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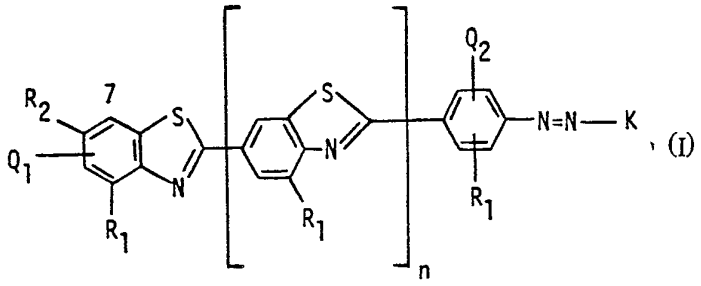
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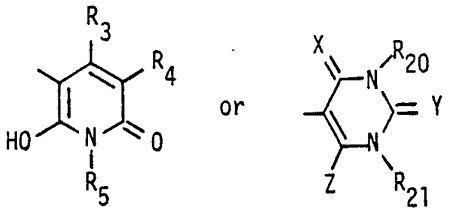
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(I)



(II) (III)

(57) Abstract

Monoazo compounds which, in one of the possible tautomeric forms, correspond to formula (I), in free acid or salt form, in which K is one of the groups (II) or (III) and the symbols are as defined in the Specification, are suitable as dyestuffs. They are used as such or in form of solid or particularly liquid aqueous dyestuff preparations for dyeing or printing hydroxy group or nitrogen containing organic substrates, such as textiles consisting of or containing cellulose material, leather or especially paper.

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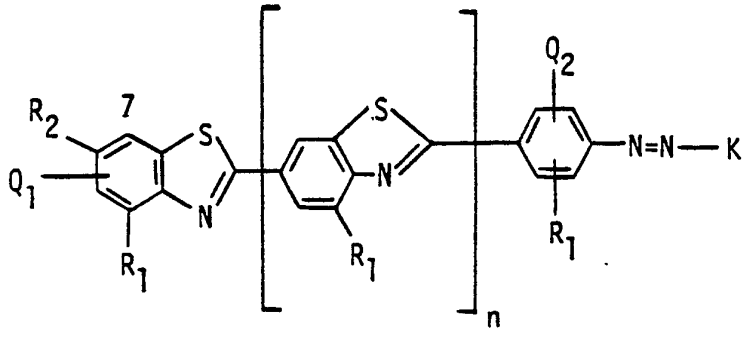
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IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

The invention relates to anionic heterocyclic compounds suitable for use as dyestuffs.

According to the invention there is provided a compound which, in one of the possible tautomeric forms, corresponds to formula I,



I

in which

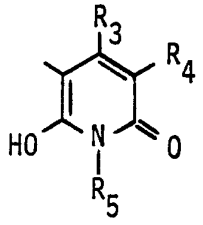
each of R_1 and R_2 is independently hydrogen, C_{1-4}alkyl, C_{1-4}alkoxy or COOM,

each of Q_1 and Q_2 is independently hydrogen or SO_3M_1,

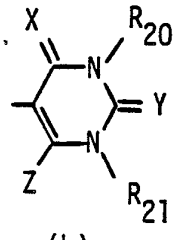
n is 0 or 1,

each of M and M_1 is independently hydrogen or a non-chromophoric cation;

K is one of the groups (a) and (b),



(a)



(b)

in which

R_3 is hydrogen, CN, NH_2, OH, C_{1-4}alkoxy, C_{1-4}alkyl, C_{2-4}alkyl monosubstituted by hydroxy or C_{1-4}alkoxy, C_{5-6}cycloalkyl; phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M; a saturated or unsaturated 5- or 6-membered heterocyclic ring containing one to three hetero atoms which is unsubstituted or further substituted by one to three C_{1-4}-alkyl groups and which is bound by a carbon or nitrogen atom directly or via a bridge member provided that any $\overset{\oplus}{N}$ is bound via a bridge member; $-COR_6$ or $-(CH_2)_{1-3}-R_7$,

