

I-19562/A

Dye mixtures, processes for their preparation and their use

The present invention relates to novel mixtures of reactive dyes, processes for their preparation and their use for dyeing or printing fibre materials.

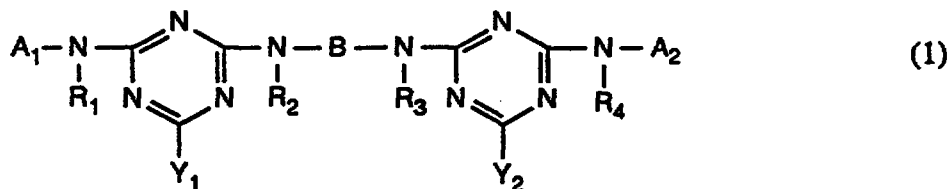
The practice of dyeing using reactive dyes has recently led to increased demands on the quality of the dyeings and the profitability of the dyeing process. There is consequently still a demand for novel reactive dyes which have improved properties, especially in respect of application.

Reactive dyes which have an adequate substantivity and at the same time a good ease of washing out of the non-fixed portions are now required for dyeing. They should furthermore have a good tinctorial yield and high reactivity, and dyeings having high degrees of fixing in particular should be produced. These requirements are not met in all properties by the known dyes.

The present invention is therefore based on the object of discovering novel improved mixtures of reactive dyes for dyeing and printing fibre materials which have the qualities characterized above to a high degree. The novel dye mixtures in particular should have high fixing yields and high fibre-dye bond stabilities, and furthermore the portions which are not fixed to the fibre should be easy to wash out. They should furthermore produce dyeings having good allround properties, for example light- and wet-fastnesses.

It has been found that this object is largely achieved by the dye mixtures defined below.

The invention therefore relates to dye mixtures which comprise at least two reactive dyes of the formula



in which A₁ and A₂ are the radical of a monoazo, polyazo, metal complex azo, anthraquinone, phthalocyanine, formazan, azomethine, dioxazine, phenazine, stilbene, triphenylmethane, xanthene, thioxanthone, nitroaryl, naphthoquinone, pyrenequinone or perylenetetracarbinide dye,

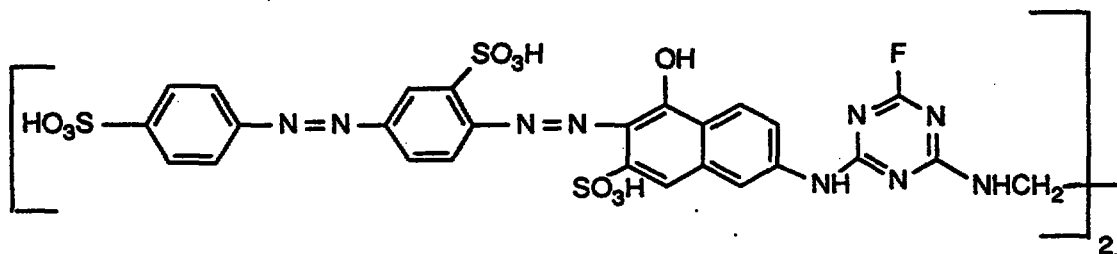
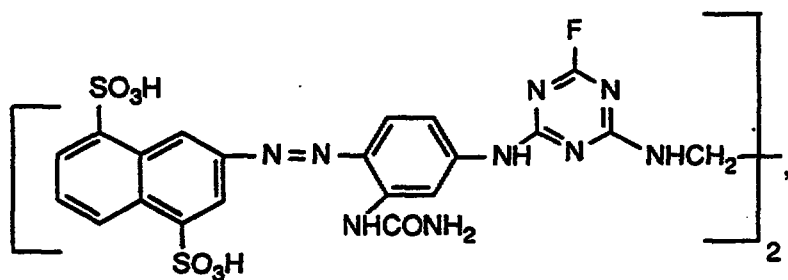
R₁, R₂, R₃ and R₄ independently of one another are hydrogen or substituted or unsubstituted C₁-C₄alkyl,

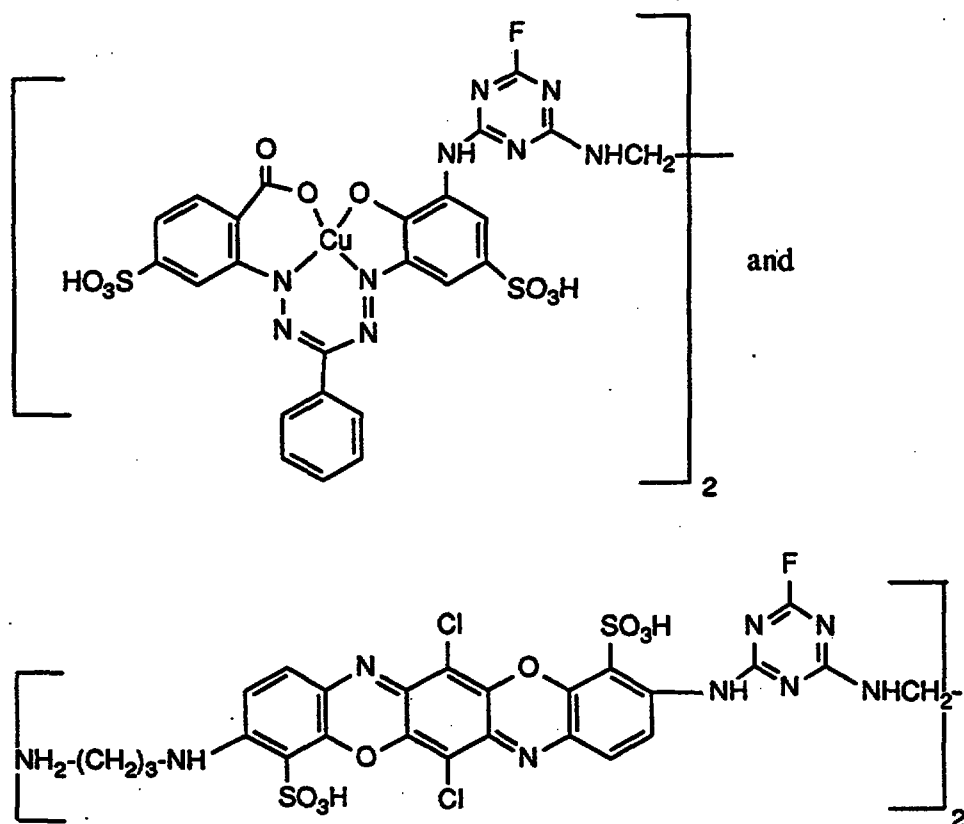
B is an aliphatic bridge member,

Y₁ and Y₂ independently of one another are halogen or carboxypyridinium,

and in at least one of the reactive dyes of the formula (1) the radicals A₁ and A₂ have the same meanings,

with the proviso that the dye mixtures do not comprise two or more of the dyestuffs of the formulae





Alkyl radicals R_1 , R_2 , R_3 and R_4 in the reactive dyes of the formula (1) are straight-chain or branched; the alkyl radicals can be further substituted, for example by halogen, hydroxyl, cyano, C_1 - C_4 alkoxy, C_1 - C_4 alkoxycarbonyl, carboxyl, sulfamoyl, sulfo or sulfato. Examples of the radicals R_1 , R_2 , R_3 and R_4 are the following: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, 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, aminosulfonylmethyl and β -sulfatoethyl. Preferably, R_1 , R_2 , R_3 and R_4 independently of one another are hydrogen, methyl or ethyl, in particular hydrogen.

The aliphatic bridge member B in the reactive dyes of the formula (1) is preferably a C_2 - C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 members from the group comprising $-NH-$, $-N(CH_3)-$ and $-O-$ and is unsubstituted or substituted by hydroxyl, sulfo or sulfato.

B is particularly preferably a C_2 - C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals, in particular a C_2 - C_6 alkylene radical, and preferably a radical of the formula $\text{---}(\text{CH}_2)_{2-6}\text{---}$, ethylene and propylene being of particular interest.

The radicals Y_1 and Y_2 in the reactive dyes of the formula (1) independently of one another are, in particular, fluorine or chlorine. Preferably, Y_1 and Y_2 have in each case identical meanings. The dye mixtures according to the invention particularly preferably comprise at least two reactive dyes of the formula (1) in which Y_1 and Y_2 have identical meanings and the reactive dyes do not differ from one another in respect of the meaning of these radicals.

The radicals A_1 and A_2 in the reactive dyes of the formula (1) can contain the substituents customary in organic dyes bonded to their basic structure.

The dye mixtures according to the invention preferably comprise at least two reactive dyes of the formula (1) in which the radicals A_1 and A_2 in each case have identical meanings. The dye mixtures according to the invention particularly preferably comprise at least two reactive dyes of the formula (1) in which the radicals A_1 and A_2 have identical meanings and the two reactive dyes do not differ from one another in respect of the meaning of these radicals.

Another preferred sub-group of dye mixtures comprises those in which the radicals A_1 and A_2 have meanings which differ from one another in at least one of the reactive dyes of the formula (1).

Examples of substituents in the radicals A_1 and A_2 are: alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl or butyl, where the alkyl radicals can be further substituted, for example by hydroxyl, sulfo or sulfato; alkoxy groups having 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy, isopropoxy or butoxy, where the alkyl radicals can be further substituted, for example by hydroxyl, sulfo or sulfato; phenyl which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo; acylamino groups having 1 to 8 carbon atoms, in particular such alkanoylamino groups, for example acetylamino or propionylamino; benzoylamino which is unsubstituted or substituted in the phenyl ring by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen or sulfo; phenylamino which is unsubstituted or substituted in the phenyl ring by C_1 - C_4 alkyl, C_1 - C_4 alkoxy,

halogen or sulfo; N,N-di- β -hydroxyethylamino; N,N-di- β -sulfatoethylamino; sulfobenzylamino; N,N-disulfobenzylamino; alkoxy carbonyl 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; amino; 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-mono- or N,N-dialkylsulfamoyl having in each case 1 to 4 carbon atoms, such as N-methylsulfamoyl, N-ethylsulfamoyl, N-propylsulfamoyl, N-isopropylsulfamoyl or N-butylsulfamoyl, where the alkyl radicals can be further substituted, for example by hydroxyl or sulfo; N-(β -hydroxyethyl)sulfamoyl; N,N-di(β -hydroxyethyl)sulfamoyl; N-phenylsulfamoyl which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl or sulfo; ureido; hydroxyl; carboxyl; sulfomethyl or sulfo and fibre-reactive radicals.

The radicals A₁ and A₂ preferably in each case contain at least one sulfo group, in particular 1 to 4 sulfo groups, and preferably 1 to 3 sulfo groups.

A reactive group in the radical A₁ or A₂ in the reactive dyes of the formula (1) is, for example, an alkanoyl or alkylsulfonyl radical substituted by an atom which can be split off or a group which can be split off, an alkenoyl or alkenesulfonyl radical which is unsubstituted or substituted by an atom which can be split off or a group which can be split off, or an alkenoyl or alkenesulfonyl radical containing a vinyl group. The alkanoyl, alkylsulfonyl and alkenesulfonyl radicals mentioned as a rule contain 2 to 8 carbon atoms and the alkenoyl radicals as a rule contain 3 to 8 carbon atoms. Radicals containing carbo- or heterocyclic 4-, 5- or 6-membered rings substituted by an atom which can be split off or a group which can be split off are further examples. Heterocyclic radicals are, for example, those which contain at least one substituent which can be split off bonded to a heterocyclic radical; inter alia, those which contain at least one reactive substituent bonded to a 5- or 6-membered heterocyclic ring, such as to a monoazine, diazine, triazine, pyridine, pyrimidine, pyridazine, pyrazine, thiazine, oxazine or asymmetric or symmetric triazine ring or to such a ring system which contains one or more fused aromatic rings, such as a quinoline, phthalazine, chinnoline [sic], quinazoline, quinoxaline, acridine, phenazine and phenanthridine ring system.

Atoms which can be split off and groups which can be split off are, in addition to others, for example, halogen, such as fluorine, chlorine or bromine, ammonium, including

hydrazinium, sulfato, thiosulfato, phosphato, acetoxy, propionoxy, azido, carboxypyridinium or thiocyanato.

Bridge members between the dye radical and the fibre-reactive radical are, in addition to the direct bond, the most diverse radicals. The bridge member is, for example, an aliphatic, aromatic or heterocyclic radical; the bridge member furthermore can be composed of various such radicals. The bridge member as a rule contains at least one functional group, for example the carbonyl group or the amino group, where the amino group can be further substituted by C₁-C₄alkyl which is unsubstituted or substituted by halogen, hydroxyl, cyano, C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, carboxyl, sulfamoyl, sulfo or sulfato. An aliphatic radical is, for example, an alkylene radical having 1 to 7 carbon atoms or branched isomers thereof. The carbon chain of the alkylene radical can be interrupted by a heteroatom, for example an oxygen atom. An aromatic radical is, for example, a phenyl radical, which can be substituted by C₁-C₄alkyl, for example methyl or ethyl, C₁-C₄alkoxy, for example methoxy or ethoxy, halogen, for example fluorine, bromine or, in particular, chlorine, carboxyl or sulfo, and a heterocyclic radical is, for example, a piperazine radical.

Examples of reactive groups are the following:

vinylsulfonyl, β -chloroethylsulfonyl, β -sulfatoethylsulfonyl, β -acetoxy-ethylsulfonyl, phosphatoethylsulfonyl, β -thiosulfatoethylsulfonyl, N-methyl-N-(β -sulfoethylsulfonyl)amino, acryloyl, mono-, di- or trichloroacryloyl, such as -CO-CCl=CH₂, -CO-CH=CH-Cl, -CO-CCl=CH-CH₃; mono-, di- or tribromoacryloyl, such as -CO-CBr=CH₂, -CO-CH=CH-Br, -CO-CBr=CH-CH₃; and -CO-CCl=CH-COOH, -CO-CH=CCl-COOH, -CO-CBr=CH-COOH, -CO-CH=CBr-COOH, -CO-CCl=CCl-COOH, -CO-CBr=CBr-COOH; precursors of the acryloyl radical and of derivatives of the acryloyl radical, such as β -chloro- or β -bromopropionyl, 3-phenylsulfonylpropionyl, 3-methylsulfonylpropionyl, 2-chloro-3-phenylsulfonylpropionyl, 2,3-dichloropropionyl, 2,3-dibromopropionyl; and 2-fluoro-2-chloro-3,3-difluorocyclobutane-1-carbonyl, 2,2,3,3-tetrafluorocyclobutane-1-carbonyl or -1-sulfonyl, β -(2,2,3,3-tetrafluorocyclobut-1-yl)acryloyl, α - or β -alkenyl- or arylsulfonylacryloyl groups, such as α - or β -methylsulfonylacryloyl, chloroacetyl, bromoacetyl, 4-(β -chloroethylsulfonyl)butyryl, 4-vinylsulfonylbutyryl, 5-(β -chloroethylsulfonyl)caproyl, 6-vinylsulfonylcaproyl; and 4-fluoro-3-nitrobenzoyl, 4-fluoro-3-nitrophenylsulfonyl, 4-fluoro-3-methylsulfonylbenzoyl, 4-fluoro-3-cyanobenzoyl, 2-fluoro-5-methylsulfonylbenzoyl.

The following fibre-reactive radicals may furthermore be mentioned as examples: mono- or dihalo-symmetric triazinyl radicals, for example 2,4-dichlorotriazin-6-yl, 2-amino-4-chlorotriazin-6-yl, 2-alkylamino-4-chlorotriazin-6-yl, such as 2-methylamino-4-chlorotriazin-6-yl or 2-ethylamino- or 3-propylamino-4-chlorotriazin-6-yl, 2- β -oxyethylamino-4-chlorotriazin-6-yl, 2-di- β -oxyethylamino-4-chlorotriazin-6-yl and the corresponding sulfuric acid half-esters, 2-diethylamino-4-chlorotriazin-6-yl, 2-morpholino- or 2-piperidino-4-chlorotriazin-6-yl, 2-cyclohexylamino-4-chlorotriazin-6-yl, 2-arylamino- and substituted arylamino-4-chlorotriazin-6-yl, such as 2-phenylamino-4-chlorotriazin-6-yl, 2-(o-, m- or p-carboxy- or sulfophenyl)amino-4-chlorotriazin-6-yl, 2-alkoxy-4-chlorotriazin-6-yl, such as 2-methoxy- or -ethoxy-4-chlorotriazin-6-yl, 2-(phenylsulfonylmethoxy)-4-chlorotriazin-6-yl, 2-aryloxy and substituted aryloxy-4-chlorotriazin-6-yl, such as 2-phenoxy-4-chlorotriazin-6-yl, 2-(p-sulfophenyl)oxy-4-chlorotriazin-6-yl, 2-(o-, m- or p-methyl- or methoxyphenyl)oxy-4-chlorotriazin-6-yl, 2-alkylmercapto- or 2-arylmercapto- or 2-(substituted aryl)mercapto-4-chlorotriazin-6-yl, such as 2- β -hydroxyethylmercapto-4-chlorotriazin-6-yl, 2-phenylmercapto-4-chlorotriazin-6-yl, 3-(4'-methylphenyl)mercapto-4-chlorotriazin-6-yl, 2-(2',4'-dinitro)phenylmercapto-4-chlorotriazin-6-yl, 2-methyl-4-chlorotriazin-6-yl, 2-phenyl-4-chlorotriazin-6-yl, 2,4-difluorotriazin-6-yl, monofluorotriazinyl radicals which are substituted by amino, alkylamino, aralkylamino or acylamino groups, where alkyl is, in particular, substituted or unsubstituted C₁-C₄alkyl, aralkyl is, in particular, substituted or unsubstituted phenyl-C₁-C₄alkyl and aryl is, in particular, phenyl or naphthyl which are unsubstituted or substituted by sulfo, C₁-C₄alkyl, C₁-C₄alkoxy, carboxylic acid groups, acylamino groups and halogen atoms, such as fluorine, chlorine or bromine, for example 2-amino-4-fluorotriazin-6-yl, 2-methylamino-4-fluorotriazin-6-yl, 2-ethylamino-4-fluorotriazin-6-yl, 2-iso-propylamino-4-fluorotriazin-6-yl, 2-dimethylamino-4-fluorotriazin-6-yl, 2-diethylamino-4-fluorotriazin-6-yl, 2- β -methoxyethylamino-4-fluorotriazin-6-yl, 2- β -hydroxyethylamino-4-fluorotriazin-6-yl, 2-di(β -hydroxyethylamino)-4-fluorotriazin-6-yl, 2- β -sulfoethylamino-4-fluorotriazin-6-yl, 2- β -sulfoethylmethylamino-4-fluorotriazin-6-yl, 2-carboxymethylamino-4-fluorotriazin-6-yl, 2- β -cyanoethylamino-4-fluorotriazin-6-yl, 2-benzolamino-4-fluorotriazin-6-yl, 2- β -phenylethylamino-4-fluorotriazin-6-yl, 2-benzylmethylamino-4-fluorotriazin-6-yl, 2-(2'-, 3'- or 4'-sulfobenzyl)amino-4-fluorotriazin-6-yl, 2-cyclohexylamino-4-fluorotriazin-6-yl, 2-(o-, m- or p-methylphenyl)amino-4-fluorotriazin-6-yl, 2-(o-, m- or

