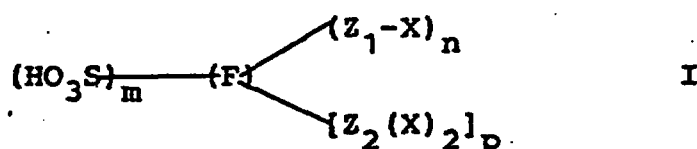


1 -

**BASIC OR CATIONIC SULPHONIC ACID
GROUP-CONTAINING AZO COMPOUNDS**

The present invention relates to basic or cationic, sulphonic acid group-containing azo compounds.

More particularly, the present invention provides compounds of formula I,



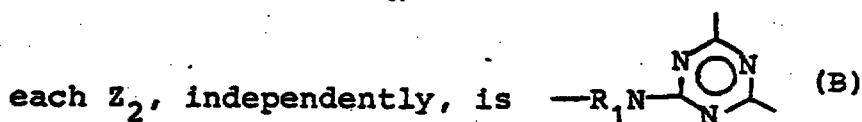
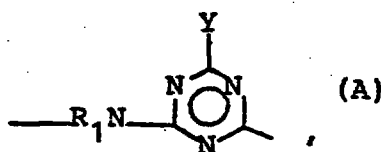
in which F is the residue of a mono or diazo compound in 1:1 metal complex form or of a tris-, diazoazoxy- or tetra-kisazo compound in metal free or in 1:1 metal complex form,

m is 1, 2 or 3,

n is 0, 1, 2, 3 or 4,

p is 0, 1, 2, 3 or 4,

each Z₁, independently, is -CO-, -SO₂- or



each R_1 , independently, is hydrogen or C_{1-4} alkyl,

each Y , independently, is Cl , OH , NH_2 , an aliphatic, cycloaliphatic or aromatic amine radical or a heterocyclic saturated amine in which the nitrogen atom is part of the heterocycle,

each X , independently, is $\text{---NR}_2\text{---Q---NR}_3\text{R}_4$

or $\text{---NR}_2\text{---Q---NR}_5^{\oplus}\text{R}_6\text{R}_7$,

each Q , independently, is a linear or branched chain C_{2-6} alkylene or $\text{---NHCOCH}_2\text{---}$,

each R_2 , independently, is hydrogen or C_{1-4} alkyl,

each R_3 and R_4 , independently, is hydrogen; C_{1-6} alkyl; cyano- or hydroxy- C_{2-6} alkyl in which the substituent is in other than 1-position; phenyl- C_{1-3} alkyl in which the phenyl nucleus is optionally substituted by a total of up to 3 substituents selected from chlorine, C_{1-4} alkyl and C_{1-4} alkoxy; C_{5-6} cycloalkyl optionally substituted

by up to three C_{1-4} alkyl groups or R_3 and R_4 together with the nitrogen atom to which they are bound form a 5- or 6-membered saturated or unsaturated heterocyclic ring which optionally contains a further heteroatom,

either, each R_5 and R_6 , independently, has one of the significances given above for R_3 and R_4 with the exception of hydrogen, and each R_7 , independently, is C_{1-4} alkyl or benzyl, or R_5 , R_6 and R_7 , together with the nitrogen atom to which they are bound form a pyridinium cation, which is optionally substituted by 1 or 2 methyl groups, with the proviso that

$$n + 2p \geq m + 1,$$

or an external salt thereof.

In the compounds of formula I the m sulfo groups may react with the X groups to form internal salts of the type $(XH)^{\oplus} SO_3^{\ominus}$ or $X^{\oplus} SO_3^{\ominus}$. The compounds of formula I have more basic and/or cationic groups than sulphonic acid groups, and the additional basic and/or cationic groups may form external salts to render the compounds water soluble.

The diazo components of the compounds of the invention may be of the aromatic carbocyclic or heterocyclic series, such as of the aniline, aminonaphthalene, aminodibenzofuran or benzothiazole series. Preferred diazo components are those of the aniline series.

The coupling components may be any of those standard for azo dyestuffs. Preferably the end coupling component is one of the naphthalene series which optionally contains 1 or 2 sulpho groups; more preferably such end coupling components are 1-naphthol-3- or -4-sulphonic acid, 5-, 6-, 7- or 8-amino-1-naphthol-3-sulphonic acid or 8-amino-1-naphthol-3,6-disulphonic acid and especially 6-amino-1-naphthol-3-sulphonic acid and derivatives thereof.

It will be appreciated that the diazo and coupling components optionally bear metallizable groups such as -OH, -OCH₃, -NH₂ and -COOH etc. ortho to the azo group. Preferred metallizable groups are -OH and -OCH₃.

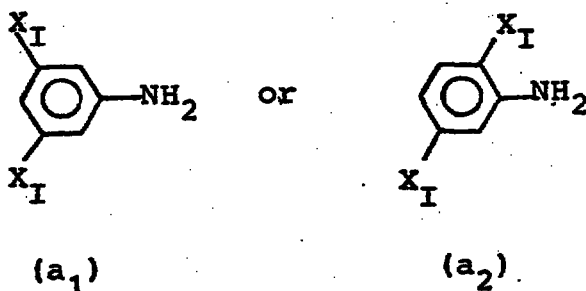
The polyazo chromophores of the compounds of the invention may be those in which the coupling components or diazo components of two mono and/or disazo compounds are directly bound to each other or are bound via a bridge member. In such compounds the components which are directly linked or linked through a bridge member are preferably of the phenylene, naphthylene or tetrahydro-

naphthylene series, most preferably of the 1,4-phenylene series.

Representative metal complexes are copper, nickel and iron, with 1:1 copper complexes being most preferred especially when the copper is bound to an oxygen atom.

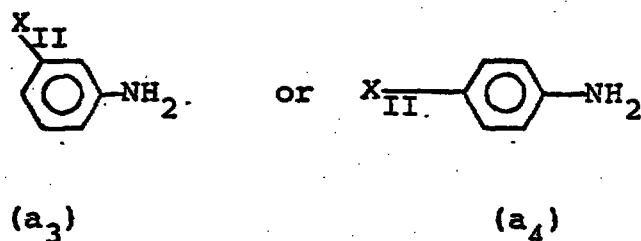
The sulpho groups may be on any of the components or even bridge members, preferably 1 or 2 sulpho groups are located on coupling components.

The groups $-Z_1-X$ and $Z_2(X)_2$ may be bound to the diazo components and/or middle components when present, and/or end coupling components. The group $-Z_1'-X$ herein-after referred to as X_I where $-Z_1'$ is $-CO-$ or $-SO_2-$ is preferably located on a diazo component. For diazo components of the aniline series the following positions may be given: -



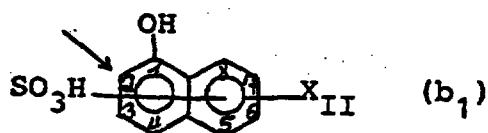
wherein when two groups X_I are present they are preferably the same and the diazo component bears no further substituent, where a diazo component of the aniline series bears a single group X_I such is preferably located meta or para to the amino group.

The groups $-Z_1-X$ or $Z_2-(X)_2$ hereinafter referred to as X_{II} where $-Z_1$ is a group of formula (A) may be located on diazo components, middle components and/or end coupling components with compounds in which an end coupling component bears such a group being especially preferred. For diazo components of the aniline series the following position may be given



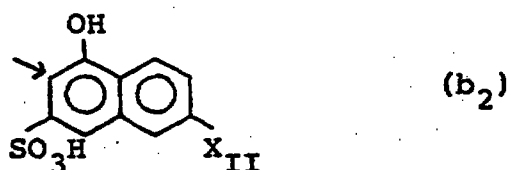
In (a₃) when a further substituent is present it is preferably located and in the 2,4 or 6-position and when 2 further substituents are present they are preferably located in the 2,5-position. In (a₄) preferably only 1 further substituent is present which is located in the 2- or 3-position.

If the end coupling component bears a group X_{II} it is preferably of formula



in which either the sulpho group is in the 3-position and X_{II} is in the 5-, 6-, 7- or 8-position or the sulpho group in the 5-position and X_{II} in the 8-position. More

preferably such end component is of formula



If the groups X_I or X_{II} are on middle components such middle component is preferably of the aniline series, preferably such group of the aniline series bears X_{II} in a position meta to the amino group or may bear a group $\text{-NHCO(CH}_2\text{)}_{1-3}\text{N(C}_{1-4}\text{alkyl)}_2$ or $\text{-NHCO(CH}_2\text{)}_{1-3}\text{N}^{\oplus}(\text{C}_{1-4}\text{alkyl)}_3\text{A}^{\ominus}$ where A[⊖] is an anion.

Any alkylene as Q is linear or branched, preferably any alkylene as Q is straight chain and most preferably is ethylene or propylene.

Any alkyl as R₁ and/or R₂ is preferably methyl.

Preferably R₁ and R₂ are R₁' and R₂' where each of R₁' and R₂', independently, is hydrogen or methyl with hydrogen being most preferred.

Preferably R₃ and R₄ are identical. Any C₁₋₆-alkyl group is straight chain or branched. Any alkyl is preferably C₁₋₄alkyl, with methyl and ethyl being most preferred. Any cyano or hydroxy substituted alkyl is preferably cyano- or hydroxy- ethyl or -propyl.

Any phenylalkyl as R₃ and/or R₄ is preferably benzyl in which the phenyl nucleus is preferably unsubstituted. Any cycloalkyl is preferably cyclohexyl and any alkyl substituent on cycloalkyl is preferably methyl.

When R_3 and R_4 together with the nitrogen atom form a heterocyclic ring they preferably form a pyrrolidine, piperidine or morpholine ring.

R_3 and R_4 are preferably R_3' and R_4' , where each of R_3' and R_4' , independently, is hydrogen, linear or branched C_{1-6} alkyl, linear 2- or 3-hydroxyethyl or -propyl, benzyl or together with the N-atom they form a pyrrolidine, piperidine or morpholine ring. More preferably each of R_3 and R_4 is R_3'' and R_4'' , where

R_3'' and R_4'' , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring; most preferably R_3 and R_4 are R_3''' and R_4''' , where each of R_3''' and R_4''' , independently, is methyl or ethyl.

The groups R_5 and R_6 are preferably the same. The preferred significances for R_3 and R_4 also apply to R_5 and R_6 with the exception that R_5 and R_6 are other than hydrogen.

Any alkyl as R_7 is preferably methyl or ethyl, especially methyl.

Preferably, either R_5 and R_6 , independently, have one of the preferred significances of R_3 and R_4 i.e. R_3' , R_4' , R_3'' , R_4'' or R_3''' and R_4''' and R_7 is R_7' , where R_7' is methyl, ethyl or benzyl, more preferably methyl; or R_5 , R_6 and R_7 together with the N-atom signify a

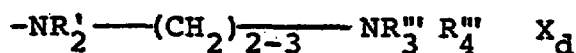
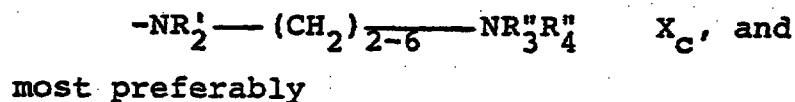
pyridinium cation.

Belonging to the cation $-NR_2-Q-NR_5^+R_6R_7$, is either a SO_3^- already present in the molecule or any non-chromophoric anion A^- which may be organic or inorganic. The nature of the anion A^- is not critical. Examples of representative anions A^- are chloride, bromide, iodide, lactate, acetate, formate, citrate, methylsulphate, ethylsulphate and hydrogensulphate.

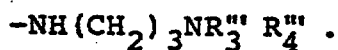
Preferred basic groups as X are



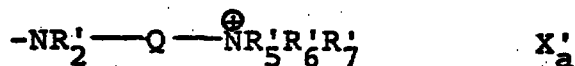
where Q' is linear or branched C_{2-6} alkylene, even more preferably



especially when R_2^1 is hydrogen and more especially

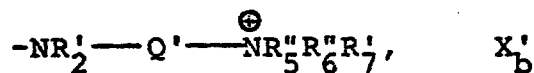


For the cationic group $-NR_2-Q-NR_5^+R_6R_7$ the groups X_a' to X_d' are preferred i.e.



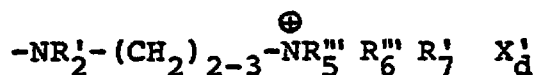
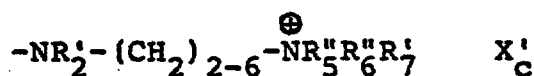
where R_5^1 and R_6^1 have one of the significances of R_3^1

and R_4' , respectively



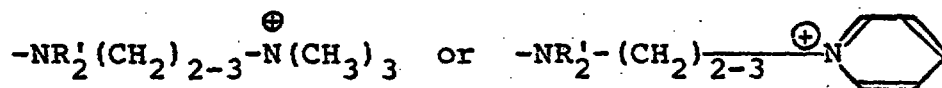
where Q' is as defined above, and

R_5'' and R_6'' have one of the significances of R_3'' and R_4'' , respectively, and



in which R_5''' and R_6''' , have one of the significances of R_3''' and R_4''' , respectively.

More preferably the cationic group is X_e where X_e is



When Y is an aliphatic amino group it is preferably a monoalkyl- or dialkylamino group in which the alkyl group contains 1 to 4 carbon atoms and is straight chain or branched and is optionally substituted by halogen (preferably chlorine or bromine), phenyl or preferably hydroxy.

Any cycloaliphatic amine radical as Y is preferably a C_{5-6} cycloalkylamino group.

Any aromatic amine radical as Y is preferably an aniline radical in which the phenyl ring is optionally substituted by 1 or 2 substituents selected

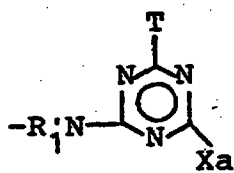
from the group consisting of halogen (preferably chlorine), C_{1-4} alkyl, C_{1-4} alkoxy, hydroxy or phenoxy.

Any heterocyclic amine radical as Y is preferably morpholine which is bound through the N-atom.

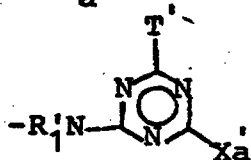
Each Y_i , independently, is preferably Y_a , where Y_a is Cl, OH, NH_2 , mono- C_{1-4} alkylamino, 2-, 3- or 4-hydroxy- C_{2-4} alkylamino, di- C_{1-2} alkylamino, bis [2-, 3- or 4-hydroxy- C_{2-4} alkyl]amino, anilino or morpholino, more preferably each Y_i , independently, is Y_b , where Y_b is Cl, OH, NH_2 , mono- C_{1-2} alkylamino, 2-, 3- or 4-hydroxy- C_{2-4} alkylamino or bis[2-, 3- or 4- hydroxy- C_{2-4} alkyl]amino.

Each X_I , independently, is preferably X_{Ia} , where X_{Ia} is $-CO-X_a$, $-CO-X'_a$, $-SO_2-X_a$ or $-SO_2-X'_a$, more preferably X_{Ib} as $-CO-X_b$, $-CO-X'_b$, $-SO_2-X_b$ or $-SO_2-X'_b$, even more preferably X_{Ic} as $-CO-X_c$ or $-CO-X'_c$ and especially X_{Id} as $-CO-X_d$ or $-CO-X'_d$ in which R'_2 is preferably hydrogen and $-CO-X'_d$ is preferably $-CO-X_e$.

Each X_{II} , independently, is preferably X_{IIa} or X'_{IIa} , where X_{IIa} is



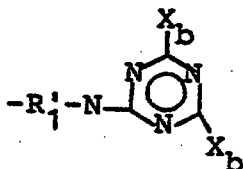
where T is X_a or Y_a , preferably Y_a is Y_b and X'_{IIa} is



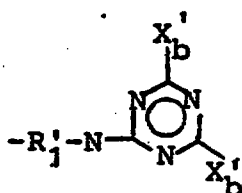
where T' is X'_a or Y_a , preferably Y_a is Y_b ;

more preferably X_{IIb} or X'_{IIb} ,

where X_{IIb} is

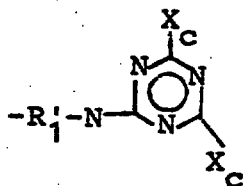


and X'_{IIb} is

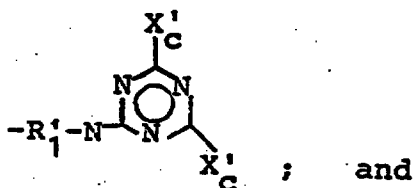


even more preferably X_{IIc} or X'_{IIc}

where X_{IIc} is



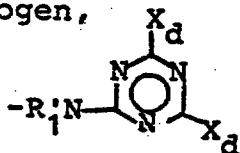
and X'_{IIc} is



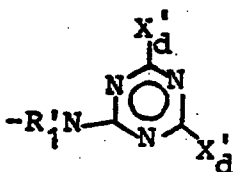
; and

most preferably X_{IIId} or X'_{IIId} in which R'_1 and R'_2 are preferably hydrogen,

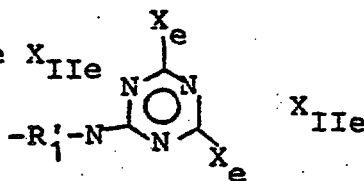
where X_{IIId} is



and X'_{IIId} is



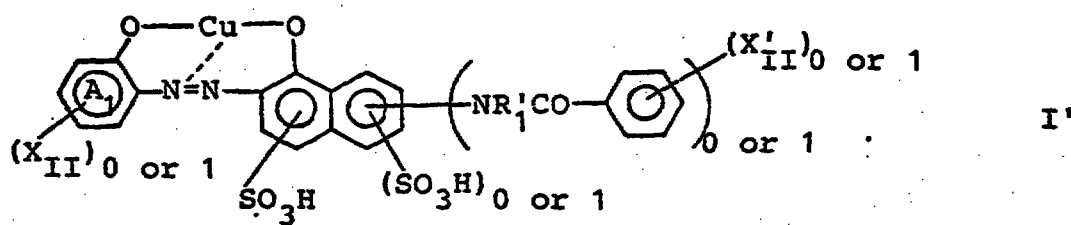
especially where X_d' is X_e to give X_{IIe}



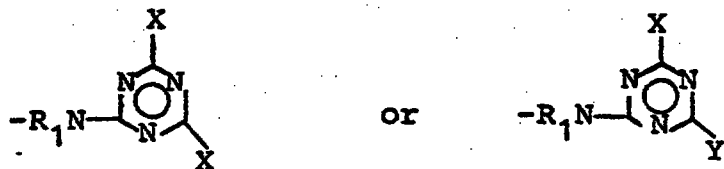
By halogen as used hereinbefore and after is meant fluorine, chlorine or bromine.

