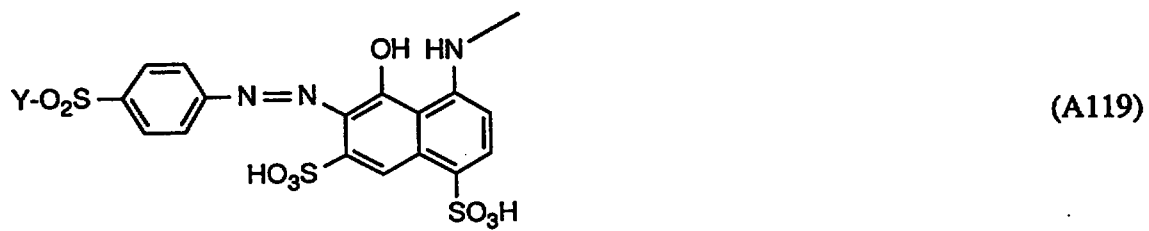


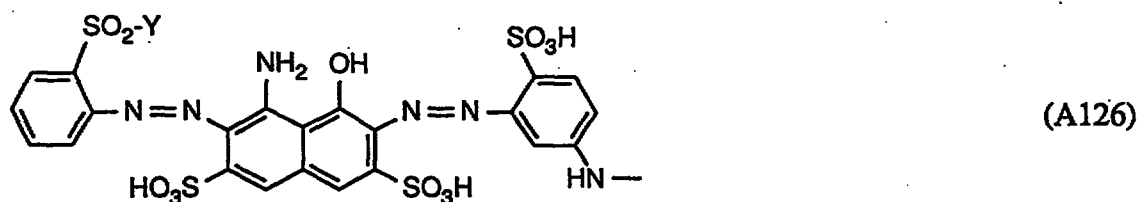
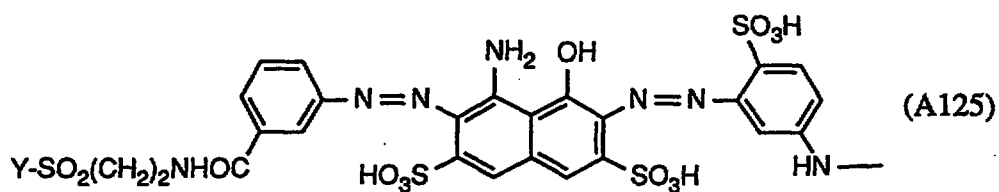
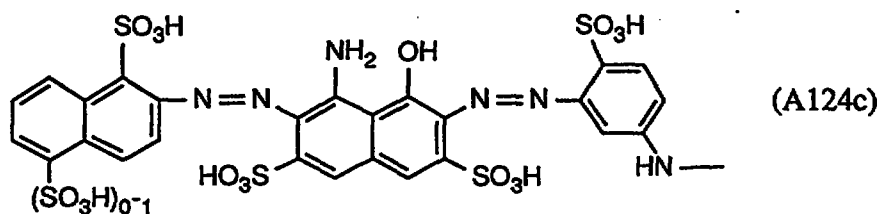
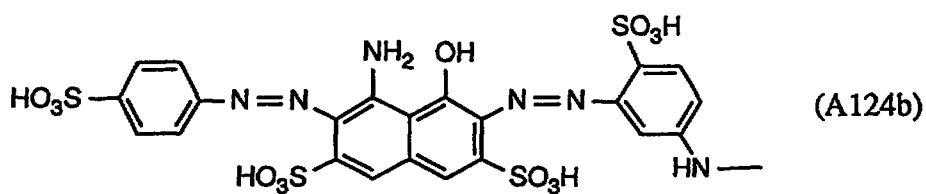
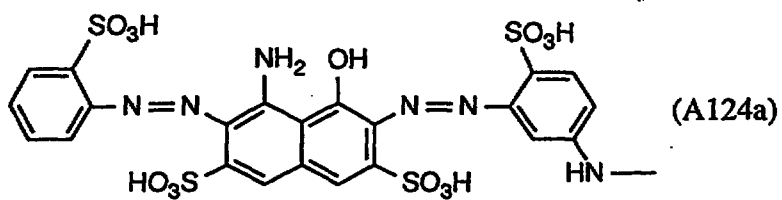
and Z' is a chromophore radical of the formula





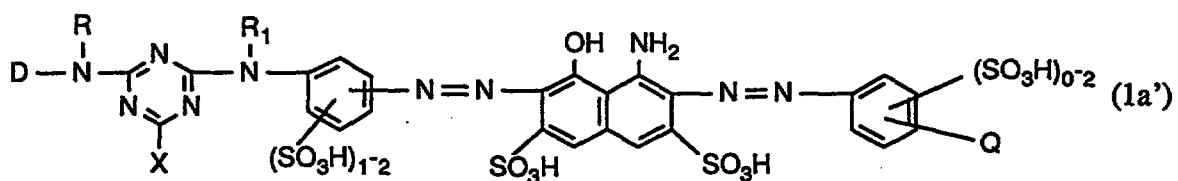






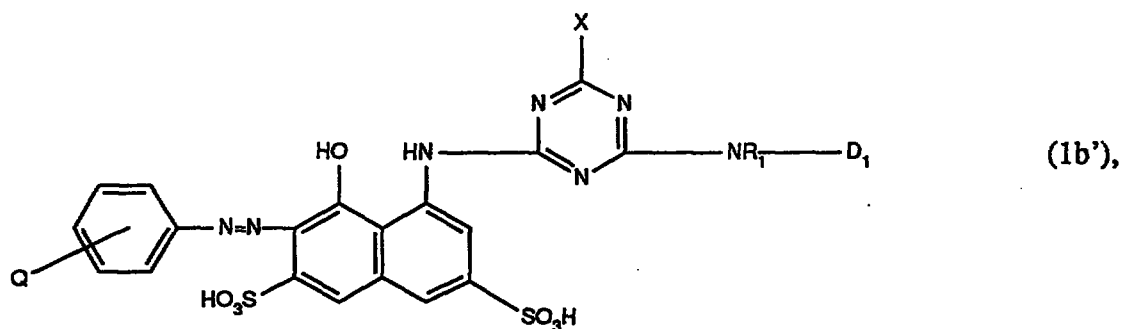
and Y is subject to the aforementioned meanings and preferences.

A preferred embodiment of the present invention concerns compounds of the formula



in which R and R₁ are each independently of the other hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the formula (2a) or (2b'') indicated above, and D is a radical of the formula (5b) indicated above which apart from sulfo carries no further substituents, or a radical of the formula (6), (21a), (23), (24) or (25) indicated above.

A further preferred embodiment of the present invention concerns compounds of the formula



in which R₁ is hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the above-indicated formula (2a) or (2b'') and D₁ is a radical of the formula (5b) indicated above which apart from sulfo contains no further substituents or is a radical of the formula (22), (23), (26) or (27) indicated above.

The compounds of the formula (1) are fibre-reactive. Fibre-reactive compounds are to be understood as meaning compounds capable of reacting with the hydroxyl groups of cellulose, the amino, carboxyl, hydroxyl and thiol groups in the case of wool and silk, or with the amino and possibly carboxyl groups of synthetic polyamides to form covalent chemical bonds.

The compounds of the formula (1) have at least two and preferably four to eight sulfo groups, which are in each case present in the form of the free acid or preferably in salt form, for example as sodium, lithium, potassium or ammonium salt. The compounds of the formula (1) can also be in the form of a mixed salt, for example in the form of a Na/Li or Na/Li/NH₄ salt.

The reactive dyes of the formula (1) can be prepared in a manner known per se, for example by reacting about a mole equivalent of an organic dye of the formula



about a mole equivalent of a compound of the formula



or suitable precursors of the compounds of the formulae (28) or (29) and about a mole equivalent of a halotriazine, preferably 2,4,6-trichloro- or 2,4,6-trifluoro-s-triazine, with one another in any desired order or, if precursors of the compounds of the formulae (28) or (29) were used, converting the resulting intermediates into the desired dyes and, if desired, following up with a further conversion reaction, for example to convert a halogen atom on the triazine into any desired radical X, where D, D₁, R, R₁ and X are subject to the meanings and preferences indicated above.

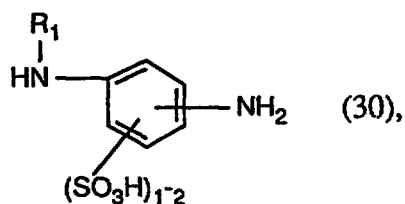
The conversion of intermediates into the final dyes, which becomes necessary on account of the use of precursors of the compounds of the formulae (28) or (29), is in particular a coupling reaction leading to azo dyes.

Since the individual above-indicated process steps can be carried out in various orders, in some instances even simultaneously, various process variants are possible. Generally the reaction is carried out in successive steps with the order of the elementary, known reactions between the individual reaction components depending on the particular conditions.

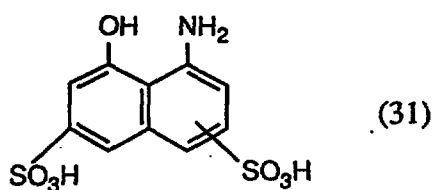
A preferred process for preparing dyes of the previously-indicated formula (1a) comprises for example reacting about 1 equivalent of an organic dye of the formula



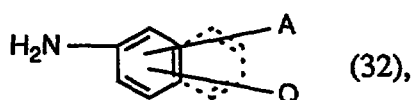
or a dye precursor, about 1 equivalent of 2,4,6-trifluoro-s-triazine (cyanuric fluoride) or 2,4,6-trichloro-s-triazine (cyanuric chloride), about 1 equivalent of the compound of the formula



about 1 equivalent of the compound of the formula

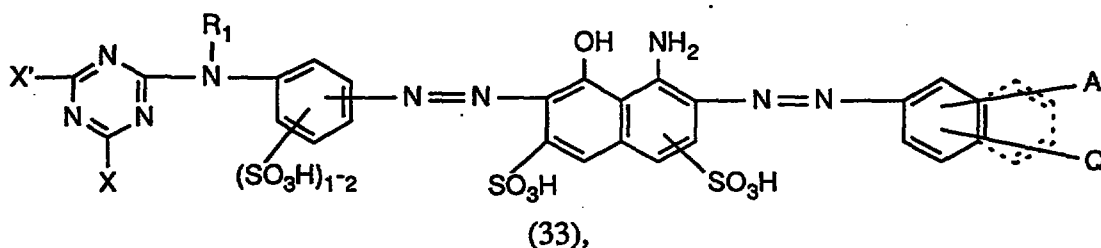


and about 1 equivalent of a compound of the formula



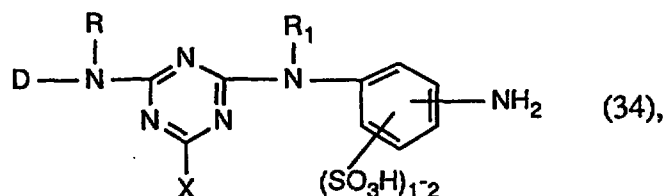
in which A, D, R, R₁ and Q are each as defined above, with one another in any desired order by diazotization and coupling or, if dye precursors are used, converting the resulting intermediates into the desired dyes with or without a further conversion reaction.

A preferred variant for preparing the compounds of the formula (1a) concerns the preparation of a compound of the formula

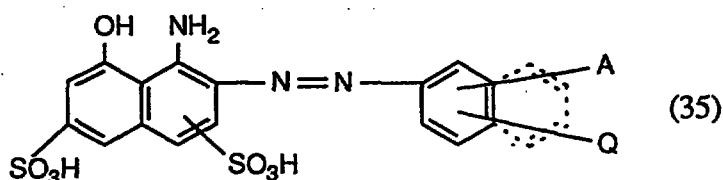


in which A, R₁, X and Q are each as defined above and X' is halogen, preferably chlorine or fluorine, and the further reaction thereof with a compound of the previously indicated formula (29). This route is especially suitable for compounds of the formula (1a) in which D is the radical of an anthraquinone, phthalocyanine, formazan or dioxazine chromophore.

A further preferred variant for preparing the compounds of the formula (1a) concerns the preparation of a compound of the formula



diazotization of this compound and coupling onto a compound of the formula



in which A, D, R, R₁, X and Q are each as defined above. This route is preferred in the synthesis of compounds of the formula (1a) in which D is the radical of a monoazo, polyazo or metal complex azo chromophore.

The invention further provides a process for dyeing and printing cellulose-containing fibre materials with the dyes of the invention. Suitable fibre materials include for example the natural cellulose fibres, such as cotton, linen and hemp, and also pulp and regenerated cellulose. The dyes are also suitable for dyeing or printing hydroxyl-containing fibres present in blend fabrics, for example blends of cotton with polyamide fibres or in particular with polyester fibres.

The dyes of the invention can be applied to and fixed on the fibre material in various ways, in particular in the form of aqueous dye solutions and print pastes. They are suitable not only for the exhaust method but also for dyeing by the padding method, whereby the material is impregnated with aqueous, salt-containing or salt-free dye solutions and the dyes are fixed after an alkali treatment or in the presence of alkali with or without heating. After fixing, the dyeings or prints are thoroughly rinsed with cold and hot water with or without an agent which has a dispersing action and promotes the diffusion of the unfixed portions. Dyeing and printing are carried out using the customary dyeing and printing processes.

The amounts in which the reactive dyes are used in the dyebaths or print pastes of the process of the invention can vary according to the desired depth of shade; generally amounts from 0.01 to 10 per cent by weight, in particular from 0.1 to 6 per cent by weight, on weight of fibre, are suitable.

The dyeing liquors may contain the generally customary additions, for example the aqueous solutions of inorganic salts, for example of alkali metal chlorides or alkali metal sulfates, alkali metal hydroxides, urea, thickenings, for example alginate thickenings, water-soluble cellulose alkyl ethers and also dispersants, levelling agents and migration coinhibitors, further sodium m-nitrobenzenesulfonate and as further thickeners for example methylcellulose, starch ethers, emulsion thickenings, preferably an alginate, e.g. sodium alginate, and also wetting agents.

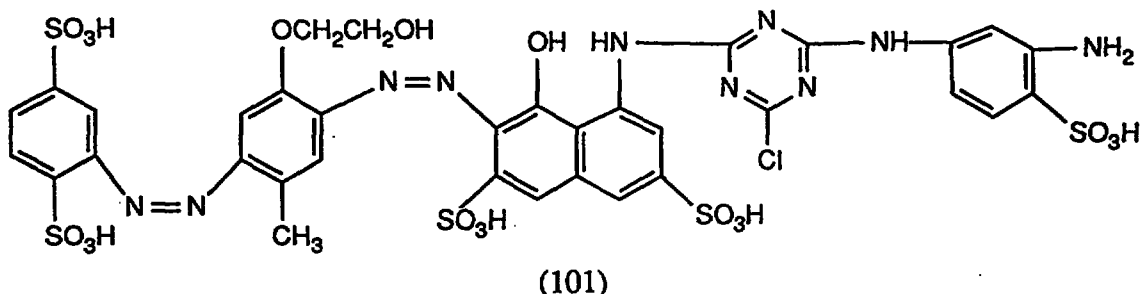
The process of the invention is preferably carried out as a dyeing by the exhaust method. In this case dyeing generally takes place from an aqueous medium at a liquor ratio of for example 2:1 to 60:1, in particular at a liquor ratio from 5:1 to 20:1, at a dyebath pH of for example 6 to 13 and at a temperature of for example 40 to 110°C, in particular at a temperature from 60 to 95°C.

The dyes of the invention are notable for good fixation and very good build-up. They are notable for a high degree of exhaustion and can be applied by the exhaust method over a very wide temperature range and are therefore also suitable for dyeing cotton-polyester blend fabrics under the conditions recommended for such fabrics. The dye mixtures of the invention are also suitable for printing, in particular cotton or blend fabrics containing for example wool or silk.

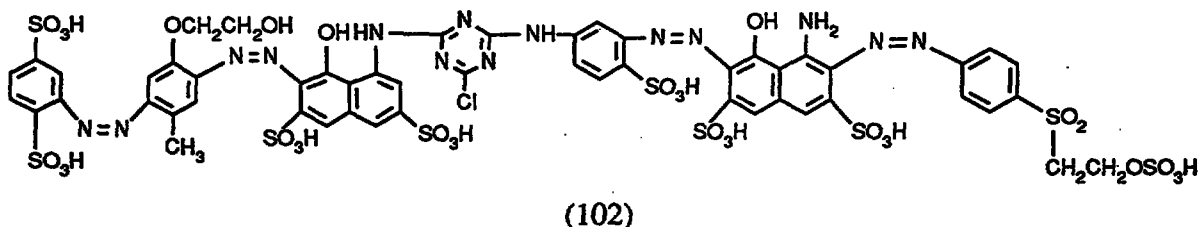
The dyeings and prints on cellulose fibre materials prepared with the dyes of the invention have a high colour strength and a high fibre-dye bond stability not only in the acid but also in the alkaline range, also good lightfastness and very good wet fastness properties, such as wash, water, seawater, cross-dyeing and perspiration fastness properties, and also good fastness to dry heating setting and pleating.