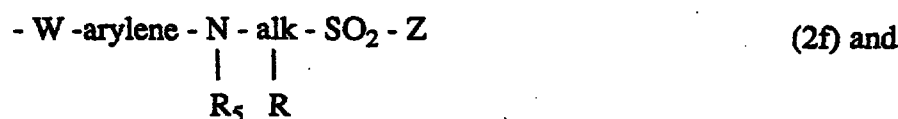
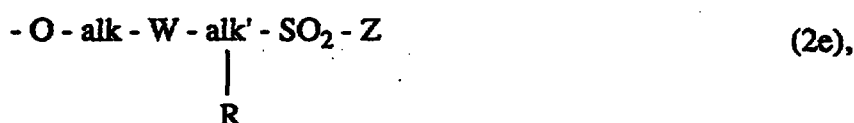
p-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2',5'-disulfophenyl)amino-4-fluorotriazin-6-yl, 2-(o-, m- or p-chlorophenyl)amino-4-fluorotriazin-6-yl, 2-(o-, m- or p-methoxyphenyl)-4-fluorotriazin-6-yl, 2-(2'-methyl-4'-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2'-methyl-5'-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2'-chloro-4'-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2'-chloro-5'-sulfophenyl)-amino-4-fluorotriazin-6-yl, 2-(2'-methoxy-4'-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(o-, m- or p-carboxyphenyl)amino-4-fluorotriazin-6-yl, 2-(2',4'-disulfophenyl)-amino-4-fluorotriazin-6-yl, 2-(3',5'-disulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2'-carboxy-4-sulfophenyl)amino-4-fluorotriazin-6-yl, 2-(2'-carboxy-4-sulfophenyl)-amino-4-fluorotriazin-6-yl, 2-(6'-sulfonaphth-2'-yl)amino-4-fluorotriazin-6-yl, 2-(4',8'-disulfonaphth-2'-yl)amino-4-fluorotriazin-6-yl, 2-(6',8'-disulfonaphth-2'-yl)amino-4-fluorotriazin-6-yl, 2-(N-methylphenyl)amino-4-fluorotriazin-6-yl, 2-(N-ethylphenyl)amino-4-fluorotriazin-6-yl, 2-(N-β-hydroxyethylphenyl)amino-4-fluorotriazin-6-yl, 2-(N-iso-propylphenyl)amino-4-fluorotriazin-6-yl, 2-morpholino-4-fluorotriazin-6-yl, 2-piperidino-4-fluorotriazin-6-yl, 2-(4',6',8'-trisulfonaphth-2'-yl)-4-fluorotriazin-6-yl, 2-(3',6',8'-trisulfonaphth-2'-yl)-4-fluorotriazin-6-yl, 2-(3',6'-disulfonaphth-1'-yl)-4-fluorotriazin-6-yl, mono-, di- or trihalogenopyrimidinyl radicals, such as 2,4-dichloropyrimidin-6-yl, 2,4,5-trichloropyrimidin-6-yl, 2,4-dichloro-5-nitro- or -5-methyl- or -5-carboxymethyl- or -5-carboxy- or -5-cyano- or -5-vinyl- or -5-sulfo- or -5-mono-, -di- or -trichloromethyl- or -5-carboalkoxypyrimidin-6-yl, 2,6-dichloropyrimidine-4-carbonyl, 2,4-dichloropyrimidine-5-carbonyl, 2-chloro-4-methylpyrimidine-5-carbonyl, 2-methyl-4-chloropyrimidine-5-carbonyl, 2-methylthio-4-fluoropyrimidine-5-carbonyl, 6-methyl-2,4-dichloropyrimidine-5-carbonyl, 2,4,6-trichloropyrimidine-5-carbonyl, 2,4-dichloropyrimidine-5-sulfonyl, 2-chloroquinoxaline-3-carbonyl, 2- or 3-monochloroquinoxaline-6-carbonyl, 2- or 3-monochloroquinoxaline-6-sulfonyl, 2,3-dichloroquinoxaline-6-carbonyl, 2,3-dichloroquinoxaline-6-sulfonyl, 1,4-dichlorophthalazine-6-sulfonyl or -6-carbonyl, 2,4-dichloroquinazoline-7- or -6-sulfonyl or -carbonyl, 2- or 3- or 4-(4',5'-dichloro-6'-pyridazin-1'-yl)phenylsulfonyl- or -carbonyl, β-(4',5'-dichloro-6'-pyridazon-1'-yl)ethylcarbonyl, N-methyl-N-(2,4-dichlorotriazin-6-yl)carbonyl, N-methyl-N-(2-methylamino-4-chlorotriazin-6-yl)carbonyl, N-methyl-N-(2-dimethylamino-4-chlorotriazin-6-yl)-carbonyl, N-methyl or N-ethyl-N-(2,4-dichlorotriazin-6-yl)aminoacetyl, N-methyl-N-(2,3-dichloroquinoxaline-6-sulfonyl)aminoacetyl,

N-methyl-N-(2,3-dichloroquinoxaline-6-carbonyl)aminoacetyl, and the corresponding bromine and fluorine derivatives of the abovementioned chlorine-substituted heterocyclic radicals, among these, for example, 2-fluoro-4-pyrimidinyl, 2,6-difluoro-4-pyrimidinyl, 2,6-difluoro-5-chloro-4-pyrimidinyl, 2-fluoro-5,6-dichloro-4-pyrimidinyl, 2,6-difluoro-5-methyl-4-pyrimidinyl, 2,5-difluoro-6-methyl-4-pyrimidinyl, 2-fluoro-5-methyl-6-chloro-4-pyrimidinyl, 2-fluoro-5-nitro-6-chloro-4-pyrimidinyl, 5-bromo-2-fluoro-4-pyrimidinyl, 2-fluoro-5-cyano-4-pyrimidinyl, 2-fluoro-5-methyl-4-pyrimidinyl, 2,5,6-trifluoro-4-pyrimidinyl, 5-chloro-6-chloromethyl-2-fluoro-4-pyrimidinyl, 2,6-difluoro-5-bromo-4-pyrimidinyl, 2-fluoro-5-bromo-6-methyl-4-pyrimidinyl, 2-fluoro-5-bromo-6-chloromethyl-4-pyrimidinyl, 2,6-difluoro-5-chloromethyl-4-pyrimidinyl, 2,6-difluoro-5-nitro-4-pyrimidinyl, 2-fluoro-6-methyl-4-pyrimidinyl, 2-fluoro-5-chloro-6-methyl-4-pyrimidinyl, 2-fluoro-5-chloro-4-pyrimidinyl, 2-fluoro-6-chloro-4-pyrimidinyl, 6-trifluoromethyl-5-chloro-2-fluoro-4-pyrimidinyl, 6-trifluoromethyl-2-fluoro-4-pyrimidinyl, 2-fluoro-5-nitro-4-pyrimidinyl, 2-fluoro-5-trifluoromethyl-4-pyrimidinyl, 2-fluoro-5-phenyl- or -5-methylsulfonyl-4-pyrimidinyl, 2-fluoro-5-carboxamido-4-pyrimidinyl, 2-fluoro-5-carbomethoxy-4-pyrimidinyl, 2-fluoro-5-bromo-6-trifluoromethyl-4-pyrimidinyl, 2-fluoro-6-carboxamido-4-pyrimidinyl, 2-fluoro-6-carbomethoxy-4-pyrimidinyl, 2-fluoro-6-phenyl-4-pyrimidinyl, 2-fluoro-6-cyano-4-pyrimidinyl, 2,6-difluoro-5-methylsulfonyl-4-pyrimidinyl, 2-fluoro-5-sulfonamido-4-pyrimidinyl, 2-fluoro-5-chloro-6-carbomethoxy-4-pyrimidinyl, 2,6-difluoro-5-trifluoromethyl-4-pyrimidinyl, 6-fluoro-5-chloropyrimidin-4-yl, 6-fluoro-5-trifluoromethylpyrimidin-4-yl, 6-fluoro-2-methylpyrimidin-4-yl, 6-fluoro-5-chloro-2-methylpyrimidin-4-yl, 5,6-difluoropyrimidin-4-yl, 6-fluoro-5-chloro-2-trifluoromethylpyrimidin-4-yl, 6-fluoro-2-phenylpyrimidin-4-yl, 6-fluoro-5-cyanopyrimidin-4-yl, 6-fluoro-5-nitropyrimidin-4-yl, 6-fluoro-5-methylsulfonylpyrimidin-4-yl, 6-fluoro-5-phenylsulfonylpyrimidin-4-yl, triazine radicals containing sulfonyl groups, such as 2,4-bis(phenylsulfonyl)triazin-6-yl, 2-(3'-carboxyphenyl)sulfonyl-4-chlorotriazin-6-yl, 2-(3'-sulfophenyl)sulfonyl-4-chlorotriazin-6-yl, 2,4-bis(3'-carboxyphenylsulfonyl)triazin-6-yl; pyrimidine rings containing sulfonyl groups, such as 2-carboxymethylsulfonylpyrimidin-4-yl, 2-methylsulfonyl-6-methylpyrimidin-4-yl, 2-methylsulfonyl-6-ethylpyrimidin-4-yl, 2-phenylsulfonyl-5-chloro-6-methylpyrimidinyl, 2,6-bis-methylsulfonylpyrimidin-4-yl, 2,6-bis-methylsulfonyl-5-chloropyrimidin-4-yl, 2,4-bis-methylsulfonylpyrimidine-

5-sulfonyl, 2-methylsulfonylpyrimidin-4-yl, 2-phenylsulfonylpyrimidin-4-yl, 2-trichloromethylsulfonyl-6-methylpyrimidin-4-yl, 2-methylsulfonyl-5-chloro-6-methylpyrimidin-4-yl, 2-methylsulfonyl-5-bromo-6-methylpyrimidin-4-yl, 2-methylsulfonyl-5-chloro-6-ethylpyrimidin-4-yl, 2-methylsulfonyl-5-chloro-6-chloromethylpyrimidin-4-yl, 2-methylsulfonyl-4-chloro-6-methylpyrimidine-5-sulfonyl, 2-methylsulfonyl-5-nitro-6-methylpyrimidin-4-yl, 2,5,6-tris-methylsulfonylpyrimidin-4-yl, 2-methylsulfonyl-5,6-dimethylpyridin-4-yl, 2-ethylsulfonyl-5-chloro-6-methylpyrimidin-4-yl, 2-methylsulfonyl-6-chloro-pyrimidin-4-yl, 2,6-bis-methylsulfonyl-5-chloropyrimidin-4-yl, 2-methylsulfonyl-6-carbonylpyrimidin-4-yl, 2-methylsulfonyl-5-sulfopyrimidin-4-yl, 2-methylsulfonyl-6-carbomethoxypyrimidin-4-yl, 2-methylsulfonyl-5-carboxypyrimidin-4-yl, 2-methylsulfonyl-5-cyano-6-methoxypyrimidin-4-yl, 2-methylsulfonyl-5-chloropyrimidin-4-yl, 2-sulfoethylsulfonyl-6-methylpyrimidin-4-yl, 2-methylsulfonyl-5-bromopyrimidin-4-yl, 2-phenylsulfonyl-5-chloro-pyrimidin-4-yl, 2-carboxymethylsulfonyl-5-chloro-6-methylpyrimidin-4-yl, 2-methylsulfonyl-6-chloropyrimidine-4- and -5-carbonyl, 2,6-bis(methylsulfonyl)pyrimidine-4- or -5-carbonyl, 2-ethylsulfonyl-6-chloropyrimidine-5-carbonyl, 2,4-bis(methylsulfonyl)pyrimidine-5-sulfonyl, 2-methylsulfonyl-4-chloro-6-methylpyrimidine-5-sulfonyl or -carbonyl, triazine rings containing ammonium groups, such as trimethylammonium-4-phenylamino- or -4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl, 2-(1,1-dimethylhydrazinium)-4-phenylamino- or -4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl, 2-(2-isopropylidene-1,1-dimethyl)hydrazinium-4-phenylamino- or -4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl, 2-N-aminopyrrolidinium or 2-aminopiperidinium-4-phenylamino- or -4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl, 2-N-aminopyrrolidinium or 2-N-aminopiperidinium-4-phenylamino- or -4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl, and furthermore 4-phenylamino- or 4-(sulfophenylamino)triazin-6-yl radicals which contain 1,4-bis-azabicyclo[2,2,2]octane or 1,2-bis-azabicyclo[0,3,3]octane bonded quaternally in the 2-position via a nitrogen bond, 2-pyridinium-4-phenylamino- or 4-(o-, m- or p-sulfophenyl)aminotriazin-6-yl and corresponding 2-oniumtriazin-6-yl radicals which are substituted in the 4-position by alkylamino, such as methylamino, ethylamino or β -hydroxyethylamino, or alkoxy, such as methoxy or alkoxy, or aroxy, such as phenoxy or sulfophenoxy groups; 2-chlorobenzothiazole-5- or -6-carbonyl or -5- or -6-sulfonyl, 2-arylsulfonyl- or -alkylsulfonylbenzothiazole-5- or -6-carbonyl or -5- or -6-sulfonyl, such as 2-methylsulfonyl- or 2-ethoxysulfonylbenzothiazole-5- or 6-sulfonyl or -carbonyl, 2-phenylsulfonylbenzothiazole-5- or -6-sulfonyl or -carbonyl and the corresponding 2-sulfobenzothiazole-5- or 6-carbonyl or -sulfonyl derivatives, containing sulfo groups in the fused-on benzene ring, 2-chlorobenzoxazole-5- or -6-carbonyl or -sulfonyl,

2-chlorobenzimidazole-5- or -6-carbonyl or sulfonyl, 2-chloro-1-methylbenzimidazole-5- or 6-carbonyl or -sulfonyl, 2-chloro-4-methyl-1,3-thiazole-5-carbonyl or -4- or -5-sulfonyl, the N-oxide of 4-chloro- or 4-nitroquinoline-5-carbonyl or also the radicals 5-chloro-2,6-difluoro-1,3-dicyanophenyl, 2,4-difluoro-1,3,5-tricyanophenyl, 2,4,5-trifluoro-1,3-dicyanophenyl, 2,4-dichloro-5-methylsulfonylpyrimidin-6-yl, 2,4-trichloro-5-ethylsulfonylpyrimidin-6-yl, 2-fluoro-5-methylsulfonyl-6'-(2'-sulfophenylamino)pyrimidin-4-yl and 2,5-dichloro-6-methylsulfonylpyrimidin-4-yl.

A group of suitable reactive groups comprises those of the formulae



in which W is a group of the formula $-\text{SO}_2-\text{NR}_5$, $-\text{CONR}_5$ or $-\text{NR}_5\text{CO}-$, R_5 is hydrogen, C_1 - C_4 alkyl which is unsubstituted or substituted by hydroxyl, sulfo,

sulfato, carboxyl or cyano, or a radical of the formula $\begin{array}{c} \text{alk} - \text{SO}_2 - \text{Z} \\ | \\ \text{R} \end{array}$,

R is hydrogen, hydroxyl, sulfo, sulfato, carboxyl, cyano, halogen, C₁-C₄alkoxycarbonyl, C₁-C₄alkanoyloxy, carbamoyl or the group -SO₂-Z,

Z is the radical -CH=CH₂ or -CH₂-CH₂-Y,

Y is a leaving group,

E is the radical -O- or -NR₇,

R₇ is hydrogen or C₁-C₄alkyl,

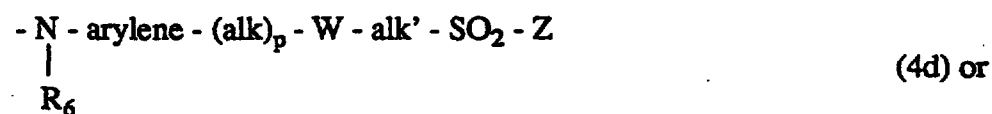
alk and alk' independently of one another are C₁-C₆alkylene,

arylene is a phenylene or naphthylene radical which is unsubstituted or substituted by sulfo, carboxyl, C₁-C₄alkyl, C₁-C₄alkoxy or halogen,

R₆ is hydrogen or C₁-C₄alkyl which is unsubstituted or substituted by carboxyl, cyano, hydroxyl, sulfo or sulfato and

X is a group which can be split off as an anion and

T is a radical of the formula



in which R, R₅, R₆, E, W, Z, alk, alk' and arylene are as defined above and p is 0 or 1.

Suitable leaving groups Y are, for example, -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, -OPO₃H₂, -OCO-CCl₃, -OCO-CHCl₂, -OCO-CH₂Cl, -OSO₂-C₁-C₄alkyl, -OSO₂-N(C₁-C₄alkyl)₂ or -OCO-C₆H₅.

Y is preferably a group of the formula -Cl, -OSO₃H, -SSO₃H, -OCO-CH₃, -OCO-C₆H₅ or -OPO₃H₂, in particular -OSO₃H.

alk and alk' independently of one another are, for example, a methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexylene radical or branched isomers thereof.

alk and alk' are preferably a C₁-C₄alkylene radical, and particularly preferably an ethylene radical.

R is preferably hydrogen or the group -SO₂-Z, in which Z is as defined above. R is particularly preferably hydrogen.

R₅ is preferably hydrogen, C₁-C₄alkyl or a group -alk-SO₂-Z, in which alk and Z are in each case as defined above. R₅ is particularly preferably hydrogen or C₁-C₄alkyl, in particular hydrogen.

R₆ is preferably hydrogen or a C₁-C₄alkyl radical, and particularly preferably hydrogen.

Arylene is preferably a 1,3- or 1,4-phenylene radical, which is unsubstituted or substituted, for example by sulfo, methyl, methoxy or carboxyl.

E is preferably -NH-, and particularly preferably -O-.

W is preferably a group of the formula -CONH- or -NHCO-.

X is, for example, fluorine, chlorine, bromine, sulfo, C₁-C₄alkylsulfonyl or phenylsulfonyl, and preferably fluorine or chlorine.

Other interesting reactive groups are those of the formula (3) in which T is a group which can be split off as an anion or is a non-reactive substituent.

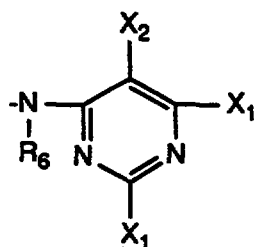
A group T which can be split off as an anion is here, for example, fluorine, chlorine, bromine, sulfo, C₁-C₄alkylsulfonyl or phenylsulfonyl, and preferably fluorine or chlorine.