The preferred halogen is chlorine.

Preferred complexes are of formula I'

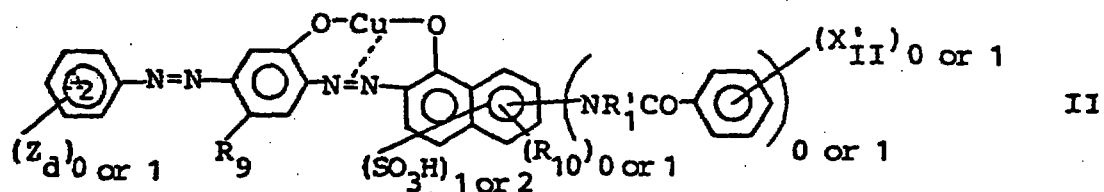


in which each of X_{II} and X'_{II} , independently, is



and the ring A_1 optionally bears 1 or 2 further substituents selected from halogen, C_{1-4} alkyl, C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$, $-SO_2R_{13}$, $-SO_2NR_1R_1$ and $-CONR_1R_1$, where R_{13} is C_{1-4} alkyl or phenyl.

Also preferred are complexes of formula II,



in which Z_d is X_{II} or signifies 1 or 2 groups X_I
 X_{II} being as defined above
and the ring A_2 is optionally substituted by up to 2
further substituents selected from halogen, C_{1-4} alkyl,
 C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$, $-SO_2R_{13}$, $-SO_2NR_1R_1$ and
 $-CONR_1R_1$, where R_{13} is C_{1-4} alkyl or phenyl,

X_{II}' is as defined above;

R_9 is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} -
alkoxy, $-NHCO(C_{1-4}alkyl)$, $-NHCONH_2$,

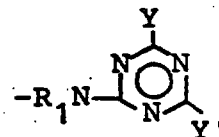
$-NHCO(CH_2)_{1-3}N(C_{1-4}alkyl)_2$ or

$-NHCO(CH_2)_{1-3}N^+(CH_3)_3 A^-$, where A^- is an anion,

or R_9 together with the two carbon atoms on the
benzene ring forms a condensed benzene ring,

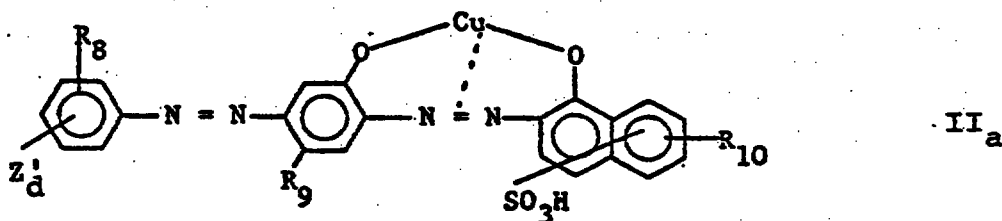
R_{10} is hydrogen; OH; $-NH_2$; $(C_{1-4}alkyl)$ carbonylamino;
benzoylamino or anilino in which the phenyl
nucleus is optionally substituted by one or

two substituents selected from halogen, NO_2 , NH_2 , C_{1-4} alkyl and C_{1-4} alkoxy; or is



in which R_1' and Y are as defined above, and Y' has one of the significances of Y with the exception of chlorine.

Further preferred complexes are of formula II_a



in which Z_d' is a group X_{IIb} or X_{IIe} , or two groups X_{Ia} or X_{Ie} which may be the same or different, and

R_8 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen, $-\text{SO}_2\text{NR}_1\text{R}_1$ or $-\text{CONR}_1\text{R}_1$ and R_9 is as defined above.

Preferably R_8 is R_8' , where R_8' is hydrogen, chlorine, methyl, methoxy, $-\text{SO}_2\text{NH}_2$ or $-\text{CONH}_2$. More preferably R_8 is R_8'' , where R_8'' is hydrogen, chlorine, methyl or methoxy, most preferably hydrogen.

R_9 is preferably R_9' , where R_9' is hydrogen, chlorine, methyl, methoxy, acetamino, $-\text{NHCONH}_2$, $-\text{NHCO}(\text{CH}_2)_{2-3}\text{N}(\text{CH}_3)_2$ or $-\text{NHCO}(\text{CH}_2)_{2-3}\text{N}^+(\text{CH}_3)_3 \text{A}^-$; more

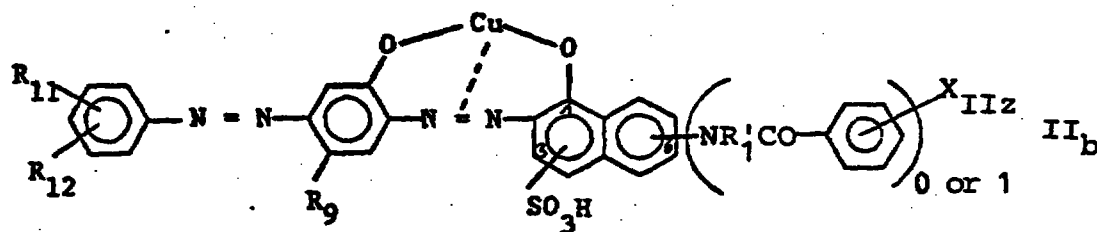
preferably R_9 is R_9'' , where R_9'' is hydrogen, methyl or methoxy.

R_{10} is preferably R_{10}' , where R_{10}' is hydrogen, NH_2 , acetylamino, benzoylamino or anilino.

Preferred compounds of formula II_a are

- (1) those where Z_d' is X_{IIc} or signifies two identical groups X_{IIc} ; where X_{IIc} and X_{II} are as defined above.
- (2) those where R_8 is R_8' , especially R_8'' ;
- (3) those of (1) and/or (2) where R_9 is R_9' , especially R_9'' ;
- (4) those of (1) to (3) where R_{10} is R_{10}' ;
- (5) those of (1) to (4) where R_8 is hydrogen;
- (6) those of (1) to (5) where Z_d' is X_{IIId} or signifies 2 identical X_{IIId} groups.

Further preferred complexes are of formula II_b



in which X_{IIz} is a group X_{IIb} or X_{IIe} ,

R_{11} is hydrogen, halogen, C_{1-4} alkyl,

C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$,

$-SO_2R_{13}$, $-SO_2NR_1R_1$ or $-CONR_1R_1$, and

R_{12} is hydrogen, halogen, C_{1-4} alkyl or

C_{1-4} alkoxy.

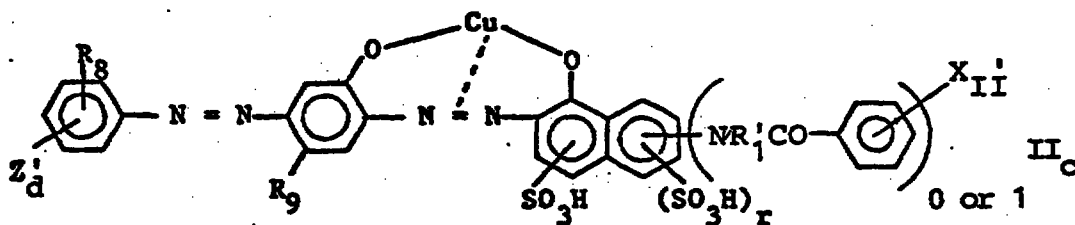
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R_{12} is preferably R_{12}' , where R_{12}' is hydrogen, chlorine, methyl or methoxy, especially hydrogen.

Preferred compounds of formula II_b are

- (1) those where R_{11} is R_{11}' and R_{12} is R_{12}' ;
- (2) those where R_9 is R_9' , especially R_9'' ;
- (3) those where X_{IIz} is X_{IIc} , especially X_{IIId} ; in which X_{IIc} and X_{IIId} are defined above;
- (4) those of (1) to (3) where R_{11} is R_{11}'' and R_{12} is hydrogen;
- (5) those of (4) where the sulpho group is in the 3-position and X_{IIz} as X_{IIc} or X_{IIId} is in the 6-position;
- (6) those of (5) where R_{11} is hydrogen.

Further preferred complexes are of formula II_c,



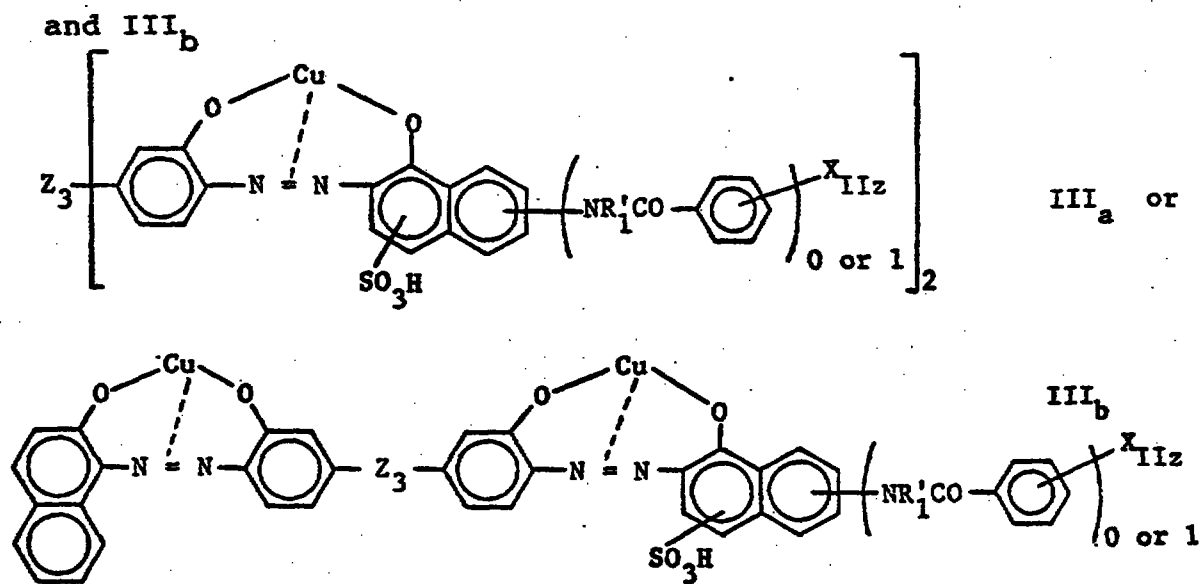
in which r is 0 or 1.

Preferred compounds of formula II_c are

- 18 -

- (1) those where R_8 is R_8' , especially R_8'' ;
- (2) those where R_9 is R_9' , especially R_9'' ;
- (3) those of (1) and/or (2) where Z_d' is X_{IIc} or 2 identical groups X_{IIc} ;
- (4) those of (1) to (3) where X_{II}' is X_{IIb} or X_{IIe} , especially X_{IIc} ;
- (5) those of (3) and/or (4) where R_8 is hydrogen;
- (6) those of (1) to (5) where Z_d' is X_{IIId} or is two identical groups X_{IIId} and X_{II}' is X_{IIId} .

Also preferred complexes are those of formulae III_a

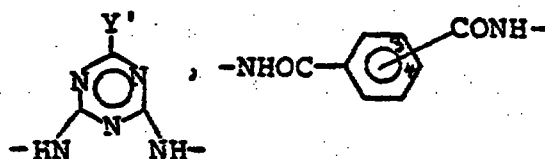


in which each X_{IIz} in the compound of formula III_a may be the same or different and are preferably the same,

Z_3 is a direct bond, $-(CH_2)_{1-3}-$, $-CH=CH-$,

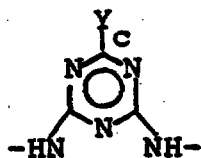
In the compounds of formula IV preferably each Z'_d is the same and R_8 is the same as R_{8a} . Any X_{IIb} or X_{IIe} as Z'_d is preferably in the 4- or 5-position of the benzene ring.

Preferred bridge members Z_4 are those Z_{4a} , where Z_{4a} is -NH-, -NHCONH-,



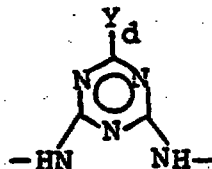
where the -CONH-group is in the 3- or 4-position, -NHCOCH₂CH₂CONH- or -NHCOCH=CHCONH-, where Y' has one of the significances of Y or X .

More preferably Z_4 is Z_{4b} , where Z_{4b} is -NH-, -NHCONH-, -NHCOCH₂CH₂CONH-, -NHCOCH=CHCONH- or



in which Y_c has one of the significances of Y_a or is X_b or X_e .

Even more preferably Z_4 is Z_{4c} , where Z_{4c} is -NH-, -NHCONH-, -NHCOCH=CHCONH- or



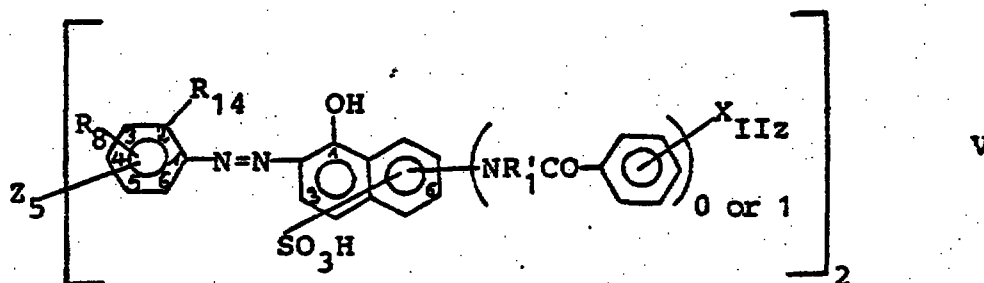
wherein Y_d has one of the significances of Y_b or is X_d or X_e .

Most preferably Z_4 is Z_{4d} , where Z_{4d} is $-NH-$ or $-NHCONH-$.

Preferred compounds of formula IV are

- (1) those where R_8 and R_{8a} are R_8'' , especially hydrogen;
- (2) those of (1) where X_{IIb} is X_{IIc} and X_{Ia} is X_{Ib} , especially X_{Ic} , preferably both are the same;
- (3) those of (2) where X_{IIb} is X_{IIId} and X_{Ia} is X_{Id} ;
- (4) those of (1) to (3) where Z_4 is Z_{4a} , preferably Z_{4b} , especially Z_{4d} .

Also preferred compounds are those of formula V,



in which Z_5 , independently, is in the 4- or 5-position of each phenyl group and signifies $-N=N-$ or $-N=N-$,

R_{14} , independently, is hydrogen or methoxy,

R_8 , independently, is hydrogen, C_{1-4} alkyl, C_{1-4} -alkoxy, halogen, $-SO_2NR_1R_1$ or $-CONR_1R_1$;

X_{IIz} , independently, is X_{IIb} or X_{IIe} ,

and copper complexes thereof.

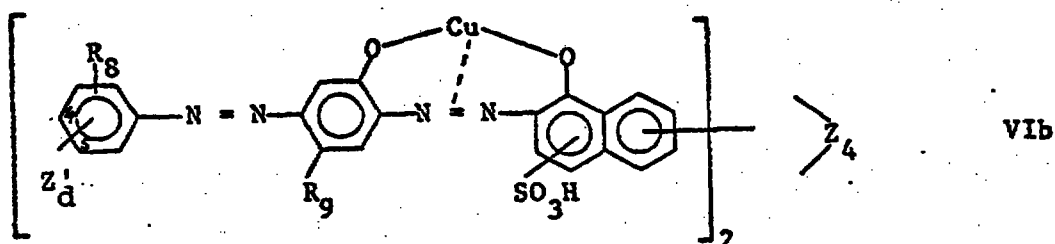
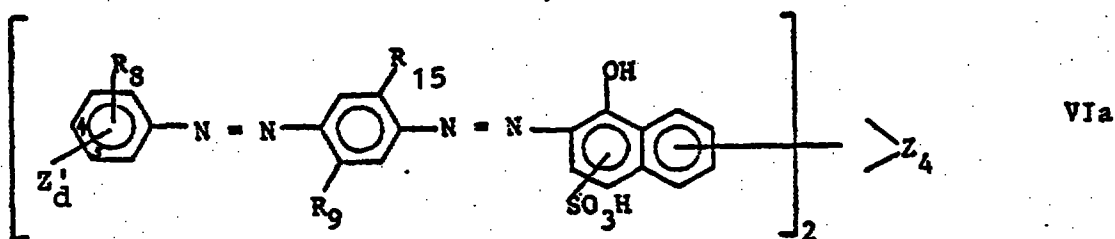
Preferred compounds and complexes of formula V are

- (1) those where R_8 is R_8'' ;
- (2) those where X_{IIz} is X_{IIc} ;
- (3) those where X_{IIz} is X_{IIId} ;
- (4) those of (1) to (3) wherein the sulpho group is in the 3-position and X_{IIz} as X_{IIc} or X_{IIId} is directly bound to the naphthalene ring in the 6-

position;

(5) those of (2) to (4) where R_8 is hydrogen.

Also preferred are compounds of formula IV_a and complexes of formula VI_b ,



in which R_{15} is hydrogen; C_{1-4} alkyl or C_{1-4} alkoxy.

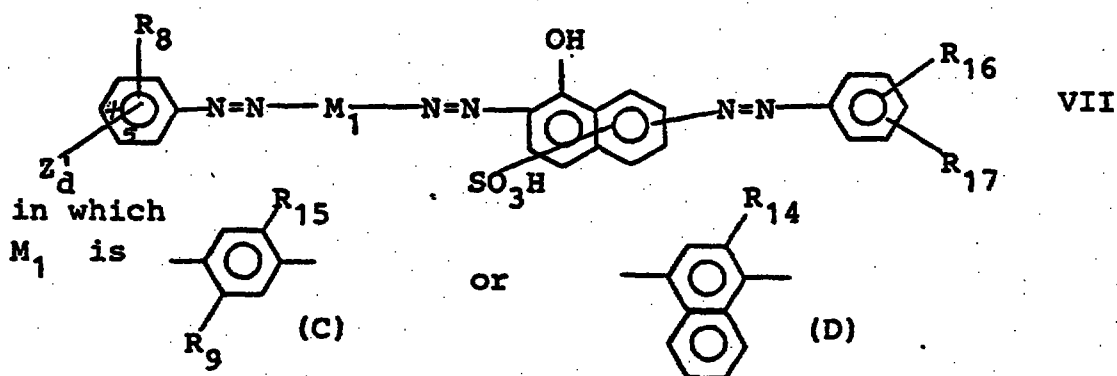
In the compounds and complexes of formulae VI_a and VI_b preferably the variables in both halves of the molecule are identical. X_{IIB} or X_{IIE} as Z'_d are preferably in the 4- or 5-position. In the compounds of formula VI_a preferably R_{15} is hydrogen, methyl or methoxy.