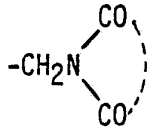
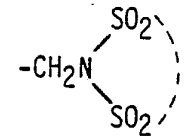
R_6 is OH, NH_2 or C_{1-4}alkoxy,

R_7 is CN, halogen, SO_3M, $-OSO_3M$, $-COR_8$ or ,

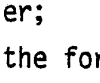
R_8 is OH, NH_2, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN or C_{1-4}alkoxy; C_{1-4}alkoxy, phenoxy, phenyl or phenyl-C_{1-4}alkyl in which the phenyl groups of the latter three groups are unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M;

R_4 is hydrogen, CN, halogen, SO_3M, NO, NO_2, $-NR_9R_{10}$, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}alkoxy, phenyl, SO_3M or $-OSO_3M$;

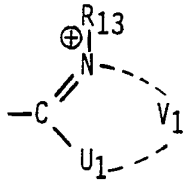
$-SO_2NH_2$, $-COR_{11}$, $-CH_2NHCOR_{12}E$, a group of the formulae

 or ,

in which the carbonyl or sulphonyl groups are bound to two carbon atoms of an aromatic ring which are in ortho position to each other;

a group of the formula  in which the $\overset{\oplus}{N}$ ion is part of a 5- or 6-membered ring containing one to three hetero atoms which is further unsubstituted or substituted by one or two methyl groups or by NH_2, $-NHC_{1-4}$alkyl or $N(C_{1-4}alkyl)_2$; or

a group of the formula



in which

R_{13} is hydrogen or C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}alkoxy or phenyl,

U_1 is S, -NH or -NC_{1-4}alkyl, and

V_1 is a group necessary to form a 5- or 6-membered ring to which ring a further 5- or 6-membered carbocyclic or heterocyclic ring containing one or two hetero atoms may be condensated,

or

both R_3 and R_4 together form a C_3- or C_4-chain which may be part of a further 5- or 6-membered ring by two vicinal chain members,

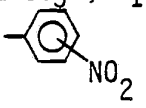
each of R_9 and R_{10} is independently hydrogen, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}-alkoxy or phenyl; or -$COR_{12}E$,

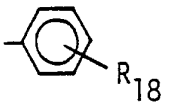
R_{11} is OH, NH_2, -NHC_{1-4}alkyl, -N$(C_{1-4}alkyl)_2$, C_{1-4}alkyl, C_{1-4}-alkoxy, phenyl or phenoxy which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M,

R_{12} is C_{1-6}alkylene,

E is hydrogen, halogen, a protonable amine group, a quaternary ammonium group or a hydrazinium group; SO_3M or -OSO_3M;

R_5 is hydrogen, CN, NO_2, -$NR_{14}R_{15}$, a saturated or unsaturated 5- or 6-membered heterocyclic ring containing one or two hetero atoms which is bound by a carbon or nitrogen atom and which is further unsubstituted or substituted by up to three methyl

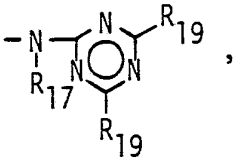
groups or by NH_2, $-NHC_{1-4}alkyl$ or $-N(C_{1-4}alkyl)_2$; $C_{1-6}alkyl$, $C_{2-4}alkenyl$, $C_{2-4}alkinyl$; $C_{1-6}alkyl$ monosubstituted by OH, CN, $C_{1-4}alkoxy$, acetamido, $-COR_{16}$, SO_3M or $-OSO_3M$; $C_{5-6}cycloalkyl$, phenyl or phenyl-$C_{1-4}alkyl$ which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from $C_{1-4}alkyl$, $C_{1-4}alkoxy$, halogen, NO_2, NH_2, COOM and SO_3M; $C_{1-6}alkylene-E_1$, $-C_{1-6}alkylene-N(R_{17})CO$- or a group of the formula