The Examples which follow illustrate the invention. The temperatures are given in degrees Celsius, and the parts and percentages are by weight, unless otherwise stated. Parts by weight relate to parts by volume as the kilogram to the litre.

Example 1: A neutral solution of 106 parts of the compound of the formula

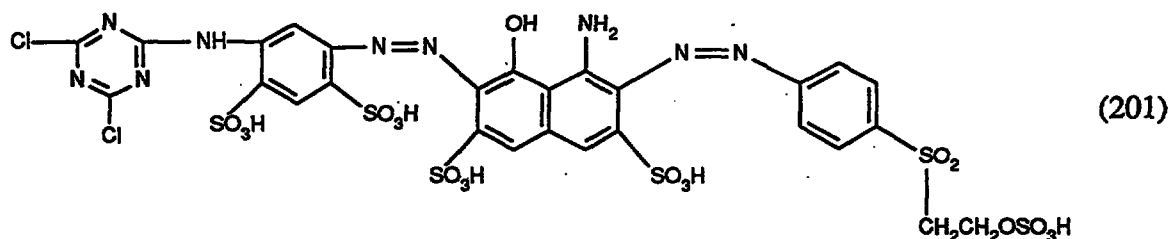


in 1000 parts of water is admixed at a temperature of about 0°C with 25 parts of 32 % hydrochloric acid and 7 parts of sodium nitrite and stirred for an hour. The excess nitrite is destroyed with a little sulfamic acid and the suspension of the diazonium salt is added dropwise into a cold neutral solution of 61 parts of 1-amino-2-[4-(2-sulfatoethylsulfonyl)phenylazo]-8-hydroxynaphthalene-3,6-disulfonic acid while the pH is kept constant by the addition of sodium hydroxide solution. The solution is warmed to room temperature, and freed of salt by dialysis, and the dye of the formula

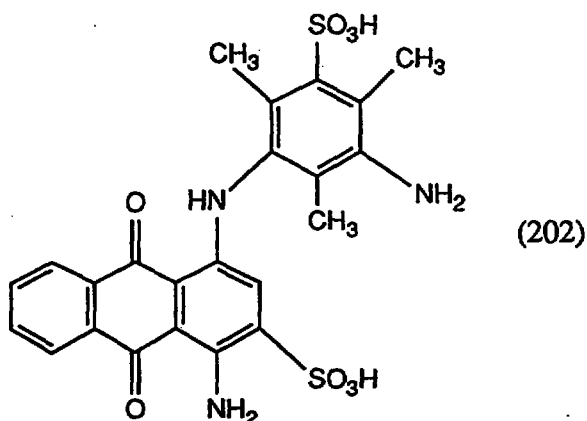


is isolated by evaporating to dryness. The powder obtained dyes cellulose in bright navy shades having good allround fastness properties.

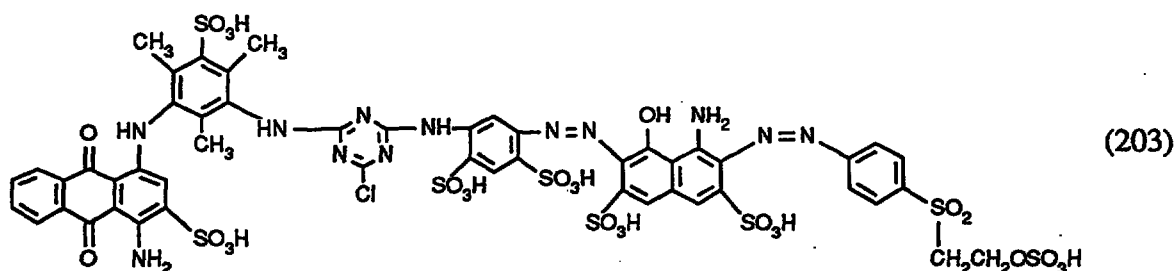
Example 2: A neutral solution of 104 parts of the compound of the formula



in 1000 parts of water is added at a temperature of about 0°C to a cold neutral solution of 53 parts of the compound of the formula

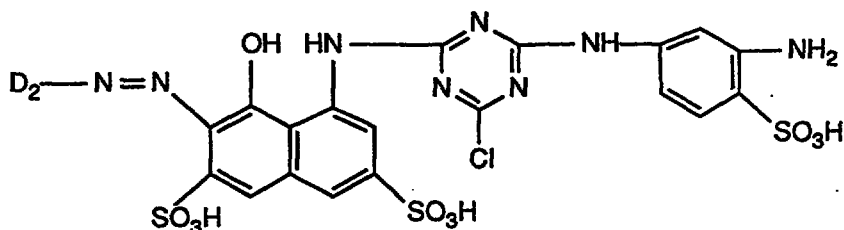


while the pH is kept constant by the addition of sodium hydroxide solution. The solution is warmed to room temperature and freed of salt by dialysis and the dye of the formula



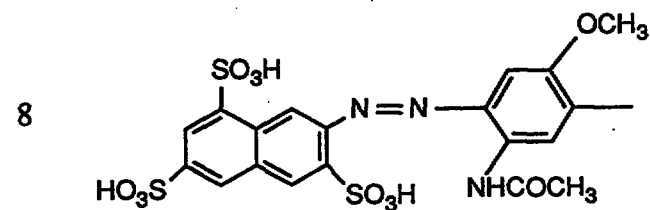
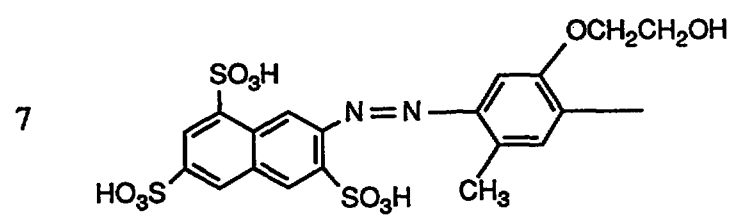
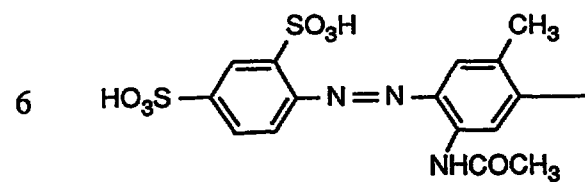
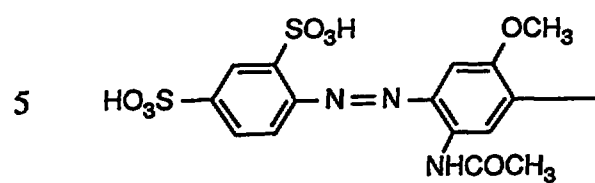
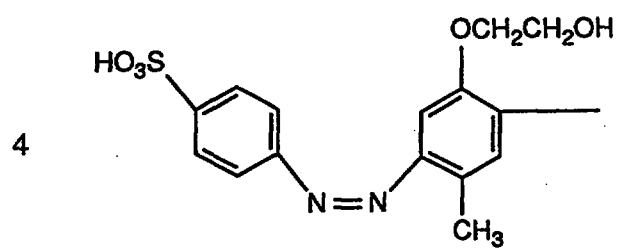
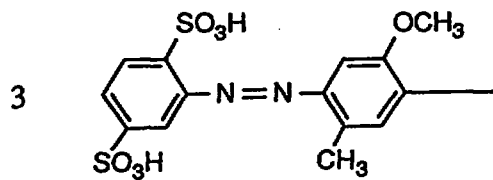
is isolated by evaporation to dryness. The powder obtained dyes cellulose in bright blue shades having good allround fastness properties.

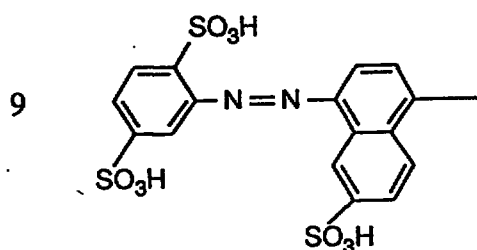
Examples 3-9: Example 1 is repeated using instead of the compound (101) a compound of the general formula



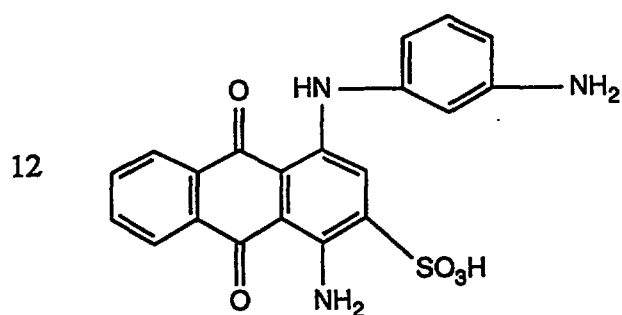
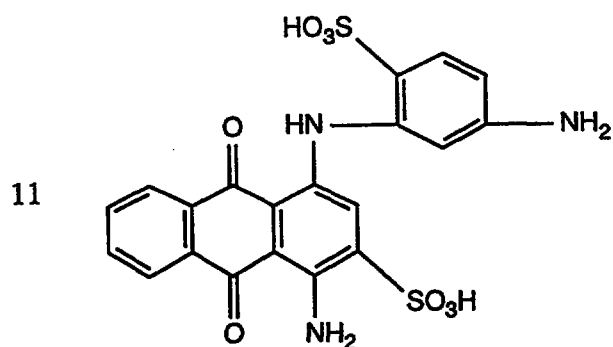
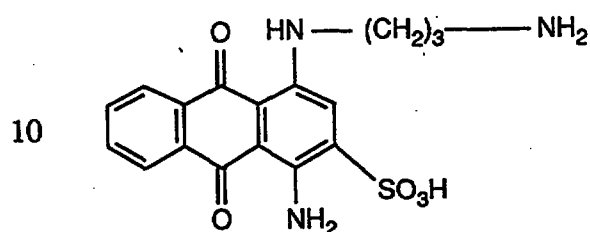
in which D₂ has the meanings specified in the table below. This results in analogous dyes

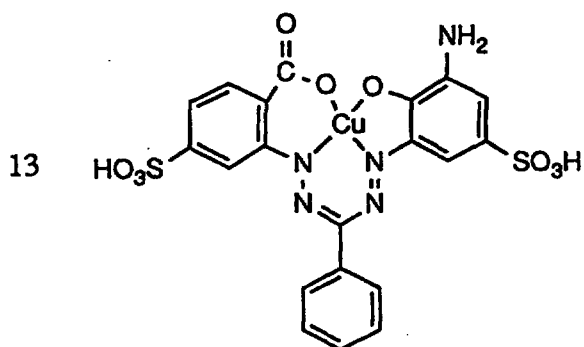
which each dye cotton with good allround fastness properties.



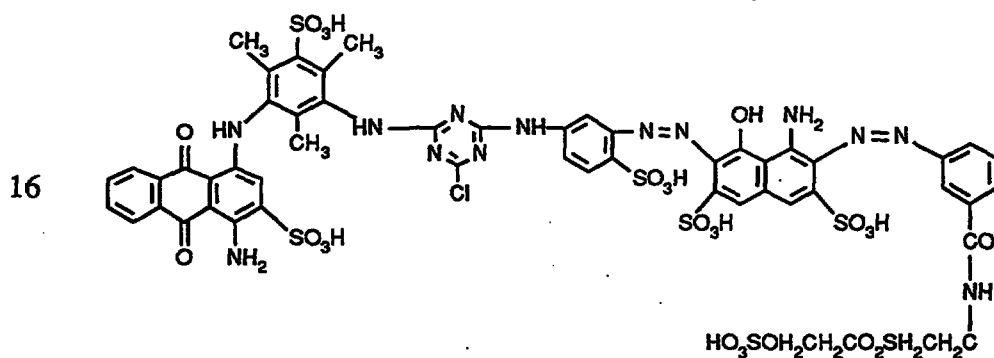
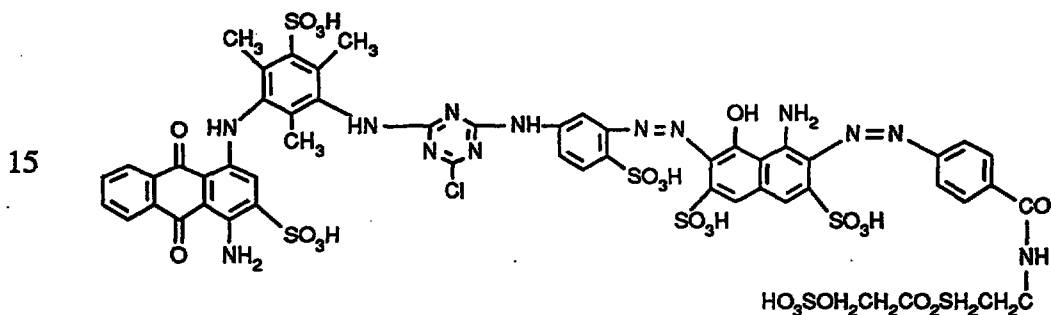
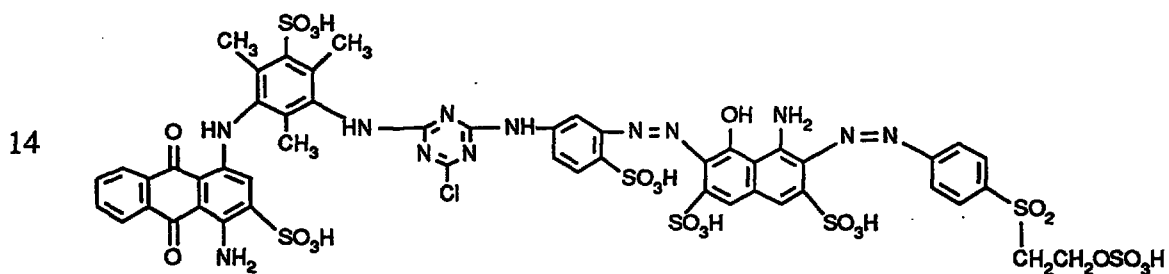


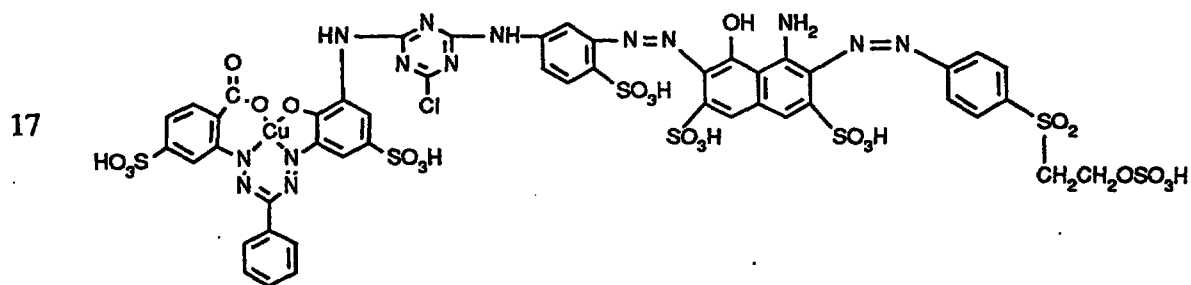
Examples 10-13: Example 2 is repeated using instead of the compound (202) the compounds mentioned in the table below. This results in analogous dyes which each dye cotton with good allround fastness properties.