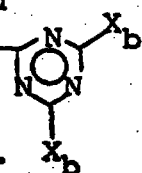
Preferred compounds and complexes of formulae VI_a and VI_b are

- (1) those where R_8 is R_8'' and R_9 is R_9'' ;
- (2) those where Z'_d is X_{IIC} or two identical groups X_{IC} ;

- (3) those where Z'_d is X_{IIId} or two identical groups X_{Id} ; where X_{Id} and X_{IIId} are defined above;
- (4) those of (1) to (3) where Z_4 is Z_{4a} , preferably Z_{4b} , especially Z_{4d} ;
- (5) those of (4) where R_8 is hydrogen.

Also preferred compounds are those of formula VII,

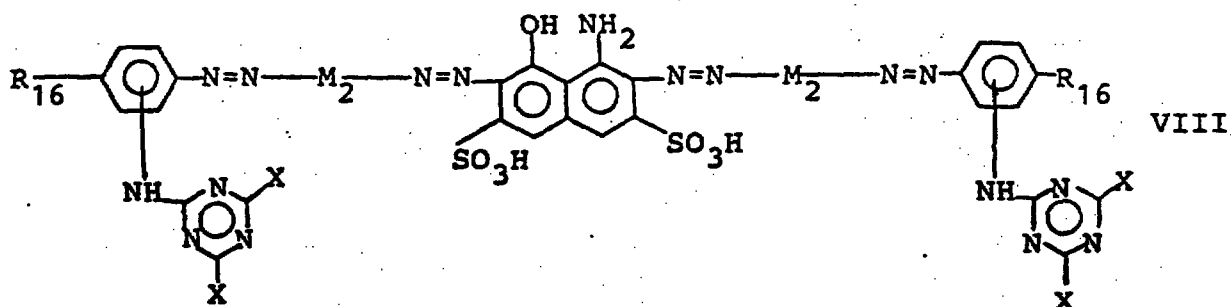


R_{16} is OH or $-NH_2$, and
 R_{17} is OH, NH_2 or $-NH-$ 
 and copper
 complexes thereof. X_b

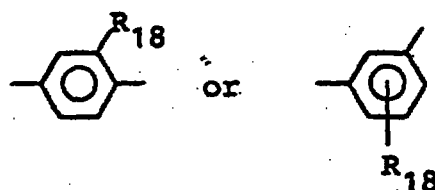
Preferred compounds of formula VII and complexes thereof are

- (1) those where R_8 is R_8'' , especially hydrogen;
- (2) those where X_{IIb} or X_{IIe} as Z'_d is in the 4- or 5-position;
- (3) M_1 is a group (C), especially when R_{15} is hydrogen, methyl or methoxy and R_9 is R_9'' .

Also preferred are compounds of formula VIII,



in which each R_{16} , independently, is OH or NH_2 and each M_2 , independently, is



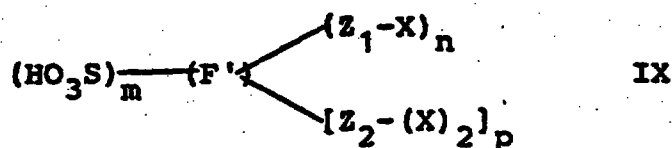
in which R_{18} is hydrogen, chlorine, methyl or methoxy, and copper complexes thereof.

Preferred compounds of formula VIII and complexes thereof are

- (1) those where R_{16} is $-NH_2$;
- (2) those where X is X_b or X_e , especially X_d , where X_b , X_d and X_e are defined above.

The compounds of the invention are preferably in salt form.

The invention also provides a process for the production of complexes of formula I, comprising reacting a compound of formula IX



in which F' is a metallizable residue with an equivalent of a metal donating compound.

Metallization is effected in accordance with known methods. Preferably coppering is effected by oxidative coppering at 40 to 70°C and a medium having a pH of 4 - 7 in the presence of Cu(II) salts or copper powder with hydrogen peroxide or another conventional oxidation agent or more preferably by demethylation coppering preferably in a medium having a pH in the range of from 3 - 9 at temperatures up to the boil.

The compounds of formula IX, may be prepared in accordance with known methods by diazotizing and coupling the corresponding starting materials. The disazoazoxy compounds may be obtained by reductive coupling of two nitro groups.

For example disazoazoxy compounds of formula V may be formed from the corresponding nitroanilines by coupling followed by connecting the two monoazo parts with azoxy bridge by reducing the nitro groups in accordance with known methods, suitably using a mild reducing agent such as glucose and an alkaline medium having a temperature of 20 to 70°C, preferably 40 to 70°C.

Trisazo or tetrakisazo compounds containing a bridge member may be made by diazotization and coupling with a compound containing such a bridge member or by

reacting two azo compounds with a compound yielding a bridging member.

Trisazo compounds are suitably prepared by coupling on either side of a tetrazo component.

It will be also be appreciated that the polyazo complexes of the invention may also be made by taking a metallized starting material and effecting a subsequent diazotization and coupling step.

The monoazo or disazo compounds of formula IX are described in DOS 2,915,323.

The compounds and complexes are isolated in accordance with known methods and may be converted to water soluble salts by reacting the basic compound with at least a stoichiometric amount of a mineral acid such as hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid or preferably an organic acid such as formic acid, acetic acid, lactic acid, citric acid, glycolic acid and methane sulphonc acid.

Further compounds containing free basic groups may be converted to quaternized compounds by reacting with corresponding alkylating agents.

The compounds and complexes of the invention, in acid addition salt form or quaternary ammonium salt form, are dyestuffs and are useful for dyeing and printing fibres, filaments and textiles comprising or consisting of cellulose e.g. cotton, or preferably for

dyeing and printing of paper, or leather, including low affinity vegetable-tanned leather, in accordance with known methods.

Cotton is preferably dyed by the exhaust method. Paper may be dyed in the stock and may be sized or unsized or paper sheet may be dip-dyed.

The dyeings obtained, especially the paper dyeings have good fastnesses especially light-fastness; wet-fastnesses and the exhaust bath is essentially colourless.

The dyestuffs have good solubility especially in cold water and are substantially pH resistant. The dyestuffs have good substantivity and build-up practically quantitatively. The dyestuffs can be added to paper stock as a dry powder or granulate and can also be used in soft water without loss of yield.

The dyes may be used to dye fibres containing wood shavings. Paper dyed with the dyes of the invention can be bleached oxidatively or reductively which is important for the recycling of waste and old paper.

The compounds and complexes may be used in the form of dye preparations. Suitable liquid, preferably aqueous, preparations may be made in accordance with known methods by dissolving in solvents optionally with the addition of assistance such methods are described in French Patent 1,572,030.

An example of a suitable liquid preparation is: -

100 parts dye,
1-100 parts, preferably 1-10 parts inorganic salt,
1-100 parts organic acid such as formic, acetic,
lactic and citric acid etc.,
100-800 parts water,
0-500 parts solvating agent (e.g. glycols such as
diethylene glycol, triethylene glycol,
hexylene glycol; glycol ethers such as
methyl cellosolve, methylcarbitol,
butylpolyglycol; urea; formamide and
dimethylformamide).

The dyes may also be made up into granulates in
accordance with known methods such as that described
in French Patent 1,581,900.

A suitable granulate preparation comprises

100 parts dye,
1-100 parts, preferably 1-10 parts inorganic salt,
and
0-800 parts standardizing agent, (preferably non-
ionic such as dextrin, sugar, grape sugar
or urea).

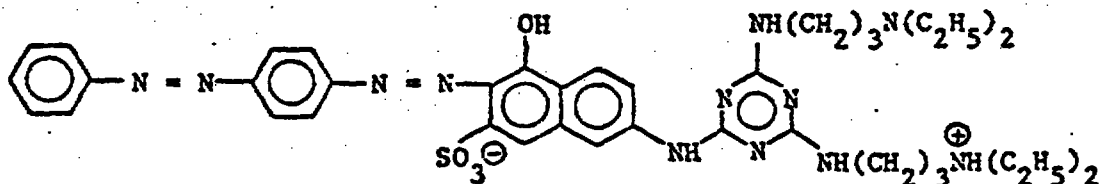
The solid preparations may contain up to 10 %
residual moisture.

The following Examples further serve to illustrate

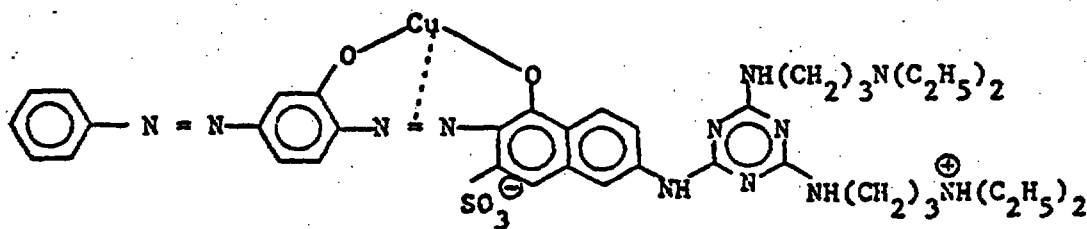
the invention. In the Examples all parts are by weight unless otherwise stated.

Example 1

39.1 Parts of the red dye of formula



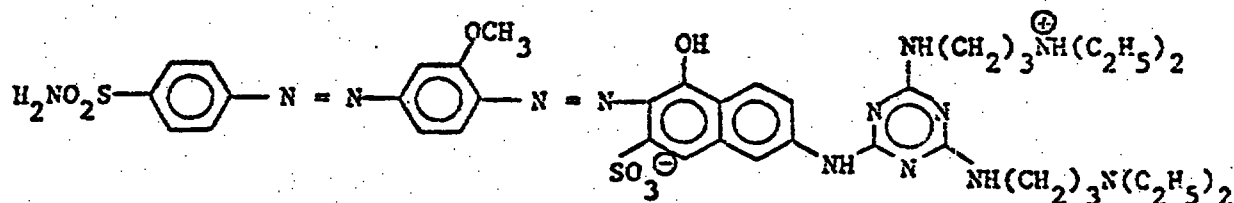
(made as described in Example 98 of DOS 2,915,323) are dissolved in 200 parts water and 50 parts acetic acid and heated to 40°C. Subsequently 15 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 100 parts water are added and then 20 parts sodium acetate are sprinkled in. 250 Parts of 5 % hydrogen peroxide solution are slowly added dropwise over 2 hours. Stirring is then effected for 8 hours at 40°C after which oxidative coppering is complete. 30 % sodium hydroxide is added till the pH is 9 to 10. The dye precipitates and is suction filtered and dried. A dye of formula



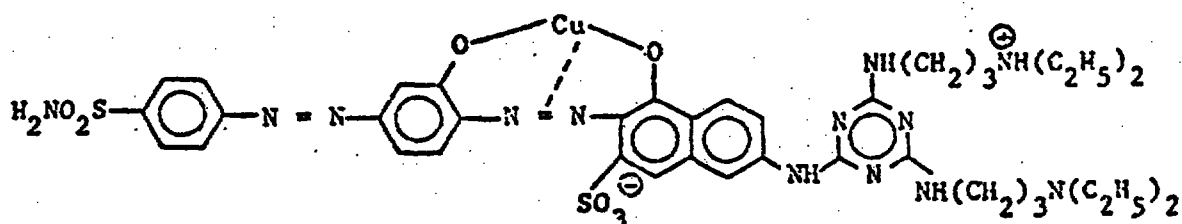
in powder form is obtained. The dye, in the form of acid addition salt, is well water soluble and dyes paper in grey-violet shades. The dyeings obtained have good wet- and light-fastnesses. The waste water is colourless.

Example 2

22.2 Parts of the red dye of formula

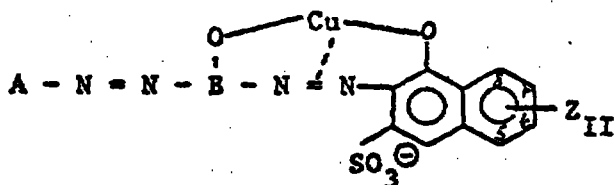


prepared in analogy to the procedure described in Example 98 of DOS 2,915,323 is suspended in 400 parts water and adjusted to pH 3.5 to 4 with sodium acetate. The whole is heated to 50°C and a solution of 10 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 parts water are added dropwise in 15 minutes. Then the temperature is raised to 95-98°C and stirring is effected for 28 hours after which the demethylation coppering is complete. In order to fully precipitate the dye 50 parts by vol. 30 % sodium hydroxide are added at 20°C, the dye is suction filtered and then dried and corresponds to the formula

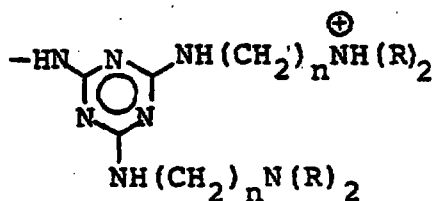


The dye, in the form of the acid addition salt, dyes paper in grey-blue shades; the dyeings have good wet- and light-fastnesses.

In analogy with the procedure of Examples 1 and 2 further dyestuffs given in Table 1 can be prepared. They correspond to the formula



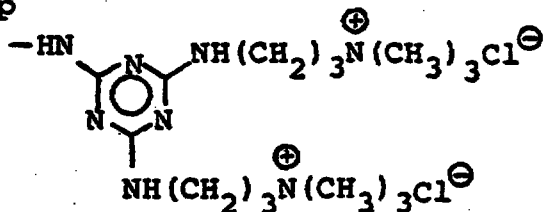
in which the symbols Z_{II} have the following significances; the group



is Z_{II} (1) to Z_{II} (6) whereby when: -

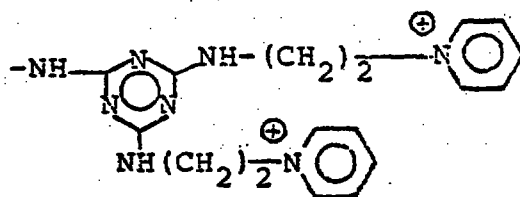
- | | | | |
|--------------|---------|-----|------------------|
| Z_{II} (1) | $n = 3$ | and | $R = CH_3$ |
| Z_{II} (2) | $n = 3$ | and | $R = C_2H_5$ |
| Z_{II} (3) | $n = 2$ | and | $R = CH_3$ |
| Z_{II} (4) | $n = 2$ | and | $R = C_2H_5$ |
| Z_{II} (5) | $n = 2$ | and | $R = CH(CH_3)_2$ |
| Z_{II} (6) | $n = 3$ | and | $R = CH_2CH_2OH$ |

the group



is Z_{II} (7) and

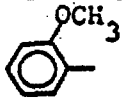
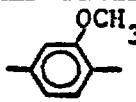
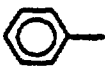
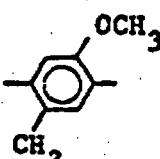
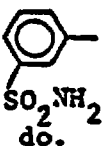
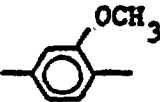
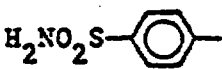
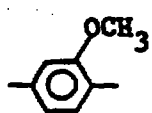
42



is Z_{II} (8).

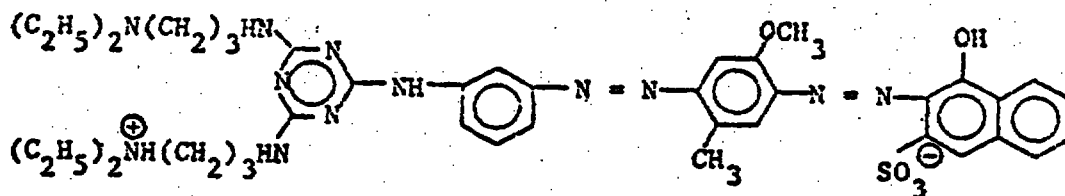
Component B is shown in unmetallized form. In the last column I the dye shade on paper is given whereby a = grey; b = grey-blue; c = brown-grey; d = blue; e = green-blue; f = steel-blue; g = reddish-blue; h = bordeaux; i = violet-blue; j = grey-violet; k = violet; l = red-brown and m = green. (This applies for all following Tables).

Table 1

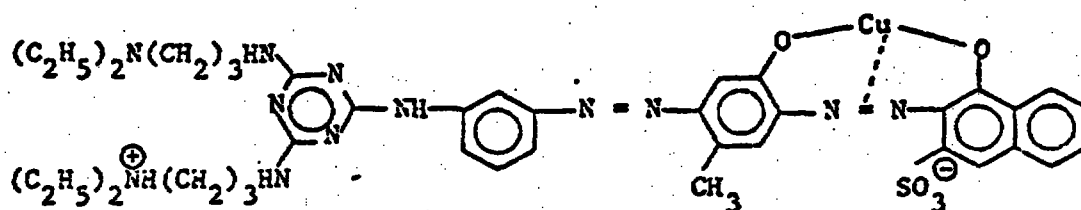
Ex. No.	A	B (unmetallized)	Z _{II}	position of Z _{II}	I
3			Z _{II} (1)	7	a
4	do.	do.	Z _{II} (2)	7	a
5	do.	do.	Z _{II} (2)	6	a
6	do.	do.	Z _{II} (7)	6	a
7	do.	do.	Z _{II} (3)	6	a
8	do.	do.	Z _{II} (4)	7	a
9	do.	do.	Z _{II} (2)	8	e
10	do.		Z _{II} (5)	6	a
11		do.	Z _{II} (1)	7	a
12	do.	do.	Z _{II} (2)	7	a
13	do.	do.	Z _{II} (1)	6	j
14	do.		Z _{II} (2)	6	d
15	do.	do.	Z _{II} (1)	6	d
16		do.	do.	6	d
17	do.		Z _{II} (2)	6	b
18		do.	Z _{II} (1)	6	b
19		do.	Z _{II} (7)	6	a
20	do.		Z _{II} (6)	7	a
21	do.	do.	Z _{II} (2)	5	a
22	do.	do.	Z _{II} (8)	6	a
23			Z _{II} (2)	6	b

Example 24

37.1 Parts of the red dye of formula



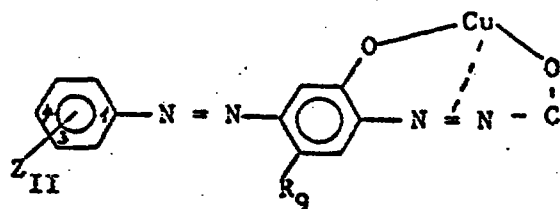
prepared in analogy with the procedure described in DOS 2,915,323 are suspended in 500 parts water and dissolved with the addition of 50 parts glacial acetic acid. The whole is heated to 90°C and 40 parts sodium acetate are added thereto. Subsequently, the copper complex is formed employing 15 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 150 parts water in analogy with the procedure described in Example 2. The dye precipitates out in filterable form, is filtered and dried. The dye powder obtained corresponds to formula



and in the form of the acid addition salt dyes paper in clear reddish-blue shades. The dyes have notable light- and wet-fastnesses.