,

each of R_{14} and R_{15} is independently hydrogen, $C_{1-4}alkyl$, $C_{1-4}alkyl$ monosubstituted by OH, halogen, CN or $C_{1-4}alkoxy$; phenyl or phenyl substituted by one or two groups selected from halogen, $C_{1-4}alkyl$ and $C_{1-4}alkoxy$,

R_{16} is OH or $C_{1-4}alkoxy$,

R_{17} is hydrogen or $C_{1-4}alkyl$,

E_1 is a protonable amine group, a quaternary ammonium group or a hydrazinium group or a group of the formula ,

R_{18} is E_2, $-NHCOR_{12}E_2$, $-SO_2NHR_{12}E_2$ or $-CONHR_{12}E_2$;

each R_{19} is independently halogen, NH_2 or an aliphatic amine group,

E_2 is a protonable amine group, a quaternary ammonium group or a hydrazinium group,

X is O or NH,

Z is OH, NH_2, methyl or ethyl,

Y is O, S or N-Y_1,

Y_1 is hydrogen, CN, $CONH_2$, $C_{1-4}alkyl$, $C_{1-4}alkyl$ monosubstituted by OH, CN, halogen or $C_{1-4}alkoxy$; phenyl or phenyl-$C_{1-4}alkyl$ which phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from halogen,

C_{1-4}alkyl, C_{1-4}alkoxy, acetamido, COOM and SO_3M; 1- or 2-naphthyl; C_{1-6}alkylene-SO_3M, C_{1-6}alkylene-OSO_3M or C_{1-6}-alkylene-COOM,

each of R_{20} and R_{21} is independently hydrogen, C_{1-4}alkyl, phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from halogen, C_{1-4}alkyl, C_{1-4}alkoxy, COOM and SO_3M; or, provided that Y is N-Y_1 where Y_1 is hydrogen, one of R_{20} and R_{21} may also have a significance additionally given for Y_1;

with the provisos that

(i) in a compound of formula I at least one sulphonic acid group is present;

(ii) when in a compound of formula I

(1) K is a group (b), in which Y is O or S,

(2) R_2 is other than COOM,

(3) one of Q_1 and Q_2 or both Q_1 and Q_2 are SO_3M_1,

and (1) to (3) occur simultaneously,

then at least one of M_1 is a quaternary ammonium cation;

(iii) when in a compound of formula I containing as K a group (b)

(1) the diazo component radical is defined as follows:

R_1 is hydrogen, R_2 is methyl, Q_1 is SO_3M_1 in the 7-position, n is 0 and Q_2 is hydrogen,

(2) X is O or NH,

(3) each of R_{20} and R_{21} is hydrogen,

(4) Y is N-Y_1 in which Y_1 is hydrogen,

and (1) to (4) occur simultaneously,

then M_1 has a significance other than hydrogen or sodium;

which compound of formula I is in free acid or salt form with the proviso that each sulphonic acid group as well as each protonable amine group can be present in ionized form.

In the specification any halogen means fluorine, chlorine or bromine, especially chlorine.

Generally, any alkyl or alkylene is linear or branched unless indicated to the contrary.

In any hydroxysubstituted alkyl group which is linked to a nitrogen atom, the hydroxy group is bound to a carbon atom other than to the C_1-atom.

Q_1 is preferably SO_3M_1 which is more preferably bound to the 7-position.

n is preferably 0.

Each R_1 is preferably R_{1a}, where each R_{1a} is independently hydrogen, C_{1-4}alkyl, methoxy or ethoxy. More preferably it is R_{1b}, where each R_{1b} is independently hydrogen, methyl, ethyl, methoxy or ethoxy. Even more preferably it is R_{1c}, where each R_{1c} is independently hydrogen or methyl. Most preferably R_1 is hydrogen.