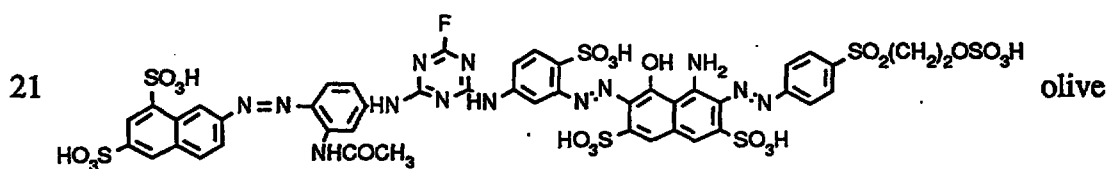
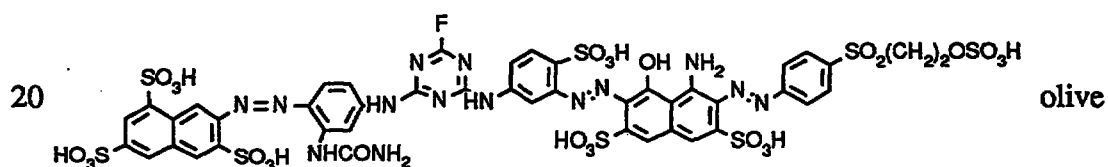
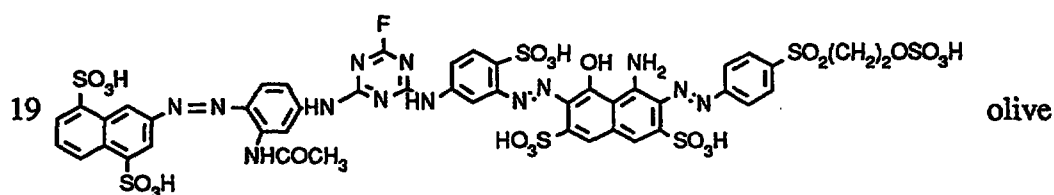
Examples 14-17: The method of Examples 1 to 13 can be used to prepare the following compounds which each dye cotton with good allround fastness properties:

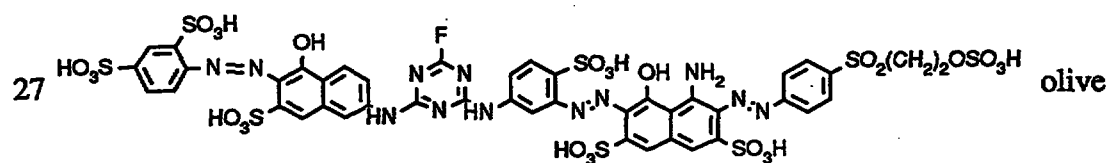
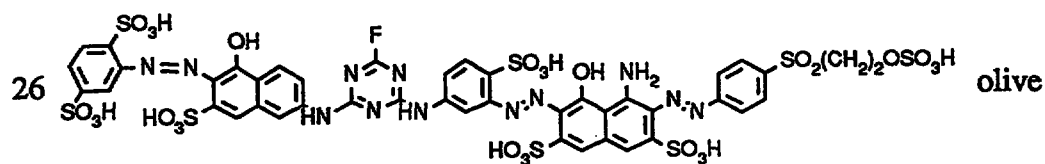
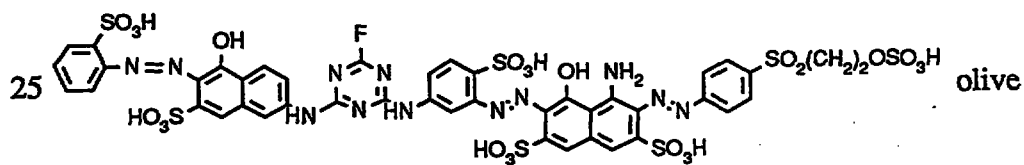
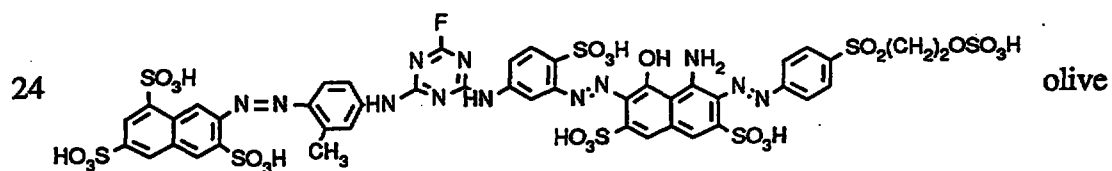
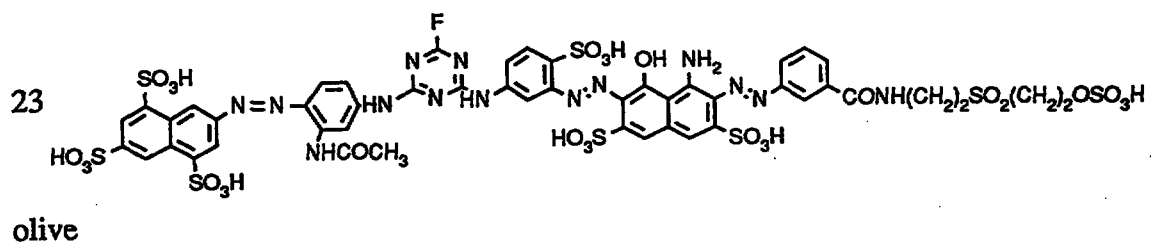
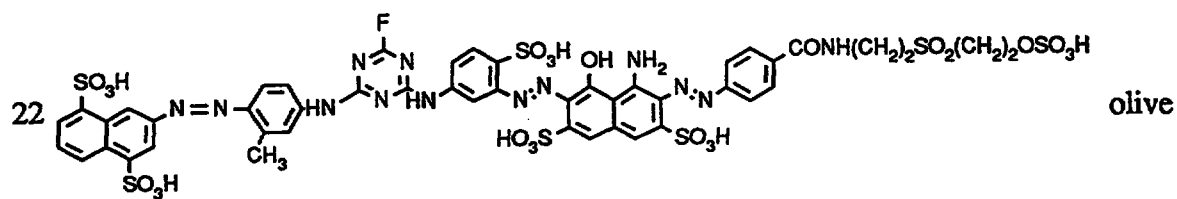


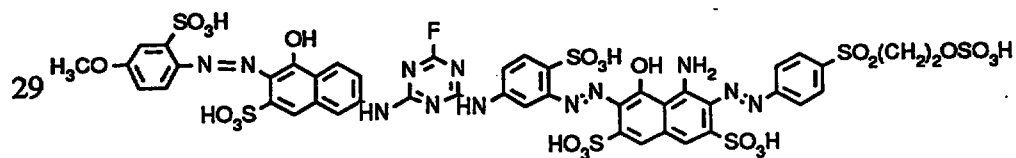
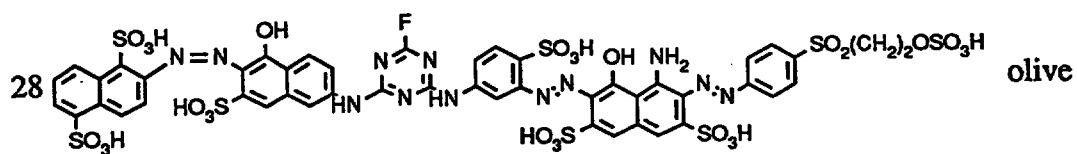


Example 18: Examples 1 to 17 are repeated using instead of the chlorotriazinyl-containing precursor the corresponding fluorotriazinyl-containing precursor. This results in the analogous fluorotriazinyl compounds.

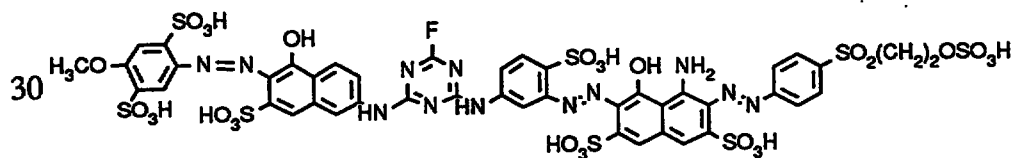
Examples 19-48: The method of Examples 1 and 2 can be used to prepare the following dyes which dye cotton with good allround fastness properties in the indicated hue:



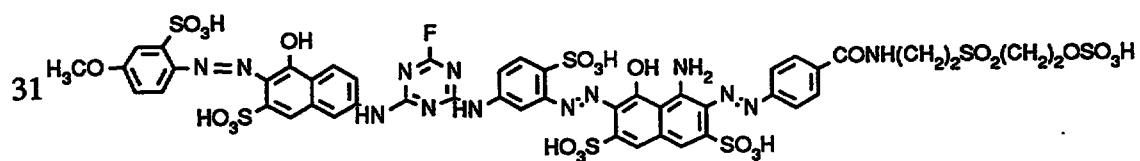




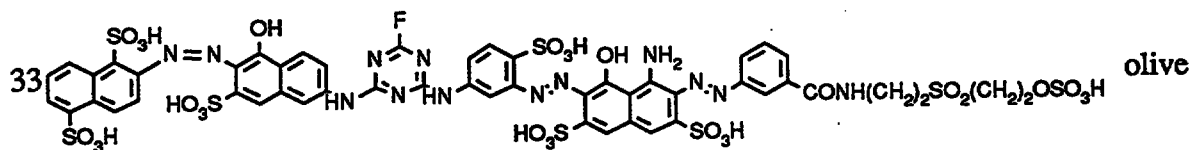
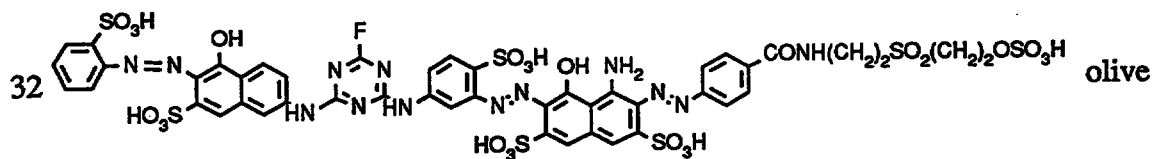
violet

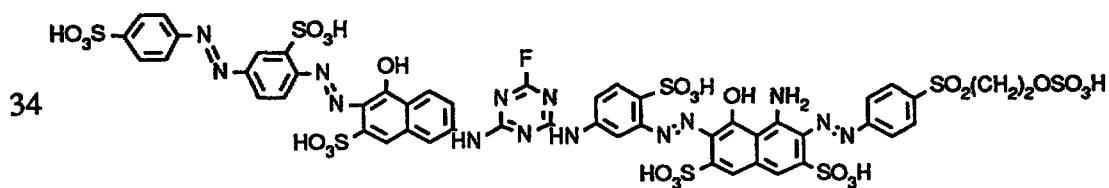


violet

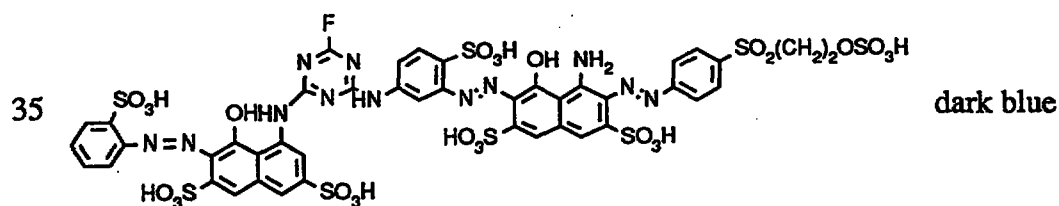


violet

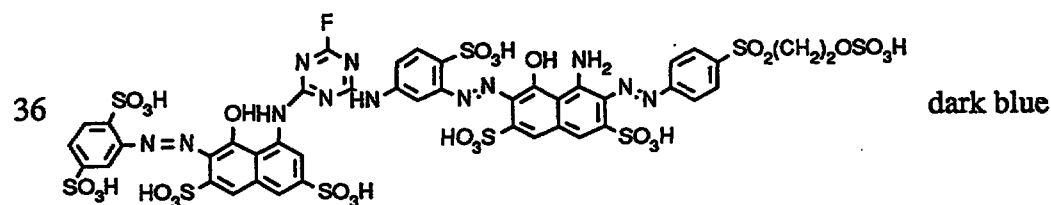




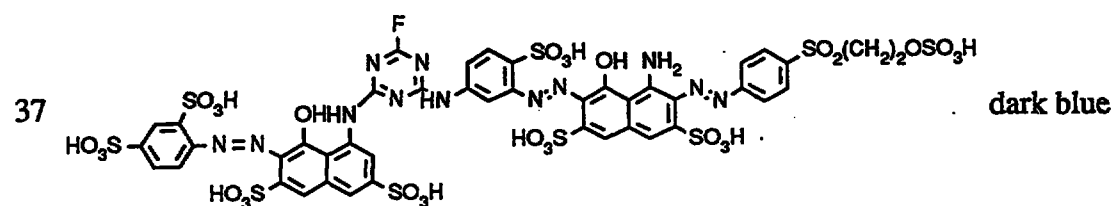
dark blue



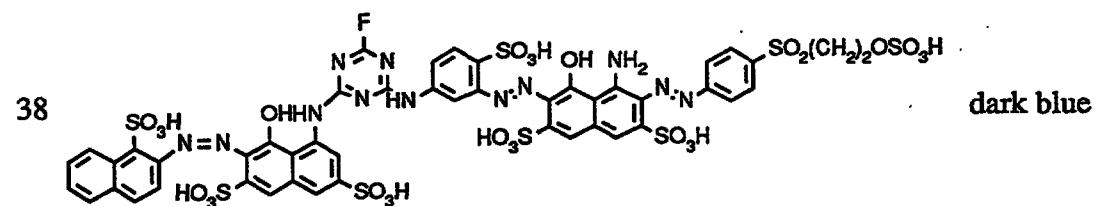
dark blue



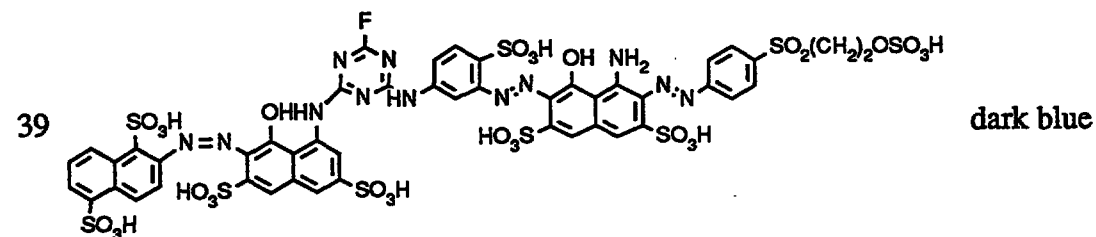
dark blue



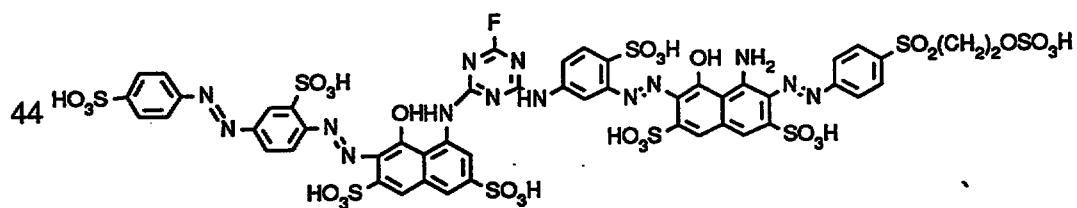
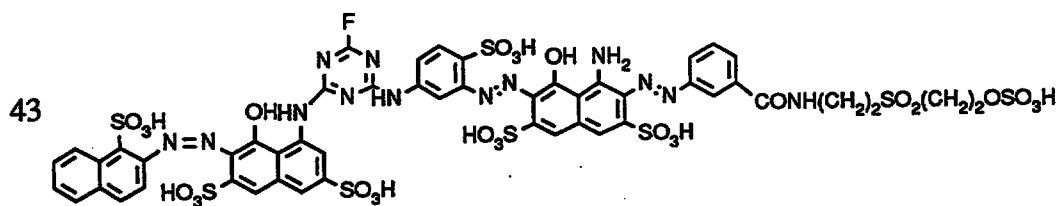
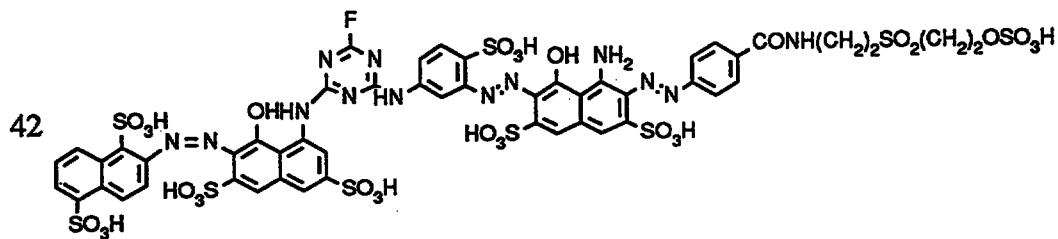
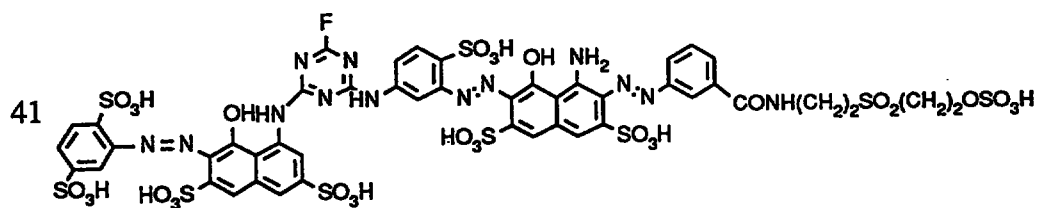
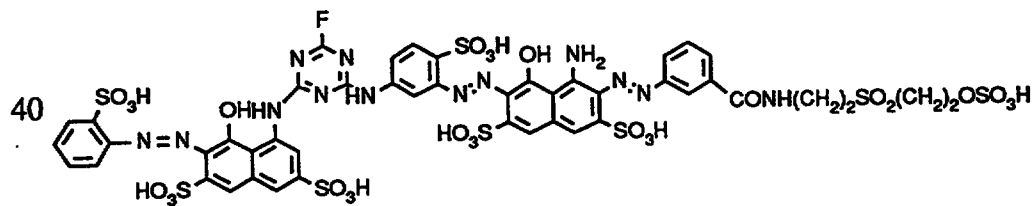
dark blue