A non-reactive substituent T can be, for example, a hydroxyl, C₁-C₄alkoxy, C₁-C₄alkylthio, amino, N-C₁-C₄alkylamino or N,N-di-C₁-C₄alkylamino, where the alkyl is unsubstituted or substituted, for example by sulfo, sulfato, hydroxyl, carboxyl or phenyl, cyclohexylamino, morpholino or N-C₁-C₄alkyl-N-phenylamino or phenylamino or naphthylamino radical, where the phenyl or naphthyl is unsubstituted or substituted, for example by C₁-C₄alkyl, C₁-C₄alkoxy, carboxyl, sulfo or halogen.

Examples of suitable non-reactive substituents T are amino, methylamino, ethylamino, β-hydroxyethylamino, N,N-di-β-hydroxyethylamino, β-sulfoethylamino, cyclohexylamino, morpholino, o-, m- or p-chlorophenylamino, o-, m- or p-methylphenylamino, o-, m- or p-methoxyphenylamino, o-, m- or p-sulfophenylamino, disulfophenylamino, o-carboxyphenylamino, 1- or 2-naphthylamino, 1-sulfo-2-naphthylamino, 4,8-disulfo-2-naphthylamino, N-ethyl-N-phenylamino, N-methyl-N-phenylamino, methoxy, ethoxy, n- or iso-propoxy and hydroxyl.

A non-reactive substituent T is preferably amino, N-C₁-C₄alkylamino, which is unsubstituted in the alkyl part or substituted by hydroxyl, sulfato or sulfo, morpholino, phenylamino or N-C₁-C₄alkyl-N-phenylamino, in which the phenyl is in each case unsubstituted or substituted by sulfo, carboxyl, methyl or methoxy. Phenylamino or N-C₁-C₄alkyl-N-phenylamino, in which the phenyl is in each case unsubstituted or substituted by sulfo, carboxyl, methyl or methoxy, are particularly preferred.

Other interesting reactive groups are pyrimidine or quinoxaline radicals, which in each case have at least one group which can be split off as an anion. Examples are the 2,3-dichloroquinoxaline-6-carbonylamino radical, the 2,4-dichloropyrimidine-5-carbonylamino radical and the radical of the formula



(5),

in which one of the radicals X_1 is a group which can be split off as an anion and the other radical X_1 is as defined and preferred for a non-reactive substituent T, or is a radical of the formulae (4a) to (4e) or a group which can be split off as an anion,

X_2 is a negative substituent and

R_6 independently is as defined under formula (3).

The radical X_1 which can be split off as an anion is preferably fluorine or chlorine.

Examples of suitable radicals X_2 are nitro, cyano, C_1 - C_4 alkylsulfonyl, carboxyl, chlorine, hydroxyl, C_1 - C_4 alkoxysulfonyl, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkoxycarbonyl or C_2 - C_4 alkanoyl, where chlorine, cyano and methylsulfonyl are preferred for X_2 .

Particularly preferred reactive groups are those of the formula (2a), in which Z is as defined and preferred above, in particular in which Z is a vinyl or β -sulfatoethyl radical, and those of the formula (3), in which T, X and R_6 are as defined and preferred above. T here is particularly preferably a non-reactive radical, in particular phenylamino or N- C_1 - C_4 alkyl-N-phenylamino, in which the phenyl is in each case unsubstituted or substituted by sulfo, carboxyl, methyl or methoxy. X here is particularly preferably fluorine or chlorine. R_6 here is particularly preferably hydrogen, methyl or ethyl, in particular hydrogen. The radical of the formula (2a) is particularly preferred as the reactive group.

Preferably, the radicals A_1 and A_2 contain no reactive groups.

A_1 and A_2 independently of one another are preferably the radical of a monoazo, disazo, anthraquinone, dioxazine, phthalocyanine or formazan dye.

Radicals of a monoazo or disazo dye are, in particular, the following:

Dye radicals of a mono- or disazo dye of the formula



In these formulae, D_1 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,

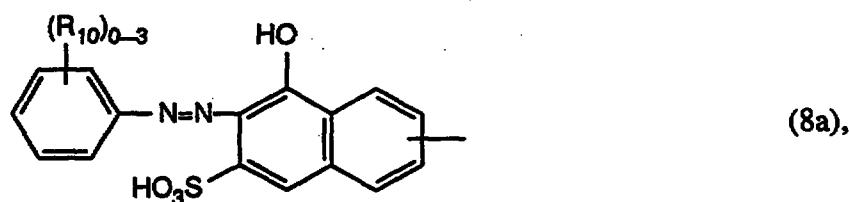
K is the radical of a coupling component of the benzene, naphthalene, pyrazolone,

6-hydroxy-2-pyridone or acetoacetic acid arylamide series and

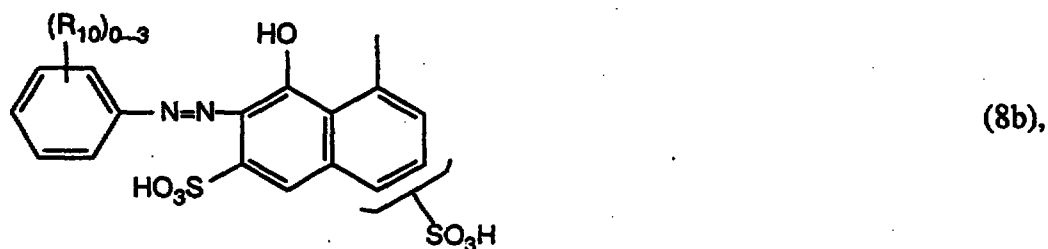
u is the number 0 or 1,

where D₁, M and K can carry the substituents customary in azo dyes, for example those defined above. Such substituents are, in particular, C₁-C₄alkyl or C₁-C₄alkoxy which are unsubstituted or further substituted by hydroxyl, sulfo or sulfato, halogen, carboxyl, sulfo, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, amino, ureido, hydroxyl, carboxyl, sulfomethyl, C₂-C₄alkanoylamino, benzoylamino which is unsubstituted or substituted in the phenyl ring by C₁-C₄alkyl, C₁-C₄alkoxy, halogen or sulfo, phenyl which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl or sulfo, and fibre-reactive radicals, where the fibre-reactive radicals are as defined and preferred above. Further examples are also the metal complexes derived from the dye radicals of the formulae (6) and (7), in particular dye radicals of a 1:1 copper complex azo dye of the benzene or naphthalene series, in which the copper atom is bonded to in each case a metallizable group on both sides in the ortho-position relative to the azo bridge.

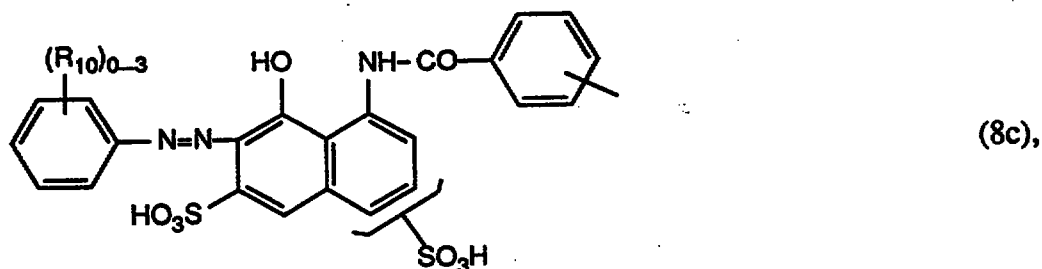
Particularly preferred radicals of a monoazo or disazo dye are the following:



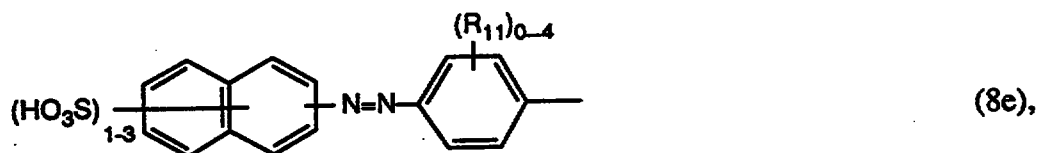
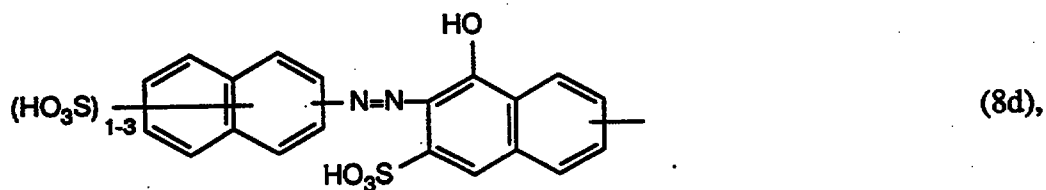
in which R₁₀ is 0 to 3 identical or different substituents from the group comprising C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl and sulfo,



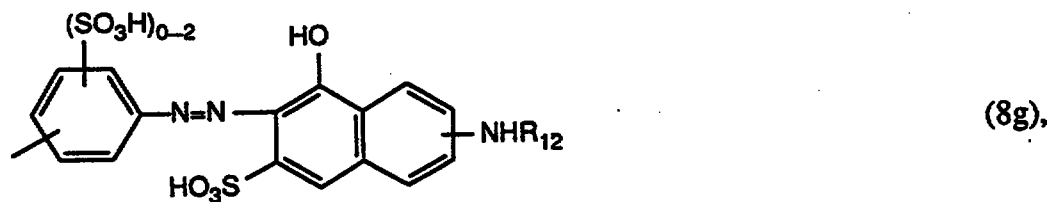
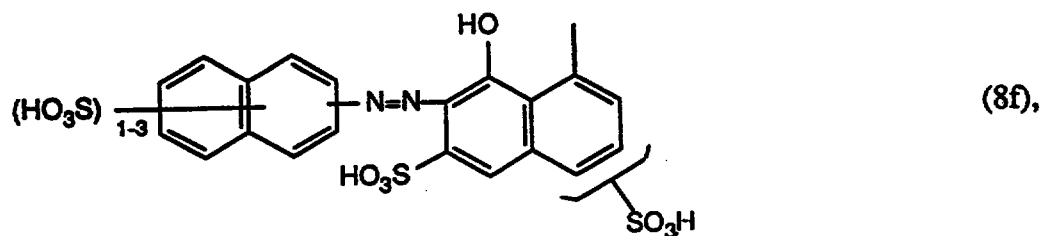
in which R₁₀ is 0 to 3 identical or different substituents from the group comprising C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl and sulfo,



in which R_{10} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,

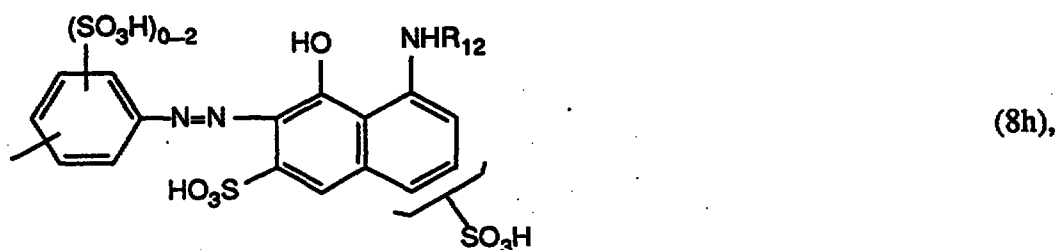


in which R_{11} is 0 to 4 identical or different substituents from the group comprising halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, amino, acetylamino, ureido, hydroxyl, carboxyl, sulfomethyl and sulfo,

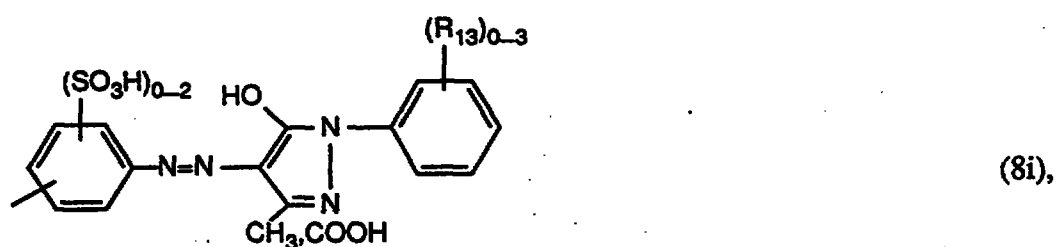


in which R_{12} is C_1 - C_4 alkanoyl, benzoyl or a halotriazinyl radical which may be further

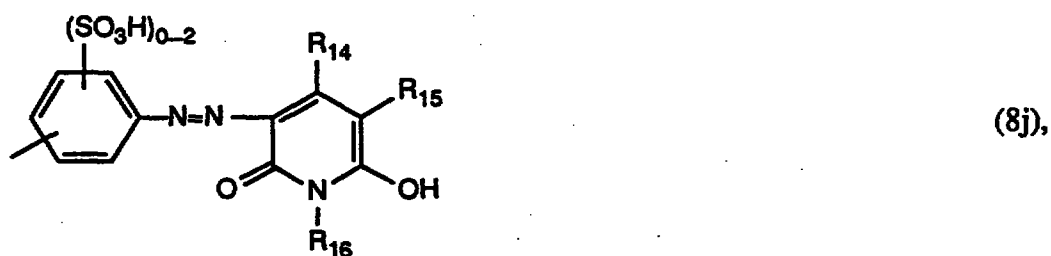
substituted,



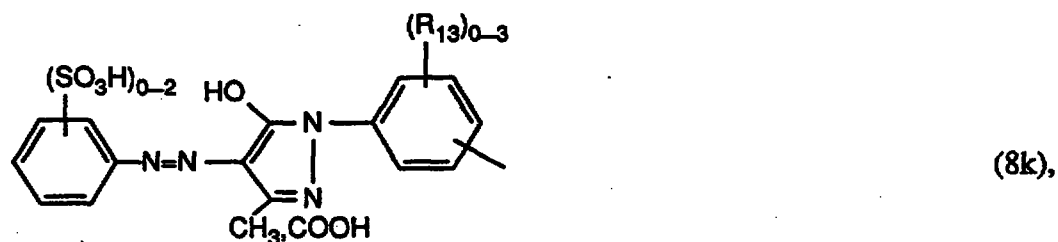
in which R_{12} is C_1 - C_4 alkanoyl, benzoyl or a halotriazinyl radical which may be further substituted,



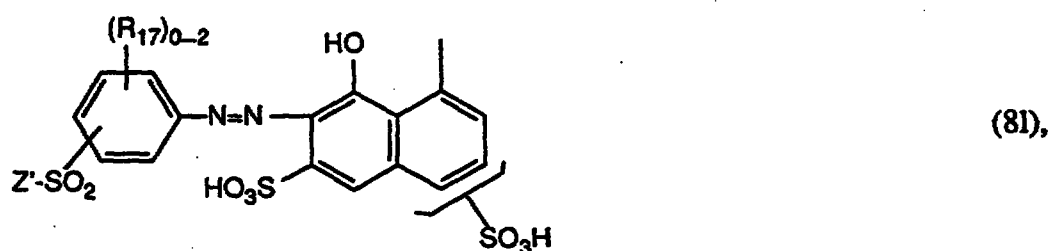
in which R_{13} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,



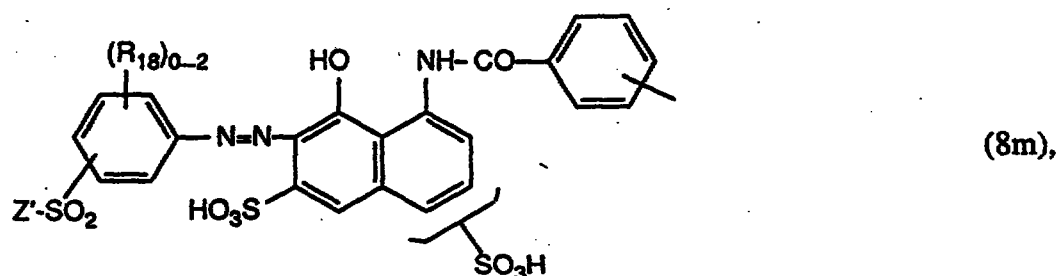
in which R_{14} and R_{16} independently of one another are hydrogen, C_1 - C_4 alkyl or phenyl,
and
 R_{15} is hydrogen, cyano, carbamoyl or sulfomethyl,



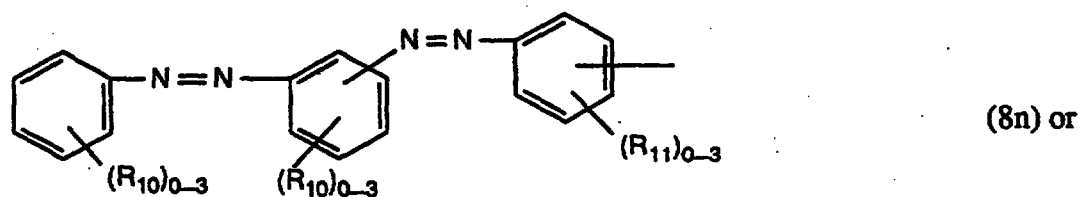
in which R_{13} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,

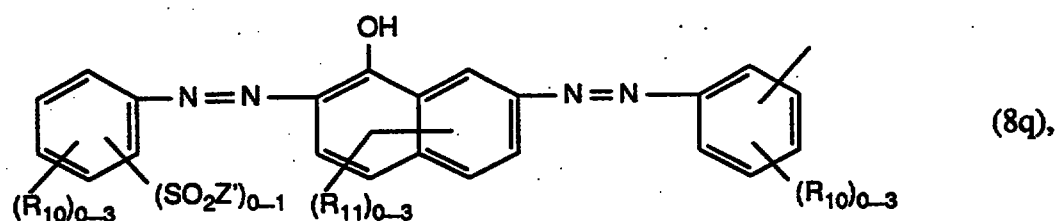
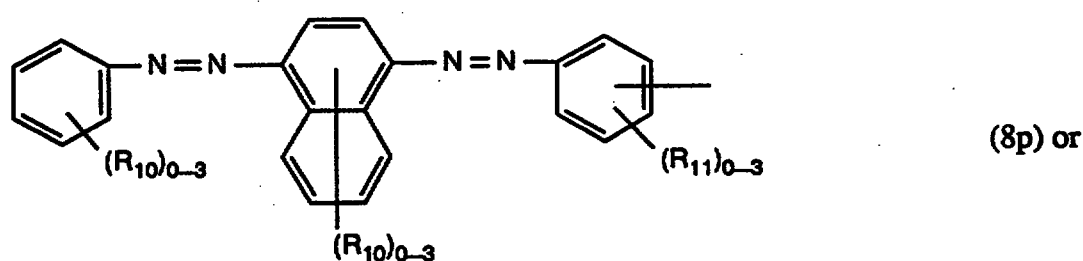
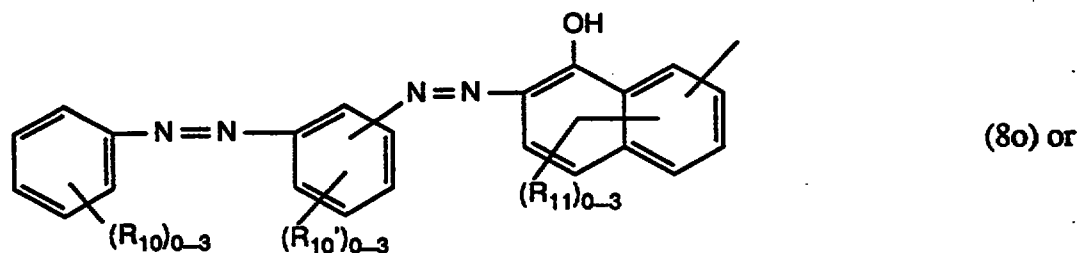


in which R_{17} is 0 to 2 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo; and Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -halogenoethyl or vinyl,



in which R_{18} is 0 to 2 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo; and Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -haloethyl or vinyl,

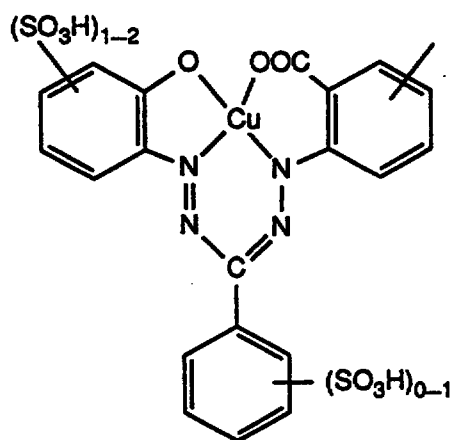




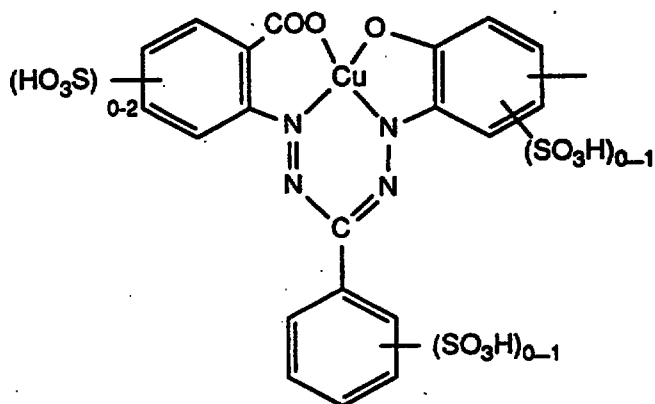
in which R_{10} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo, R_{10}' is as defined for R_{10} and can additionally be C_1 - C_4 hydroxyalkoxy or C_1 - C_4 sulfatoalkoxy, R_{11} is 0 to 3 identical or different substituents from the group comprising halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, amino, acetylamino, ureido, hydroxyl, carboxyl, sulfomethyl and sulfo and Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -haloethyl or vinyl.