R_2 is preferably R_{2a}, where R_{2a} is C_{1-4}alkyl, C_{1-4}alkoxy or COOM. More preferably it is R_{2b}, where R_{2b} is methyl, methoxy, ethoxy or COOM. Most preferably R_2 is methyl.

Q_2 when defined as SO_3M_1 is preferably bound to a carbon atom which is in ortho- position to the azo group.

Any alkyl or alkoxy as R_3 preferably contains 1 or 2 carbon atoms and is most preferably methyl or methoxy. Any substituted alkyl is preferably a C_{2-3}alkyl group monosubstituted by hydroxy or C_{1-2}alkoxy. Any cycloalkyl is preferably cyclohexyl.

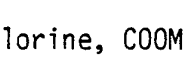
Preferably, in any substituted phenyl or phenylalkyl group the phenyl group contains one or two groups selected from methyl, methoxy, chlorine, COOM and SO_3M.

Any heterocyclic ring as R_3 is preferably morpholine, pyrrolidine, piperidine, piperazine or N-methylpiperazine (when saturated) which is bound by a carbon or nitrogen atom, or is pyridine, triazine, pyridazine, pyrimidine or pyrazine (when unsaturated) which is bound by a carbon or nitrogen atom where in the latter

case (when bound by a nitrogen atom) a methylene bridge is present.

R_6 is preferably R_{6a}, where R_{6a} is OH, NH_2, methoxy or ethoxy. More preferably it is R_{6b}, where R_{6b} is OH or NH_2.

R_7 is preferably R_{7a}, where R_{7a} is CN, chlorine, SO_3M, $-OSO_3M$,  or $-COR_{8a}$, where R_{8a} is OH, NH_2, methyl, ethyl, methoxy or ethoxy; more preferably it is R_{7b}, where R_{7b} is SO_3M, $-OSO_3M$,  or $-COR_{8b}$, where R_{8b} is OH or NH_2.

R_3 is preferably R_{3a}, where R_{3a} is hydrogen, CN, NH_2, OH; methyl, ethyl, hydroxyethyl, C_{1-2}alkoxyethyl, methoxy, ethoxy, cyclohexyl; phenyl or phenyl-C_{1-2}alkyl in which the phenyl group is unsubstituted or substituted by one or two groups selected from methyl, methoxy, chlorine, COOM and SO_3M;  , $-COR_{6a}$ or $-(CH_2)_{1-2}R_{7a}$. More preferably R_3 is R_{3b}, where R_{3b} is NH_2, methyl, ethyl, hydroxyethyl, cyclohexyl, phenyl, phenyl-C_{1-2}alkyl, $-COR_{6b}$ or $-CH_2R_{7b}$. Even more preferably R_3 is R_{3c}, where R_{3c} is NH_2, methyl, hydroxyethyl, phenylethyl or $-CH_2SO_3M$. Most preferably R_3 is methyl.

Any protonable amine or quaternary ammonium group as E, E_1 or E_2 is preferably a group B, where B is a primary amine group, a secondary or tertiary aliphatic, cycloaliphatic, aromatic or saturated, unsaturated or partially unsaturated heterocyclic amine group which latter group is attached by the N-atom or a carbon atom; or a quaternary ammonium group corresponding to the above.

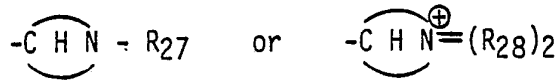
Any aliphatic amine group as B is preferably a mono-C_{1-4}-alkyl- or a di-(C_{1-4}alkyl)-amine group. The alkyl group may be monosubstituted by halogen, hydroxy, cyano, C_{1-4}alkoxy or phenyl. Any cycloaliphatic amine group is preferably C_{5-6}cycloalkylamino, the cycloalkyl group of which is unsubstituted or may be substituted by one or two C_{1-2}alkyl groups.

Any aromatic amine group is preferably phenylamino, the phenyl ring of which is unsubstituted or substituted by one or two

groups selected from halogen, C_{1-4}alkyl, C_{1-4}alkoxy, SO_3M and COOM.