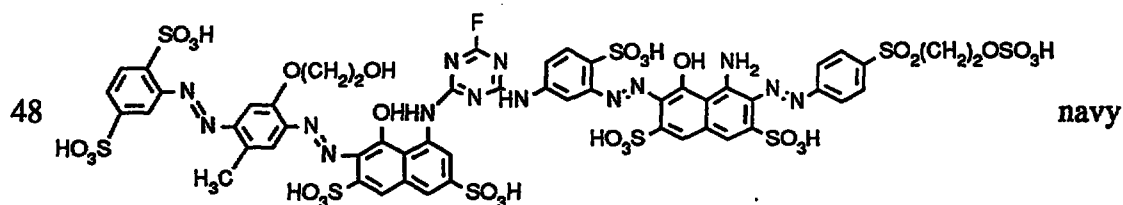
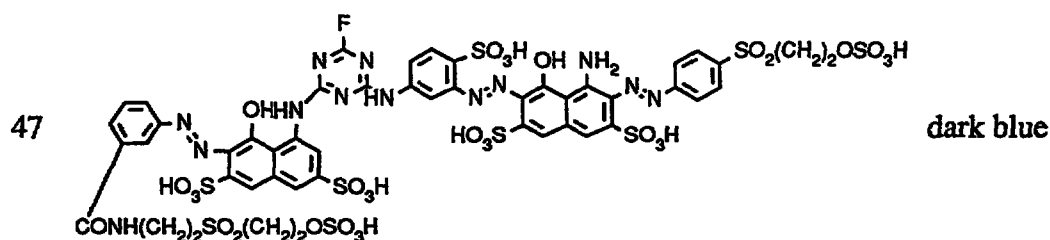
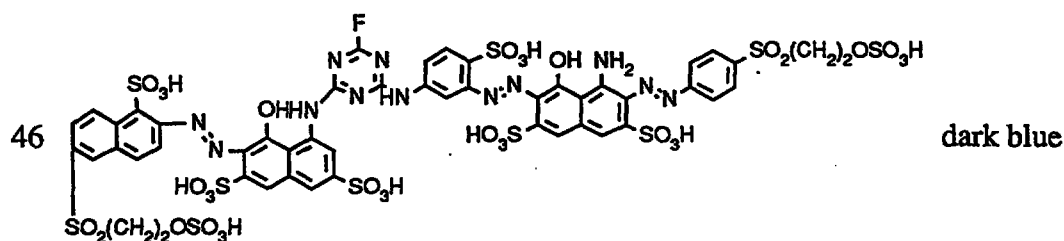
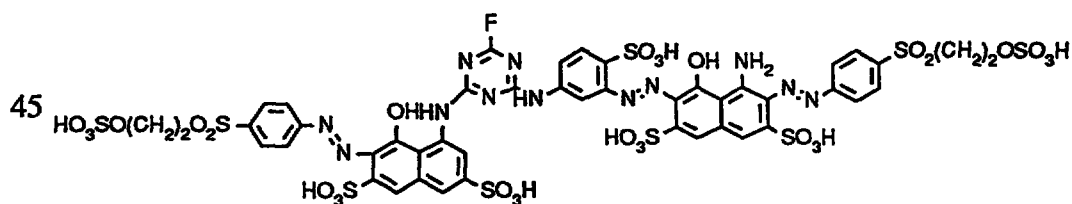


dark blue



dark blue

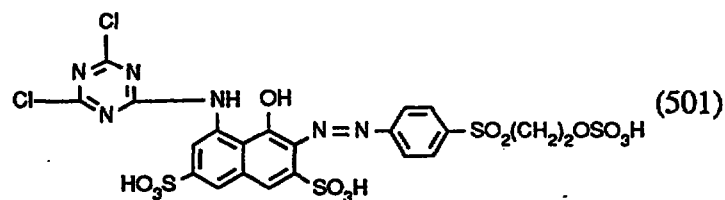




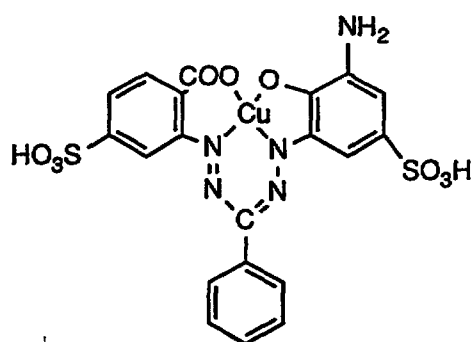
Example 49: Examples 19 to 48 are repeated using instead of the fluorotriazinyl-containing precursor in each case the corresponding chlorotriazinyl-containing precursor. This results in the analogous chlorotriazinyl compounds.

Example 50: 18.45 parts of cyanuric chloride are suspended in 150 parts of ice water and stirred. 38.5 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid, dissolved in 180 parts of water, are added dropwise at 0 to 2°C. The resulting hydrochloric acid is neutralized by the addition of 2 N sodium hydroxide solution. After the condensation has ended, 28 parts of 4-amino(2-sulfatoethylsulfonyl)benzene are diazotized in a conventional manner using sodium nitrite in hydrochloric acid and coupled at pH 2.5-6

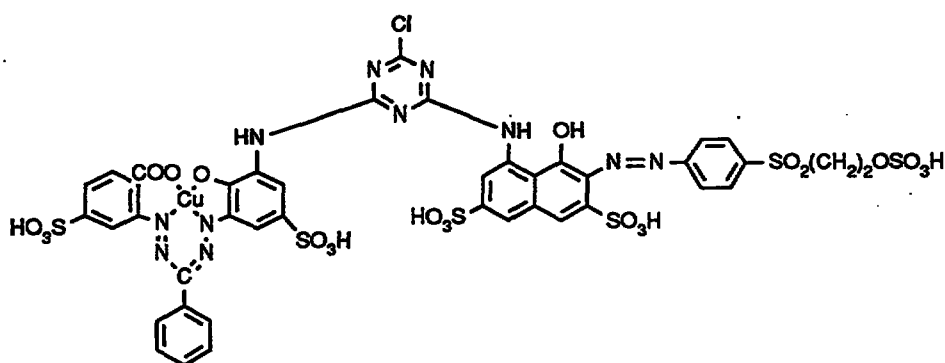
and 0-5°C. The resulting compound of the formula



is subsequently condensed with 59.5 parts of the compound of the formula

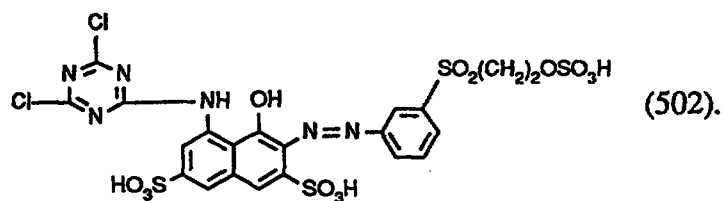


in the course of about 3 hours at pH 6-7 and room temperature. The reaction mixture is subsequently stirred for about 16 hours, and then the precipitated dye is filtered off and washed with water and acetone; the dye conforms to the formula

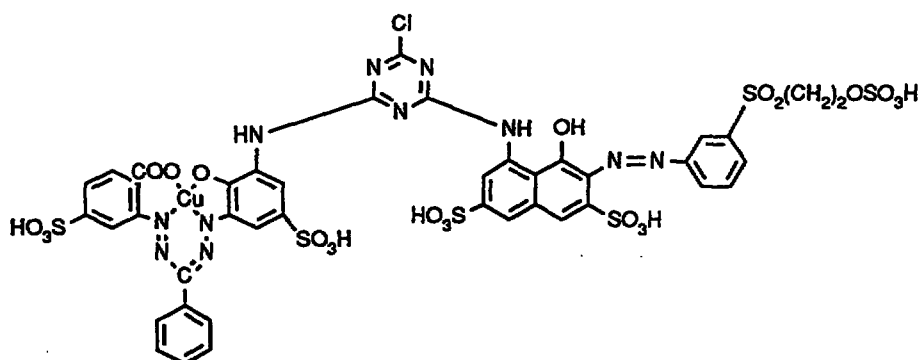


and dyes cotton in bright blue shades.

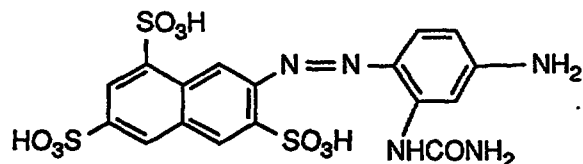
Example 50a: Example 50 is repeated using instead of the compound of the formula (501) the analogous amount of the compound of the formula



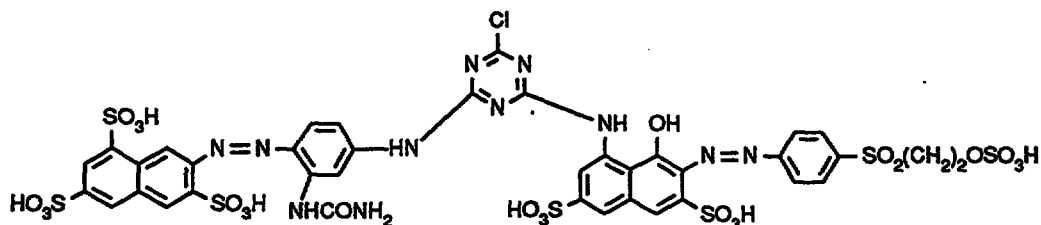
This results in the compound of the formula



Example 51: The product of the formula (501) prepared as described in Example 50 is condensed in the course of about 3.5 hours at 20 to 30°C and pH 6.5 and 6.75 with 54.5 parts of the monoazo compound of the formula



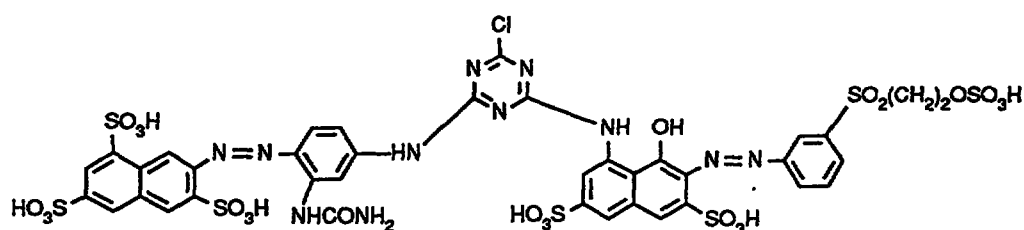
After subsequent stirring at room temperature and pH 6.5 for about 16 hours, the dye is filtered off and washed; it conforms to the formula



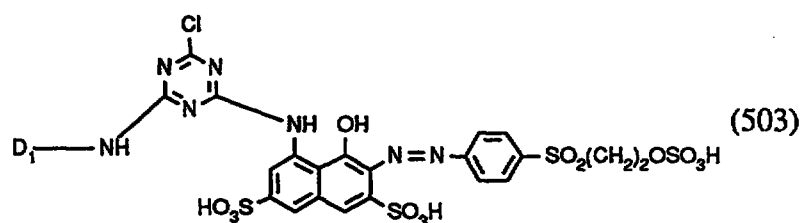
and dyes cotton in a scarlet shade with good allround fastness properties.

Example 51a: Example 51 is repeated using instead of the compound of the formula

(501) the analogous amount of the compound of the formula (502). This results in the compound of the formula



Examples 52-68: The method of example 50 or 51 can be used to prepare further dyes of the formula

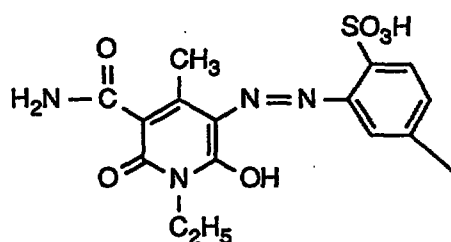


in which D_1 is as defined in the table:

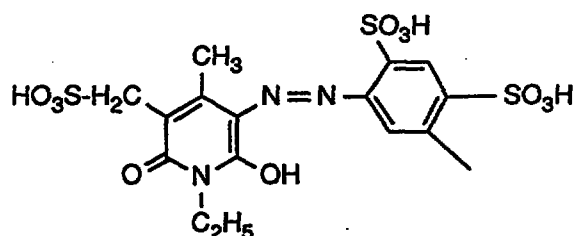
Ex.:

$$D_1$$

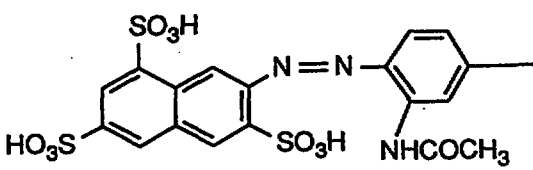
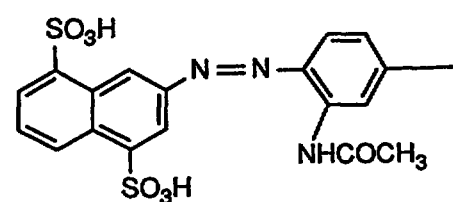
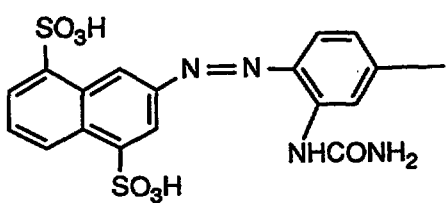
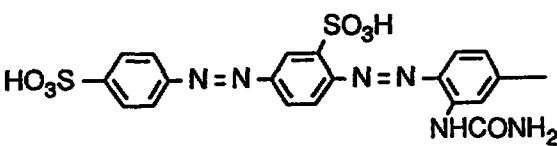
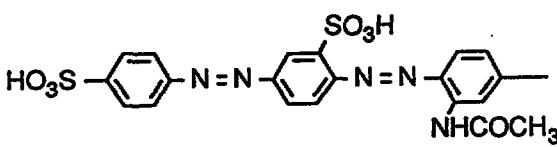
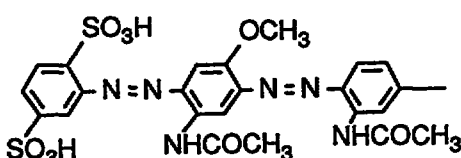
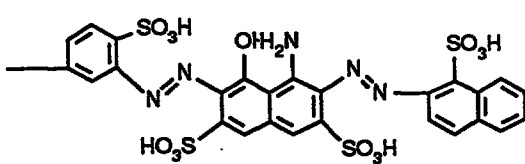
Hue

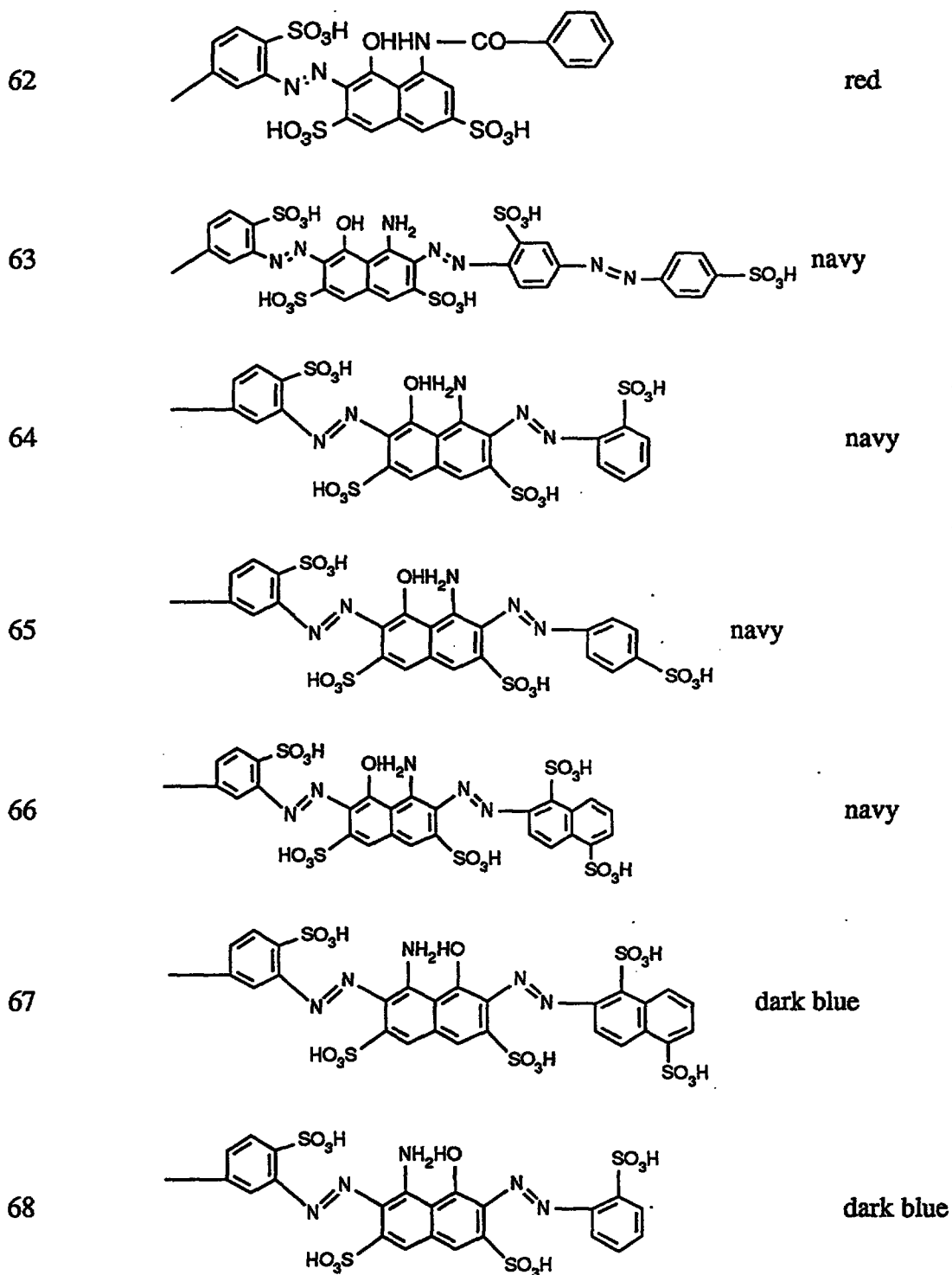


orange



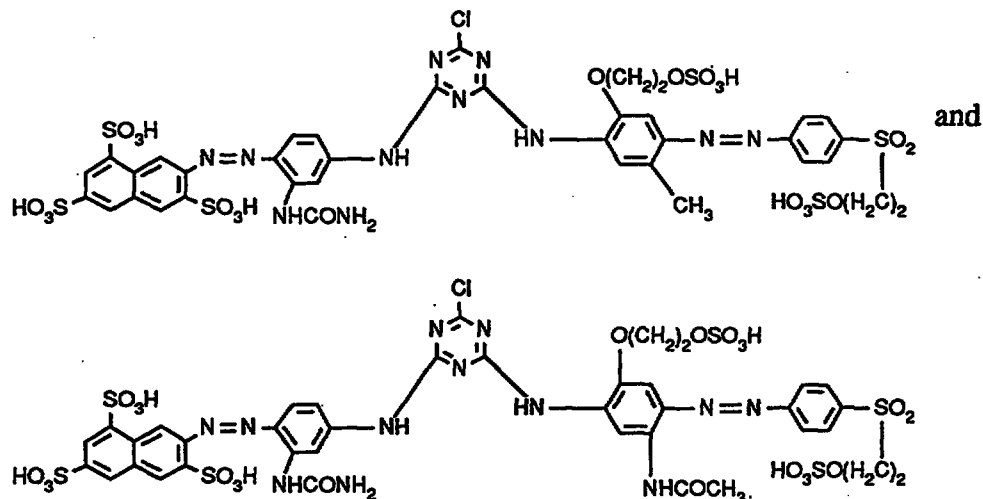
orange

54		scarlet
55		scarlet
56		scarlet
57		brown
58		brown
59		brown
60		brown
61		navy