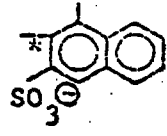
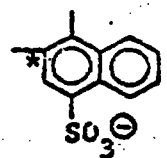
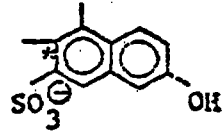
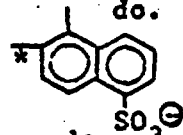
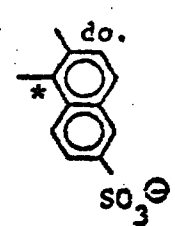
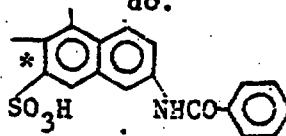
In analogy with the procedure described in Example 24 further copper complexes given in Table 2

can be prepared. The dyes correspond to the formula



in which Z_{II} has the same significances as given above.

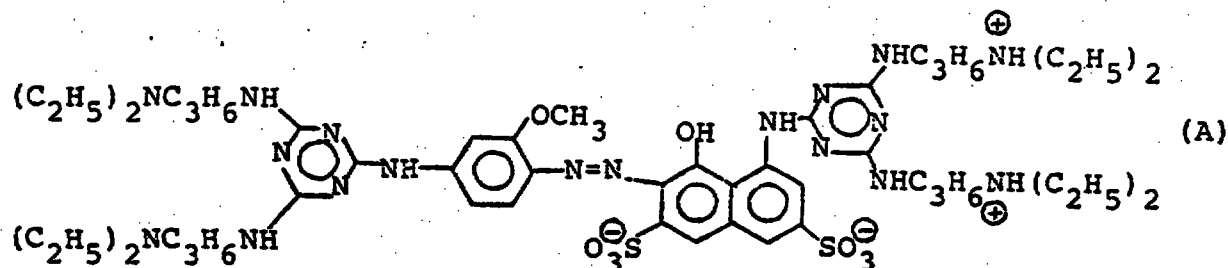
Table 2

Ex. No.	Z _{II}	position of Z _{II}	R ₉	C	I
25	Z _{II} (1)	3	CH ₃		g
26	Z _{II} (2)	3	OCH ₃	do.	f
27	Z _{II} (7)	3	do.	do.	f
28	Z _{II} (2)	3	H	do.	d
29	Z _{II} (1)	3	CH ₃		g
30	Z _{II} (2)	3	do.	do.	g
31	Z _{II} (4)	3	do.	do.	g
32	Z _{II} (1)	3	OCH ₃	do.	b
33	Z _{II} (2)	3	do.	do.	b
34	Z _{II} (2)	3	H	do.	l
35	Z _{II} (7)	3	H	do.	l
36	Z _{II} (1)	4	OCH ₃	do.	m
37	Z _{II} (2)	4	do.	do.	m
38	Z _{II} (2)	3	do.		e
39	do.	3	CH ₃	do.	k
40	Z _{II} (1)	3	do.		b
41	Z _{II} (2)	3	do.	do.	b
42	do.	3	OCH ₃	do.	e
43	Z _{II} (1)	3	CH ₃		c
44	Z _{II} (2)	3	do.	do.	c
45	do.	4	-NHCOCH ₃	do.	d
46	Z _{II} (8)	3	H	do.	c
47	Z _{II} (2)	3	H		d
48	do.	3	CH ₃	do.	d

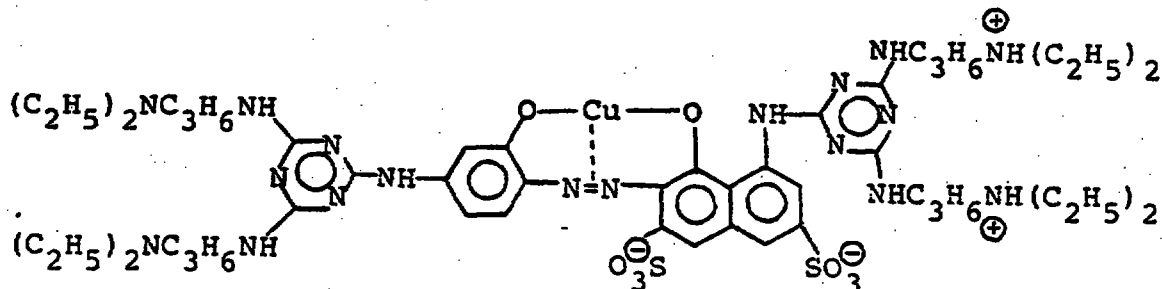
The asterisk denotes the C-atom bound to the azo group.

Example 49

The dye of formula (A)



is demethylated and coppered in analogy with the procedure described in Example 2. The dye of formula



obtained dyes, in acid addition salt form, paper in clear blue shades. The dyes obtained have notable light- and wet-fastnesses.

The dye of formula (A) can be obtained as follows:

- a) 37.1 Parts of 2,4-bis(3'-N,N-diethylaminopropylamino)-6-chloro-s-triazine are stirred in 200 parts water with sufficient hydrochloric acid to give a clear solution having a pH of 6 to 7. 31.9 Parts 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) are added. The suspension is heated to 80°C. During this time 15 parts sodium acetate are added portionwise. After 3 hours a solution is obtained

in which according to the thin layer chromatography no further H-acid is detectable. Stirring is effected at room temperature whereby the reaction product crystallises out. The product is suction filtered and dried.

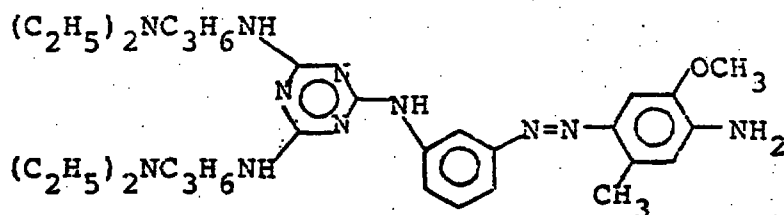
- b) 47.3 Parts 4-[2',4'-bis(3"-N,N-diethylaminopropyl-amino)-s-triazine-6'-yl-amino]-2-methoxy-aniline are acidified with hydrochloric acid in 250 parts water at 0 to 5°C and are reacted with 25 parts of a 4N sodium nitrite solution. This diazo solution is dropped into a soda alkaline solution containing 80 parts of the product obtained under a) such that the pH is maintained at 8 to 8.5. A blue dye solution is obtained which is stirred for a further 2 hours. Subsequently, the dye of formula (A) is precipitated with 400 parts 30 % sodium hydroxide, filtered and dried.

Examples 50 and 51

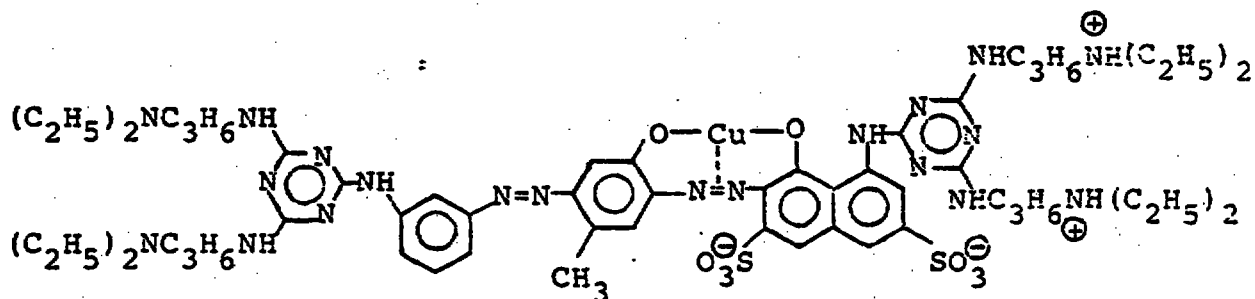
Using 3'- respectively 4'-aminobenzoyl-H-acid instead of H-acid and proceeding as described in Example 49, the corresponding copper complexes are obtained which, in acid addition salt form, dye paper in blue shades with good fastnesses, especially light-fastness.

Example 52

Using the diazo component of formula

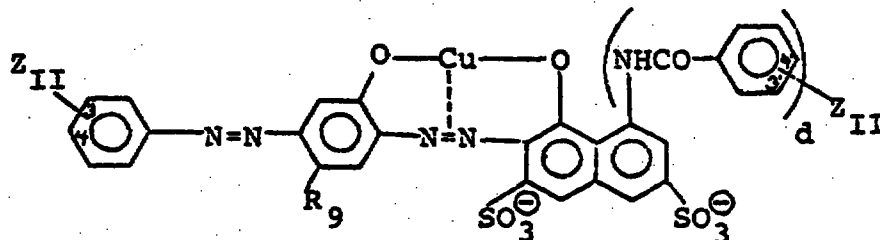


instead of that of Example 49 and proceeding as described in Example 2, the dye of formula



is obtained which, in acid addition salt form, dyes paper in green-blue shades. The paper dyeings have good wet-fastnesses and excellent light-fastness.

In analogy to the procedure of Example 52 further copper complexes given in Table 3 may be prepared. The dyes correspond to the formula



and dye paper in the shade as given under I. The dyes

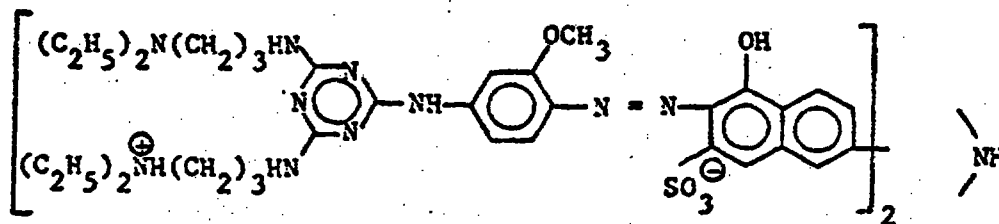
show good wet- and light-fastnesses.

Table 3

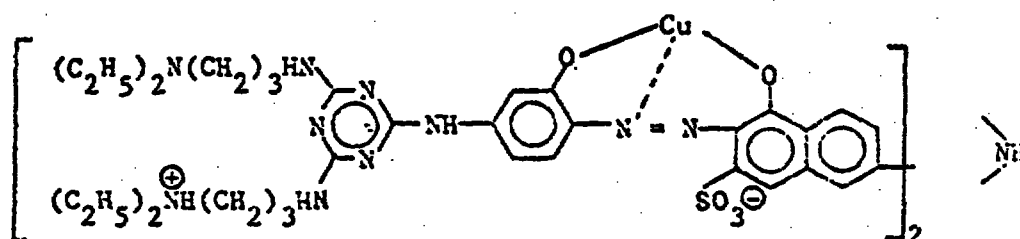
Ex. No.	Z _{II}	d	position of Z _{II}	R ₉	I
53	Z _{II} (2)	0	4; -	CH ₃	e
54	Z _{II} (1)	0	4; -	do.	e
55	do.	1	4; 3'	do.	e
56	Z _{II} (2)	1	4; 3'	do.	e
57	Z _{II} (1)	1	3; 3'	OCH ₃	d
58	do.	1	3; 4'	do.	f
59	Z _{II} (2)	1	3; 3'	do.	d
60	do.	1	4; 3'	CH ₃	e
61	do.	1	4; 3'	H	d
62	do.	0	4; -	OCH ₃	e
63	Z _{II} (1)	0	3; -	do.	e
64	Z _{II} (2)	0	3; -	do.	e
65	Z _{II} (1)	0	3; -	H	d
66	Z _{II} (7)	0	3; -	CH ₃	e
67	Z _{II} (8)	0	4; -	OCH ₃	e

Example 68

7.7. Parts of the violet dye of formula

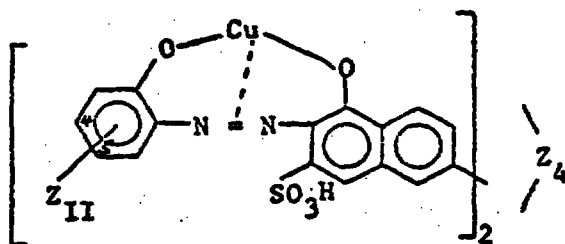


prepared in analogy with the procedure described in Example 55 of DOS 2,915,323 are stirred in 150 parts water and adjusted to pH 4 with glacial acetic acid. Then demethylation coppering is carried out in accordance with the procedure of Example 2. The dye of formula



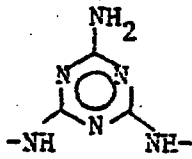
is obtained which, in the acid addition salt form, dyes paper in reddish-blue shades with good fastnesses, especially wet-, alcohol- and light-fastness.

In analogy to the procedure of Example 68 further dyes given in Table 4 of general formula



can be prepared.

Table 4

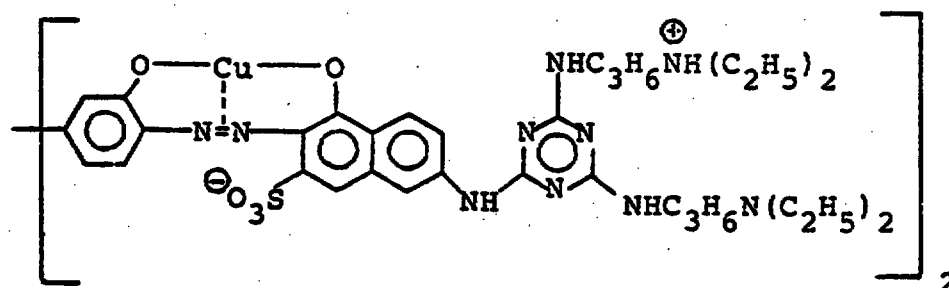
Ex. No.	Z _{II}	position of Z _{II}	Z ₄	I
69	Z _{II} (1)	4	-NH-	d
70	Z _{II} (7)	4	do.	d
71	Z _{II} (1)	5	do.	b
72	Z _{II} (2)	5	do.	b
73	Z _{II} (1)	4	-NHCONH-	i
74	Z _{II} (2)	4	do.	i
75	Z _{II} (4)	4	do.	i
76	Z _{II} (2)	5	do.	j
77	Z _{II} (8)	4	do.	i
78	Z _{II} (1)	4		i
79	Z _{II} (2)	5	do.	j

Example 80

150 Parts 2,4-bis-(3'-N,N-diethylaminopropylamino)-6-chloro-s-triazine are suspended in 500 parts water and adjusted to pH 6 - 7 with hydrochloric acid. 96 parts 2-amino-5-hydroxynaphthalene-7-sulfonic acid are added to the solution and the suspension is heated to 88 to 90°C. The pH is held at 2 - 2.2 by the addition of 60 parts crystalline sodium acetate. After 3 hours the

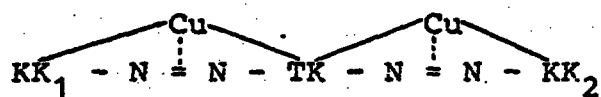
condensation is complete. The coupling solution is cooled to room temperature.

48.8 Parts 4,4'-diamino-3,3'-dimethoxy-1,1'-diphenyl are stirred in 300 parts water, 200 parts ice and 120 parts 30 % hydrochloric acid. Then a concentrated aqueous solution of 30 parts sodium nitrite are added dropwise and stirring is effected for 1 hour. A clear yellow tetrazo solution is obtained. The coupling solution is set with 200 parts ice and coupled with the above tetrazo solution at pH 8. After 4 to 6 hours coupling is complete. The pH is adjusted to 6 - 7 with 40 parts glacial acetic acid and then a solution of 110 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 300 parts water and 250 parts 25 % ammonia are added and the temperature is raised to 95 to 97°C. After 5 hours coppering is complete. After cooling to room temperature the whole is made alkaline with 270 parts 30 % sodium hydroxide and then filtered. The dye of formula



is obtained which, in acid addition salt form, dyes paper in navy-blue shades. The wet- and light-fastnesses are notable.

In analogy to the procedure of Example 80 further dyes given in Table 5 of general formula



can be prepared.

Table 5

Ex. No.	TK (unmetallized)	KK ₁ (unmetallized)	KK ₂ (unmetallized)	I
81				g
82	do.		do.	g
83	do.	do.	= KK ₁	d
84	do.		= KK ₁	e
85	do.		= KK ₁	e
86	do.		= KK ₁	g
87	do.		= KK ₁	g
88	do.		= KK ₁	b
89	do.		= KK ₁	b
90			= KK ₁	i
91	do.		= KK ₁	i
92	do.		= KK ₁	k
93	do.		= KK ₁	k

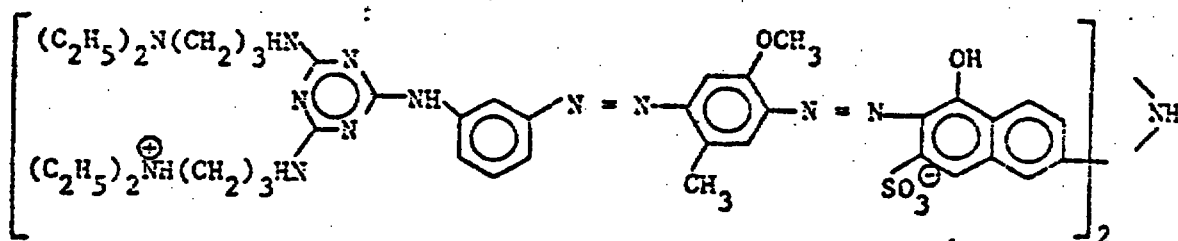
Table 5 (continued)

Ex. No.	TK (unmetallized)	KK ₁ (unmetallized)	KK ₂ (unmetallized)	I
94			= KK ₁	h
95	do.		= KK ₁	h
96		do.	= KK ₁	d
97			= KK ₁	i

Example 98

44.3 Parts 3-[2',4'-bis(3"-N,N-diethylaminopropyl-amino)-s-triazine-6'-yl-amino]aniline are dissolved in 500 parts water with the addition of 50 parts 30 % hydrochloric acid and diazotized at 0 to 5°C with 27 parts 4N sodium nitrite solution. After 1 hour the excess nitrite is destroyed with amidosulphonic acid. 13.7 Parts 2-amino-1-methoxy-4-methylbenzol are added and the pH fixed at 4 by adding sodium acetate. After 3 to 4 hours coupling is complete. The reaction mixture is

adjusted to acidic with hydrochloric acid and then 25 parts 4N sodium nitrite solution are added at room temperature. This diazo solution is added to a solution containing 23 parts 2,2'-dinaphthylamino-5,5'-dihydroxy-7,7'-disulphonic acid in such a way that the pH remains at 7.5 - 8. The blue dye suspension is stirred for 3 hours and then coupling is complete. The precipitated dye which is filtered and dried corresponds to the formula.