The radicals of the formulae (8a) to (8q) can also contain, as further substituents in the phenyl or naphthyl rings, a radical of the formula $-SO_2Z'$ in which Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -haloethyl or vinyl. Z' is preferably β -sulfatoethyl or vinyl, in particular vinyl.

The radical of a formazan dye is preferably a dye radical of the formula

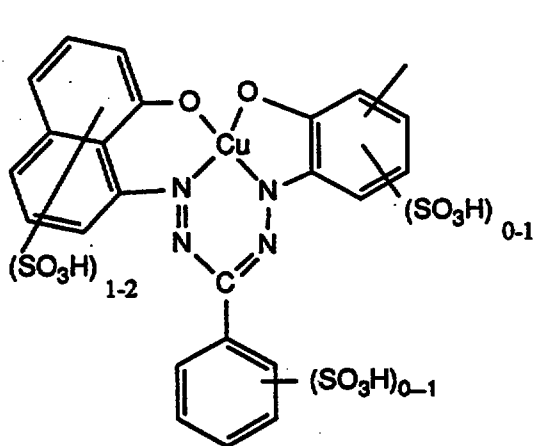


(8r)

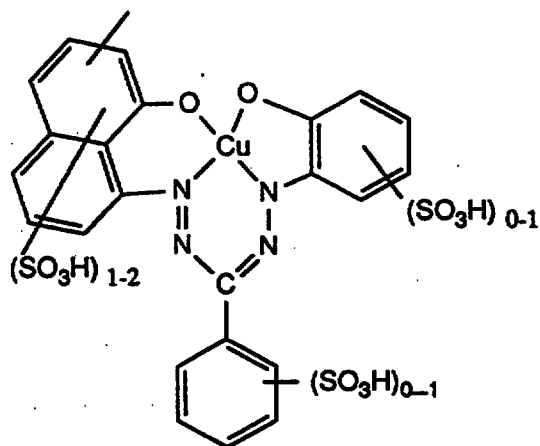


(8s) or

or



(8t)

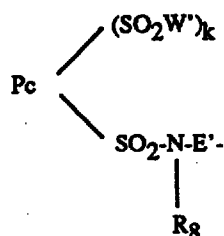


(8u),

or

in which the benzene nuclei contain no further substituents or are further substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylsulfonyl, halogen or carboxyl.

The radical of a phthalocyanine dye is preferably a radical of the formula



(9),

in which Pc is the radical of a metal phthalocyanine, in particular the radical of a copper

phthalocyanine or nickel phthalocyanine;

W' is -OH and/or -NR₉R₉';

R₉ and R₉' independently of one another are hydrogen or C₁-C₄alkyl which is unsubstituted or substituted by hydroxyl or sulfo;

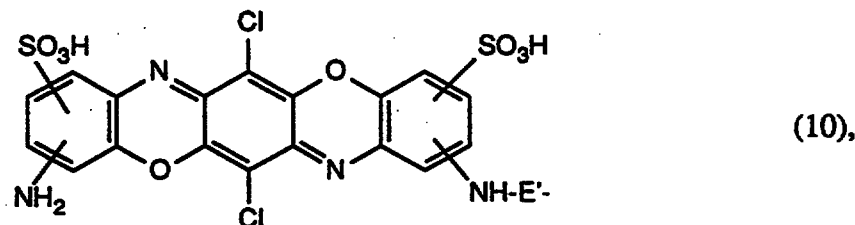
R₈ is hydrogen or C₁-C₄alkyl;

E' is a phenylene radical which is unsubstituted or substituted by C₁-C₄alkyl, halogen, carboxyl or sulfo, or a C₂-C₆alkylene radical; and

k is 1 to 3.

R₉ and R₉' are preferably hydrogen. E' is preferably a phenylene radical which is unsubstituted or substituted by C₁-C₄alkyl, halogen, carboxyl or sulfo. Pc is preferably the radical of a copper phthalocyanine.

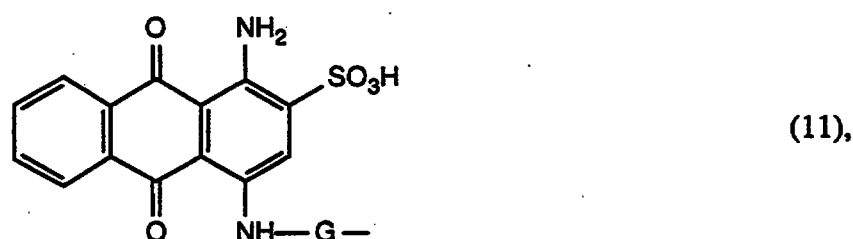
The radical of a dioxazine dye is preferably a radical of the formula



in which E' is a phenylene radical which is unsubstituted or substituted by C₁-C₄alkyl, halogen, carboxyl or sulfo, or a C₂-C₆alkylene radical, and

the outer benzene rings in the formula (10) contain no further substituents or are further substituted by C₁-C₄alkyl, C₁-C₄alkoxy, acetamino, nitro, halogen, carboxyl, sulfo or -SO₂-Z', in which Z' is β-sulfatoethyl, β-thiosulfatoethyl, β-phosphatoethyl, β-acyloxyethyl, β-haloethyl or vinyl.

The radical of an anthraquinone dye is preferably a radical of the formula



in which G is a phenylene, cyclohexylene, phenylenemethylene or C₂-C₆alkylene radical, and in which the anthraquinone nucleus can be substituted by a further sulfo group and a phenyl radical G can be substituted by C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl or sulfo, and the dye preferably contains at least 2 sulfo groups. G is preferably a phenyl radical which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl or sulfo.

A₁ and A₂ are particularly preferably radicals of the formulae (8a) to (8u), (9), (10) or (11). The radicals Y₁, Y₂, R₁, R₂, R₃, R₄ and B of the reactive dyes of the formula (1) are as defined and preferred above here.

The reactive dyes of the formula (1) which the dye mixtures according to the invention comprise are, in particular those in which

Y₁ and Y₂ independently of one another are fluorine or chlorine,

R₁, R₂, R₃ and R₄ independently of one another are hydrogen, methyl or ethyl, in particular hydrogen,

B is a C₂-C₁₂alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals, and

A₁ and A₂ are radicals of the formulae (8a) to (8u), (9), (10) or (11).

The dye mixtures according to the invention comprise at least two reactive dyes of the formula (1), which can differ in respect of the meanings of the radicals Y₁, Y₂, R₁, R₂, R₃, R₄, A₁, A₂ and B. The dye mixtures according to the invention preferably comprise at least two reactive dyes of the formula (1) which differ from one another only in respect of the meanings of the radicals A₁, A₂, R₂, R₃ and/or B. The dye mixtures according to the invention particularly preferably comprise at least two reactive dyes of the formula (1) which differ from one another only in respect of the meanings of the radicals R₂, R₃ and/or B. The dye mixtures according to the invention particularly preferably comprise at least two reactive dyes of the formula (1) which differ from one another only in respect of the meaning of the radical B.

The dye mixtures which comprise at least two reactive dyes of the formula (1) which differ from one another only in respect of the meaning of at least one of the radicals A₁ and A₂ furthermore are of interest.

Particularly important dye mixtures are those which comprise at least two reactive dyes of the formula (1) in which

R_1, R_2, R_3 and R_4 are hydrogen, methyl or ethyl,

B is a C_2-C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals, and the reactive dyes of the formula (1) differ only in respect of the meaning of the bridge member B and/or the meaning of the radicals R_2 and R_3 .

Especially important dye mixtures are those which comprise at least two reactive dyes of the formula (1) in which

R_1, R_2, R_3 and R_4 are hydrogen,

B is a C_2-C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals, and the reactive dyes of the formula (1) differ only in respect of the meaning of the bridge member B .

Dye mixtures which are of special interest are those which comprise two reactive dyes of the formula (1), wherein the ratio of the reactive dyes of the formula (1) is preferably 5:95 to 95:5, in particular 10:90 to 90:10 and preferably 40:60 to 60:40.

The reactive dyes of the formula (1) are known or can be prepared analogously to known dyes.

The reactive dyes of the formula (1) can thus be obtained by reacting radicals of the formulae



or corresponding dye intermediates, at least one halotriazine compound and at least one diamine of the formula



in which $A_1, A_2, R_1, R_2, R_3, R_4$ and B are as defined under formula (1), with one another in any sequence, or, if dye intermediates are used, by converting the resulting intermediates into the desired dyes, and if appropriate then carrying out a further conversion reaction.

The preparation of the end dyes from intermediates is, in particular, a coupling reaction which leads to azo dyes. The coupling reactions are carried out by processes known per se.

Since the individual process steps defined above can be carried out in various sequences, if appropriate in some cases also at the same time, various process variants are possible. The reaction is in general carried out stepwise in succession, the sequence of the simple reactions between the individual reaction components advantageously depending on the particular conditions.

One process variant comprises subjecting one of the radicals of the formulae (12a) and (12b) to a condensation reaction with a halotriazine compound, subjecting the resulting product to a condensation reaction with a diamine of the formula (13) and reacting the resulting reaction product with the other radical of the formulae (12b) and (12a), which has first been subjected to a condensation reaction with a halotriazine compound.

The present invention furthermore relates to a process for the preparation of dye mixtures according to the invention. These can be carried out, on the one hand, by mixing the individual components, or as described above for the preparation of the reactive dyes of the formula (1), where at least two radicals of the formulae (12a), (12b) or (13) which differ from one another or at least two halotriazine compounds which differ from one another are used. Preferably, only different diamines of the formula (13), which differ only in respect of the bridge member B, are used; in particular, two such diamines of the formula (13) which differ from one another. Furthermore, two radicals of the formulae (12a) and/or (12b) which differ from one another are preferably used.

If the radicals of the formulae (12a) and (12b) have, for example, identical meanings, these radicals are preferably subjected to a condensation reaction with a halotriazine compound and the resulting product is subjected to a condensation reaction with at least two diamines of the formula (13).

If only one diamine of the formula (13) is used, a mixture, for example, of compounds of the formulae (12a) and (12b) which differ from one another is first subjected to a condensation reaction with a halotriazine compound and the resulting reaction mixture is then reacted with a diamine of the formula (13).

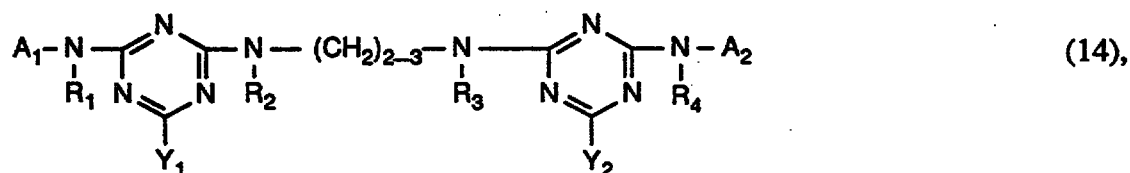
The halotriazine compounds used are preferably cyanuric halides, for example cyanuric

chloride or cyanuric fluoride. A carboxypyridinium compound is as a rule introduced after a condensation reaction on the corresponding cyanuric halides.

The compounds of the formulae (12a), (12b) and (13) and the halotriazine compounds are known or can be obtained analogously to known compounds.

The individual condensation reactions are carried out, for example, by a process known per se, as a rule in aqueous solution, at a temperature of, for example, 0 to 50°C and a pH of, for example, 4 to 10.

The present invention furthermore relates to the novel reactive dyes of the formula



in which A₁ and A₂ are the radical of a monoazo, polyazo, metal complex azo, anthraquinone, phthalocyanine, formazan, azomethine, dioxazine, phenazine, stilbene, triphenylmethane, xanthene, thioxanthone, nitroaryl, naphthoquinone, pyrenequinone or perylenetetracarbinide dye,

R₁, R₂, R₃ and R₄ independently of one another are hydrogen, methyl or ethyl, Y₁ and Y₂ independently of one another are halogen or carboxypyridinium and at least one of the radicals R₂ and R₃ is methyl or ethyl.

The reactive dyes of the formula (14) can be prepared by the process described above for the reactive dyes of the formula (1), wherein a diamine of the formula (13) in which at least one of the radicals R₂ and R₃ is methyl or ethyl is used.

The radicals A₁, A₂, Y₁, Y₂, R₁ and R₄ are as defined and preferred above for the reactive dyes of the formula (1) here.

Preferably, at least one of the radicals R₂ and R₃ is methyl.

The dyes of the formula (1) and (14) which contain a sulfo or sulfato group are either in the form of their free acid or, preferably, in the form of salts thereof. Salts are, for

example, the alkali metal, alkaline earth metal or ammonium salts or the salts of an organic amine. Examples are the sodium, lithium, potassium or ammonium salts or the salt of mono-, di- or triethanolamine.

The dye mixtures according to the invention and the dyes according to the invention are suitable for dyeing and printing the most diverse materials, such as fibre material containing hydroxyl groups or containing nitrogen. Examples are silk, leather, wool, polyamide fibres and polyurethanes, and in particular all types of cellulosic fibre materials. Such cellulosic fibre materials are, for example, the natural cellulosic fibres, such as cotton, linen and hemp, and cellulose and regenerated cellulose. The dye mixtures according to the invention and the dyes according to the invention are also suitable for dyeing or printing the fibres containing hydroxyl groups which are contained in blend fabrics, for example mixtures of cotton with polyester fibres or polyamide fibres. The dye mixtures according to the invention and the dyes according to the invention are particularly suitable for dyeing or printing cellulosic fibre materials. They can furthermore be used for dyeing or printing natural or synthetic polyamide fibre materials.

The dye mixtures according to the invention and the dyes according to the invention can be applied to the fibre material and fixed on the fibre in various ways, in particular in the form of aqueous dye solutions and printing pastes. They are suitable both for the exhaust method and for dyeing by the pad-dyeing method, in which the goods are impregnated with aqueous dye solutions, which contain salts if appropriate, and the dyes are fixed after an alkali treatment or in the presence of alkali, if appropriate under the action of heat. They are particularly suitable for the so-called cold pad-batch process, in which the dye is applied to the padder together with the alkali and is then fixed by storage at room temperature for several hours. After fixing, the dyeings or prints are rinsed thoroughly with cold and hot water, if appropriate with the addition of an agent which has a dispersing action and promotes diffusion of the non-fixed portions.

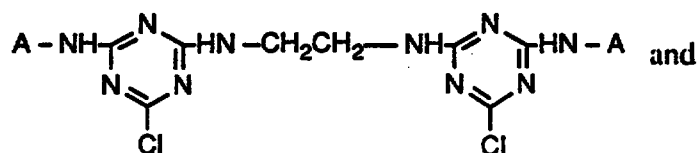
The dyes according to the invention, and in particular the dye mixtures according to the invention, have a high reactivity, good fixing capacity and a very good build-up capacity. They can therefore be used by the exhaust dyeing method at low dyeing temperatures, and require only short steaming times in the pad-steam process. The degrees of fixing are high and the non-fixed portions can easily be washed out, the difference between the degree of exhaustion and degree of fixing being remarkably small, i.e. the soaping loss is very low. The dyes according to the invention, and in particular the dye mixtures according to the

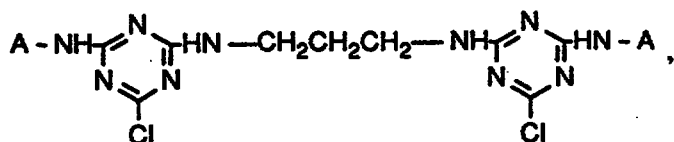
invention, are also particularly suitable for printing, in particular on cotton, and also for printing nitrogen-containing fibres, for example wool or silk or blend fabrics which comprise wool or silk.

The dyeings and prints produced with the dyes according to the invention, and in particular those produced with the dye mixtures according to the invention, have a high colour strength and a high fibre-dye bond stability both in the acid and in the alkaline range, and furthermore a good light-fastness and very good wet-fastness properties, such as fastnesses to washing, water, sea water, crossdyeing and perspiration, as well as a good fastness to pleating, fastness to ironing and fastness to rubbing.

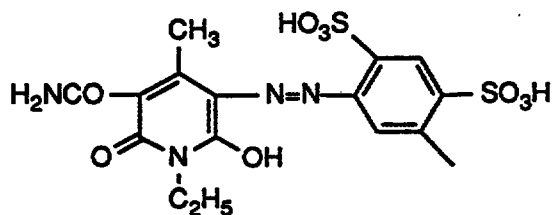
The following examples serve to illustrate the invention. Temperatures are stated in degrees Celsius and parts and percentages by weight, unless stated otherwise. Parts by weight bear the same relation to parts by volume as the kilogram to the litre.