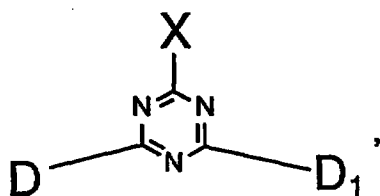
Example 69: Examples 50 to 68 are repeated using instead of the chlorotriazinyl-containing precursor of the formula (503) in each case the corresponding fluorotriazinyl-containing precursor. This results in the analogous fluorotriazinyl compounds.

Examples 70-72: The method of Example 50 or 51 can be used to prepare the dyes of the formula



which each dye cotton in a yellow shade with good allround fastness properties.

Examples 73-82: The method of Example 50 or 51 can be used to prepare further dyes of the formula



in which X, D and D₁ are each as defined in the table:

Ex.:	D ₁ :	X:	D:	Y:	Hue:
73	A14	Cl	A109	-CH=CH ₂	orange
74	A11	Cl	A109	-(CH ₂) ₂ OSO ₃ H	orange
75	A14	F	A109	-CH=CH ₂	orange

76	A11	F	A109	$-(CH_2)_2OSO_3H$	orange
77	A4	Cl	A109	$-(CH_2)_2OSO_3H$	orange
78	A2	Cl	A109	$-(CH_2)_2OSO_3H$	orange
79	A57	Cl	A109	$-(CH_2)_2OSO_3H$	violet
80	A57	Cl	A123	$-(CH_2)_2OSO_3H$	navy
81	A57	F	A113	$-(CH_2)_2OSO_3H$	violet
82	A75	Cl	A109	$-(CH_2)_2OSO_3H$	blue

The meanings of the radicals A1 to A126 are specified in the description.

Example 83: 2 parts of the dye of Example 1 are dissolved in 400 parts of water; 1500 parts of a solution containing 53 g of sodium chloride per litre are added. This dyebath is entered at 40°C with 100 parts of a cotton fabric. After 45 minutes 100 parts of a solution containing 16 g of sodium hydroxide and 20 g of anhydrous Na_2CO_3 per litre are added. The temperature of the dyebath is held at 40°C for a further 45 minutes. Then the fabric, which has been dyed navy, is rinsed, soaped off at the boil for a quarter of an hour with a nonionic detergent, rinsed once more and dried. The dyeing obtained has very good fastness properties.

Example 84: 2 parts of the dye of Example 1 are dissolved in 400 parts of water; 1500 parts of a solution containing 53 g of sodium chloride per litre are added. This dyebath is entered at 35°C with 100 parts of a cotton fabric. After 20 minutes 100 parts of a solution containing 16 g of sodium hydroxide and 20 g of anhydrous Na_2CO_3 per litre are added. The temperature of the dyebath is held at 35°C for a further 15 minutes. The temperature is then raised over 20 minutes to 60°C. The temperature is held at 60°C for a further 35 minutes. Thereafter the fabric, which has been dyed navy, is rinsed, soaped off at the boil for a quarter of an hour with a nonionic detergent, rinsed once more and dried. The dyeing obtained has very good fastness properties.

Example 85: 8 parts of the dye of Example 1 are dissolved in 400 parts of water; 1400 parts of a solution containing 100 g of sodium sulfate per liter are added. This dyebath is entered at 25°C with 100 parts of a cotton fabric. After 10 minutes 200 parts of a solution containing 150 g of trisodium phosphate per litre are added. Then the temperature of the dyebath is raised to 60°C over 10 minutes. The temperature is held at 60°C for a further 90 minutes. Thereafter the fabric, which has been dyed navy, is rinsed, soaped off at the boil for a quarter of an hour with a nonionic detergent, rinsed once more and dried. The dyeing obtained has very good fastness properties.

Example 86: 4 parts of the dye of Example 1 are dissolved in 50 parts of water. 50 parts of a solution containing 5 g of sodium hydroxide and 20 g of anhydrous Na_2CO_3 per litre are added. The solution obtained is used for padding a cotton fabric to a wet pick-up of 70 % of its weight and the fabric is then wound onto a batching roller. It is stored in that state at room temperature for 3 hours. Thereafter the fabric, which has been dyed navy, is rinsed, soaped off at the boil for a quarter of an hour with a nonionic detergent, rinsed once more and dried. The dyeing obtained has very good fastness properties.

Example 87: 6 parts of the dye of Example 1 are dissolved in 50 parts of water. 50 parts of a solution containing 16 g of sodium hydroxide and 0.04 l of 38°Bé waterglass are added. The solution obtained is used for padding a cotton fabric to a wet pick-up of 70 % of its weight and the fabric is then wound onto a batching roller. It is stored in that state at room temperature for 10 hours. Thereafter the fabric, which has been dyed navy, is rinsed, soaped off at the boil for a quarter of an hour with a nonionic detergent, rinsed once more and dried. The dyeing obtained has very good fastness properties.

Example 88: 2 parts of the dye of Example 1 are dissolved in 100 parts of water with 0.5 part of sodium m-nitrobenzenesulfonate. The solution obtained is used for impregnating a cotton fabric to a wet pick-up of 75 % of its weight and the fabric is then dried. The fabric is then impregnated with a 20°C solution containing 4 g of sodium hydroxide and 300 g of sodium chloride per litre, squeezed off to a weight increase of 75 %, the navy dyeing is steamed at 100-102°C for 30 seconds, rinsed, soaped off at the boil for a quarter of an hour in a 0.3 % solution of a nonionic detergent, rinsed and dried. The dyeing obtained has very good fastness properties.

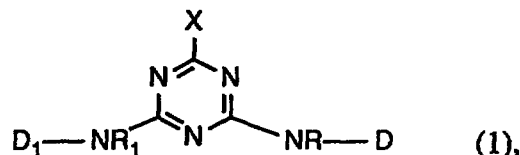
Example 89: 3 parts of the dye of Example 1 are sprinkled with rapid stirring into 100 parts of a stock thickening containing 50 parts of 5 % sodium alginate thickening,

27.8 parts of water, 20 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 1.2 parts of sodium bicarbonate. The resulting print paste is used for printing a cotton fabric, which is then dried and steamed at 102°C in saturated steam for 2 minutes. The fabric bearing the navy print is then rinsed, if desired soaped off at the boil and rinsed once more, and subsequently dried. The print obtained has very good fastness properties.

Example 90: 5 parts of the dye of Example 1 are sprinkled with rapid stirring into 100 parts of a stock thickening containing 50 parts of 5 % sodium alginate thickening, 36.5 parts of water, 10 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 2.5 parts of sodium bicarbonate. The resulting print paste, the stability of which corresponds to the industrial requirements, is used for printing a cotton fabric, which is then dried and steamed at 102°C in saturated steam for 8 minutes. The fabric bearing the navy print is then rinsed, if desired soaped off at the boil and rinsed once more, and subsequently dried. The print obtained has very good fastness properties.

Patent claims

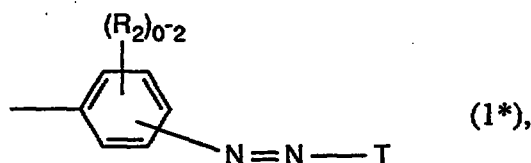
1. A compound of the formula



where

D is the radical of a monoazo, polyazo, metal complex azo, anthraquinone, triphenldioxazine, phthalocyanine or formazan chromophore that contains at least one sulfo group,

D₁ is the radical of a monoazo chromophore of the formula



where (R₂)₀₋₂ represents 0 to 2 identical or different radicals R₂ selected from the group consisting of sulfo, sulfomethyl, hydroxyl, carboxyl, halogen, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C₂-C₄alkanoylamino, ureido, C₁-C₄alkyl, C₁-C₄alkoxy, or C₁-C₄alkoxy substituted by C₁-C₄alkoxy, hydroxyl or sulfato in the alkyl moiety, and T is the radical of a diazo component or coupling component of the benzene or naphthalene series or of the heterocyclic series, or is the radical of a polyazo, metal complex azo, anthraquinone, triphenldioxazine, phthalocyanine or formazan chromophore, and at least one of the radicals D and D₁ contains a fibre-reactive radical -SO₂-Y,

Y is vinyl or a radical -CH₂-CH₂-U and U is a leaving group,

X is fluorine, chlorine, bromine, 3-carboxy-1-pyridinyl or 3-carbamoyl-1-pyridinyl, and R and R₁ are each independently of the other hydrogen or unsubstituted or halogen-, hydroxyl-, cyano-, C₁-C₄alkoxy-, C₁-C₄alkoxycarbonyl-, carboxyl-, sulfo- or sulfato-substituted C₁-C₄alkyl,

with the proviso that the radical -NR- is not bonded to an NH₂-substituted phenylene radical when D is the radical of a monoazo or disazo chromophore.

2. A compound according to claim 1, wherein R and R₁ are each independently of the



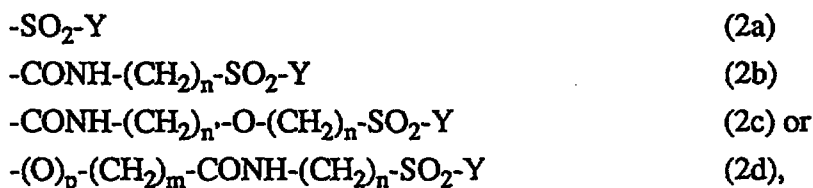
THIS SHEET HAS BEEN
REPLACED



other methyl, ethyl or in particular hydrogen.

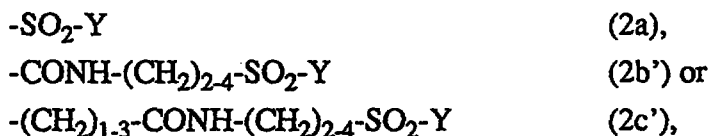
3. A compound according to claim 1 or 2, wherein X is chlorine or fluorine.

4. A compound according to any one of claims 1 to 3, wherein D and/or D₁ contain at least one fibre-reactive radical of the formula



where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl.

5. A compound according to any one of claims 1 to 4, wherein D or D₁ carries a fibre-reactive radical of the formula



where Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl.

6. A compound according to any one of claims 1 to 5, wherein D or D₁ carries a fibre-reactive radical of the formula



where Y is vinyl or β -sulfatoethyl.

7. A compound according to any one of claims 1 to 6, wherein D and D₁ are each independently of the other further substituted by one or more radicals selected from the

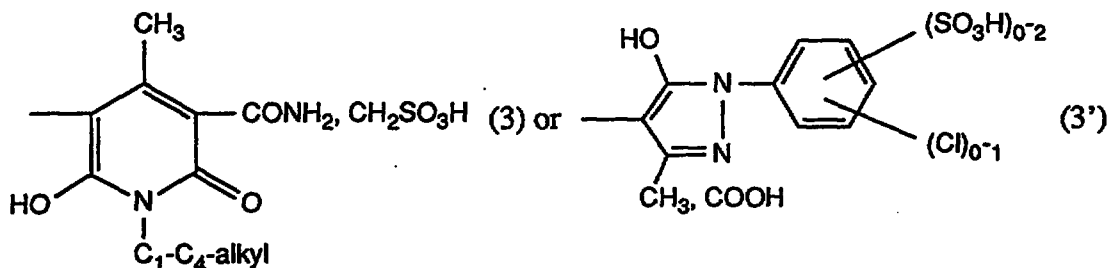




group consisting of C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkoxy substituted by hydroxyl, C₁-C₄alkoxy or sulfato in the alkyl moiety, acylamino groups having 1 to 8 carbon atoms, phenylamino, N,N-di-β-hydroxyethylamino, N,N-di-β-sulfatoethylamino, sulfobenzylamino, N,N-disulfobenzylamino, alkoxycarbonyl having 1 to 4 carbon atoms in the alkoxy radical, alkylsulfonyl having 1 to 4 carbon atoms, trifluoromethyl, nitro, cyano, halogen, carbamoyl, N-alkylcarbamoyl having 1 to 4 carbon atoms in the alkyl radical, sulfamoyl, N-alkylsulfamoyl having 1 to 4 carbon atoms, N-(β-hydroxyethyl)-sulfamoyl, N,N-di-(β-hydroxyethyl)sulfamoyl, N-phenylsulfamoyl, ureido, hydroxyl, carboxyl, sulfomethyl and sulfo.

8. A compound according to any one of claims 1 to 7, wherein D₁ is a radical of the formula (1*) where (R₂)₀₋₂ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy and T is a phenyl or naphthyl radical which is unsubstituted or substituted by sulfo, methyl, methoxy, chlorine or a radical of the formula (2a) or (2b'') indicated in claim 6, as radical of a diazo component.

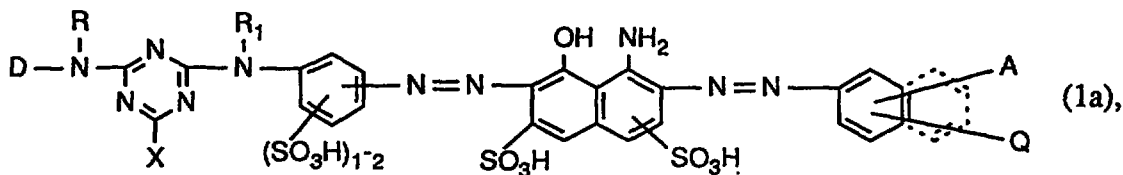
9. A compound according to any one of claims 1 to 7, wherein D₁ is a radical of the formula (1*) where (R₂)₀₋₂ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy and T is unsubstituted or for example C₁-C₂alkyl-, C₁-C₂alkoxy-, halogen-, carboxyl-, sulfo-, hydroxyl-, amino-, N-mono-C₁-C₄alkylamino-, N,N-di-C₁-C₄alkylamino-, C₂-C₄alkanoylamino- or benzoylamino-substituted phenyl or naphthyl or a radical of the formula



as radical of a coupling component.

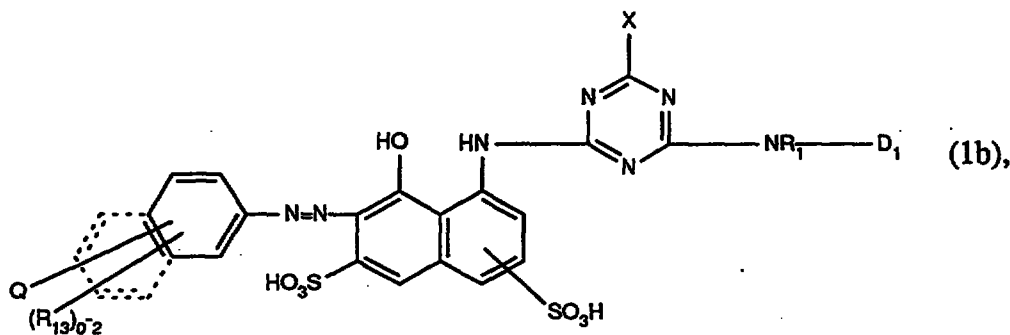
10. A compound according to claim 1 of the formula





where D, R, R₁ and X are each as defined in claim 1, A is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di-C₁-C₄alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di-C₁-C₄alkylsulfamoyl, C₁-C₄alkylsulfonyl or C₁-C₄alkoxycarbonyl and Q is a radical of the formula (2a), (2b), (2c) or (2d) indicated in claim 4.