The dye, in the acid addition salt form, dyes paper in navy-blue shades with good fastnesses.

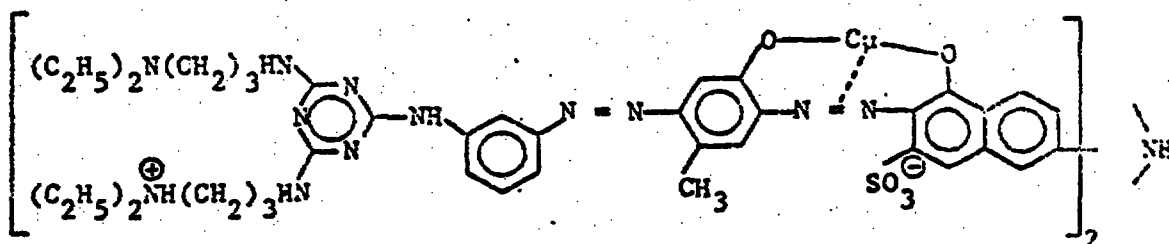
Examples 99 - 113

In analogy to the procedure of Example 98 further unmetallized tetrakisazo dyes can be prepared employing instead of the diazo component having the group $Z_{II}(2)$ in position 3 a diazo component with $Z_{II}(2)$ in position 4 or one with the group $Z_{II}(1)$, $Z_{II}(3)$ to $Z_{II}(8)$ in position 3 or 4. They all dye paper in navy-blue shades.

Example 114

10 Parts of the dyestuff powder of Example 98 are stirred in 200 parts water and dissolved with the addition of 4 parts glacial acetic acid. Subsequently, demethylation and coppering is carried out according to

the process of Example 2. The precipitated dye is filtered and dried at 60°C in vacuo. The dye corresponding to formula



is obtained in form of a powder which in an acid addition to salt form, dyes paper in grey-blue shades with good light- and wet-fastnesses.

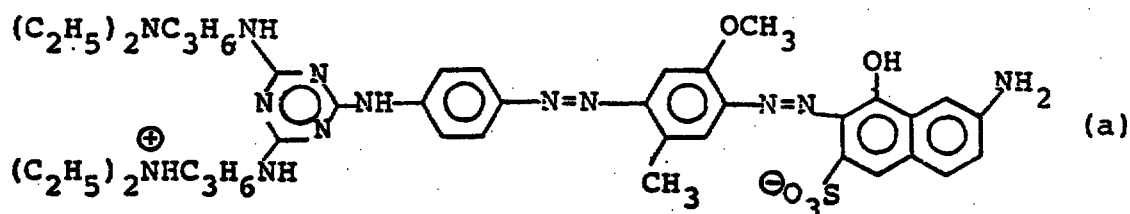
Examples 115 - 129

In analogy to Example 114 further copper complexes are obtained by employing instead of the diazo component having the group $Z_{II}(2)$ in position 3, a diazo component with $Z_{II}(2)$ in position 4 or with the group $Z_{II}(1)$, $Z_{II}(3)$ to $Z_{II}(8)$ in position 3 or 4. These all dye paper in grey-blue shades.

Example 130

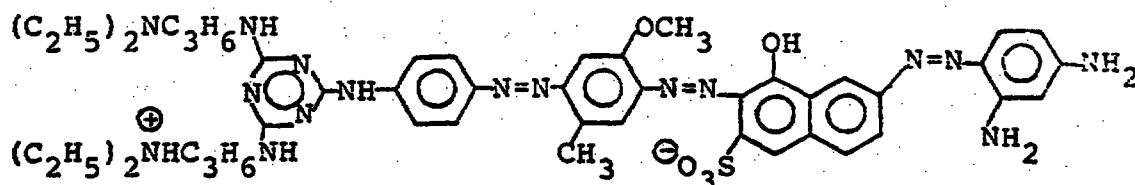
83 Parts of 4-[2',4'-bis(3"-N,N-diethylamino-propylamino)-s-triazine-6'-yl-amino] aniline are dissolved in 500 parts water and 100 parts 30 % hydrochloric acid and at 0 to 5°C diazotized with 47 parts of a 4N sodium nitrite solution. After 1 hour the excess nitrite is decomposed with amido sulphonic acid. 25.8 Parts 2-amino-1-methoxy-4-methylbenzol are added thereto and the whole is stirred; the pH is kept at

3.5 by the addition of approximately 100 parts sodium acetate. Coupling is complete after a short time. Stirring is effected for 2 hours. Subsequently, 50 parts 30 % hydrochloric acid are added and a further 45 parts of 4N sodium nitrite solution are added dropwise at 15 to 20°C. After diazotization is ended the pH is brought down to 6.5. 45 Parts 2-amino-8-hydroxy-naphthalene-6-sulfonic acid are then added and the pH is raised to 8 - 9 with 30 % sodium hydroxide solution whereby coupling takes place. A disazoamino compound of formula (a)



is obtained. As soon as coupling is complete 150 parts sodium chloride are added whereby the dyestuff completely precipitates. It is suction filtered and then stirred in 2000 parts water. Then 100 parts 30 % hydrochloric acid are added and 45 parts of a 4 N sodium nitrite solution is added dropwise. The excess nitrite is decomposed with amido sulphonie acid. Then 21 parts of 1,3-diaminobenzene (dissolved in water and hydrochloric acid) are poured in and the pH is adjusted at pH 3,5-4 with sodium acetate. Coupling takes place

and the dye precipitates out. After the reaction is complete the dye is filtered. The dye of formula

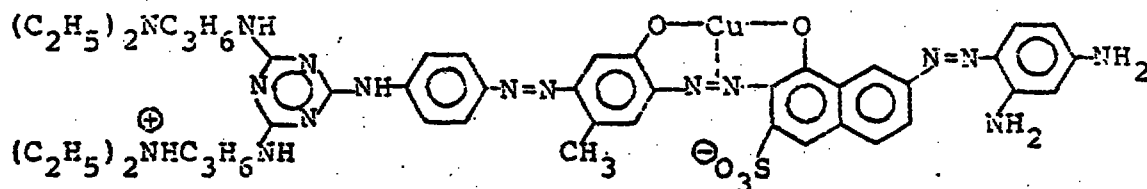


which is obtained in a form of a wet presscake is dried. The dye, in the form of an acid addition salt, dyes paper in neutral black tones. The dyeings dyed on sized and unsized paper show perfect wet-fastnesses and the waste water is colourless.

Example 131

17 Parts of the compound (a) of Example 130 are suspended in 200 parts water and reacted with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (dissolved in 50 parts water and 15 parts 25 % aqueous ammonia). The whole is heated to 95 to 97°C and is stirred at this temperature for 7 hours. The so-obtained copper complex is filtered hot and a wet presscake is obtained which is stirred in 250 parts water and 15 parts 30 % hydrochloric acid. Then 18 parts 1 N sodium nitrite solution are added dropwise over a period of 1 hour. After diazotization is completed 2 parts 1,3-diaminobenzene are added and the pH is adjusted to 3.5 to 4 with sodium acetate and the whole is allowed to couple for 3 hours. 100 Parts sodium chloride and then 15 parts 30 % sodium hydroxide solution are added to precipitate the dye.

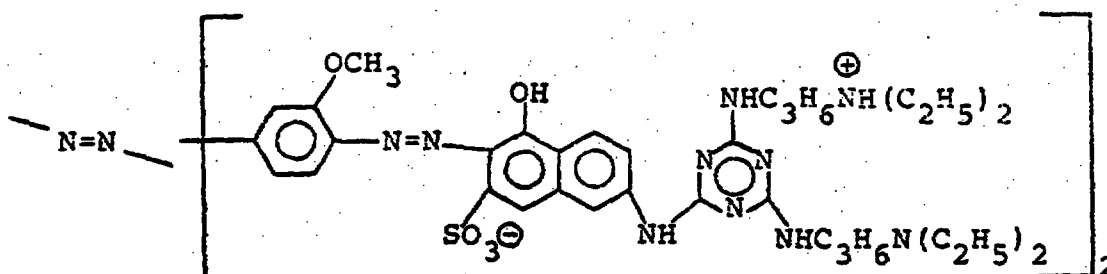
After filtration the dye of formula



is obtained as a wet presscake; the dyestuff is dried. The dyestuff, in the form of an acid addition salt, dyes paper in greenish black shades. The dyeings have good light- and wet-fastnesses and the waste water is essentially colourless.

Example 132

6,8 Parts 4,4'-diamino-3,3'-dimethoxy-azobenzene are dissolved in 100 parts water with 12 parts hydrochloric acid and cooled to 0°C. 12 Parts 4N sodium nitrite solution are added dropwise thereto. The tetrazo solution is added dropwise to a soda-alkaline solution containing 28 parts 2-[2',4'-bis(3"-N,N-diethylamino-propylamino)-s-triazine-6-yl-amino]-5-hydroxy-naphthalene-7-sulfonic acid whereby the pH is held at 8 - 8.5 by the addition of soda solution. A blue suspension is obtained which is stirred for several hours. Subsequently, 50 parts 30 % sodium hydroxide solution are added and the dyestuff precipitates, is filtered and dried. The dyestuff of formula



which is obtained in powder form dyes, in the acid addition salt form, paper in navy-blue shades. The dyes have good fastnesses.

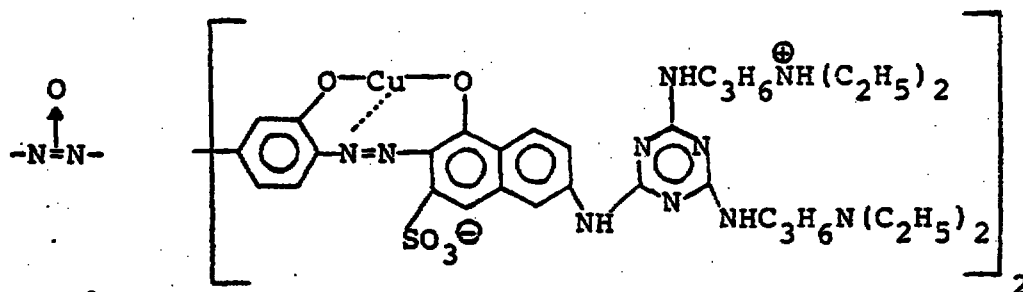
Example 133

When the dyestuff of Example 132 is coppered by demethylation in accordance with the procedure described in Example 2 the corresponding copper complex is obtained, which, in acid addition salt form, dyes paper in blue shades with good fastnesses.

Example 134

17 Parts 2-amino-1-methoxy-5-nitrobenzene are suspended in 300 parts water and 25 parts hydrochloric acid are added thereto. Subsequently, it is cooled to 0°C and 27 parts 4N sodium nitrite solution are added dropwise. Stirring is effected for 3 hours and the yellow solution is filtered clear. This diazo solution is added dropwise to a solution containing 56 parts 2-[2',4'-bis(3"-N,N-diethylaminopropylamino)-s-triazine-6'-yl-amino]-5-hydroxynaphthalene-7-sulfonic acid

with the pH being held at 3 - 3,5 by the portionwise addition of sodium acetate. After 3 hours the diazo solution is no longer detectable. 20 vol. % sodium chloride are added to the orange-red dyestuff solution and the pH is adjusted to c. 11 with sodium hydroxide solution. The precipitated dye is filtered. The wet paste obtained is stirred in 600 parts water. The whole is heated to 60°C and the pH is adjusted to 7,5 - 8 with hydrochloric acid upon which everything goes into solution. 30 Parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (dissolved in 70 parts water and 50 parts ammonia) are added and the dyestuff suspension is heated to 95 to 98°C. After 2 to 3 hours coppering is complete. 50 Parts sodium hydroxide solution are added and a solution of 15 parts glucose and 50 parts water are added dropwise over 10 minutes. Stirring is effected for 1 hour at 90°C and the whole is cooled to room temperature. The precipitated dye is filtered and dried. The dye of formula



is obtained as a dark powder which, in the acid addition salt form, dyes paper in navy-blue shades with good fastnesses.

Example 135

Proceeding as described in Example 134 but reducing the dyestuff with glucose in alkaline medium before coppering, the corresponding uncoppered dyestuff is obtained which, in the acid addition salt form, dyes paper in violet-blue shades with good wet-fastnesses. By effecting coppering by demethylation the dye can be converted to the copper complex which is identical with Example 134.

In analogy with the procedures described in Examples 132 to 135 further metal-free respectively metallized dyes can be obtained. The dyes are given in Table 6 and correspond in metal-free form to formula

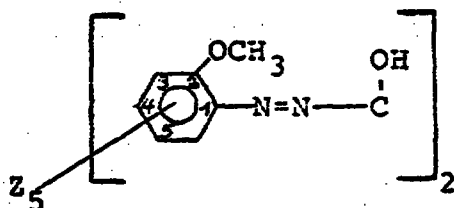


Table 6

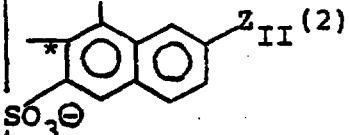
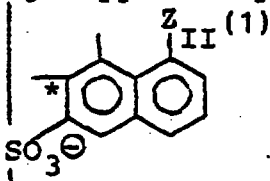
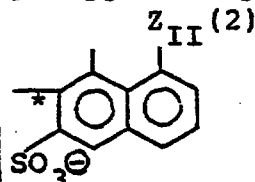
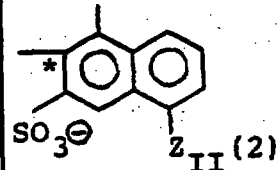
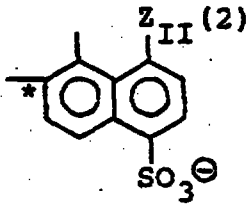
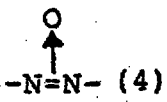
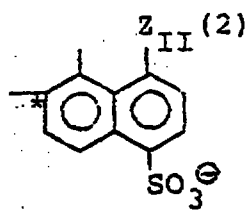
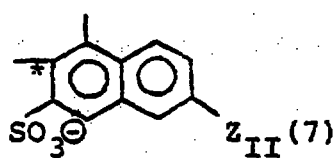
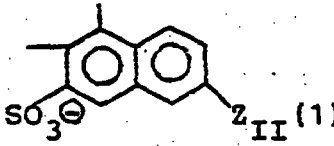
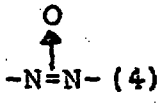
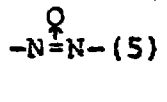
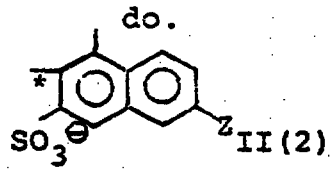
Ex. No.	Z ₅ (position)	C	I
136	-N=N- (4)		f
137	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{-N=N-} \end{array}$ (4)	do.	b
138	corresponding copper complex of Example 136		f
139	corresponding copper complex of Example 137		b
140	-N=N- (4)		e
141	corresponding copper complex of Example 140		e
142	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{-N=N-} \end{array}$ (4)		e
143	corresponding copper complex of Example 142		e
144	-N=N- (4)		d
145	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{-N=N-} \end{array}$ (4)	do.	d
146	corresponding copper complex of Example 144		d
147	corresponding copper complex of Example 145		d
148	-N=N- (4)		b

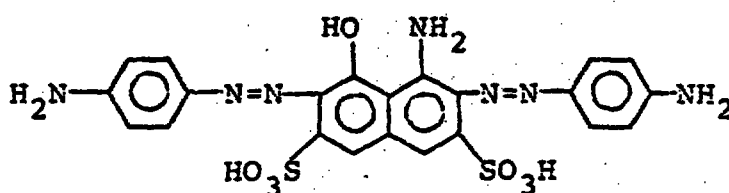
Table No. 6 continued

Ex. No:	Z ₅ (position)	C	I
149	 (4)		j
150	corresponding copper complex of Example 148		b
151	corresponding copper complex of Example 149		j
152	-N=N- (4)		d
153	do.		d
154	 (4)	do.	i
155	 (5)		orange
156	corresponding copper complex of Example 152		d
157	corresponding copper complex of Example 153		d
158	corresponding copper complex of Example 154		i

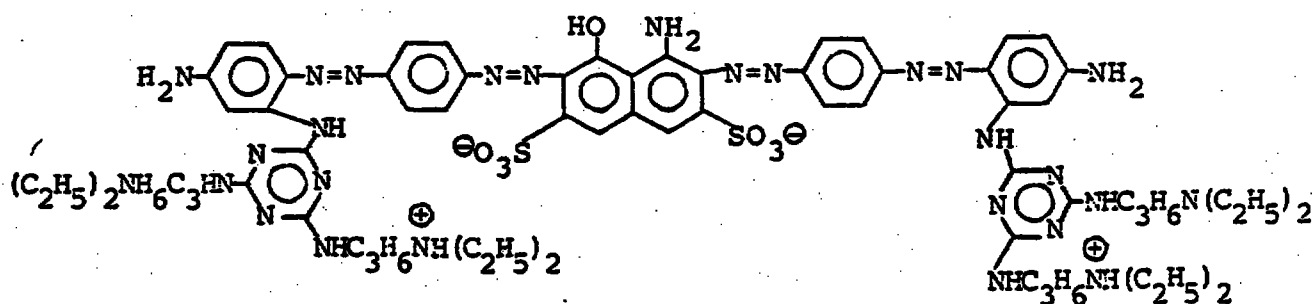
In Table 6 the asterisk denotes the C-atom bound to the azo group.