Example 1: 19 parts of cyanuric chloride are stirred vigorously into 50 parts of water, with the addition of a wetting agent and 5 parts of disodium hydrogen phosphate, at a temperature of 0°C. A neutral solution of 27 parts of 4,6-diaminobenzene-1,3-disulfonic acid in 200 parts of water is added dropwise to the mixture, during which the pH is kept at a value of 4.5 by addition of sodium hydroxide solution. When the reaction has ended, 25 parts of 32% hydrochloric acid and 7 parts of sodium nitrite are added, the mixture is stirred for 30 minutes and the excess nitrite is destroyed with sulfamic acid. The suspension is added dropwise to a neutral solution of 20 parts of 1-ethyl-6-hydroxy-4-methyl-2-pyridonecarboxylamide in 50 parts of water, during which the pH is kept constant at a value of 7 by addition of an aqueous sodium hydroxide solution. A solution of 1.5 parts of ethane-1,2-diamine and 1.8 parts of propane-1,3-diamine in 30 parts of water is then added dropwise such that the pH does not exceed a value of 9. Towards the end of the reaction, the mixture is then heated to a temperature of 40°C. When the condensation reaction has ended, the resulting product is precipitated by addition of sodium chloride, filtered off with suction and dried. A dye mixture which comprises the dyes, shown in the form of the free acid, of the formulae



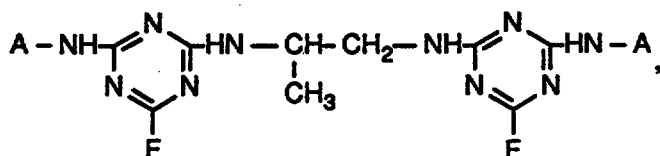
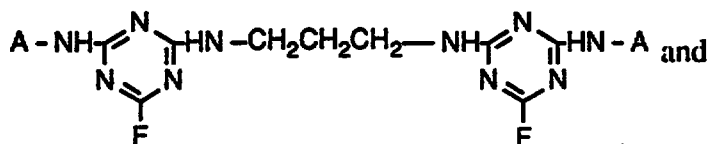


in which A is in each case a radical of the formula

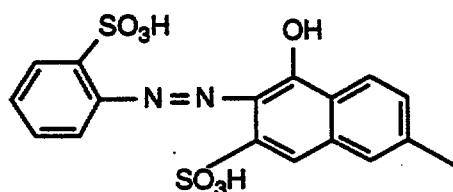


in a ratio of about 1:1 is obtained. The resulting dye mixture dyes cotton in brilliant yellow colour shades.

Example 2: 14 parts of cyanuric fluoride are added dropwise to a neutral solution of 42 parts of 7-amino-4-hydroxy-3-(2-sulfophenylazo)naphthalene-2-sulfonic acid and 5 parts of sodium dihydrogen phosphate in 500 parts of water at a temperature below 2°C; during this operation, the pH is kept constant by addition of aqueous sodium hydroxide solution. When the reaction has ended, a solution of 1.8 parts of 1-methylethane-1,2-diamine and 1.8 parts of propane-1,3-diamine in 30 parts of water is added dropwise such that the pH does not exceed a value of 9.5, and the pH is kept constant at a value of 9.5 by addition of sodium hydroxide solution. The mixture is allowed to warm to room temperature, the solution is freed from the salt by dialysis and the resulting product is evaporated. A dye mixture which comprises the dyes, shown in the form of the free acid, of the formulae



in which A is in each case a radical of the formula



in a ratio of about 1:1 is obtained. The resulting dye mixture dyes cotton in brilliant orange colour shades.

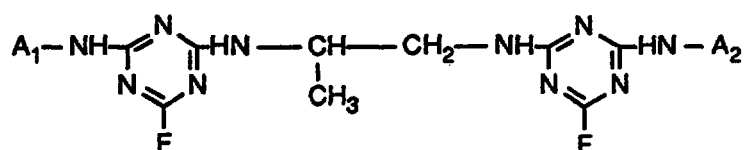
Example 3: 14 parts of cyanuric fluoride are added dropwise to a neutral solution of 50 parts of 7-amino-4-hydroxy-3-(2,5-disulfophenylazo)naphthalene-2-sulfonic acid and 5 parts of disodium hydrogen phosphate in 500 parts of water at a temperature below 2°C; during this operation, the pH is kept constant by addition of aqueous sodium hydroxide solution. When the reaction has ended, a solution of 7.2 parts of propane-1,2-diamine in 90 parts of water is added dropwise such that the pH does not exceed a value of 7, and the pH is kept at a value of 7.

A solution of 7-[4-(2-aminopropylamino)-6-fluoro-1,3,5]-triazin-2-ylamino]-4-hydroxy-3-(2,5-disulfophenylazo)naphthalene-2-sulfonic acid (solution 1) is obtained.

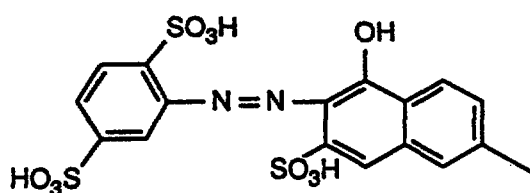
14 parts of cyanuric fluoride are added dropwise to a neutral solution of 45 parts of 7-amino-4-hydroxy-3-(4-methoxy-2-sulfophenylazo)naphthalene-2-sulfonic acid and 5 parts of disodium hydrogen phosphate in 500 parts of water at a temperature below 2°C; during this operation, the pH is kept constant by addition of aqueous sodium hydroxide solution.

A solution of 7-(4,6-difluoro-1,3,5-triazin-2-ylamino)-4-hydroxy-3-(4-methoxy-2-sulfophenylazo)naphthalene-2-sulfonic acid is obtained (solution 2).

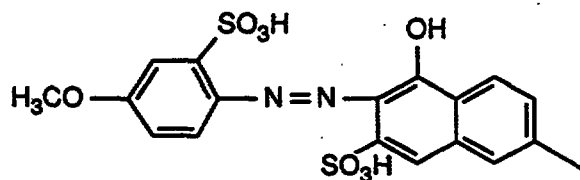
Solution 2 is added to solution 1 and the pH is increased to and kept at a value of 8.5. The mixture is allowed to warm to room temperature, the solution is freed from the salt by dialysis and the resulting product is evaporated. A dye which, in the form of the free acid, corresponds to the compound of the formula



in which A_1 is a radical of the formula



and A_2 is a radical of the formula



is obtained. The resulting dye dyes cotton in brilliant orange colour shades.

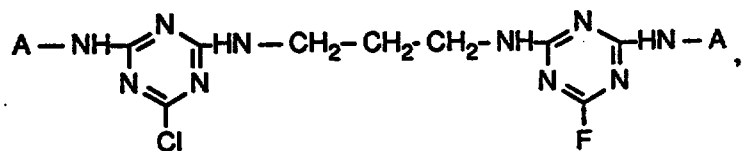
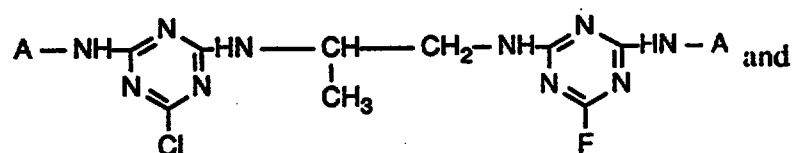
Example 4: 14 parts of cyanuric fluoride are added dropwise to a neutral solution of 27 parts of 4,6-diaminobenzene-1,3-disulfonic acid and 5 parts of disodium hydrogen phosphate in 270 parts of water at a temperature below 2°C; during this operation, the pH is kept constant by addition of aqueous sodium hydroxide solution. When the reaction has ended, a solution of 3.6 parts of 1-methylethane-1,2-diamine and 3.6 parts of propane-1,3-diamine in 65 parts of water is added dropwise such that the pH does not exceed a value of 7.5, the pH is kept constant at a value of 7.5 by addition of aqueous sodium hydroxide solution and the mixture is allowed to warm to room temperature.

A solution of 4-amino-6-[4-(3-aminopropylamino)-6-fluoro-1,3,5-triazin-2-ylamino]benzene-1,3-disulfonic acid and 4-amino-6-[4-(2-amino-1-methylethylamino)-6-fluoro-1,3,5-triazin-2-ylamino]benzene-1,3-disulfonic acid is obtained (solution 1).

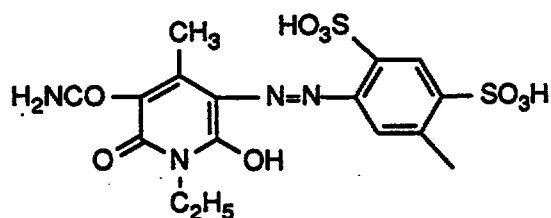
19 parts of cyanuric chloride are stirred vigorously in 50 parts of water, with the addition of a wetting agent and 5 parts of disodium hydrogen phosphate, at a temperature of 0°C. A neutral solution of 27 parts of 4,6-diaminobenzene-1,3-disulfonic acid in 220 parts of water is added dropwise to this mixture; during this operation, the pH is kept constant at a value of 4.5 by addition of aqueous sodium hydroxide solution.

A solution of 4-amino-6-[4,6-dichloro-1,3,5-triazin-2-ylamino]-benzene-1,3-disulfonic acid is obtained (solution 2).

Solution 2 is added to solution 1 and the pH is increased to a value of 8.5 and kept constant with aqueous sodium hydroxide solution. Towards the end of the reaction, the mixture is heated to a temperature of 40°C. When the reaction has ended, the mixture is cooled to a temperature of 0°C. 50 parts of 32% hydrochloric acid and 14 parts of sodium nitrite are then added and the mixture is stirred for 30 minutes. The suspension is added dropwise to a neutral solution of 40 parts of 1-ethyl-6-hydroxy-4-methyl-2-pyridonecarboxamide in 100 parts of water, during which the pH is kept constant at a value of 7 by addition of aqueous sodium hydroxide solution. When the coupling has ended, the resulting product is precipitated by addition of potassium chloride, filtered off with suction and dried. A dye mixture which comprises the dyes, shown in the form of the free acid, of the formulae

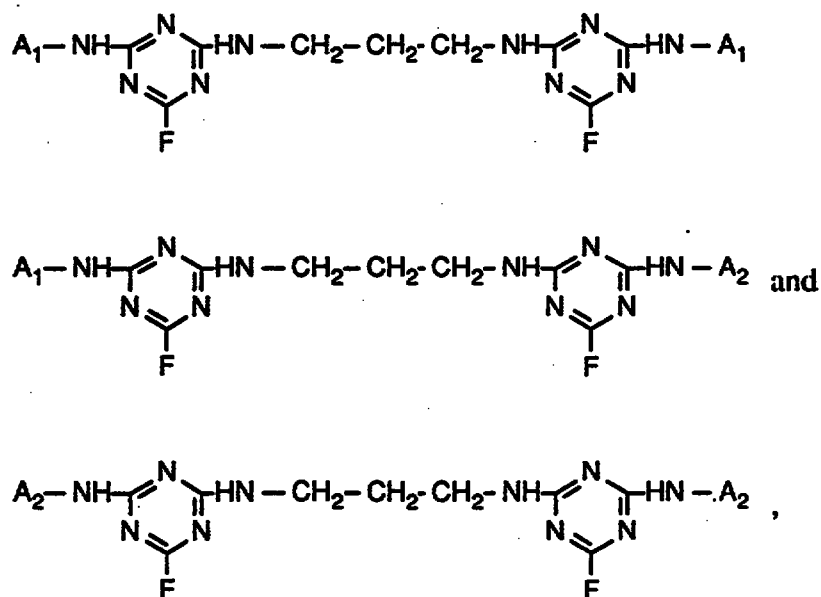


in which A is in each case a radical of the formula

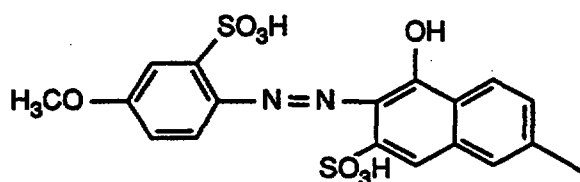


in a ratio of about 1:1 is obtained. The resulting dye mixture dyes cotton in brilliant yellow colour shades.

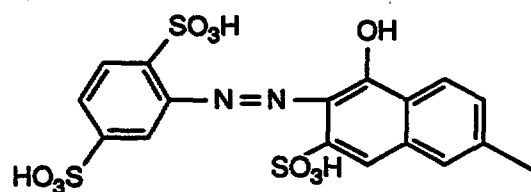
Example 5: 28 parts of cyanuric fluoride are added dropwise to a neutral solution of 50 parts of 7-amino-4-hydroxy-3-(2,5-disulfophenylazo)naphthalene-2-sulfonic acid and 45 parts of 7-amino-4-hydroxy-3-(4-methoxy-2-sulfophenylazo)naphthalene-2-sulfonic acid and 10 parts of sodium tripolyphosphate in 1000 parts of water at a temperature below 2°C; during this operation, the pH is kept at a value of 7 by addition of aqueous sodium hydroxide solution. When the reaction has ended, a solution of 7.4 parts of propane-1,3-diamine in 65 parts of water is added dropwise such that the pH does not exceed a value of 9.5, and the pH is then kept constant at a value of 9.5 by addition of aqueous sodium hydroxide solution. The mixture is allowed to warm to room temperature, the solution is freed from the salt by dialysis and the resulting product is evaporated. A dye mixture which comprises the dyes, shown in the form of the free acid, of the formulae



in which A₁ is in each case a radical of the formula

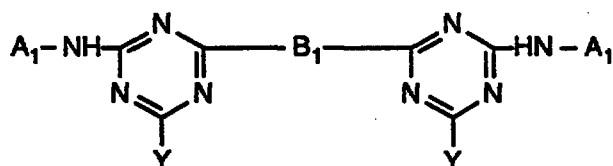


and A_2 is in each case a radical of the formula

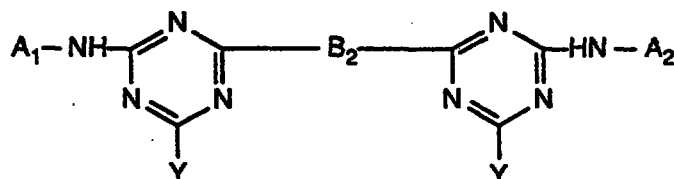


in a ratio of 0.5:1:0.5 is obtained. The resulting dye mixture dyes cotton in brilliant orange colour shades.

Examples 6 to 270: The dye mixtures shown in the following Table 1 can be obtained by mixing a dye of the formula

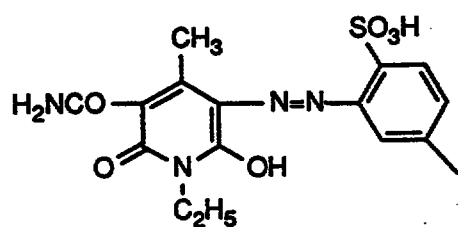


with a dye of the formula

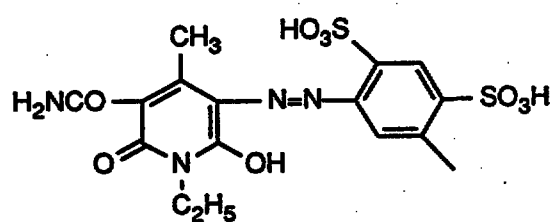


in which A_1 , A_2 , B_1 , B_2 and Y are as defined in Table 1.

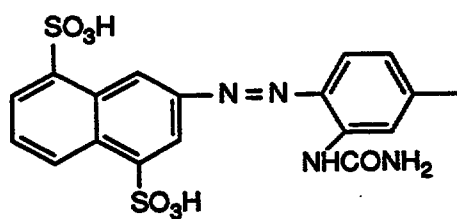
The radicals A_1 and A_2 are labelled with upper case letters A to Z5 and are as defined below in Table 1:



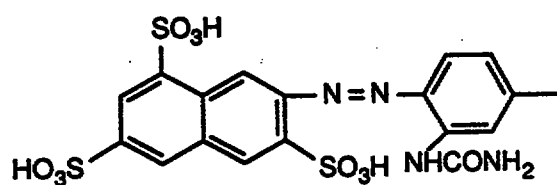
A



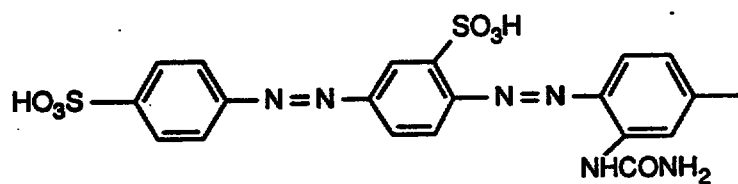
B



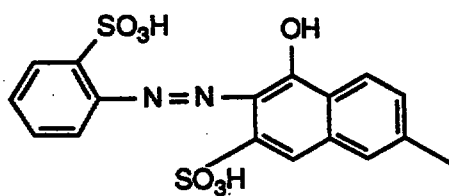
C



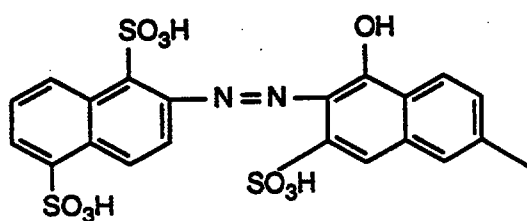
D



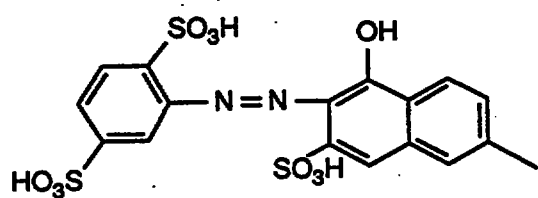
E



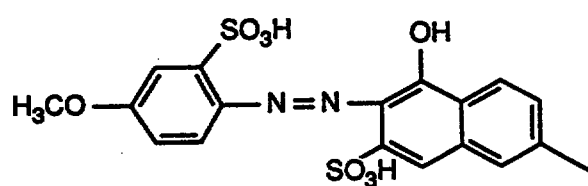
F



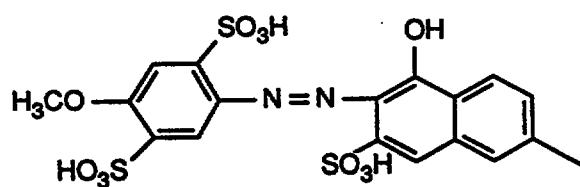
G



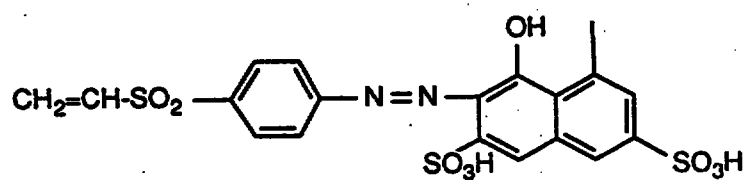
H



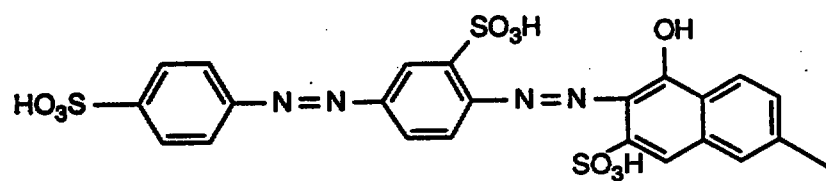
I



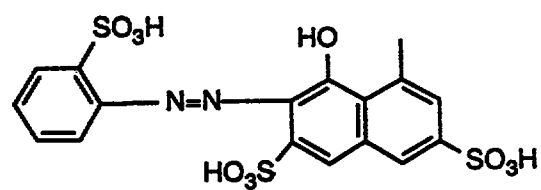
J



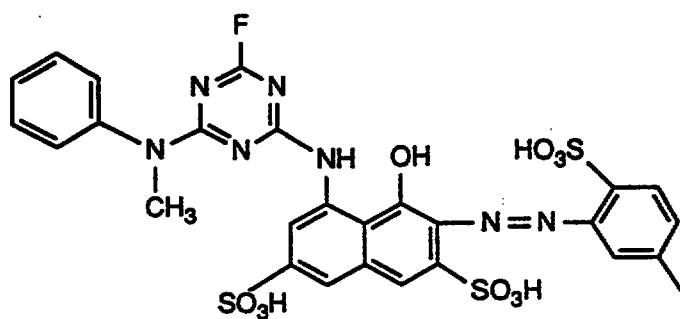
K



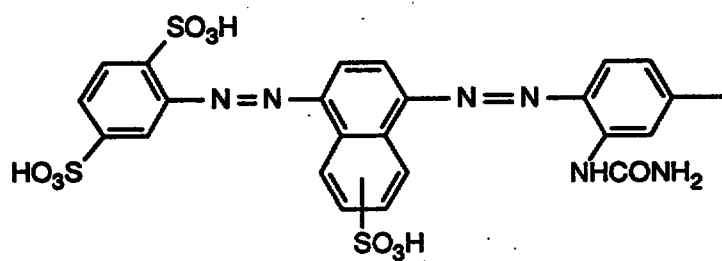
L



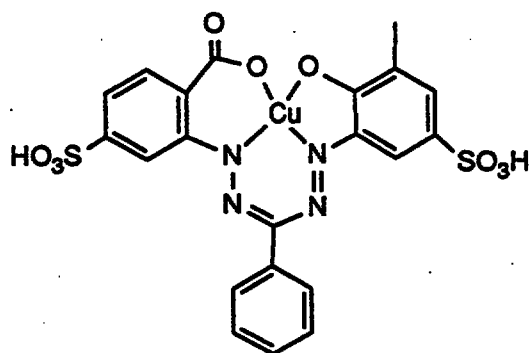
M



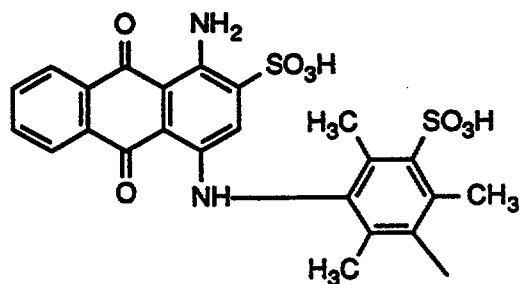
N



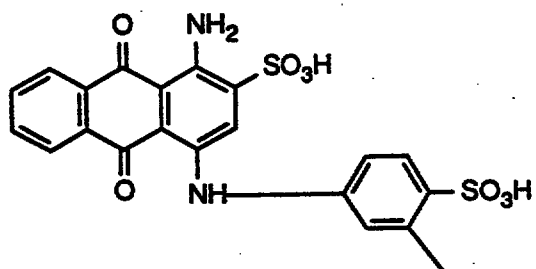
O



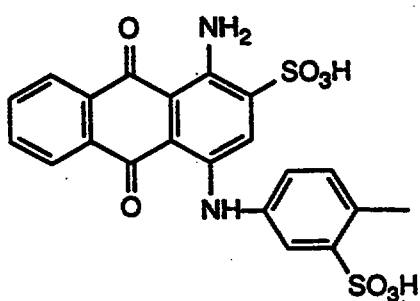
P



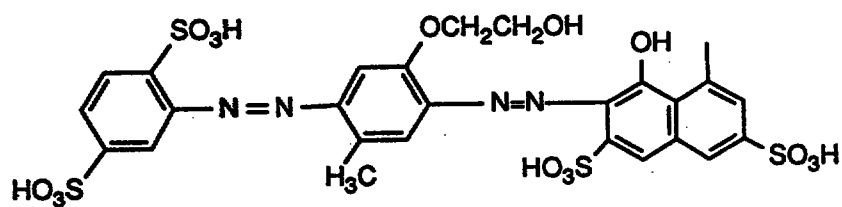
Q



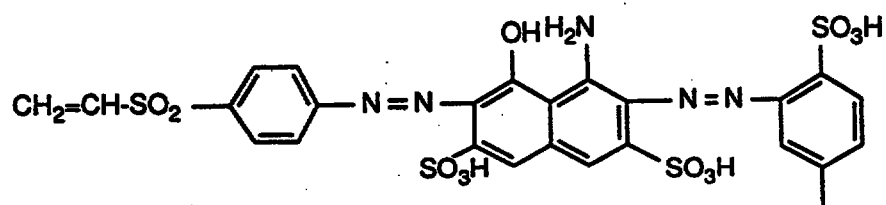
R



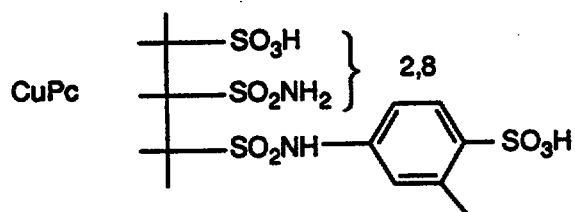
S



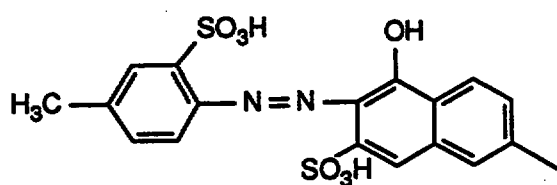
T



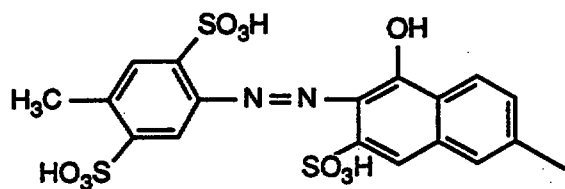
U



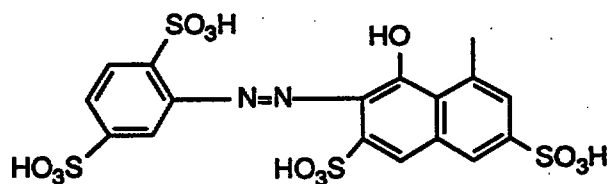
V



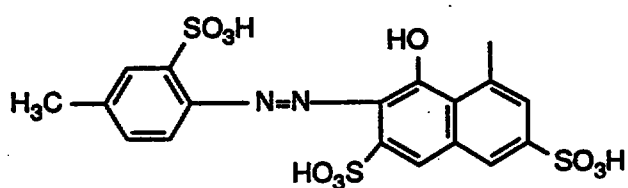
W



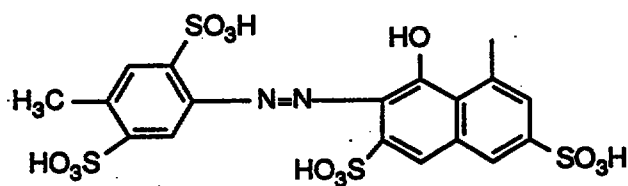
X



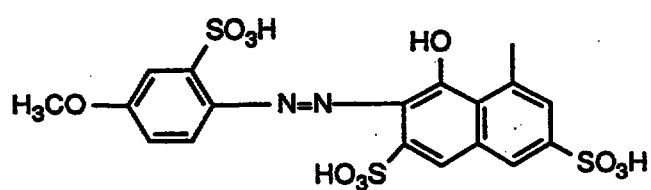
Y



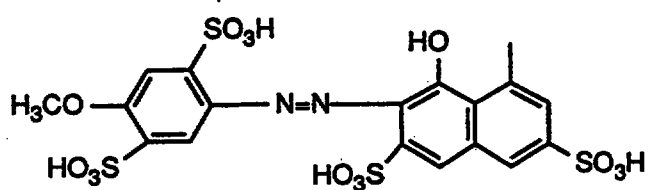
Z



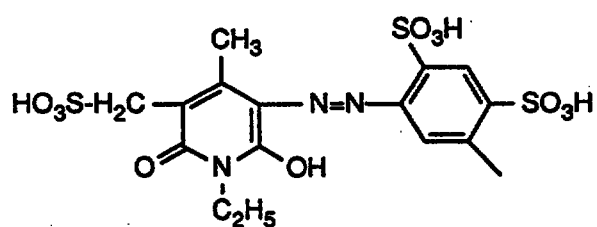
Z1



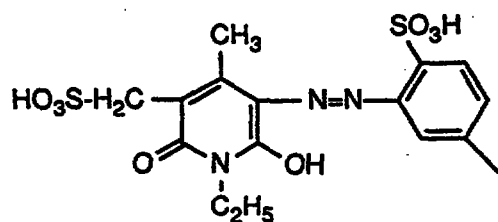
Z2



Z3

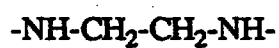


Z4

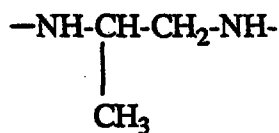


Z5

The radicals B_1 and B_2 are labelled with lower case letters a to l and are as defined below in Table 1:



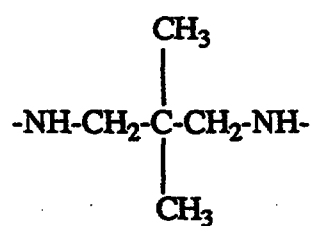
a



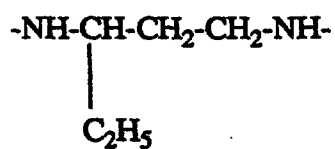
b



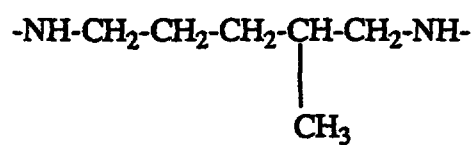
c



d



e



f



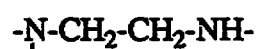
g



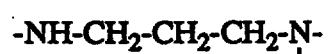
h



i



j



k



l

Table 1

Ex-ample	A ₁	A ₂	B ₁	B ₂	Y	Colour shade on cotton
6	A	B	a	c	Chlorine	greenish-tinged yellow
7	A	C	a	e	Chlorine	yellow
8	A	D	a	f	Chlorine	reddish-tinged yellow
9	A	P	a	g	Chlorine	green
10	A	Q	a	h	Chlorine	green
11	A	R	b	e	Chlorine	green
12	A	S	b	f	Chlorine	green
13	A	T	b	g	Chlorine	green
14	A	U	b	h	Chlorine	green
15	A	V	a	c	Chlorine	green
16	B	C	a	e	Chlorine	yellow
17	B	D	a	f	Chlorine	reddish-tinged yellow
18	B	P	a	g	Chlorine	green
19	B	Q	a	h	Chlorine	green
20	B	R	b	e	Chlorine	green
21	B	S	b	f	Chlorine	green
22	B	T	b	g	Chlorine	green
23	B	U	b	h	Chlorine	green
24	B	V	a	c	Chlorine	green
25	C	D	a	e	Chlorine	golden yellow
26	C	L	a	f	Chlorine	reddish-tinged orange
27	C	M	a	g	Chlorine	reddish-tinged orange
28	C	P	a	h	Chlorine	olive
29	C	Q	b	e	Chlorine	olive
30	C	R	b	f	Chlorine	olive
31	C	S	b	g	Chlorine	olive
32	C	Y	a	b	Chlorine	yellowish-tinged red
33	C	Z	a	c	Chlorine	yellowish-tinged red
34	C	Z1	a	d	Chlorine	yellowish-tinged red
35	C	Z2	a	e	Chlorine	red
36	C	Z3	a	i	Chlorine	red

37	D	P	b	h	Chlorine	olive
38	D	Q	a	c	Chlorine	olive
39	D	R	a	e	Chlorine	olive
40	D	S	a	f	Chlorine	olive
41	E	L	a	g	Chlorine	scarlet
42	E	O	a	h	Chlorine	brown
43	E	T	b	e	Chlorine	olive
44	E	U	b	f	Chlorine	olive
45	F	G	b	g	Chlorine	orange
46	F	H	b	h	Chlorine	orange
47	F	I	a	c	Chlorine	reddish-tinged orange
48	F	J	a	e	Chlorine	reddish-tinged orange
49	F	L	a	f	Chlorine	scarlet
50	F	M	a	g	Chlorine	scarlet
51	F	N	a	h	Chlorine	scarlet
52	F	W	a	j	Chlorine	scarlet
53	F	X	b	c	Chlorine	scarlet
54	F	Y	b	d	Chlorine	yellowish-tinged red
55	F	Z	b	i	Chlorine	yellowish-tinged red
56	F	Z1	b	k	Chlorine	yellowish-tinged red
57	F	Z2	b	l	Chlorine	red
58	F	Z3	c	d	Chlorine	red
59	G	H	b	e	Chlorine	scarlet
60	G	I	b	f	Chlorine	red-orange
61	G	J	b	g	Chlorine	red-orange
62	G	L	b	h	Chlorine	scarlet
63	G	M	a	c	Chlorine	scarlet
64	G	N	a	e	Chlorine	scarlet
65	G	W	c	i	Chlorine	scarlet
66	G	X	c	k	Chlorine	scarlet
67	G	Y	c	l	Chlorine	yellowish-tinged red
68	G	Z	a	b	Chlorine	yellowish-tinged red
69	G	Z1	b	a	Chlorine	yellowish-tinged red
70	G	Z2	c	a	Chlorine	red
71	G	Z3	d	a	Chlorine	red
72	H	I	a	f	Chlorine	red-orange

73	H	J	a	g	Chlorine	red-orange
74	H	L	a	h	Chlorine	scarlet
75	H	M	b	e	Chlorine	scarlet
76	H	N	b	f	Chlorine	scarlet
77	H	Y	e	a	Chlorine	yellowish-tinged red
78	H	Z	i	a	Chlorine	yellowish-tinged red
79	H	Z1	j	a	Chlorine	yellowish-tinged red
80	H	Z2	c	b	Chlorine	red
81	H	Z3	d	b	Chlorine	red
82	I	J	b	g	Chlorine	scarlet
83	I	L	b	h	Chlorine	red
84	I	M	a	c	Chlorine	red
85	I	N	a	e	Chlorine	red
86	I	Y	i	b	Chlorine	red
87	I	Z	k	b	Chlorine	red
88	I	Z1	l	b	Chlorine	red
89	I	Z2	d	c	Chlorine	red
90	I	Z3	i	c	Chlorine	red
91	J	L	a	f	Chlorine	red
92	J	M	a	g	Chlorine	red
93	J	N	a	h	Chlorine	red
94	J	Y	k	c	Chlorine	red
95	J	Z	l	c	Chlorine	red
96	J	Z1	a	b	Chlorine	red
97	J	Z2	a	c	Chlorine	red
98	J	Z3	a	d	Chlorine	red
99	K	L	b	e	Chlorine	red
100	K	M	b	f	Chlorine	red
101	K	N	b	g	Chlorine	red
102	K	P	b	h	Chlorine	violet
103	K	S	a	c	Chlorine	violet
104	K	U	a	e	Chlorine	claret
105	K	V	a	f	Chlorine	claret
106	K	Y	a	e	Chlorine	red
107	K	Z	a	i	Chlorine	red
108	K	Z1	a	j	Chlorine	red

109	K	Z2	b	a	Chlorine	red
110	K	Z3	b	c	Chlorine	red
111	L	M	a	g	Chlorine	red
112	L	N	a	h	Chlorine	red
113	L	P	b	e	Chlorine	violet
114	L	S	b	f	Chlorine	violet
115	L	U	b	g	Chlorine	violet
116	L	V	b	h	Chlorine	violet
117	L	Y	b	d	Chlorine	red
118	L	Z	d	i	Chlorine	red
119	L	Z1	b	k	Chlorine	red
120	L	Z2	b	l	Chlorine	red
121	L	Z3	b	d	Chlorine	red
122	M	N	a	c	Chlorine	red
123	M	P	a	e	Chlorine	violet
124	M	S	a	f	Chlorine	violet
125	M	U	a	g	Chlorine	violet
126	M	V	a	h	Chlorine	violet
127	N	P	b	e	Chlorine	violet
128	N	S	b	f	Chlorine	violet
129	N	U	b	g	Chlorine	violet
130	N	V	b	h	Chlorine	violet
131	P	Q	a	c	Chlorine	blue
132	P	R	a	e	Chlorine	blue
133	P	S	a	f	Chlorine	blue
134	P	T	a	g	Chlorine	blue
135	P	U	a	h	Chlorine	blue
136	Q	R	b	e	Chlorine	blue
137	Q	S	b	f	Chlorine	blue
138	Q	T	b	g	Chlorine	blue
139	Q	U	b	h	Chlorine	blue
140	R	S	a	c	Chlorine	blue
141	R	T	a	e	Chlorine	blue
142	R	U	a	f	Chlorine	blue
143	S	T	a	g	Chlorine	blue
144	S	U	a	h	Chlorine	blue

145	T	U	a	c	Chlorine	navy blue
146	Y	N	a	b	Chlorine	red
147	Z	N	b	c	Chlorine	red
148	Z1	N	a	d	Chlorine	red
149	Z2	N	c	d	Chlorine	bluish-tinged red
150	Z3	N	a	i	Chlorine	bluish-tinged red
151	Y	P	a	b	Chlorine	violet
152	Z	P	b	c	Chlorine	violet
153	Z1	P	a	d	Chlorine	violet
154	Z2	P	c	d	Chlorine	violet
155	Z3	P	a	i	Chlorine	violet
156	Y	S	a	b	Chlorine	violet
157	Z	S	b	c	Chlorine	violet
158	Z1	S	a	d	Chlorine	violet
159	Z2	S	c	d	Chlorine	violet
160	Z3	S	a	i	Chlorine	violet
161	Y	U	a	b	Chlorine	violet
162	Z	U	b	c	Chlorine	violet
163	Z1	U	a	d	Chlorine	violet
164	Z2	U	c	d	Chlorine	violet
165	Z3	U	a	i	Chlorine	violet
166	Y	V	a	b	Chlorine	brown
167	Z	V	b	c	Chlorine	brown
168	Z1	V	a	d	Chlorine	brown
169	Z2	V	c	d	Chlorine	brown
170	Z3	V	a	i	Chlorine	brown
171	W	M	b	a	Chlorine	yellowish-tinged red
172	W	Y	c	a	Chlorine	red-brown
173	W	Z	d	a	Chlorine	yellowish-tinged red
174	W	Z1	e	a	Chlorine	yellowish-tinged red
175	W	Z2	i	a	Chlorine	red
176	W	Z3	j	a	Chlorine	red
177	W	N	c	b	Chlorine	red
178	W	L	d	b	Chlorine	red
179	W	J	i	b	Chlorine	scarlet
180	W	I	k	b	Chlorine	scarlet