11. A compound according to claim 1 of the formula



where D₁, R₁ and X are each as defined in claim 1, (R₁₃)₀₋₂ represents 0 to 2 identical or different radicals selected from the group consisting of methyl, methoxy, chlorine and sulfo and Q is a radical of the formula (2a), (2b), (2c) or (2d) indicated in claim 4.

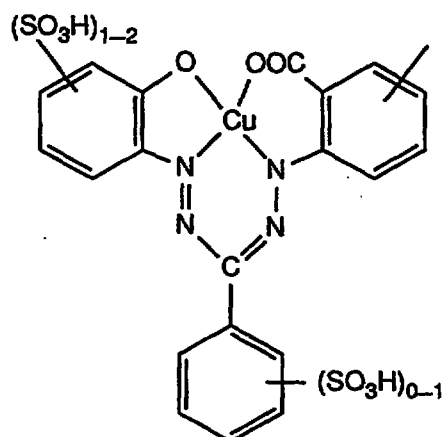
12. A compound according to any one of claims 1 to 10, wherein D is
a) a radical of the formula



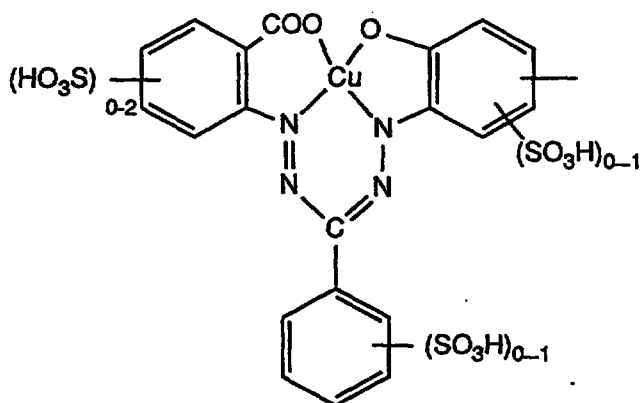
THIS SHEET HAS BEEN
REPLACED



- 65 -



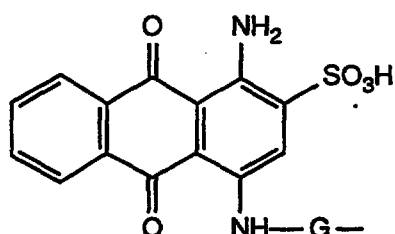
(5a) or



(5b),

where the benzene nuclei are unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkylsulfonyl having 1 to 4 carbon atoms, halogen, carboxyl or a fibre-reactive radical of the formula (2a), (2b), (2c) or (2d) indicated in claim 4,

b) a radical of the formula



(6),

where G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and the anthraquinone nucleus is unsubstituted or substituted by a further sulfo group, and G as phenyl radical is unsubstituted or substituted by alkyl having 1 to 4 carbon atoms,

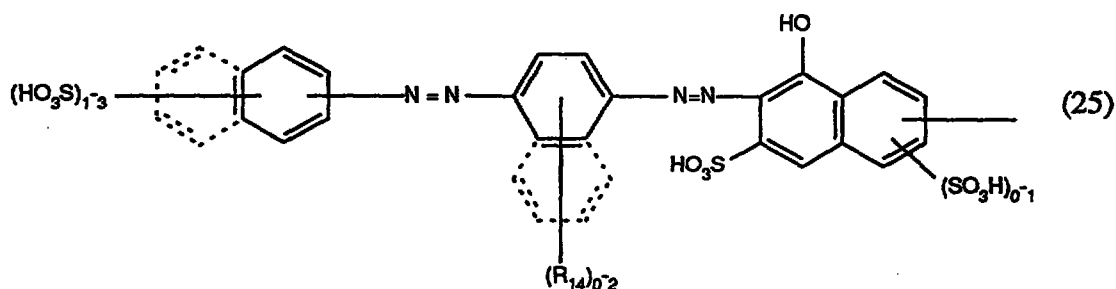
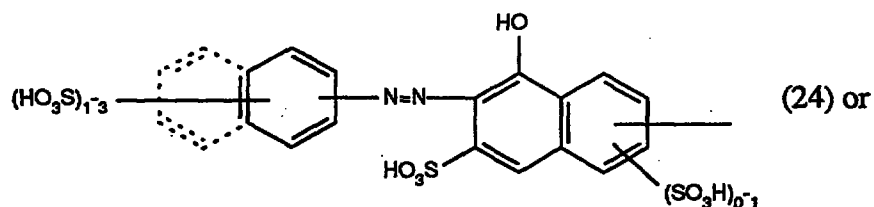
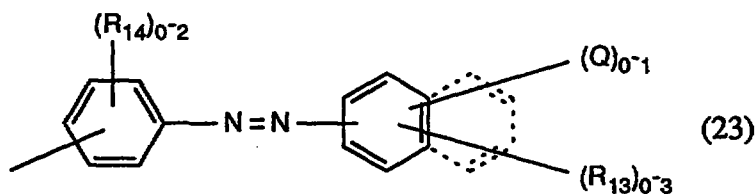
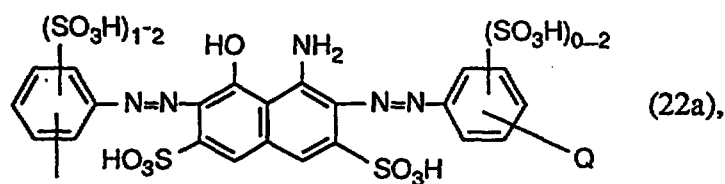
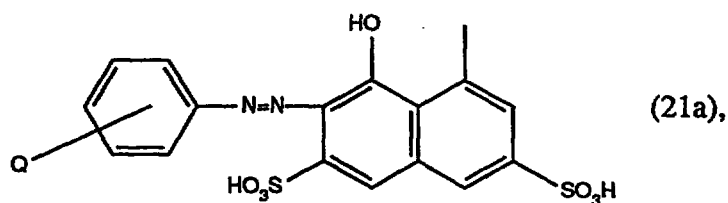


THIS SHEET HAS BEEN
REPLACED



alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo,

or c) a radical of the formula



where $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, and Q is



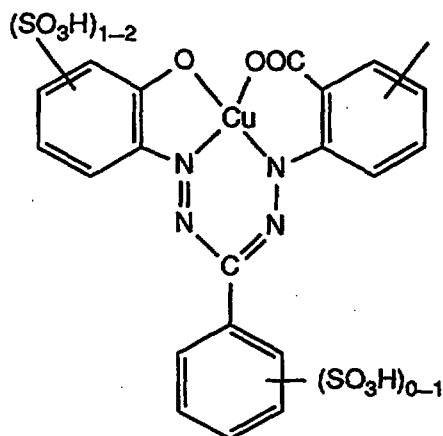
THIS SHEET HAS BEEN
REPLACED



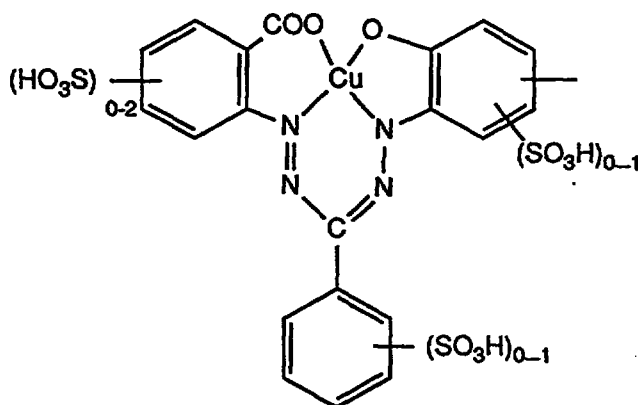
a radical of the formula (2a) or (2b'') indicated in claim 6.

13. A compound according to any one of claims 1 to 7 and 11, wherein D_1 is

a) a radical of the formula



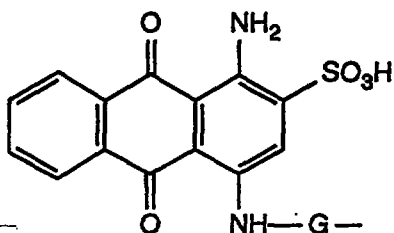
(5a) or



(5b),

where the benzene nuclei are unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkylsulfonyl having 1 to 4 carbon atoms, halogen, carboxyl or a fibre-reactive radical of the formula (2a), (2b), (2c) or (2d) indicated in claim 4,

b) a radical of the formula



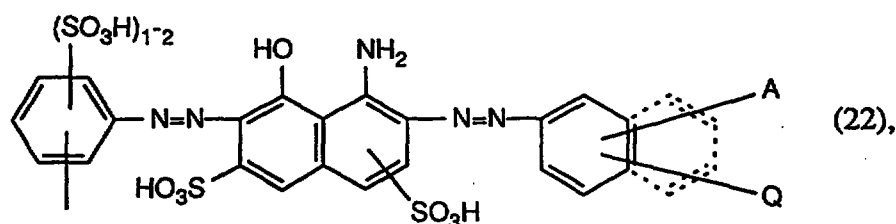
(6),





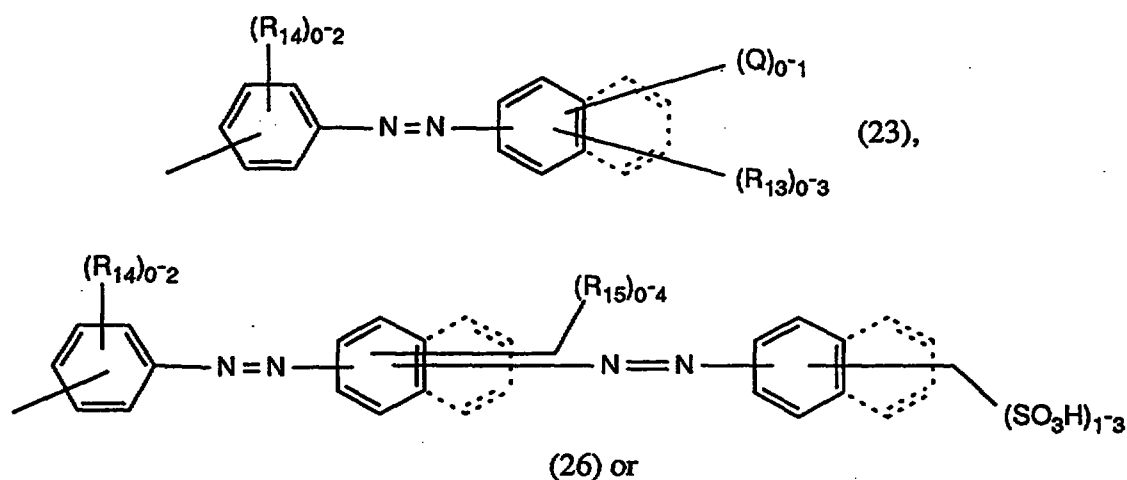
where G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and the anthraquinone nucleus is unsubstituted or substituted by a further sulfo group, and G as phenyl radical is unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo,

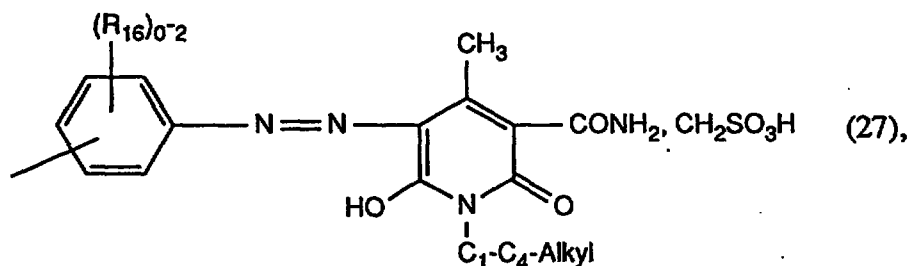
c) a radical of the formula



where A is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di-C₁-C₄alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di-C₁-C₄alkylsulfamoyl, C₁-C₄alkylsulfonyl or C₁-C₄alkoxycarbonyl and Q is a radical of the formula (2a), (2b), (2c) or (2d) indicated in claim 4,

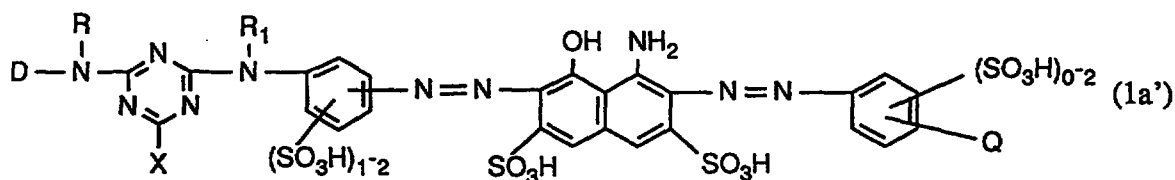
or d) a radical of the formula





where $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals R_{14} selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, $(R_{15})_{0-4}$ represents 0 to 4 identical or different radicals selected from the group consisting of sulfo, hydroxyl, amino, methoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, methyl, acetylamino, benzoylamino, propionylamino and ureido, and $(R_{16})_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, methyl, methoxy and chlorine.

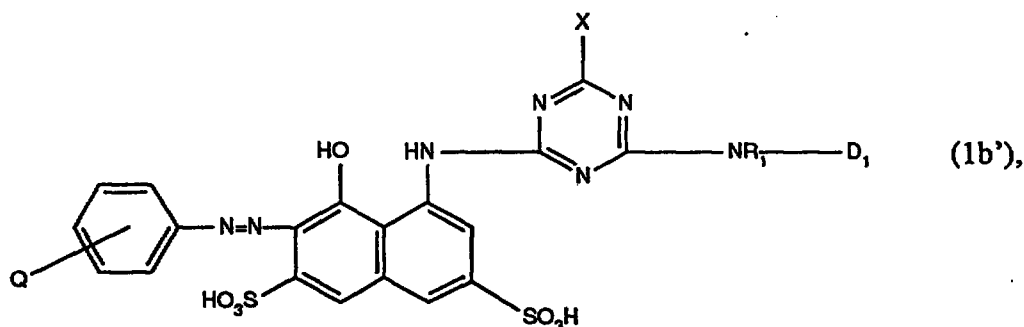
14. A compound according to claim 10 of the formula



where R and R_1 are each independently of the other hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the formula (2a) or (2b') indicated in claim 6, and D is a radical of the formula (5b) indicated in claim 12 which apart from sulfo carries no further substituents, or a radical of the formula (6), (21a), (23), (24) or (25) indicated in claim 12.

15. A compound according to claim 11 of the formula





where R_1 is hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the above-indicated formula (2a) or (2b'') and D_1 is a radical of the formula (5b) indicated in claim 13 which apart from sulfo contains no further substituents or is a radical of the formula (22), (23), (26) or (27) indicated in claim 13.

16. A process for preparing a compound of the formula (1) according to claim 1, which comprises reacting a mole equivalent of an organic dye of the formula



a mole equivalent of the compound of the formula



or suitable precursors of the compounds of the formulae (28) or (29) and a mole equivalent of a halotriazine, preferably 2,4,6-trichloro- or 2,4,6-trifluoro-s-triazine, with one another in any desired order or, if precursors of the compounds of the formulae (28) or (29) were used, converting the resulting intermediates into the desired dyes and, if desired, following up with a further conversion reaction, where D, D_1 , R and R_1 are each as defined in claim 1.

17. A process for dyeing and printing cellulose-containing fibre materials, which comprises treating the fibre materials in aqueous solution with a dye of the formula (1) according to claim 1.

18. A process according to claim 11, wherein the cellulose-containing fibre materials are cotton.





- 71 -

19. The use of dyes of the formula (1) according to claim 1 for dyeing and printing cellulose-containing fibre materials.

FD 4.1/LIP

This Sheet Has Been Replaced



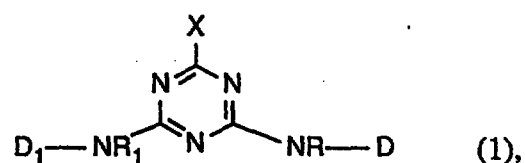
THIS SHEET HAS BEEN
REPLACED

1-19560/A/19660

Fibre-reactive dyes and preparation and use thereof

Abstract

The invention relates to compounds of the formula



where the variables are each as defined in the claims. The compounds are suitable for use as dyes, in particular for dyeing and printing cellulose-containing fibre materials and produce dyeings and prints having good allround fastness properties.