Example 159

28 parts of the compound of formula



(obtained by diazotization of 4-nitroaniline and coupling with 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid followed by reduction with sodium sulfide) are stirred in 900 parts water and reacted with 25 parts 30 % hydrochloric acid. 25 Parts 4N sodium nitrite solution are added to this suspension dropwise over 2 hours. Stirring is effected for a further 2 hours and then 1 part amido sulphonic acid is added. 45 Parts 2,4-bis(3'-N,N-diethylaminopropylamino)-6-(3'-aminophenylamino)-s-triazine are stirred in 100 parts water and are dissolved with 25 parts 30 % hydrochloric acid. 60 Parts sodium acetate are added and subsequently the above tetrazo solution is added dropwise over 2 hours to this preparation. The pH is slowly adjusted to 9 by the addition of 70 parts of 30 % sodium hydroxide solution whereupon the dyestuff for the most part precipitates. After filtration the dyestuff of formula



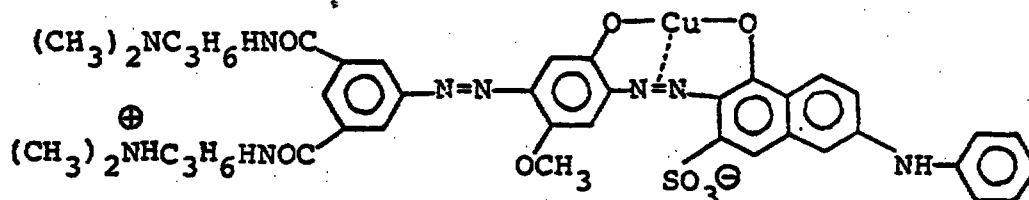
which is obtained as a wet presscake, is dried. The dye, in the acid addition salt form, dyes paper in neutral dark black shades and builds-up well on both sized and unsized paper giving dyeings with good wet-fastnesses.

Example 160

16 Parts 5-aminobenzene-1,3-dicarboxylic acid-di-(3'-N',N'-dimethylaminopropyl)-amide are stirred into 200 parts water and are dissolved with 30 parts of 30 % hydrochloric acid. 100 Parts ice are added and 12 parts 4N sodium nitrite solution are added dropwise. The excess nitrite is decomposed with amido sulphonic acid. 7 Parts of 1-amino-2,5-dimethoxybenzene are added to the weakly yellow diazo solution whereupon a yellow-red dyestuff solution is formed. After 15 minutes the pH is adjusted to 4 by the addition of sodium acetate. Coupling is complete after a further 2 hours. The dye is isolated by the addition of 100 parts 30 % sodium hydroxide solution and is subsequently dissolved in 400 parts water and 25 parts 30 % hydrochloric acid. 11 Parts 4N sodium nitrite solution are added and stirring is effected for 1 hour. 15 Parts 2-phenylamino-5-hydroxynaphthalene-7-sulfonic acid are stirred in 600 parts water and the pH is adjusted to 9 with 30 % sodium hydroxide solution. The above diazo solution is added thereto and the pH is kept at 9 with sodium hydroxide.

- 60 -

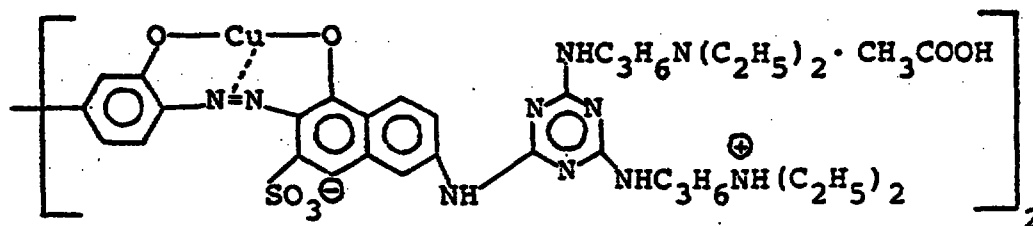
Coupling is finished after a short time and the dyestuff precipitates. The dye is suction filtered and stirred in 600 parts water. Then 12 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (dissolved in 200 parts water and 150 parts 25 % aqueous ammonia) are added, the suspension obtained is heated to 97 to 98°C. After 8 hours coppering is complete and the dyestuff which is filtered and is obtained in the form of a wet presscake, is of formula



The dye, in the acid addition salt form, dyes paper in violet-blue shades with good light- and wet-fastnesses.

Example 161

30.2 Parts of the dyestuff powder of Example 80 are stirred in 500 parts water and reacted in 2.4 parts glacial acetic acid. The dye goes completely into solution. Subsequently, the dyestuff solution is evaporated to dryness. The dyestuff which corresponds to the formula



is obtained in powder form and has good solubility in cold water.

Instead of employing the glacial acetic acid of Example 161 hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, lactic acid and other inorganic or preferably organic acids can be used for forming external salts. The dyes of the above Examples may also be converted to the acid addition salt form in analogous manner.

Example 162

80 Parts of the dyestuff salt of Example 161 are added at room temperature to a solution of 20 parts dextrin, 20 parts glacial acetic acid and 500 parts water and are stirred to a homogeneous suspension. By spray drying blue granulates are obtained which are well soluble in water and dye paper in blue shades. The dyes of the other Examples can also be converted to granulates in analogous manner.

Example 163

200 Parts of the dye presscake of Example 80 are stirred in 440 parts water and the pH is adjusted to 5 with 34 parts glacial acetic acid. The so-obtained solution is heated to 80°C and is filtered clear (employing kieselgur or Hyflo). After cooling 700 parts of a ready-to-use dyestuff solution is obtained, which is storage stable over several months both in cool and

warm atmospheres. The dyes of the other Examples can be converted to stable liquid preparations in analogous manner.

Application Example A

70 Parts of chemically bleached sulphite cellulose obtained from pinewood and 30 parts of chemically bleached sulphite cellulose obtained from birchwood are ground in 2000 parts of water in a Hollander. 0.5 Parts of the dyestuff from Example 80 (as an acid addition salt, e.g. according to Example 161) are sprinkled into this pulp. Paper is produced from this pulp after mixing for 20 minutes. The absorbent paper which is obtained in this manner is dyed in a blue shade. The waste water is practically colourless.

Application Example B

0.5 Parts of the dyestuff from Example 80 (as an acid addition salt, e.g. according to Example 161) are dissolved in 100 parts of hot water and cooled to room temperature. This solution is added to 100 parts of chemically bleached sulphite cellulose which have been ground in a Hollander with 200 parts of water. Sizing takes place after thorough mixing for 15 minutes. The paper which is produced from this material has a blue shade and good light- and wet-fastnesses.

Application Example C

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

0.5 parts of the dyestuff from Example 80 (as an acid addition salt, e.g. according to Example 161)

0.5 parts of starch and
99.0 parts of water.

The excess dyestuff solution is squeezed out through two rollers. The dried length of paper is dyed in a blue shade.

The dyestuffs of the remaining Examples may also be used for dyeing according to Application Examples A to C in the acid addition salt form or in the form of solid or liquid preparations.

Application Example D

100 Parts freshly tanned and neutralised chrome leather are agitated for 30 minutes in a vessel with a dyebath of 250 parts water at 55°C and 0.5 parts of the dyestuff of Examples 1, 2 or 80, in acid addition salt form, and then treated in the same bath for 30 minutes with 2 parts of an anionic fatty liquor based on sulphonated train oil. The leather is then dried and prepared in the normal way, giving a leather evenly dyed in a grey-

violet (grey-blue and blue, respectively) shade.

Other low affinity vegetable-tanned leathers can similarly be dyed by known methods.

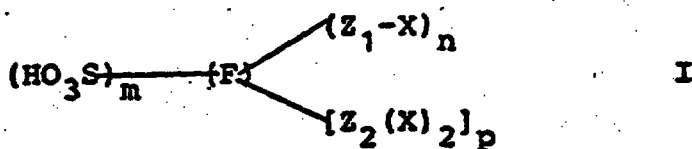
Application Example E

2 Parts of the dyestuff of Example 2 in acid addition salt form are dissolved in 4000 parts demineralised water at 40°C. 100 Parts of a pre-wetted cotton textile substrate are added, and the bath is raised to boiling point over 30 minutes and held at the boil for 1 hour. After rinsing and drying, a greyish-blue dyeing is obtained having good light- and wet-fastnesses. The dye exhausts practically quantitatively, and the waste water is almost colourless.



CLAIMS

1. A compound of formula I,



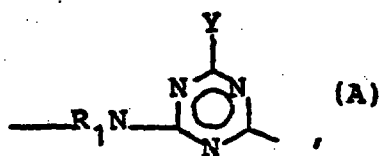
in which F is the residue of a mono or disazo compound in 1:1 metal complex form or of a tris-, disazoazoxy- or tetra-kisazo compound in metal free or in 1:1 metal complex form,

m is 1, 2 or 3,

n is 0, 1, 2, 3 or 4,

p is 0, 1, 2, 3 or 4,

each Z_1 , independently, is ---CO--- , $\text{---SO}_2\text{---}$ or



each Z_2 , independently, is $\text{---R}_1\text{N---} \begin{array}{c} \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \quad \text{(B)}$

each R_1 , independently, is hydrogen or C_{1-4} alkyl,

each Y, independently, is Cl, OH, NH_2 , an

aliphatic, cycloaliphatic or aromatic



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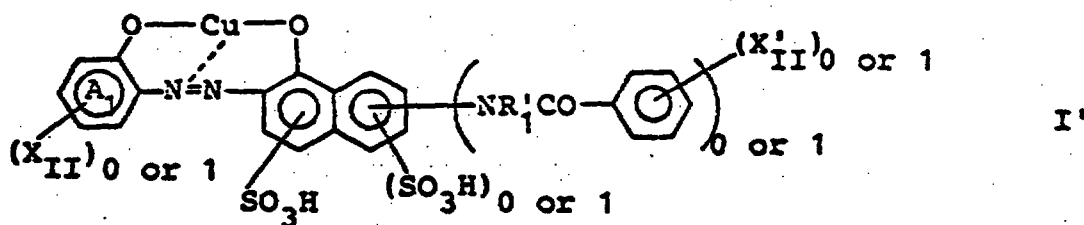
amine radical or a heterocyclic saturated amine in which the nitrogen atom is part of the heterocycle, each X, independently, is $-NR_2-Q-NR_3R_4$

or $-NR_2-Q-NR_5R_6R_7$,

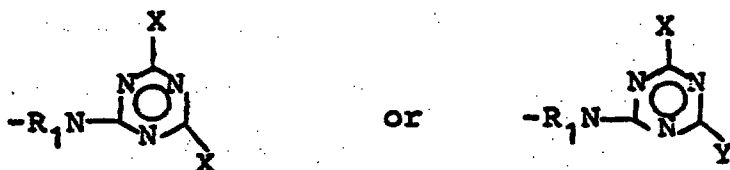
each Q, independently, is a linear or branched chain C_{2-6} alkylene or $-NHCOCH_2-$, each R_2 , independently, is hydrogen or C_{1-4} alkyl,

each R_3 and R_4 , independently, is hydrogen; C_{1-6} alkyl; cyano- or hydroxy- C_{2-6} alkyl in which the substituent is in other than 1-position; phenyl- C_{1-3} alkyl in which the phenyl nucleus is optionally substituted by a total of up to 3 substituents selected from chlorine, C_{1-4} alkyl and C_{1-4} alkoxy; C_{5-6} cycloalkyl optionally substituted by up to three C_{1-4} alkyl groups or R_3 and R_4 together with the nitrogen atom to which they are bound form a 5- or 6-membered saturated or unsaturated heterocyclic ring which optionally contains a further heteroatom,

2. A complex according to Claim 1 of formula I'



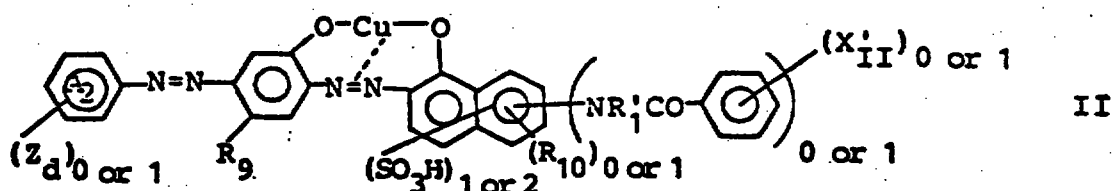
in which each of X_{II} and X'_{II} , independently, is



and R_1 is hydrogen or methyl,
and the ring A_1 optionally bears 1 or 2 further substituents selected from halogen, C_{1-4} alkyl, C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$, $-SO_2R_{13}$, $-SO_2NR_1R_1$ and $-CONR_1R_1$, where R_{13} is C_{1-4} alkyl or phenyl.



3. A complex according to Claim 1 of formula II,



in which Z_d is X_{II} or one or two groups X_I , and each of X_{II} and X'_{II} , independently, is $-Z_1''-X$ or

$-Z_2-(X)_2$ wherein Z_1'' is a group of formula (A) defined in Claim 1;

X_I is $-Z_1'-X$ wherein Z_1' is $-CO-$ or $-SO_2-$,

the ring A_2 is optionally substituted

by up to 2 further substituents

selected from halogen, C_{1-4} alkyl,

C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$, $-SO_2R_{13}$,

$-SO_2NR_1R_1$ and $-CONR_1R_1$, where R_{13} is

C_{1-4} alkyl or phenyl,

R_9 is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} -alkoxy, $-NHCO(C_{1-4}alkyl)$, $-NHCONH_2$,

$-NHCO(CH_2)_{1-3}N(C_{1-4}alkyl)_2$ or

$-NHCO(CH_2)_{1-3}N^+(CH_3)_3 A^-$, where A^- is an anion;

or R_9 together with the carbon atom to which it is

attached and the ortho carbon atom on the

benzene ring forms a condensed benzene ring;

R_{10} is hydrogen; OH; $-NH_2$; $(C_{1-4}alkyl)carbonylamino$;

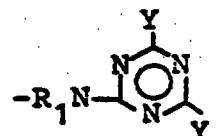
benzoylamino or anilino in which the phenyl

nucleus is optionally substituted by one or

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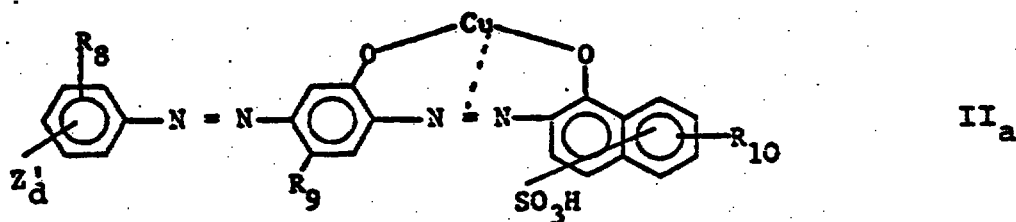


two substituents selected from halogen, NO_2 , NH_2 , C_{1-4} alkyl and C_{1-4} alkoxy; or is



in which R_1' is hydrogen or methyl, and Y' has one of the significances of Y with the exception of chlorine.

4. A complex according to Claim 1, of formula II_a ,



in which Z_d' is X_{IIb} or X_{IIe} or two groups X_{Ia} or X_{Ie} which may be the same or different;

R_8 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen, $-\text{SO}_2\text{NR}_1\text{R}_1$ or $-\text{CONR}_1\text{R}_1$;

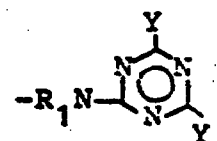
R_9 is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-\text{NHCO}(\text{C}_{1-4}\text{alkyl})$, $-\text{NHCONH}_2$, $-\text{NHCO}(\text{CH}_2)_{1-3}\text{N}(\text{C}_{1-4}\text{alkyl})_2$ or



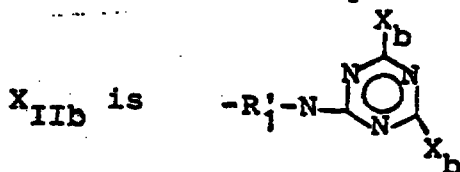
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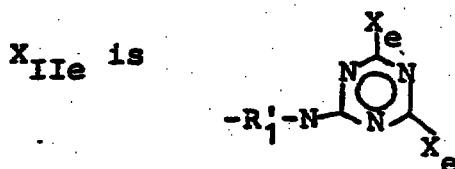
$-\text{NHCO}(\text{CH}_2)_{1-3} \text{N}^+(\text{CH}_3)_3 \text{A}^\ominus$, where $\text{A}^\ominus$ is an anion,
or R_9 together with the two carbon atoms on the
benzene ring forms a condensed benzene ring
 R_{10} is hydrogen; OH; $-\text{NH}_2$; $(\text{C}_{1-4} \text{ alkyl})$ carbonylamino;
benzoylamino or anilino in which the phenyl
nucleus is optionally substituted by one or
two substituents selected from halogen, NO_2 ,
 NH_2 , $\text{C}_{1-4} \text{ alkyl}$ and $\text{C}_{1-4} \text{ alkoxy}$; or is



in which 'Y' has one of the significances of Y
with the exception of chlorine,



in which X_b is $\text{NR}'_2-\text{Q}'-\text{NR}''_3\text{R}''_4$



in which X_e is $-\text{NR}'_2(\text{CH}_2)_{2-3} \text{N}^+(\text{CH}_3)_3$ or
 $-\text{NR}'_2(\text{CH}_2)_{2-3} \text{N}^+(\text{C}_6\text{H}_5)$

X_{Ia} is $-\text{COX}_a$ or $-\text{SO}_2\text{X}_a$,

X_{Ie} is $-\text{COX}_e$,

wherein X_a is $-\text{NR}'_2-\text{Q}-\text{NR}''_3\text{R}''_4$

each of R'_1 and R'_2 , independently, is hydrogen or methyl,
each of R''_3 and R''_4 , independently, is hydrogen, linear or
branched $\text{C}_{1-6} \text{ alkyl}$, linear 2- or 3-hydroxy-

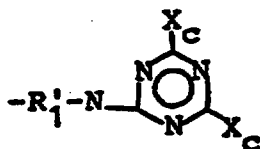


ethyl or -propyl, benzyl or together with the N-atom they form a pyrrolidine, piperidine or morpholine ring;

each of R_3'' and R_4'' , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring;

Q' is a linear or branched C_{2-6} alkylene.

5. A complex according to Claim 4, in which Z_d' is X_{IIC} or two identical groups I_{IC} , where X_{IIC} is



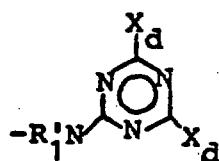
and X_{IC} is $-COX_C$

where X_C is $-NR_2'- (CH_2)_{2-6}NR_3''R_4''$, in R_2' , R_3'' and R_4'' are defined in Claim 4.