Any heterocyclic amine group as B which is attached by the N-atom or a carbon atom is preferably a saturated, unsaturated or partially unsaturated 5- or 6-membered ring which contains one or two hetero atoms and may be further substituted by one or two C_{1-4}alkyl groups.

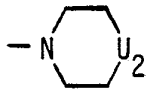
More preferably B is B_1, where B_1 is a protonable amine group $-NR_{22}R_{23}$ or a quaternary ammonium group $-\overset{\oplus}{N}R_{24}R_{25}R_{26}$, or B_1 forms a protonable or quaternary 5- or 6-membered saturated heterocyclic ring of the formula



or a corresponding protonable or quaternary 5- or 6-membered unsaturated or partially unsaturated heterocyclic ring,

each of R_{22} and R_{23}, independently, is hydrogen, C_{1-4}alkyl, C_{2-4}alkyl monosubstituted by hydroxy, C_{1-4}alkoxy, halogen or cyano; phenyl-C_{1-4}alkyl, the phenyl group of which is unsubstituted or substituted by one to three groups selected from chlorine, C_{1-4}alkyl and C_{1-4}alkoxy, or C_{5-6}cycloalkyl, or

R_{22} and R_{23}, together with the N-atom to which they are attached, attached, form a heterocyclic ring of the formula



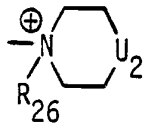
in which

U_2 is the direct bond, $-CH_2-$, $-O-$, $-S-$, $-SO_2-$, $-SO-$, $-NH-$, $-N(C_{1-4}alkyl)-$ or $-\overset{\oplus}{N}(C_{1-4}alkyl)_2-$,

each of R_{24} and R_{25} has independently one of the cyclic or non-cyclic significances of R_{22} and R_{23} except hydrogen, and

R_{26} is C_{1-4}alkyl or phenyl-C_{1-4}alkyl, or

R_{24}, R_{25} and R_{26}, together with the N-atom to which they are attached, form a pyridinium group unsubstituted or substituted by one or two methyl groups, or a ring of the formula



in which R_{26} and U_2 are as defined above,

R_{27} is hydrogen or C_{1-4}alkyl and

each of R_{28}, independently, is C_{1-4}alkyl.

Even more preferably B is B_2, where B_2 is a group $-NR_{22a}R_{23a}$ or $-\overset{\oplus}{N}R_{24a}R_{25a}R_{26a}$,

each of R_{22a} and R_{23a}, independently, is hydrogen, C_{1-2}alkyl, unbranched hydroxy-C_{2-3}alkyl or benzyl or both R_{22a} and R_{23a}, together with the N-atom to which they are attached, form a pyrrolidine, piperidine, morpholine, piperazine or N-methylpiperazine group,

each of R_{24a} and R_{25a} has independently one of the non-cyclic or cyclic significances of R_{22a} and R_{23a} except hydrogen, and

R_{26a} is methyl, ethyl or benzyl, or

R_{24a}, R_{25a} and R_{26a}, together with the N-atom to which they are attached, form a pyridinium group unsubstituted or substituted by one or two methyl groups.

Most preferably B is B_3, where B_3 is a group $-NR_{22b}R_{23b}$ or $-\overset{\oplus}{N}R_{24b}R_{25b}R_{26b}$,

each of R_{22b} and R_{23b} is hydrogen, methyl or ethyl or both R_{22b} and R_{23b}, together with the N-atom to which they are attached, form a piperidine, morpholine, piperazine or N-methylpiperazine ring;

each of R_{24b} and R_{25b} is methyl or ethyl or both R_{24b} and R_{25b}, together with the N-atom to which they are attached, has one of the cyclic significances of R_{22b} and R_{23b},

R_{26b} is methyl or ethyl or

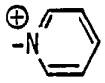
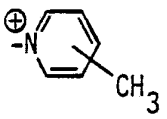
R_{24b}, R_{25b} and R_{26b}, together with the N-atom to which they are attached, form a pyridinium group unsubstituted or substituted by one or two methyl groups.