This Sheet Has Been Replaced



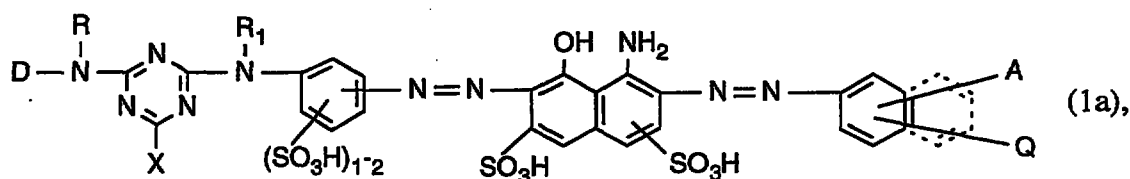
THIS SHEET HAS BEEN
REPLACED



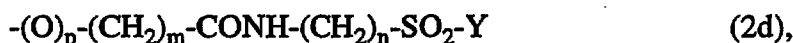
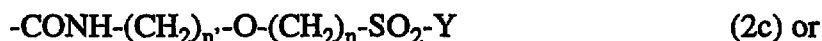
11 OCT 2000

New claims 1 to 17:

1. A compound of the formula



where D is the radical of a monoazo, polyazo, metal complex azo, anthraquinone, triphendioxazine, phthalocyanine or formazan chromophore that contains at least one sulfo group, A is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di-C₁-C₄alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di-C₁-C₄alkylsulfamoyl, C₁-C₄alkylsulfonyl or C₁-C₄alkoxycarbonyl, Q is a radical of the formula



where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is vinyl, β-bromoethyl, β-chloroethyl, β-acetoxyethyl, β-phenoxyethyl, β-phosphatoethyl, β-sulfatoethyl or β-thiosulfatoethyl, X is fluorine, chlorine, bromine, 3-carboxy-1-pyridinyl or 3-carbamoyl-1-pyridinyl, and R and R₁ are each independently of the other hydrogen or unsubstituted or halogen-, hydroxyl-, cyano-, C₁-C₄alkoxy-, C₁-C₄alkoxycarbonyl-, carboxyl-, sulfo- or sulfato-substituted C₁-C₄alkyl, with the proviso that the radical -NR- is not bonded to an NH₂-substituted phenylene radical when D is the radical of a monoazo or disazo chromophore.

2. A compound according to claim 1, wherein R and R₁ are each independently of the other methyl, ethyl or hydrogen.

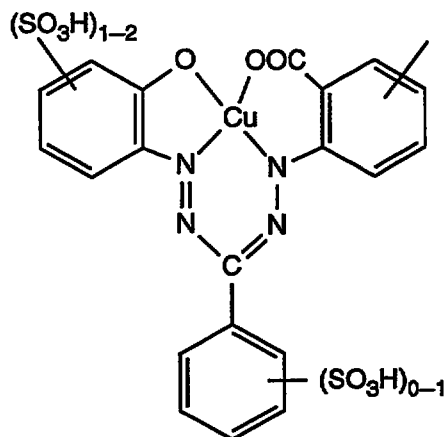


11 OCT 2000

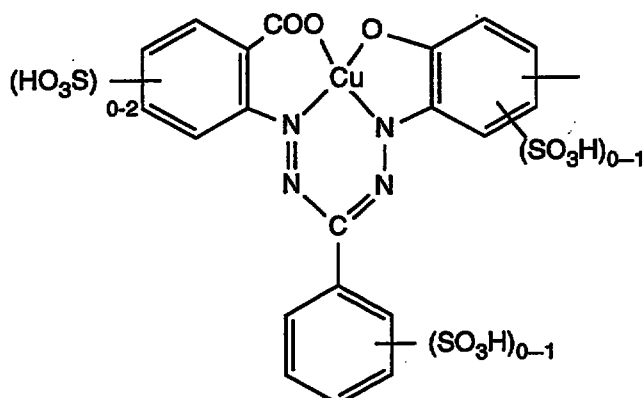
3. A compound according to claim 1 or 2, wherein X is chlorine or fluorine.

4. A compound according to any one of claims 1 to 3, wherein D is

a) a radical of the formula

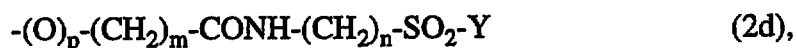
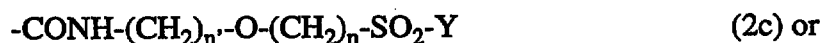


(5a) or



(5b),

where the benzene nuclei are unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkylsulfonyl having 1 to 4 carbon atoms, halogen, carboxyl or a fibre-reactive radical of the formula

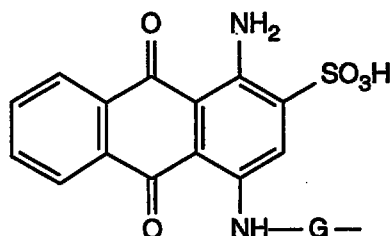


where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl,



11 OCT 2000

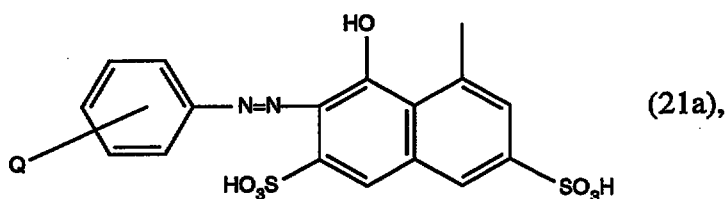
b) a radical of the formula



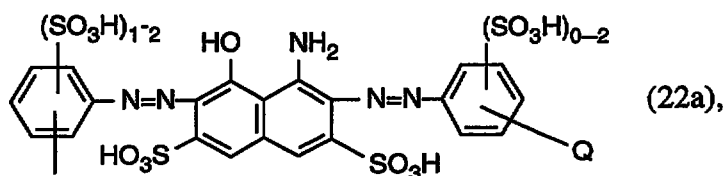
(6),

where G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and the anthraquinone nucleus is unsubstituted or substituted by a further sulfo group, and G as phenyl radical is unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo,

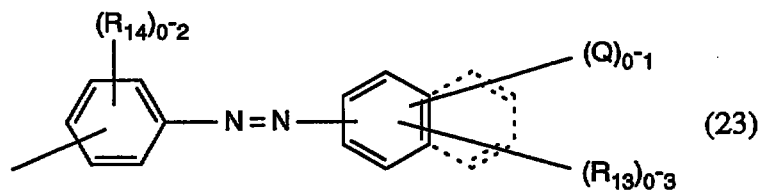
or c) a radical of the formula



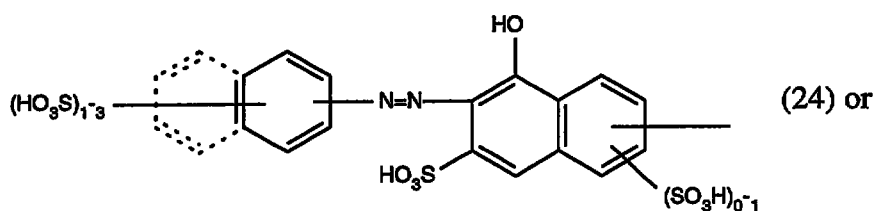
(21a),



(22a),



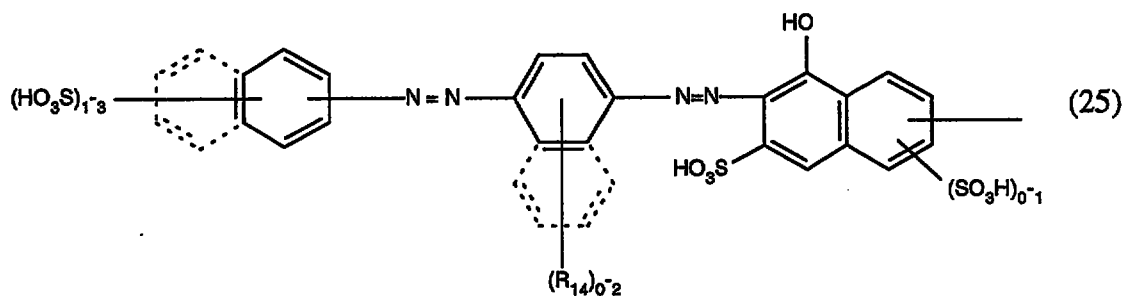
(23)



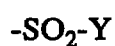
(24) or



11 OCT 2000



where $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals R_{14} selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, and Q is a radical of the formula



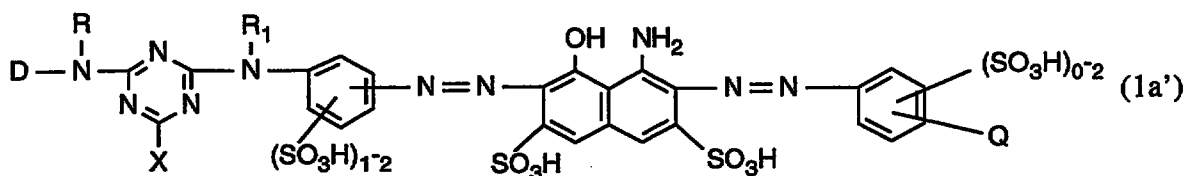
(2a) or



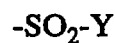
(2b''),

where Y is vinyl or β -sulfatoethyl.

5. A compound according to claim 1 of the formula



where R and R_1 are each independently of the other hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the formula



(2a) or



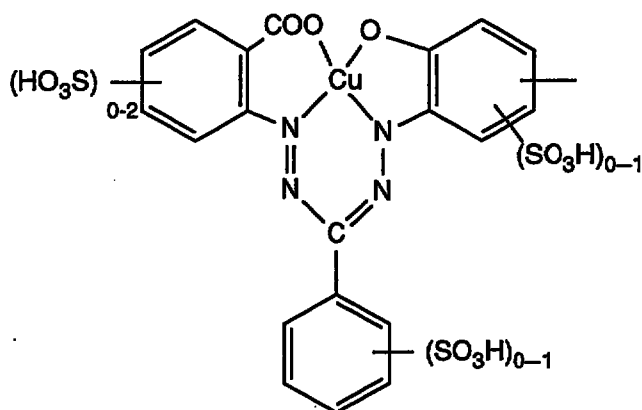
(2b''),

where Y is vinyl or β -sulfatoethyl, and D is a radical of the formula



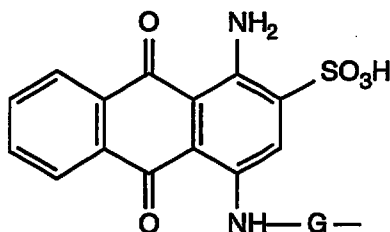
1.1 OCT 2000

65



(5b),

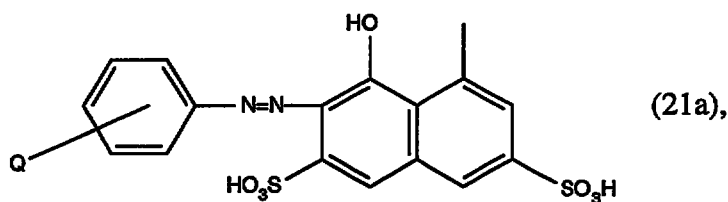
or is a radical of the formula



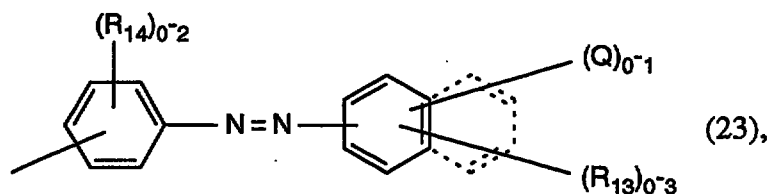
(6),

where G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and the anthraquinone nucleus is unsubstituted or substituted by a further sulfo group, and G as phenyl radical is unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo,

or is a radical of the formula



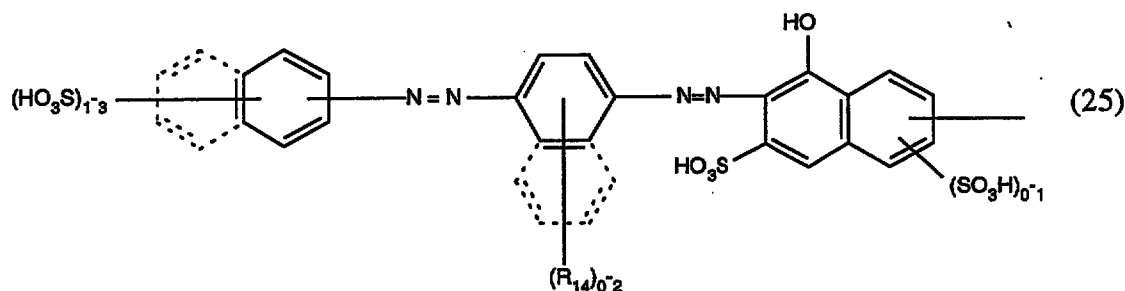
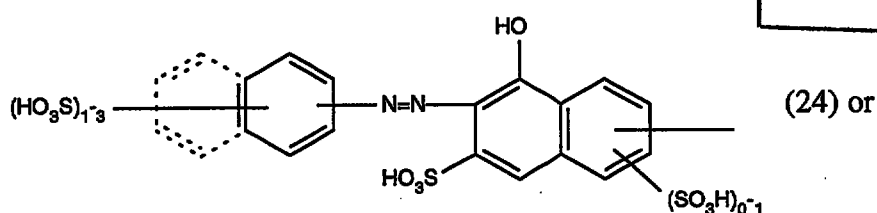
(21a),



(23),



11 OCT 2000

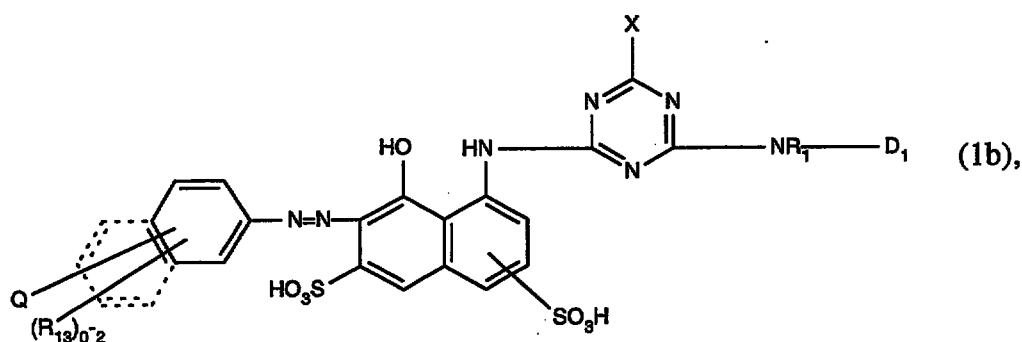


where $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals R_{14} selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, and Q is a radical of the formula (2a) or (2b'') indicated above.

6. A process for dyeing and printing a cellulose-containing fibre material, which comprises treating the fibre material in an aqueous solution with a dye of the formula (1a) according to claim 1.

7. A process according to claim 6, wherein the cellulose-containing fibre material is cotton.

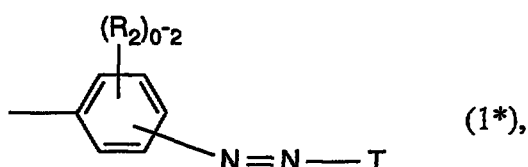
8. A compound of the formula



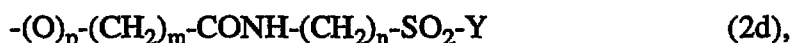
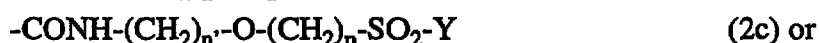
where D_1 is the radical of a monoazo chromophore of the formula



11 OCT 2000



where $(R_2)_{0-2}$ represents 0 to 2 identical or different radicals R_2 selected from the group consisting of sulfo, sulfomethyl, hydroxyl, carboxyl, halogen, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_2 - C_4 alkanoylamino, ureido, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or C_1 - C_4 alkoxy substituted by C_1 - C_4 alkoxy, hydroxyl or sulfato in the alkyl moiety, and T is the radical of a diazo component or coupling component of the benzene or naphthalene series or of the heterocyclic series, or D_1 is the radical of a polyazo, metal complex azo, anthraquinone, triphenyldioxazine, phthalocyanine or formazan chromophore, X is fluorine, chlorine, bromine, 3-carboxy-1-pyridinyl or 3-carbamoyl-1-pyridinyl, R_1 is hydrogen or unsubstituted or halogen-, hydroxyl-, cyano-, C_1 - C_4 alkoxy-, C_1 - C_4 alkoxycarbonyl-, carboxyl-, sulfo- or sulfato-substituted C_1 - C_4 alkyl, $(R_{13})_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of methyl, methoxy, chlorine and sulfo and Q is a radical of the formula



where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl.