6. A complex according to Claim 4 or Claim 5, in which R_8 is hydrogen, chlorine, methyl, methoxy, $-SO_2NH_2$ or $-CONH_2$.

7. A complex according to any one of Claims 4 to 6, in which R_9 is hydrogen, methyl or methoxy.

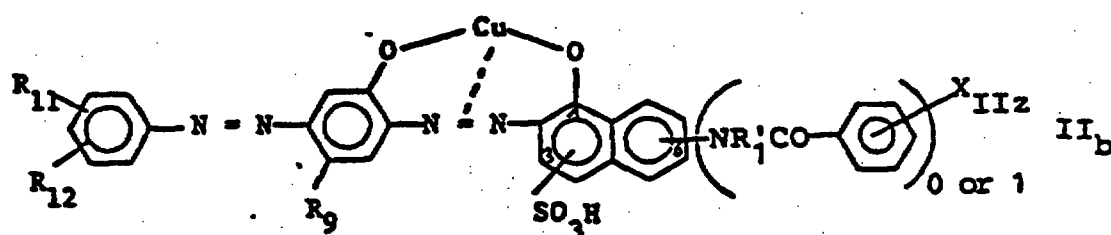
8. A complex according to any one of Claims 4 to 7, in which R_{10} is hydrogen, NH_2 , acetylamino, benzoylamino or anilino, R_8 is hydrogen and Z_d' is X_{IIId} or is two identical X_{Id} groups where X_{IIId} is



and X_{Id} is $-COX_d$

in which X_d is $-NR'_2-(CH_2)_{2-3}NR'''_3R''''_4$ wherein each of R'''_3 and R''''_4 , independently, is methyl or ethyl and R'_2 is defined in Claim 4.

9. A complex according to Claim 1, of formula II_b ,



in which X_{IIz} is a group X_{IIb} or X_{IIe} ,

R_{11} is hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, phenoxy, $-NHCOR_{13}$, $-SO_2R_{13}$, $-SO_2NR_1R_1$ or $-CONR_1R_1$, and

R_{12} is hydrogen, halogen, C_{1-4} alkyl or C_{1-4} alkoxy,

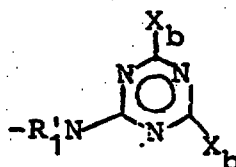
R_9 is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-NHCO(C_{1-4}$ alkyl), $-NHCONH_2$, $-NHCO(CH_2)_{1-3}N-(C_{1-4}alkyl)_2$ or $-NHCO(CH_2)_{1-3}N^+(CH_3)_3 A^\ominus$, where $A^\ominus$ is an anion,

or R_9 together with the carbon atom to which it is attached and the unsubstituted ortho carbon atoms on the benzene ring forms a condensed benzene ring;

R'_1 is hydrogen or methyl;

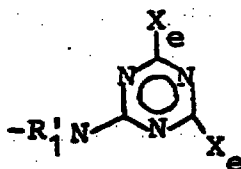


X_{IIb} is



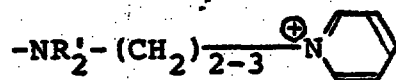
, and

X_{IIe} is



in which X_b is -NR'₂-Q'-NR'₃R'₄ and

X_e is -NR'₂-(CH₂)₂₋₃[⊕]N(CH₃)₃ or



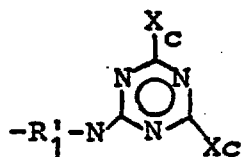
each of R'₁ and R'₂, independently, is hydrogen or methyl,
each of R'₃ and R'₄, independently, is hydrogen, linear or
branched C₁₋₄alkyl, 2-hydroxyethyl or
together with the N-atom they form a
piperidine or morpholine ring;

Q' is a linear or branched C₂₋₆alkylene.

10. A complex according to Claim 9, in which R₁₁
is hydrogen, chlorine, methyl, methoxy, acetilamino,
benzoylamino, SO₂NH₂ or -CONH₂ and R₁₂ is hydrogen,
chlorine, methyl or methoxy.

11. A complex according to Claim 9 or Claim 10,
in which R₉ is hydrogen, methyl or methoxy.

12. A complex according to any one of Claims 9 to
11, in which X_{IIz} is X_{IIc} where X_{IIc} is

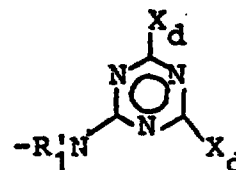


in which X_c is $-NR'_2-(CH_2)_{2-6}NR''_3R''_4$.

13. A complex according to any one of Claims 9 to 12, in which R_{11} is hydrogen, chlorine, methyl, methoxy, acetyl-amino or benzoylamino and R_{12} is hydrogen.

14. A complex according to any one of Claims 9 to 13, in which the sulfo group is in the 3-position and X_{IIz} is in the 6-position.

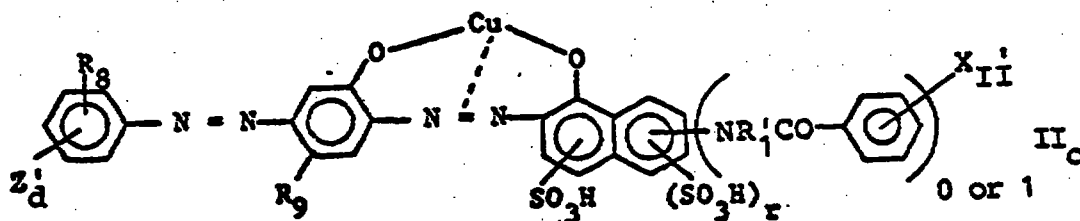
15. A complex according to any one of Claims 9 to 14, in which X_{IIz} is $X_{II d}$ where $X_{II d}$ is



in which X_d is $-NR'_2-(CH_2)_{2-3}NR''_3R''_4$ wherein each of R''_3 and R''_4 , independently, is methyl or ethyl.

16. A complex according to any one of Claims 9 to 15, in which R_{11} is hydrogen.

17. A complex according to Claim 1 of formula II_c



in which R_8 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen,

$-\text{SO}_2\text{NR}_1\text{R}_1$ or $-\text{CONR}_1\text{R}_1$;

R_9 is either hydrogen, halogen, C_{1-4} alkyl,

C_{1-4} alkoxy, $-\text{NHCO}(\text{C}_{1-4}\text{alkyl})$, $-\text{NHCONH}_2$,

$-\text{NHCO}(\text{CH}_2)_{1-3}\text{N}(\text{C}_{1-4}\text{alkyl})_2$ or

$-\text{NHCO}(\text{CH}_2)_{1-3}\text{N}^+(\text{CH}_3)_3 \text{A}^-$, where A^- is an anion;

or R_9 together with the two carbon atoms on the benzene ring forms a condensed benzene ring;

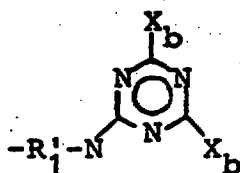
r is 0 or 1;

R'_1 is hydrogen or methyl;

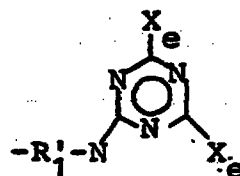
Z'_d is a group X_{IIb} or X_{IIe} or two groups

X_{Ia} or X_{Ie} wherein

X_{IIb} is



X_{IIe} is

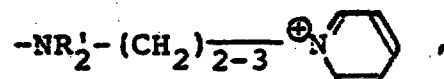


X_{Ia} is $-\text{SO}_2\text{X}_a$ or $-\text{COX}_a$,

X_{Ie} is $-\text{COX}_e$, wherein

X_b is $-\text{NR}'_2-\text{Q}'-\text{NR}''_3\text{R}_4$

X_e is $-\text{NR}'_2-(\text{CH}_2)_{2-3}\text{N}^+(\text{CH}_3)_3$ or



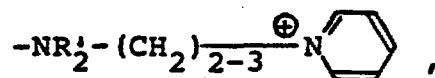
X_a is $-\text{NR}'_2-\text{Q}-\text{NR}''_3\text{R}_4$,

X_e is $-\text{NR}'_2-(\text{CH}_2)_{2-3}\text{N}^+(\text{CH}_3)_3$ or



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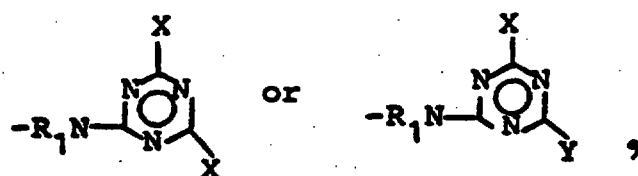


each of R_1^1 and R_2^1 , independently, is hydrogen or methyl, each of R_3^1 and R_4^1 , independently, is hydrogen, linear or branched C_{1-6} alkyl, linear 2- or 3-hydroxyethyl or -propyl, benzyl or together with the N-atom they form a pyrrolidine, piperidine or morpholine ring;

each of R_3^2 and R_4^2 , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring;

Q^1 is a linear or branched C_{2-6} alkylene;

X_{II}^1 is



and the other symbols are defined in Claim 1.

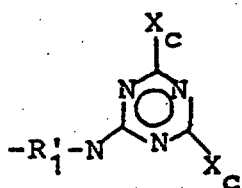
18. A complex according to Claim 17, in which R_8 is hydrogen, chlorine, methyl or methoxy.

19. A complex according to Claim 17 or Claim 18, in which R_9 is hydrogen, methyl or methoxy.

20. A complex according to any one of Claims 17 to 19, in which Z_d^1 is X_{IIc} or two identical groups X_{Ic}

in which X_{IIc} is defined in Claim 12 and X_{Ic} is defined in Claim 5.

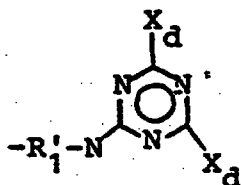
21. A complex according to any one of Claims 17 to 20, X_{II}^1 is X_{IIb} or X_{IIe} , in which X_{IIb} and X_{IIe} are defined in Claim 4.



wherein X_C is $-NR'_2-(CH_2)_{2-6}-NR''_3R''_4$, and X_{IC} is $-CO-X_C$.

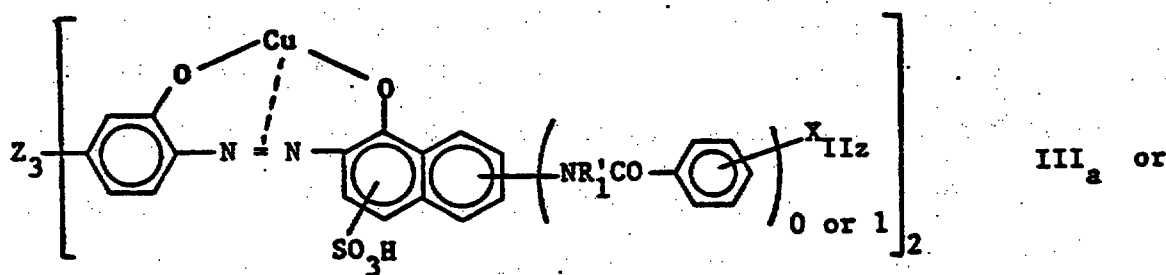
22. A complex according to Claim 21, in which $X_{II'}$ is X_{IIC} as defined in Claim 20.

23. A complex according to any one of Claims 17 to 22, in which Z_d' is X_{IIId} or two identical groups X_{Id} where X_{IIId} is

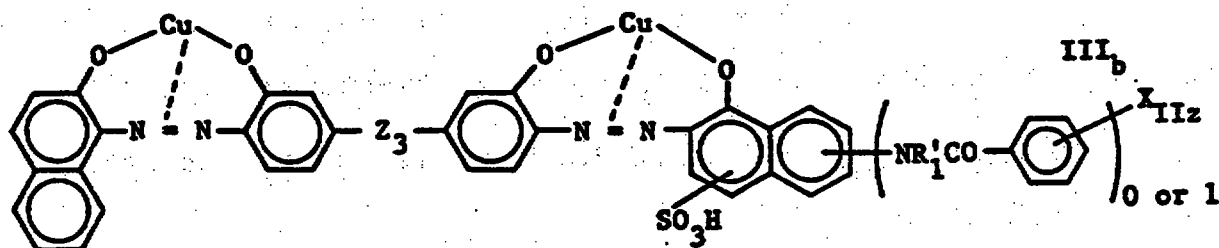


and X_{Id} is $-COX_d$ in which X_d is $-NR'_2-(CH_2)_{2-3}-NR''_3R''_4$, in which each R''_3 and R''_4 , independently, is methyl or ethyl and in which R'_1 and R'_2 are defined in Claim 4.

24. A complex according to Claim 1 of formula III_a or III_b



III_a or

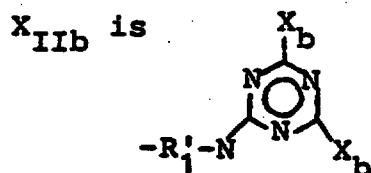


III_b

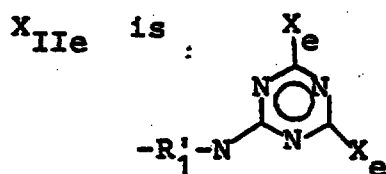


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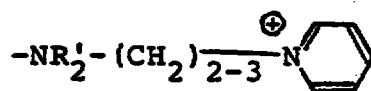
in which X_{IIz} is X_{IIb} or X_{IIe} and such groups in the complex of formula III_a are the same or different,



in which X_b is $-NR'_2-Q'-R''_3R''_4$;



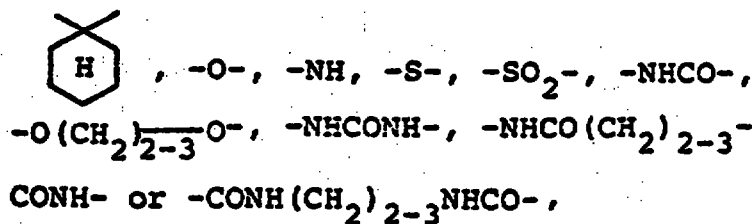
in which X_e is $-NR'_2-(CH_2)_{2-3}-\overset{\oplus}{N}(CH_3)_3$ or



each of R'_1 and R'_2 , independently, is hydrogen or methyl, each of R''_3 and R''_4 , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring;

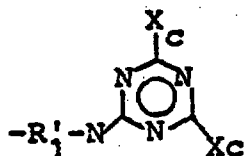
Q' is a linear or branched C_{2-6} alkylene,

Z_3 is a direct bond, $-(CH_2)_{1-3}-$, $-CH=CH-$,





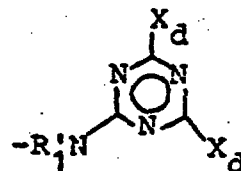
25. A complex according to Claim 24, in which X_{IIz} is X_{IIc} where X_{IIc} is



in which X_c is $-NR'_2-(CH_2)_{2-6}-NR''_3R''_4$.

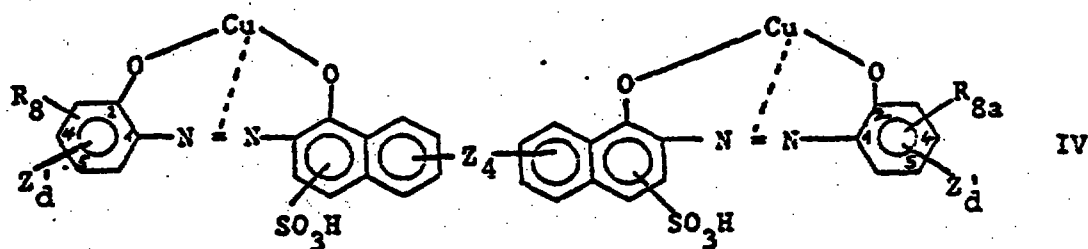
26. A complex according to Claim 24 or Claim 25, in which Z_3 is a direct bond, $-(CH_2)_2-$, $-NHCO-$, $-NHCONH-$ or $-NHCO(CH_2)_2CONH-$.

27. A complex according to any one of Claims 24 to 26, in which X_{IIz} is X_{IIId} where X_{IIId} is



in which X_d is $-NR'_2-(CH_2)_{2-3}-NR'''_3R'''_4$ wherein each of R'''_3 and R'''_4 , independently, is methyl or ethyl.

28. A complex according to Claim 1, of formula IV.

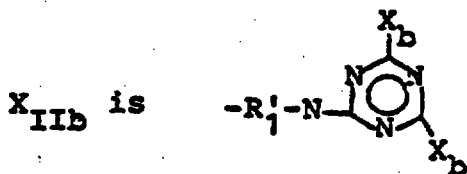




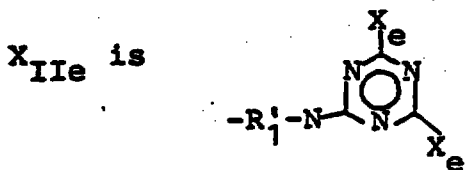
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in which each Z_d' , independently, is a group X_{IIb} or X_{IIe} ,
or two groups X_{Ia} or X_{Ie} , which may be
the same or different,

R_8 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy,
halogen, $-SO_2NR_1R_1$ or $-CONR_1R_1$;



in which X_b is $NR_2'-Q'-NR_3''R_4''$



X_{Ia} is $-COX_a$ or $-SO_2X_a$,

X_{Ie} is $-COX_e$,

wherein X_a is $-NR_2'-Q-NR_3'R_4'$

each of R_1' and R_2' , independently, is hydrogen or methyl,

each of R_3' and R_4' , independently, is hydrogen, linear or

branched C_{1-6} alkyl, linear 2- or 3-hydroxy-

ethyl or -propyl, benzyl or together with the

N-atom they form a pyrrolidine, piperidine

or morpholine ring;

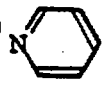
each of R_3'' and R_4'' , independently, is hydrogen, linear

or branched C_{1-4} alkyl, 2-hydroxyethyl or

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together with the N-atom they form a piperidine or morpholine ring;

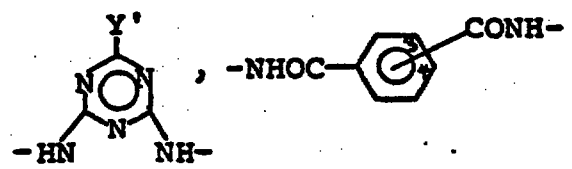
X_e is $-NR_2'(CH_2)_{2-3}-N^+(CH_3)_3$ or $-NR_2'-(CH_2)_{2-3}-N^+$ ,

Q' is a linear or branched C_{2-6} alkylene,

R_{8a} has one of the significances of R_8 ,

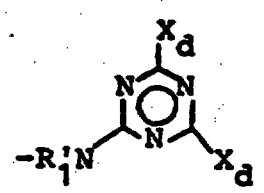
and Z_4 is a divalent nitrogen-containing bridge member.