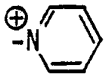
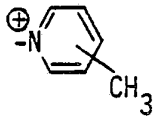
E ist preferably E_a, where E_a is hydrogen, chlorine, a group B_2 or SO_3M; more preferably it is E_b, where E_b is hydrogen, chlorine, a group B_3 or SO_3M.

Each of R_9 and R_{10} is preferably R_{9a} and R_{10a}, where each of R_{9a} and R_{10a} is independently hydrogen, C_{1-2}alkyl, C_{1-2}alkyl monosubstituted by OH, C_{1-2}alkoxy or phenyl, or $-COR_{12a}E_a$, in which R_{12a} is C_{1-2}alkylene. More preferably each of R_9 and R_{10} is R_{9b} and R_{10b}, where each of R_{9b} and R_{10b} is independently hydrogen, methyl or $-COR_{12a}E_b$.

R_{11} is preferably R_{11a}, where R_{11a} is OH, NH_2, $-NHCH_3$, $-N(CH_3)_2$, methyl, ethyl, methoxy or ethoxy. More preferably it is R_{11b}, where R_{11b} is NH_2, methyl, ethyl, methoxy or ethoxy.

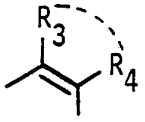
R_4 is preferably R_{4a}, where R_{4a} is hydrogen, CN, chlorine, bromine, SO_3M, $-NR_{9a}R_{10a}$, C_{1-2}alkyl, C_{1-2}alkyl monosubstituted by OH, phenyl, SO_3M or $-OSO_3M$; $-COR_{11a}$, $-CH_2NHCOR_{12a}B_2$ or a group $-\overset{\oplus}{N}=$ forming a pyridine, pyrimidine or benzimidazole ring which is further unsubstituted or monosubstituted by methyl, NH_2, $-NHCH_3$ or $-N(CH_3)_2$. More preferably R_4 is R_{4b}, where R_{4b} is hydrogen, CN, $-NHR_{10b}$, $-COR_{11b}$, $-CH_2NHCOCH_2B_3$ or a group of the formulae

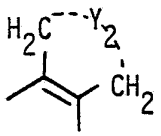
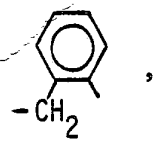
 or . Even more preferably R_4 is R_{4c},

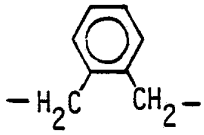
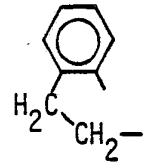
where R_{4c} is hydrogen, CN, $-NHCOCH_2E_b$, $-CONH_2$,  or .

Most preferably R_4 is R_{4d}, where R_{4d} is hydrogen or CN.

It is also preferred that R_3 and R_4 together with the carbon atoms to which they are attached form part of a further ring which corresponds to the formula

; for example they form a ring of the formula

 in which Y_2 is $-(CH_2)_{1-2}-$, ,

 or .

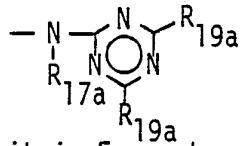
R_{14} and R_{15} are preferably R_{14a} and R_{15a}, where each of R_{14a} and R_{15a} is independently hydrogen, methyl, ethyl or phenyl.

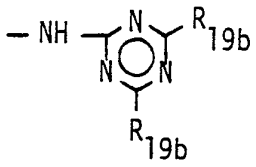
R_{16} is preferably R_{16a}, where R_{16a} is OH, methoxy or ethoxy.

R_{17} is preferably R_{17a}, where R_{17a} is hydrogen or methyl.