9. A compound according to claim 8, wherein D_1 is a radical of the formula (1*) where $(R_2)_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy and T is a phenyl or naphthyl radical which is unsubstituted or substituted by sulfo, methyl, methoxy, chlorine or a radical of the formula

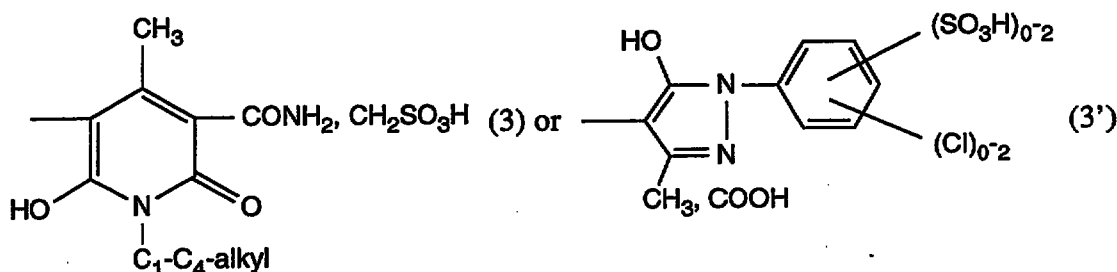




11 OCT 2000

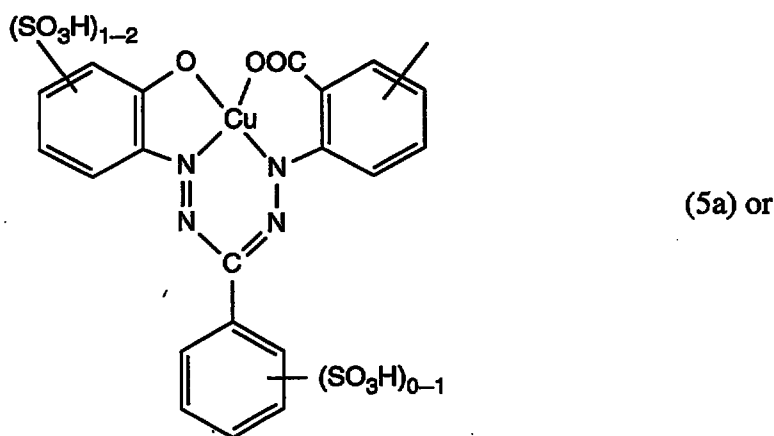
where Y is vinyl or β -sulfatoethyl, as radical of a diazo component.

10. A compound according to claim 8, wherein D_1 is a radical of the formula (1*) where $(R_2)_{0-2}$ represents 0 to 2 identical or different radicals selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy and T is unsubstituted or C_1 - C_2 alkyl-, C_1 - C_2 alkoxy-, halogen-, carboxyl-, sulfo-, hydroxyl-, amino-, N-mono- C_1 - C_4 alkylamino-, N,N-di- C_1 - C_4 alkylamino-, C_2 - C_4 alkanoylamino- or benzoylamino-substituted phenyl or naphthyl or a radical of the formula



as radical of a coupling component.

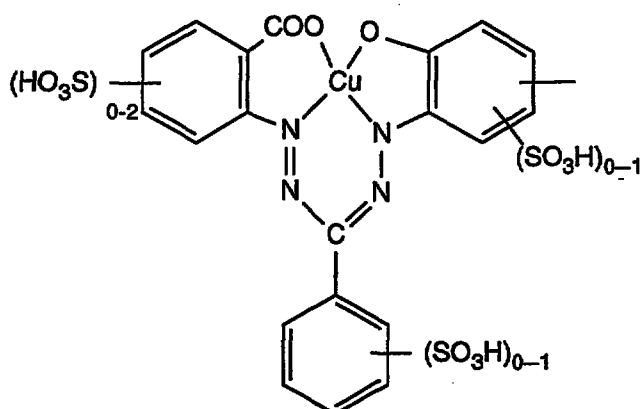
11. A compound according to claim 8, wherein D_1 is
a) a radical of the formula





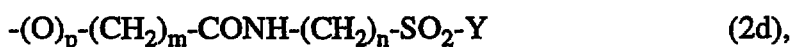
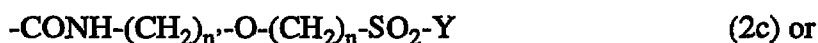
11 OCT 2000

69



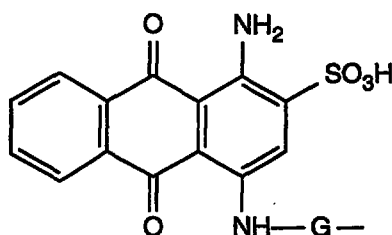
(5b),

where the benzene nuclei are unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, alkylsulfonyl having 1 to 4 carbon atoms, halogen, carboxyl or a fibre-reactive radical of the formula



where n, n' and m are each independently of the others an integer from 1 to 6, p is 0 or 1, and Y is vinyl, β -bromoethyl, β -chloroethyl, β -acetoxyethyl, β -phenoxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl,

b) a radical of the formula



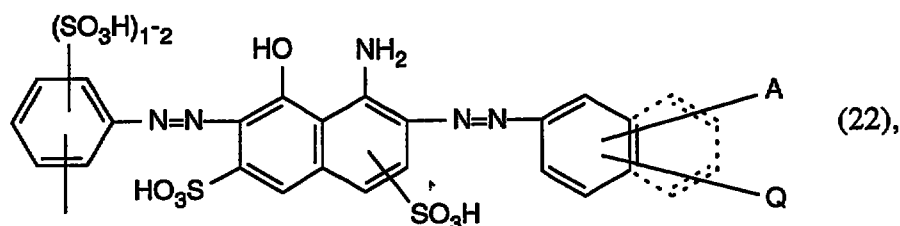
(6),

where G is a phenylene, cyclohexylene, phenylenemethylene or C_2 - C_6 alkylene radical, and the anthraquinone nucleus is unsubstituted or substituted by a further sulfo group, and G as phenyl radical is unsubstituted or substituted by alkyl having 1 to 4 carbon atoms, alkoxy having 1 to 4 carbon atoms, halogen, carboxyl or sulfo,



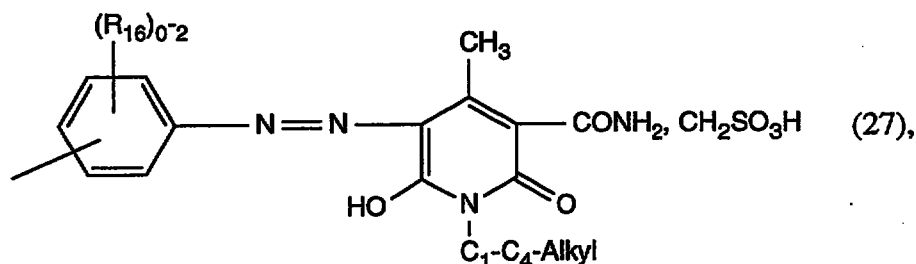
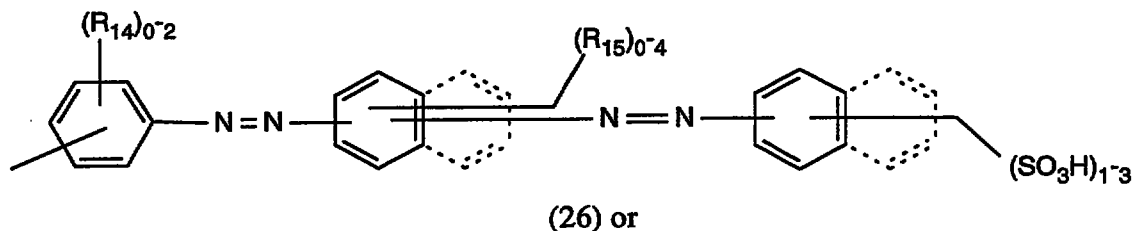
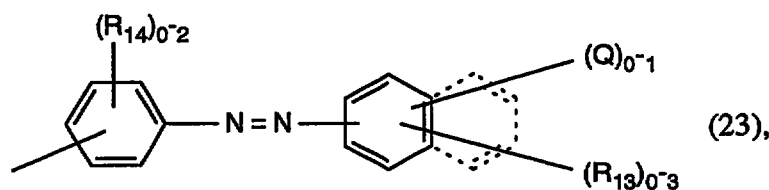
11 OCT 2000

c) a radical of the formula



where A is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di-C₁-C₄alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di-C₁-C₄alkylsulfamoyl, C₁-C₄alkylsulfonyl or C₁-C₄alkoxycarbonyl and Q is a radical of the formula (2a), (2b), (2c) or (2d) indicated above,

or d) a radical of the formula



where (R₁₃)₀₋₃ represents 0 to 3 identical or different radicals R₁₃ selected from the group consisting of methyl, methoxy, chlorine and sulfo, (R₁₄)₀₋₂ represents 0 to 2 identical or different radicals R₁₄ selected from the group consisting of sulfo, acetyl amino, propionyl amino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, (R₁₅)₀₋₄



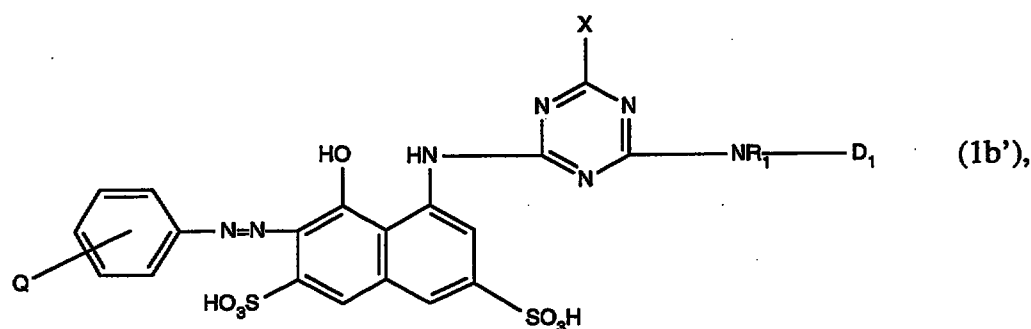
11 OCT 2000

represents 0 to 4 identical or different radicals R_{15} selected from the group consisting of sulfo, hydroxyl, amino, methoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, methyl, acetylamino, benzoylamino, propionylamino and ureido, $(R_{16})_{0-2}$ represents 0 to 2 identical or different radicals R_{16} selected from the group consisting of sulfo, methyl, methoxy and chlorine, and Q is a radical of the formula (2a), (2b), (2c) or (2d) indicated above.

12. A compound according to any one of claims 8 to 11, wherein R_1 is methyl, ethyl or hydrogen.

13. A compound according to any one of claims 8 to 12, wherein X is chlorine or fluorine.

14. A compound according to claim 8 of the formula



where R_1 is hydrogen, methyl or ethyl, X is chlorine or fluorine, Q is a radical of the formula

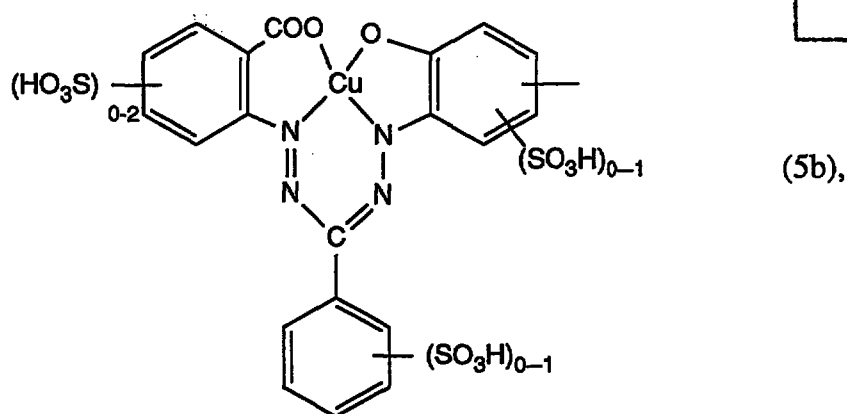


where Y is vinyl or β -sulfatoethyl, and D_1 is a radical of the formula

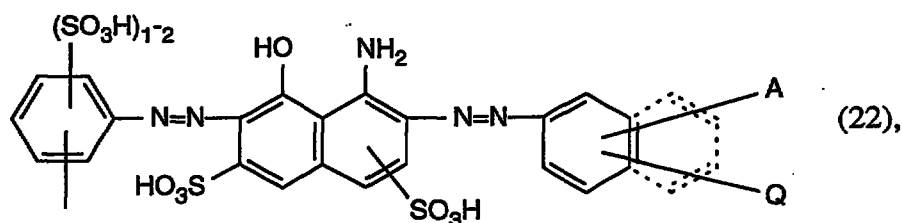


11 OCT 2000

72

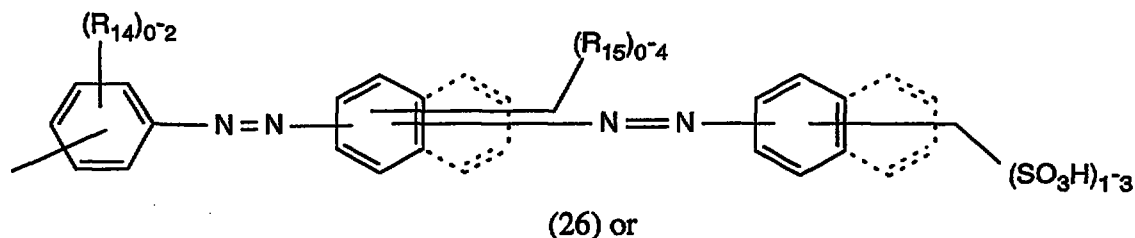
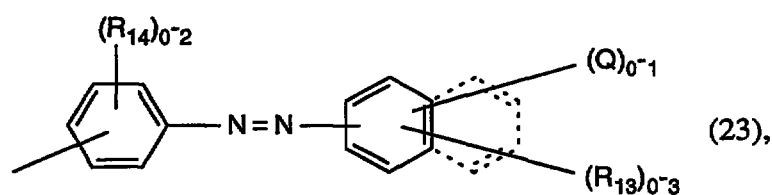


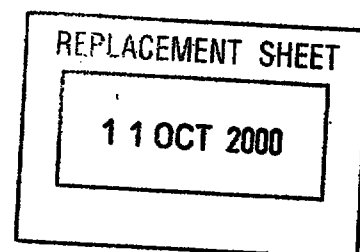
or is a radical of the formula



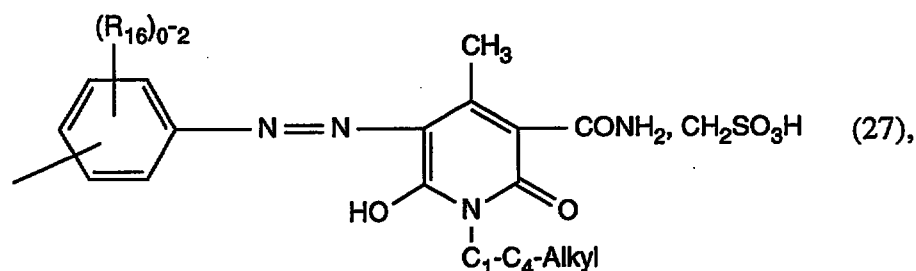
where A is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, sulfo, carboxyl, trifluoromethyl, nitro, cyano, hydroxyl, carbamoyl, N-mono- or N,N-di-C₁-C₄alkylcarbamoyl, sulfamoyl, N-mono- or N,N-di-C₁-C₄alkylsulfamoyl, C₁-C₄alkylsulfonyl or C₁-C₄alkoxycarbonyl and Q is a radical of the formula (2a) or (2b'') indicated above,

or is a radical of the formula





73



where $(R_{13})_{0-3}$ represents 0 to 3 identical or different radicals R_{13} selected from the group consisting of methyl, methoxy, chlorine and sulfo, $(R_{14})_{0-2}$ represents 0 to 2 identical or different radicals R_{14} selected from the group consisting of sulfo, acetylamino, propionylamino, ureido, methyl, methoxy, 2-hydroxyethoxy and 2-sulfatoethoxy, $(R_{15})_{0-4}$ represents 0 to 4 identical or different radicals R_{15} selected from the group consisting of sulfo, hydroxyl, amino, methoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, methyl, acetylamino, benzoylamino, propionylamino and ureido, $(R_{16})_{0-2}$ represents 0 to 2 identical or different radicals R_{16} selected from the group consisting of sulfo, methyl, methoxy and chlorine, and Q is a radical of the formula (2a) or (2b'') indicated above.

15. A compound according to claim 14 of the formula (1b'), where D_1 is a radical of the formula (5b).

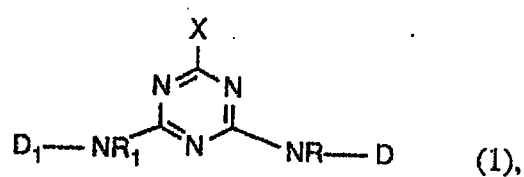
16. A process for dyeing and printing a cellulose-containing fibre material, which comprises treating the fibre material in an aqueous solution with a dye of the formula (1b) according to claim 8.

17. A process according to claim 16, wherein the cellulose-containing fibre material is cotton.

11 OCT 2000

Fibre-reactive dyes and preparation and use thereofAbstract

The invention relates to compounds of the formula



where the variables are each as defined in the claims. The compounds are suitable for use as dyes, in particular for dyeing and printing cellulose-containing fibre materials and produce dyeings and prints having good allround fastness properties.