181	X	M	l	b	Chlorine	yellowish-tinged red
182	X	Y	d	c	Chlorine	scarlet
183	X	Z	i	c	Chlorine	yellowish-tinged red
184	X	Z1	k	c	Chlorine	yellowish-tinged red
185	X	Z2	l	c	Chlorine	red
186	X	Z3	a	b	Chlorine	red
187	X	N	a	c	Chlorine	red
188	X	L	a	d	Chlorine	red
189	X	J	a	e	Chlorine	scarlet
190	X	I	a	i	Chlorine	scarlet
191	A	A	a	c	Chlorine	yellow
192	B	B	a	c	Chlorine	yellow
193	C	C	a	c	Chlorine	golden yellow
194	D	D	a	c	Chlorine	golden yellow
195	E	E	a	c	Chlorine	orange
196	F	F	a	c	Chlorine	orange
197	G	G	a	c	Chlorine	orange
198	H	H	a	c	Chlorine	orange
199	I	I	a	c	Chlorine	scarlet
200	J	J	a	c	Chlorine	scarlet
201	K	K	a	c	Chlorine	red
202	L	L	a	c	Chlorine	red
203	M	M	a	c	Chlorine	red
204	N	N	a	c	Chlorine	red
205	O	O	a	c	Chlorine	brown
206	P	P	a	c	Chlorine	blue
207	Q	Q	a	c	Chlorine	blue
208	R	R	a	c	Chlorine	blue
209	S	S	a	c	Chlorine	blue
210	T	T	a	c	Chlorine	blue
211	U	U	a	c	Chlorine	navy blue
212	V	V	a	c	Chlorine	turquoise blue
213	W	W	a	c	Chlorine	scarlet
214	X	X	a	c	Chlorine	scarlet
215	Y	Y	a	c	Chlorine	red
216	Z	Z	a	c	Chlorine	red

217	Z1	Z1	a	c	Chlorine	red
218	Z2	Z2	a	c	Chlorine	bluish-tinged red
219	Z3	Z3	a	c	Chlorine	bluish-tinged red
220	A	A	a	b	Chlorine	yellow
221	B	B	a	d	Chlorine	gelb
222	C	C	a	e	Chlorine	golden yellow
223	D	D	a	i	Chlorine	golden yellow
224	E	E	a	j	Chlorine	orange
225	F	F	b	a	Chlorine	orange
226	G	G	b	c	Chlorine	orange
227	H	H	b	d	Chlorine	orange
228	I	I	b	i	Chlorine	scarlet
229	J	J	b	k	Chlorine	scarlet
230	K	K	b	l	Chlorine	red
231	L	L	c	a	Chlorine	red
232	M	M	c	b	Chlorine	red
233	N	N	c	d	Chlorine	red
234	O	O	c	i	Chlorine	brown
235	P	P	c	k	Chlorine	blue
236	Q	Q	c	l	Chlorine	blue
237	R	R	d	a	Chlorine	blue
238	S	S	d	b	Chlorine	blue
239	T	T	d	c	Chlorine	blue
240	U	U	e	a	Chlorine	navy blue
241	V	V	i	a	Chlorine	turquoise blue
242	W	W	i	b	Chlorine	scarlet
243	X	X	i	c	Chlorine	scarlet
244	Y	Y	j	a	Chlorine	red
245	Z	Z	k	b	Chlorine	red
246	Z1	Z1	k	c	Chlorine	red
247	Z2	Z2	l	b	Chlorine	bluish-tinged red
248	Z3	Z3	l	c	Chlorine	bluish-tinged red
249	Z4	B	a	c	Chlorine	greenish-tinged yellow
250	Z4	C	a	e	Chlorine	yellow
251	Z4	D	a	f	Chlorine	reddish-tinged yellow
252	Z4	P	a	g	Chlorine	green

253	Z4	Q	a	h	Chlorine	green
254	Z4	R	b	e	Chlorine	green
255	Z4	S	b	f	Chlorine	green
256	Z4	T	b	g	Chlorine	green
257	Z4	U	b	h	Chlorine	green
258	Z4	V	a	c	Chlorine	green
259	Z4	Z4	a	c	Chlorine	yellow
260	Z5	B	a	c	Chlorine	greenish-tinged yellow
261	Z5	C	a	e	Chlorine	yellow
262	Z5	D	a	f	Chlorine	reddish-tinged yellow
263	Z5	P	a	g	Chlorine	green
264	Z5	Q	a	h	Chlorine	green
265	Z5	R	b	e	Chlorine	green
266	Z5	S	b	f	Chlorine	green
267	Z5	T	b	g	Chlorine	green
268	Z5	U	b	h	Chlorine	green
269	Z5	V	a	c	Chlorine	green
270	Z5	Z5	a	c	Chlorine	yellow

Corresponding dye mixtures in which Y is fluorine instead of chlorine can be obtained in a manner analogous to Examples 6 to 270.

The dye mixtures shown in Table 1 in which the individual dyes differ only in respect of the meanings of the bridge members B₁ and B₂ can also be obtained in a manner analogous to Example 4.

The individual dyes of the dye mixtures shown in Table 1 can be obtained analogously to Example 3.

Dyeing instructions

2 parts of dye mixture obtained according to Example 1 are dissolved in 400 parts of water; 1500 parts of a solution which contains 53 g of sodium chloride per litre are added. 100 parts of cotton fabric are introduced into this dye bath at 40°C. After 45 minutes, 100 parts of a solution which contains 16 g of sodium hydroxide and 20 g of calcined sodium carbonate per litre are added. The temperature of the dye bath is kept at 40°C for a further

45 minutes. Thereafter, the dyed goods are rinsed, soaped at the boil with a nonionic detergent for a quarter of an hour, rinsed again and dried.

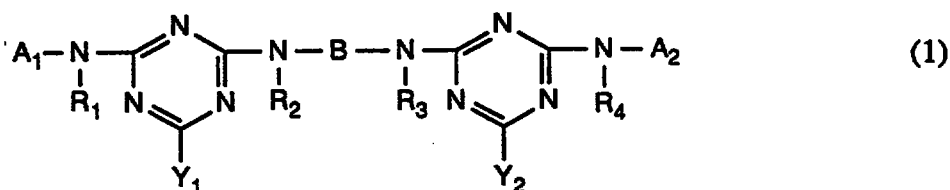
Printing instructions

3 parts of the dye mixture obtained according to Example 2 are sprinkled, with rapid stirring, into 100 parts of a stock thickener comprising 50 parts of 5% sodium alginate thickener, 27.8 parts of water, 20 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 1.2 parts of sodium bicarbonate. A cotton fabric is printed with the printing paste thus obtained and dried and the resulting printed material is steamed in saturated steam at 102°C for 2 minutes. The printed fabric is then rinsed, soaped at the boil, if appropriate, and rinsed again, and then dried.



Patent claims

1. A dye mixture which comprises at least two reactive dyes of the formula



in which A₁ and A₂ are the radical of a monoazo, polyazo, metal complex azo, anthraquinone, phthalocyanine, formazan, azomethine, dioxazine, phenazine, stilbene, triphenylmethane, xanthene, thioxanthone, nitroaryl, naphthoquinone, pyrenequinone or perylenetetracarbinide dye,

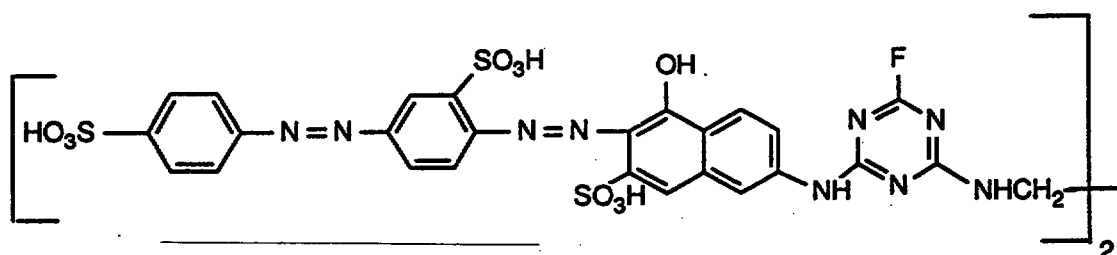
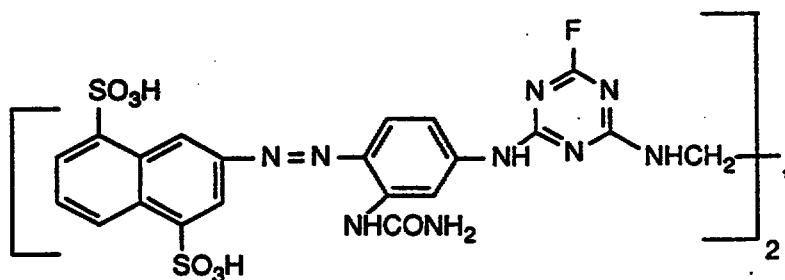
R₁, R₂, R₃ and R₄ independently of one another are hydrogen or substituted or unsubstituted C₁-C₄alkyl,

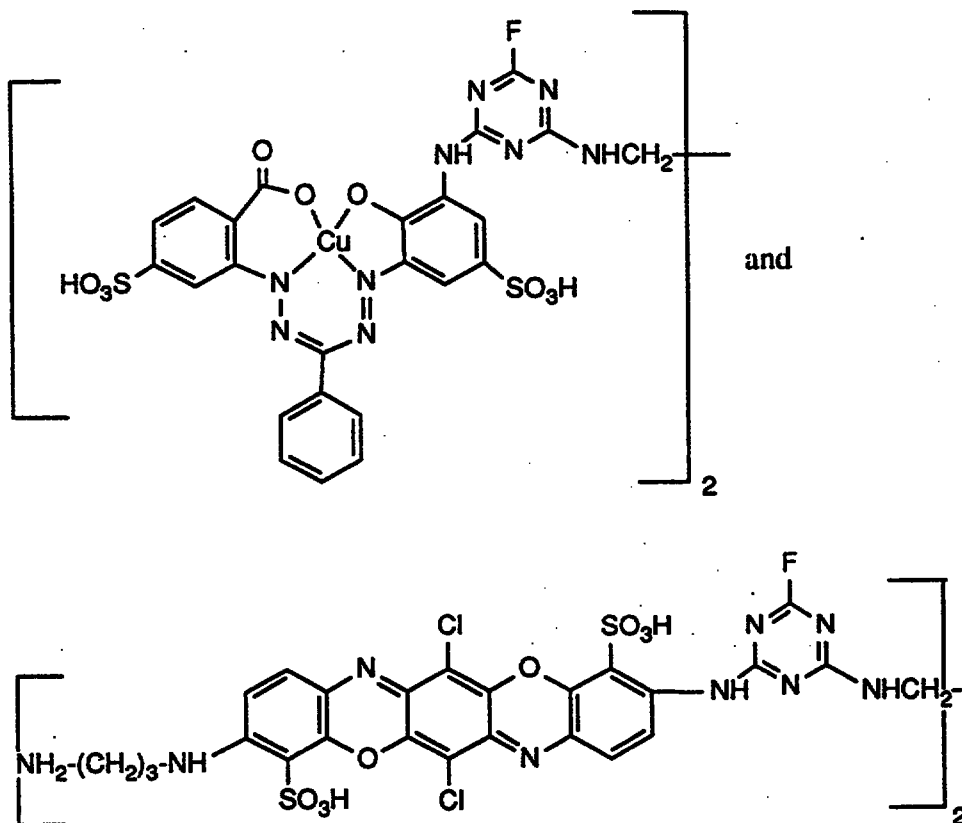
B is an aliphatic bridge member,

Y₁ and Y₂ independently of one another are halogen or carboxypyridinium,

and in at least one of the reactive dyes of the formula (1) the radicals A₁ and A₂ have the same meanings,

with the proviso that the dye mixture does not comprise two or more of the dyestuffs of the formulae





2. A dye mixture according to claim 1,
in which Y_1 and Y_2 independently of one another are fluorine or chlorine.
3. A dye mixture according to claim 1 or 2,
in which R_1 , R_2 , R_3 and R_4 independently of one another are hydrogen, methyl or ethyl, in particular hydrogen.
4. A dye mixture according to any one of claims 1 to 3,
in which B is a C_2 - C_{12} alkylene radical which can be interrupted by 1, 2 or 3 members from the group comprising -NH-, -N(CH₃)- and -O- and is unsubstituted or substituted by hydroxyl, sulfo or sulfato.
5. A dye mixture according to any one of claims 1 to 4,
in which B is a C_2 - C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals.

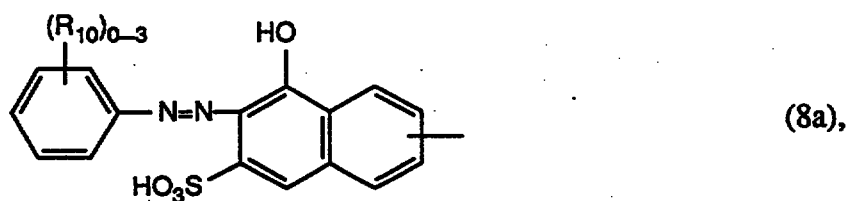




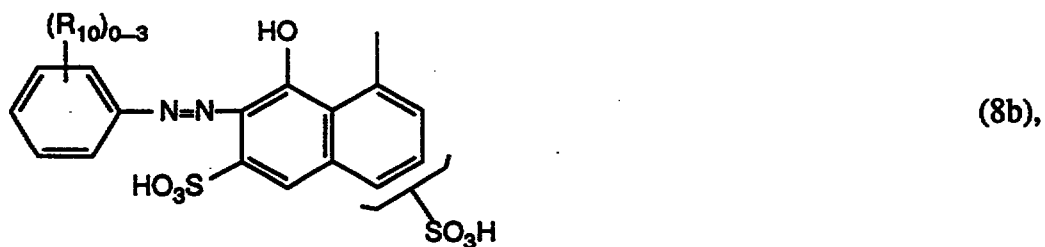
6. A dye mixture according to any one of claims 1 to 5,
in which B is a C₂-C₆alkylene radical.

7. A dye mixture according to any one of claims 1 to 6,
in which A₁ and A₂ are the radical of a monoazo, disazo, anthraquinone, dioxazine,
phthalocyanine or formazan dye.

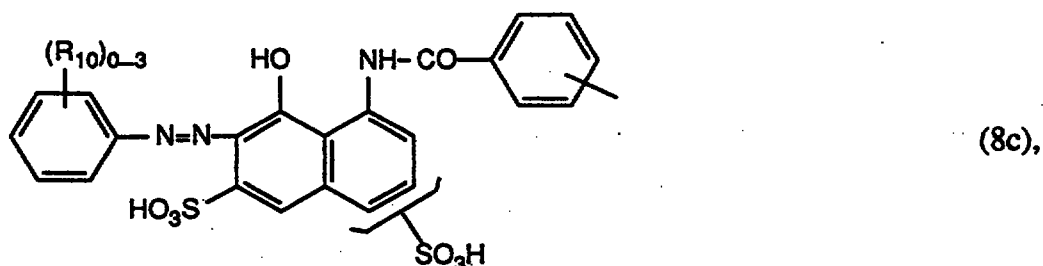
8. A dye mixture according to any one of claims 1 to 7,
in which A₁ and A₂ independently of one another are radicals of the formulae



in which R₁₀ is 0 to 3 identical or different substituents from the group comprising
C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl and sulfo,

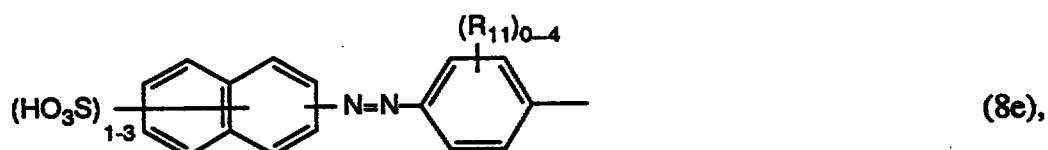
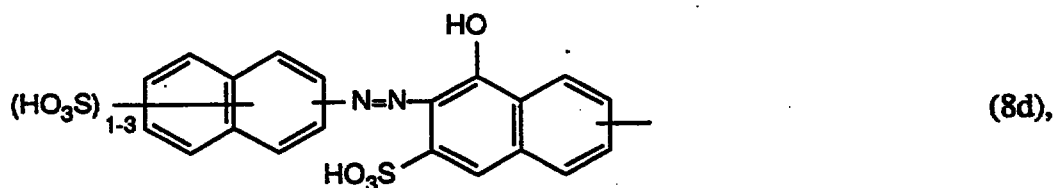


in which R₁₀ is 0 to 3 identical or different substituents from the group comprising
C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl and sulfo,

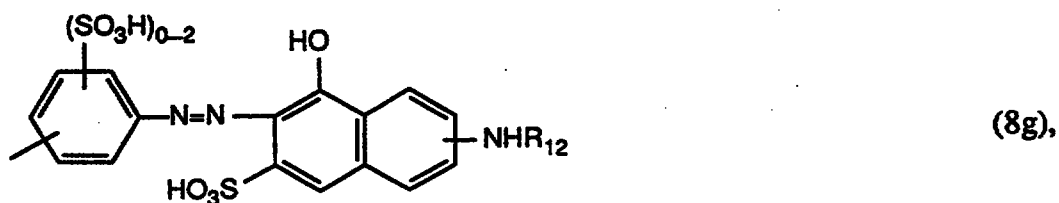
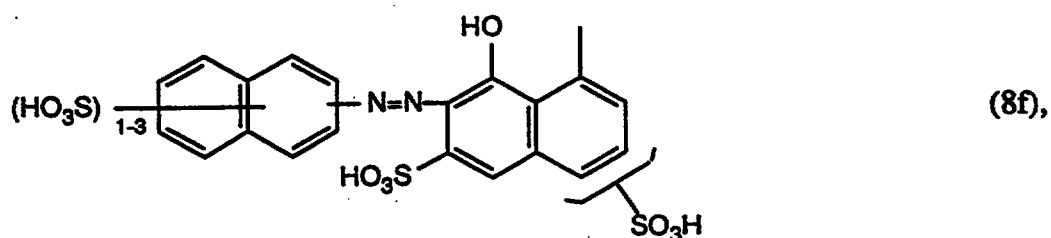




in which R_{10} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,

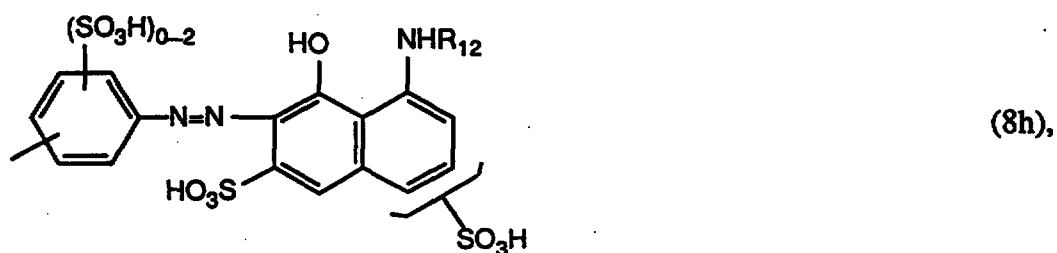


in which R_{11} is 0 to 4 identical or different substituents from the group comprising halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, amino, acetylamino, ureido, hydroxyl, carboxyl, sulfomethyl and sulfo,