29. A complex according to Claim 28, in which Z_4 is Z_{4a} , where Z_{4a} is $-NH-$, $-NHCONH-$,



where the CONH group is in the 3- or 4-position, $-NHCOCH_2CH_2CONH-$ or $-NHCOCH=CHCONH-$, where Y' has one of the significances of Y or X .

30. A complex according to Claim 28 or Claim 29, in which X_{IIb} is X_{IIId} , where X_{IIId} is



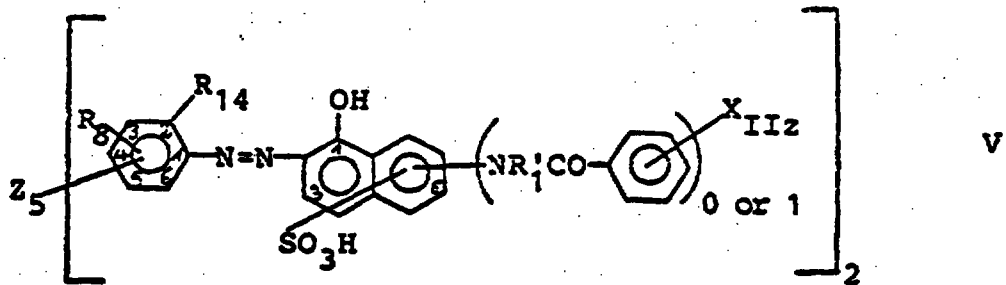
in which X_d is $-NR_2'-(CH_2)_{2-3}-NR_3'' R_4'''$ wherein each of R_3'' and R_4''' , independently, is methyl or ethyl, or in which the two groups X_{Ia} are two identical groups $-COX_d$ and X_d is defined in Claim 27.

31. A complex according to any one of Claims 28 to



30, in which Z_4 is $-NH-$ or $-NHCONH-$.

32. A compound according to Claim 1, of formula V



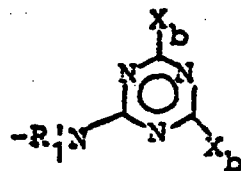
in which Z_5 , independently, is in the 4- or 5-position of each phenyl group and signifies $-N=N-$ or $-N=\overset{\text{O}}{\text{N}}-$,

R_{14} , independently, is hydrogen or methoxy,

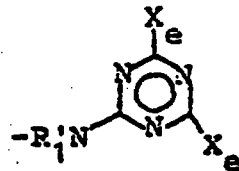
R_8 , independently, is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen, $-\text{SO}_2\text{NR}_1\text{R}_1$ or $-\text{CONR}_1\text{R}_1$;

X_{IIz} , independently, is X_{IIb} or X_{IIe} , where

X_{IIb} is

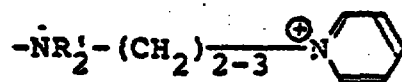


X_{IIe} is



in which X_b is $-\text{NR}'_2-\text{Q}'-\text{NR}''_3\text{R}_4$ and

X_e is $-\text{NR}'_2-(\text{CH}_2)_{2-3}-\overset{\oplus}{\text{N}}(\text{CH}_3)_3$ or



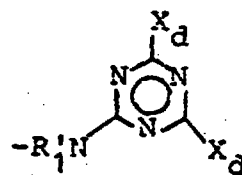


each of R_1' and R_2' , independently, is hydrogen or methyl, each of R_3'' and R_4'' , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring;

Q' is a linear or branched C_{2-6} alkylene; or a copper complex thereof.

33. A compound or complex according to Claim 32, in which R_8 , independently, is hydrogen, chlorine, methyl or methoxy.

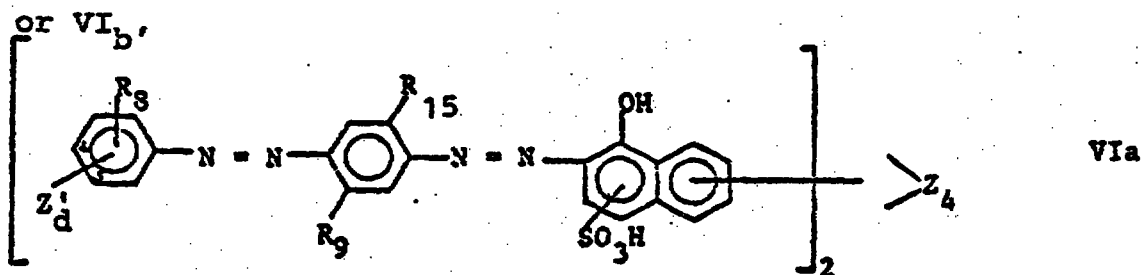
34. A compound or complex according to Claim 32 or Claim 33, in which X_{II2} , independently, is X_{IIId} , where X_{IIId} is



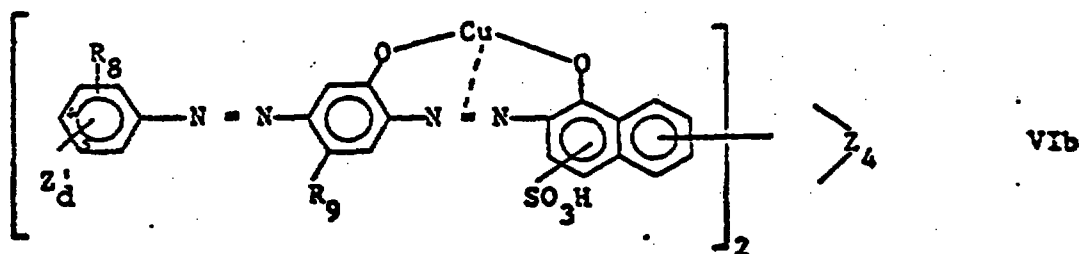
in which X_d is $-NR_2'-(CH_2)_{2-3}NR_3'''R_4'''$ wherein each of R_3''' and R_4''' , independently, is methyl or ethyl.

35. A compound or complex according to any one of Claims 32 to 34, in which the sulfo group is in the 3-position and X_{II2} is directly bound in the 6-position of the naphthalene ring.

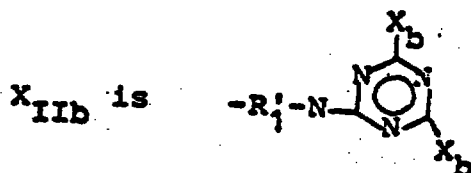
36. A compound according to Claim 1, of formula VI_a



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wherein R_8 , independently, is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen, $-SO_2NR_1R_1$ or $-CONR_1R_1$;
 R_9 , independently, is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-NHCO(C_{1-4}alkyl)$, $-NHCONH_2$, $-NHCO(CH_2)_{1-3}N(C_{1-4}alkyl)_2$ or $-NHCO(CH_2)_{1-3}N^+(CH_3)_3 A^-$, where A^- is an anion,
 or each R_9 , independently, together with the two carbon atoms on the benzene ring forms a condensed benzene ring,
 R_{15} , independently, is hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy,
 Z'_d , independently, is a group X_{IIb} or X_{IIe} or two groups X_{Ia} or X_{Ie} which may be the same or different, where

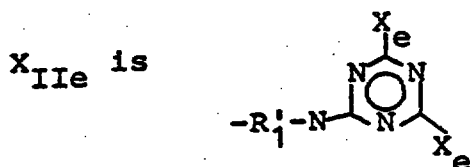


in which X_b is $NR'_2-Q'-NR'_3R'_4$,

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X_{Ia} is $-COX_a$ or $-SO_2X_a$,

X_{Ie} is $-COX_e$,

wherein X_a is $-NR_2'-Q-NR_3'R_4'$

each of R_1' and R_2' , independently, is hydrogen or methyl,

each of R_3' and R_4' , independently, is hydrogen, linear or branched C_{1-6} alkyl, linear 2- or 3-hydroxyethyl or -propyl, benzyl or together with the N-atom they form a pyrrolidine, piperidine or morpholine ring;

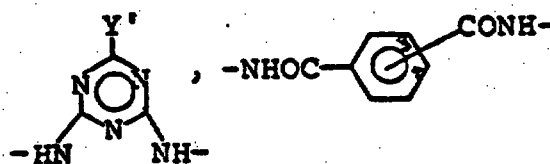
each of R_3'' and R_4'' , independently, is hydrogen, linear or branched C_{1-4} alkyl, 2-hydroxyethyl or together with the N-atom they form a piperidine or morpholine ring;

X_e is $-NR_2'(CH_2)_{2-3}-N^+(CH_3)_3$ or $-NR_2'-(CH_2)_{2-3}-N^+$ 

Q' is a linear or branched C_{2-6} alkylene,

Z_4 is a divalent nitrogen-containing bridge member.

37. A compound according to Claim 36, in which Z_4 is $-NH-$, $-NHCONH-$,

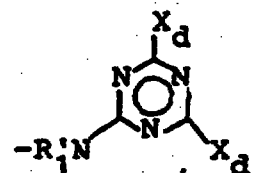




where the CONH group is in the 3- or 4-position,
-NHCOCH₂CH₂CONH- or -NHCOCH=CHCONH-, where Y' has one
of the significances of Y or X.

38. A compound according to Claim 36 or Claim 37,
in which the compounds are symmetrical and Z'_d is in the
4- or 5-position, R₈ is hydrogen, chlorine, methyl or
methoxy and R₉ is hydrogen, methyl or methoxy.

39. A compound according to any one of Claims
36 to 38, in which Z'_d is X_{IId} or two identical groups
X_{Id}, where X_{IId} is



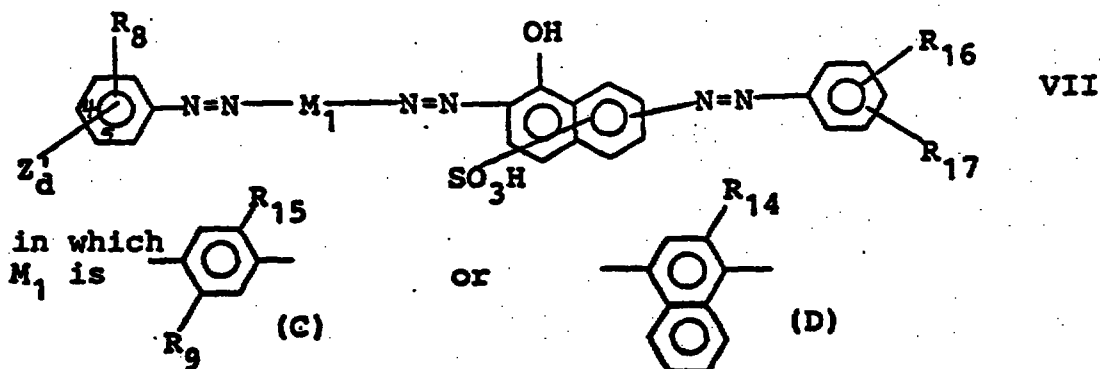
and X_{Id} is -COX_d,

in which X_d is -NR'₂-(CH₂)₂₋₃-NR'''R₄''',

where each of R₃''' and R₄''', independently, is methyl or
ethyl and R'₂ is defined in Claim 4.

40. A compound according to any one of Claims 36
to 39, in which Z₄ is -NH- or -NHCONH-.

41. A compound according to Claim 1, of formula VII,



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R_8 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy, halogen, $-SO_2NR_1R_1$ or $-CONR_1R_1$;

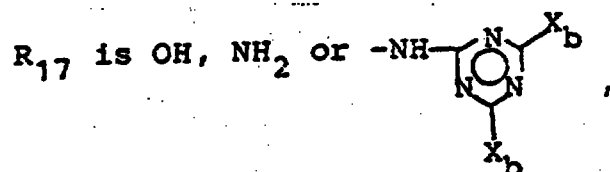
R_9 is either hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy, $-NHCO(C_{1-4}alkyl)$, $-NHCONH_2$, $-NHCO(CH_2)_{1-3}N(C_{1-4}alkyl)_2$ or $-NHCO(CH_2)_{1-3}N^+(CH_3)_3 A^-$, where A^- is an anion,

or R_9 together with the two carbon atoms on the benzene ring forms a condensed benzene ring,

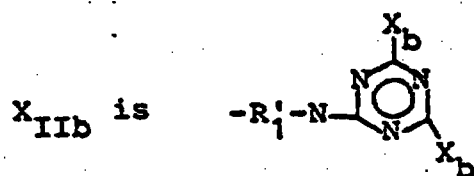
R_{14} is hydrogen or methoxy,

R_{15} is hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy,

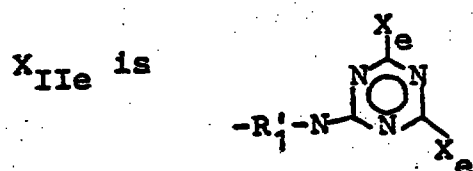
R_{16} is OH or $-NH_2$, and



Z'_d is X_{IIb} or X_{IIe} or two groups X_{Ia} or X_{Ie} which may be the same or different,



X_b is $-NR'_2-Q'-NR'_3R_4$,



X_{Ia} is $-COX_a$ or $-SO_2X_a$,



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X_{Ie} is $-COX_e$,

wherein X_a is $-NR'_2-Q-NR'_3R'_4$

each of R'_1 and R'_2 , independently, is hydrogen or methyl,

each of R'_3 and R'_4 , independently, is hydrogen, linear or

branched C_{1-6} alkyl, linear 2- or 3-hydroxy-

ethyl or -propyl, benzyl or together with the

N-atom they form a pyrrolidine, piperidine

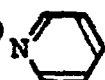
or morpholine ring;

each of R'_3 and R'_4 , independently, is hydrogen, linear

or branched C_{1-4} alkyl, 2-hydroxyethyl or

together with the N-atom they form a

piperidine or morpholine ring;

X_e is $-NR'_2'(CH_2)_{2-3}-N^+(CH_3)_3$ or $-NR'_2'-(CH_2)_{2-3}-N^+$ ,

Q' is a linear or branched C_{2-6} alkylene,

or a copper complex thereof.

42. A compound or complex according to Claim 41,
in which R_8 is hydrogen.

43. A compound or complex according to Claim 41
or Claim 42, in which Z'_d as X_{IIb} or X_{IIe} is in the 4- or 5-
position where X_{IIb} and X_{IIe} are defined in Claim 4.

44. A compound or complex according to any one
of Claims 41 to 43, in which M_1 is (C) where R_{15} is
hydrogen, methyl or methoxy and R_9 is hydrogen, methyl or
methoxy.

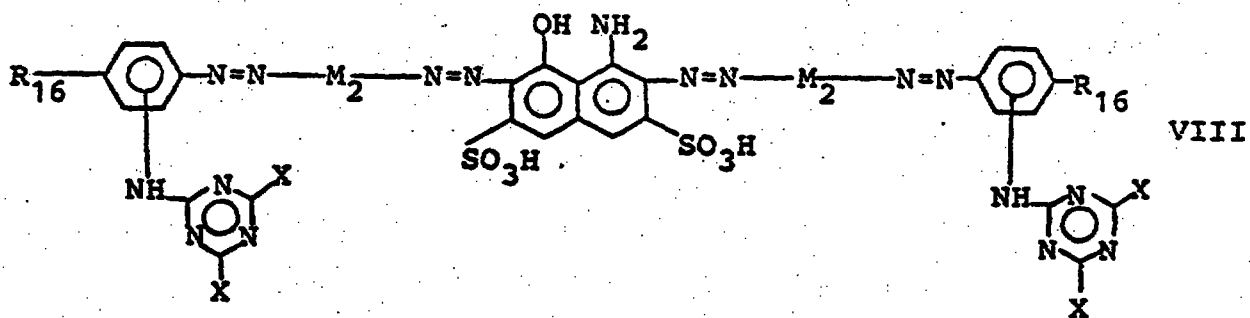
(98)



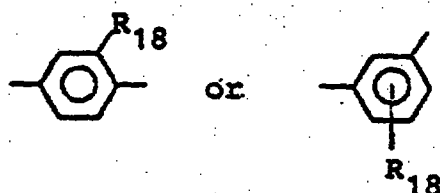
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45. A compound according to Claim 1, of formula

VIII



in which each M_2 , independently, is



in which R_{18} is hydrogen, chlorine, methyl or methoxy;

R_{16} , independently, is OH or NH_2 ;

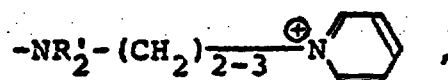
or a copper complex thereof.

46. A compound or complex according to Claim 45,
in which R_{16} is NH_2 .

47. A compound or complex according to Claim 45 or
Claim 46, in which X is X_b or X_e , where

X_b is $-NR'_2-Q'-NR''_3R''_4$ and

X_e is $-NR'_2-(CH_2)_{2-3}-N^+(CH_3)_3$ or





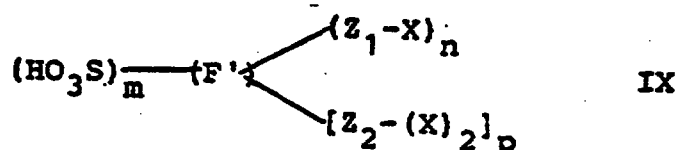
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R_2' is hydrogen or methyl,
 Q' is a linear or branched C_{2-6} alkylene and
each of R_3'' and R_4'' , independently, is hydrogen, linear
or branched C_{1-4} alkyl, 2-hydroxyethyl or
together with the N-atom they form a piperidine
or morpholine ring.

48. A compound or complex according to any one of
the preceding claims in salt form.

49. A process for the production of a complex
of formula I as defined in Claim 1 comprising reacting
a compound of formula IX,



in which F' is a metallizable residue with an equivalent
of a metal donating compound.

50. A process for the production of a compound
of formula I as defined in Claim 1, substantially as
hereinbefore described with reference to any one of
Examples 1 to 160.

51. A compound of formula I, whenever obtained
by a process according to Claim 50.

52. A process for dyeing or printing substrates
consisting of or comprising leather, paper or cotton
comprising employing a compound or complex according to
any one of Claims 1 to 47, in external salt form.

1a



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53. A process according to Claim 52, substantially as hereinbefore described with reference to any one of Examples A to E.

54. Dyed or printed substrates whenever obtained by a process according to Claim 52 or Claim 53.