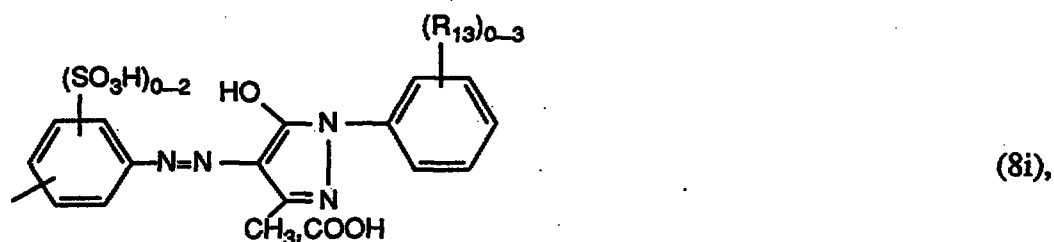


in which R_{12} is C_1 - C_4 alkanoyl, benzoyl or a halotriazinyl radical which may be further substituted,

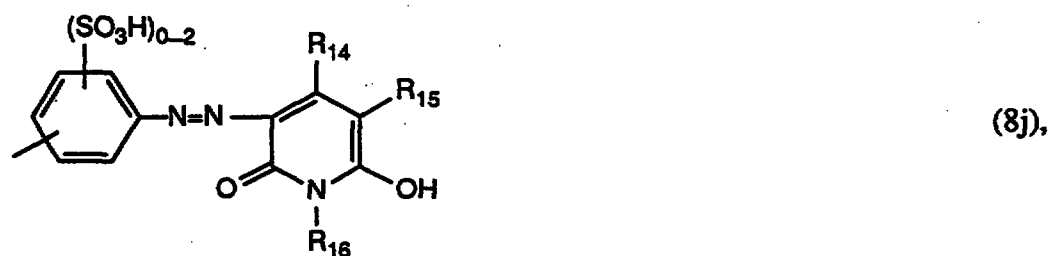




in which R_{12} is C_1 - C_4 alkanoyl, benzoyl or a halotriazinyl radical which may be further substituted,

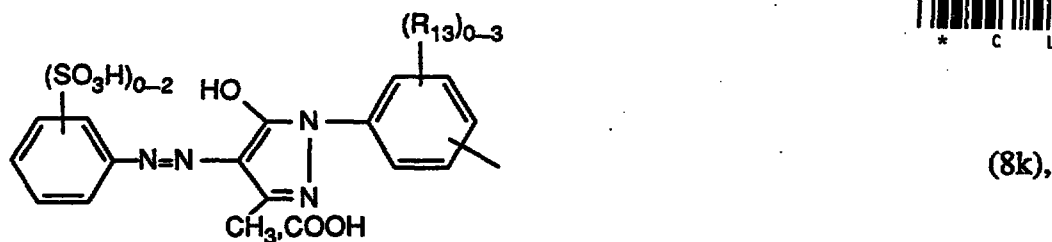


in which R_{13} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,



in which R_{14} and R_{16} independently of one another are hydrogen, C_1 - C_4 alkyl or phenyl, and

R_{15} is hydrogen, cyano, carbamoyl or sulfomethyl,

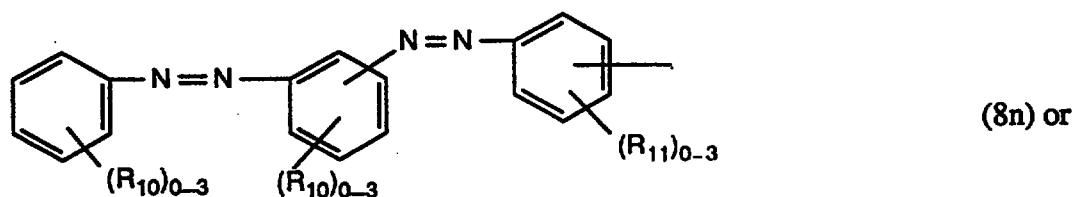
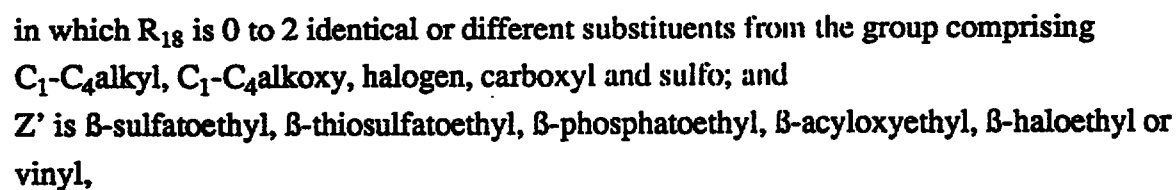
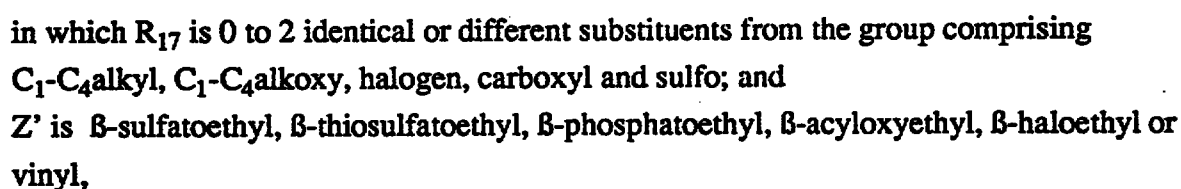


in which R_{13} is 0 to 3 identical or different substituents from the group comprising



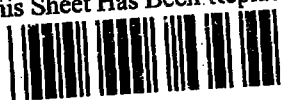


C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxyl and sulfo,

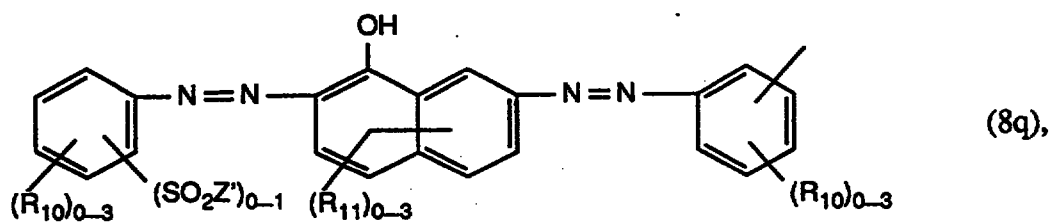
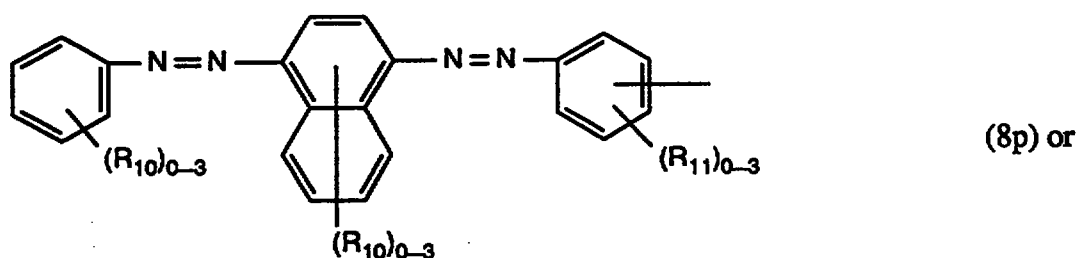
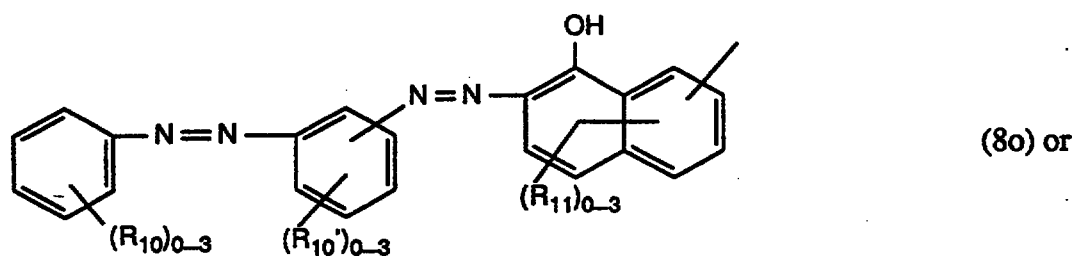


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in which R_{10} is 0 to 3 identical or different substituents from the group comprising C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl and sulfo,

R_{10}' is as defined for R_{10} and can additionally be C_1 - C_4 hydroxyalkoxy or C_1 - C_4 sulfatoalkoxy,

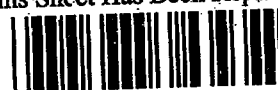
R_{11} is 0 to 3 identical or different substituents from the group comprising halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, amino, acetylamino, ureido, hydroxyl, carboxyl, sulfomethyl and sulfo and

Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -haloethyl or vinyl,

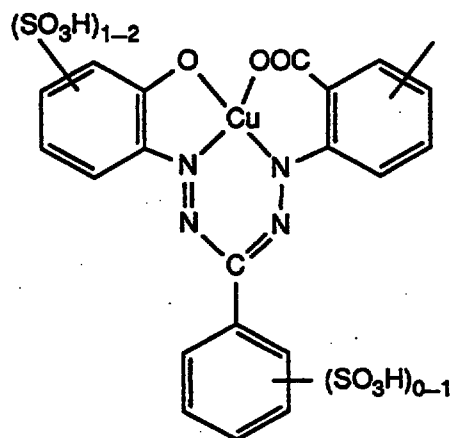


* C L M S *

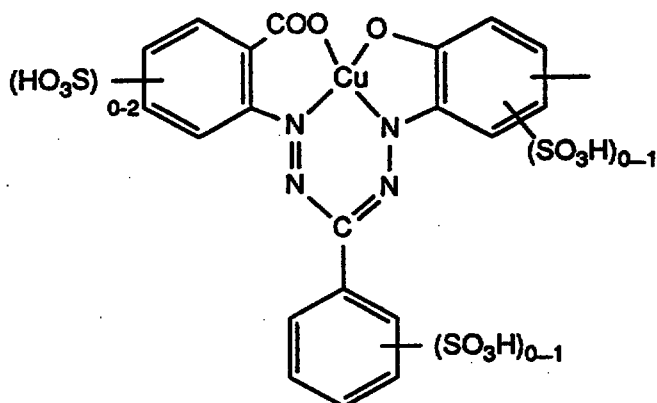
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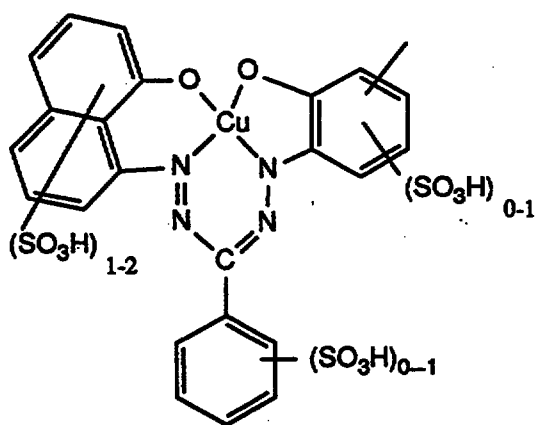
- 58 -



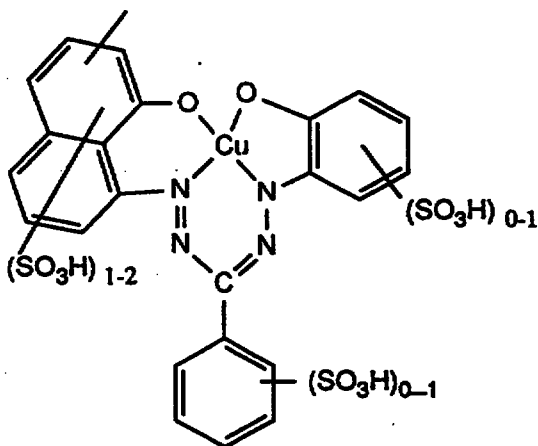
(8r)



(8s) or

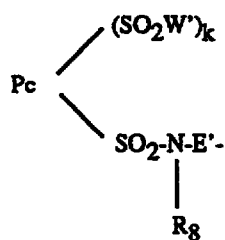


(8t)



(8u),

in which the benzene nuclei contain no further substituents or are further substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylsulfonyl, halogen or carboxyl,



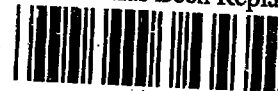
(9),

in which Pc is the radical of a metal phthalocyanine, in particular the radical of a copper phthalocyanine or nickel phthalocyanine;

W' is -OH and/or -NR₉R₉';



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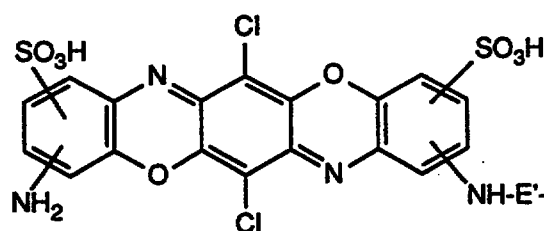


R_9 and R_9' independently of one another are hydrogen or C_1 - C_4 alkyl which is unsubstituted or substituted by hydroxyl or sulfo;

R_8 is hydrogen or C_1 - C_4 alkyl;

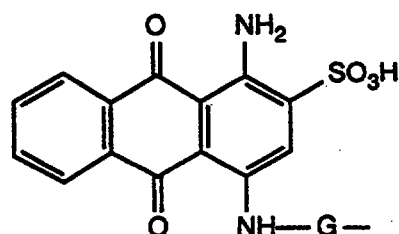
E' is a phenylene radical which is unsubstituted or substituted by C_1 - C_4 alkyl, halogen, carboxyl or sulfo, or a C_2 - C_6 alkylene radical; and

k is 1 to 3,



(10),

in which E' is a phenylene radical which is unsubstituted or substituted by C_1 - C_4 alkyl, halogen, carboxyl or sulfo, or a C_2 - C_6 alkylene radical, and the outer benzene rings in the formula (10) contain no further substituents or are further substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, acetamino, nitro, halogen, carboxyl, sulfo or $-SO_2-Z'$, in which Z' is β -sulfatoethyl, β -thiosulfatoethyl, β -phosphatoethyl, β -acyloxyethyl, β -haloethyl or vinyl, or



(11),

in which G is a phenylene, cyclohexylene, phenylenemethylene or C_2 - C_6 alkylene radical, and in which the anthraquinone nucleus can be substituted by a further sulfo group and a phenyl radical G is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxyl or sulfo.

9. A dye mixture according to any one of claims 1 to 8,

in which the radicals A_1 and A_2 in each case contain at least one sulfo group.

10. A dye mixture according to any one of claims 1 to 9, which contains at least two reactive dyes of the formula (1) in which A_1 and A_2 in each case have identical meanings.



11. A dye mixture according to any one of claims 1 to 10, which comprises at least two reactive dyes of the formula (1) which differ only in respect of the meaning of the bridge member B or the meaning of the radicals R_2 and R_3 .

12. A dye mixture according to claim 11, which comprises at least two reactive dyes of the formula (1) which differ only in respect of the meaning of the bridge member B.

13. A dye mixture according to any one of claims 1 to 10, which comprises at least two reactive dyes of the formula (1) in which

R_1 , R_2 , R_3 and R_4 are hydrogen,

B is a C_2 - C_{12} alkylene radical, which can be interrupted by 1, 2 or 3 -O- radicals,

and the reactive dyes of the formula (1) differ only in respect of the meaning of the bridge member B.

14. A process for the preparation of a dye mixture according to claim 1, which comprises reacting radicals of the formulae



or corresponding dye intermediates, at least one halotriazine compound and at least one diamine of the formula



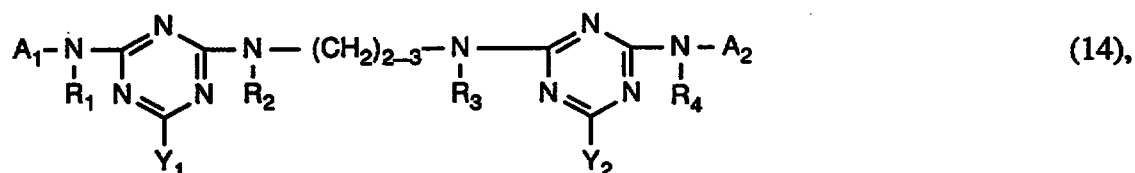
in which A_1 , A_2 , R_1 , R_2 , R_3 , R_4 and B are as defined in claim 1, with one another in any sequence, or, if dye intermediates are used, converting the resulting intermediates into the desired dyes, and if appropriate then carrying out a further conversion reaction, where at least two radicals of the formulae (12a), (12b) or (13) which differ from one another or at least two halotriazine compounds which differ from one another are used.

15. The use of a dye mixture according to any one of claims 1 to 13 or of a dye mixture obtained according to claim 14 for dyeing or printing fibre materials containing hydroxyl

groups or containing nitrogen.

16. The use according to claim 15 for dyeing or printing cellulosic fibre materials or natural or synthetic polyamide fibre materials.

17. A reactive dye of the formula



in which A₁ and A₂ are the radical of a monoazo, polyazo, metal complex azo, anthraquinone, phthalocyanine, formazan, azomethine, dioxazine, phenazine, stilbene, triphenylmethane, xanthene, thioxanthone, nitroaryl, naphthoquinone, pyrenequinone or perylenetetracarbibimide dye,

R₁, R₂, R₃ and R₄ independently of one another are hydrogen, methyl or ethyl, Y₁ and Y₂ independently of one another are halogen or carboxypyridinium and at least one of the radicals R₂ and R₃ is methyl or ethyl.

18. The use of a reactive dye of the formula (14) according to claim 17 for dyeing or printing fibre materials containing hydroxyl groups or containing nitrogen.

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