Any aliphatic amine group as R_{19} is preferably a mono-C_{1-4}-alkyl- or di-(C_{1-4}alkyl)-amine group, in which the alkyl groups may be monosubstituted by halogen, OH, CN, C_{1-4}alkoxy or phenyl.

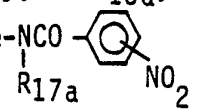
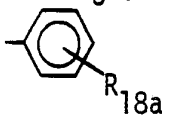
Each R_{19} is preferably R_{19a}, where each R_{19a} is independently fluorine, chlorine, NH_2, $-NHC_{1-2}$alkyl or $-N(C_{1-2}alkyl)_2$, in which the alkyl groups are unsubstituted or monosubstituted by OH, CN or C_{1-2}alkoxy. More preferably each R_{19} is R_{19b}, where each R_{19b} is independently chlorine, NH_2, $-NHCH_3$, $-N(CH_3)_2$, $-NHCH_2CH_2OH$ or $-N(CH_2CH_2OH)_2$.

E_1 is preferably E_{1a}, where E_{1a} is a group B_2 or a group of the formula  ;

more preferably it is E_{1b}, where E_{1b} is a group B_3 or a group of the formula  .

E_2 is preferably E_{2a}, where E_{2a} is a group B_2. More preferably it is E_{2b}, where E_{2b} is a group B_3.

R_{18} is preferably R_{18a}, where R_{18a} is E_{2a}, $-NHCOR_{12a}E_{2a}$, $-SO_2NHR_{12a}E_{2a}$ or $-CONHR_{12a}E_{2a}$; more preferably it is R_{18b}, where R_{18b} is E_{2b}, $-NHCOR_{12a}E_{2b}$ or $-CONHR_{12a}E_{2b}$.

R_5 is preferably R_{5a}, where R_{5a} is hydrogen, $-NR_{14a}R_{15a}$, phenyl, phenyl-C_{1-2}alkyl, cyclohexyl; C_{1-4}alkyl, C_{1-4}alkyl monosubstituted by OH, CN, C_{1-2}alkoxy, $-COR_{16a}$, SO_3M or $-OSO_3M$; $-C_{1-3}$alkylene-E_{1a}, $-C_{1-3}$alkylene- or  .

More preferably R_5 is R_{5b}, where R_{5b} is hydrogen, $-NHR_{15a}$, phenyl, phenyl-C_{1-2}alkyl, methyl, ethyl, C_{1-2}alkyl monosubstituted by SO_3M

or $-COR_{16a}$, $-(CH_2)_{1-3}-E_{1b}$, $-(CH_2)_{1-3}-NHCO-C_6H_4-NO_2$ or $-C_6H_4-R_{18b}$.

Most preferably R_5 is hydrogen.

X is preferably O.

Z is preferably Z_a, where Z_a is OH or NH_2.

Preferably, the phenyl group of any phenyl or phenylalkyl as Y_1 (when substituted) is substituted by one or two groups selected from chlorine, methyl, methoxy, COOM and SO_3M.

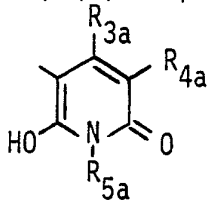
Y_1 is preferably Y_{1a}, where Y_{1a} is hydrogen, CN, $CONH_2$, methyl, ethyl, C_{2-4}alkyl monosubstituted by OH, CN, chlorine or C_{1-2}alkoxy; phenyl or phenyl-C_{1-2}alkyl, the phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from chlorine, methyl, methoxy, COOM and SO_3M; C_{2-4}alkylene-SO_3M, C_{2-4}alkylene-OSO_3M or C_{2-4}alkylene-COOM. More preferably it is Y_{1b}, where Y_{1b} is hydrogen, CN, $CONH_2$, methyl, ethyl, 2-hydroxyethyl, phenyl, phenyl-C_{1-2}alkyl, C_{2-4}alkylene-SO_3M or C_{2-4}alkylene-COOM. Even more preferably it is Y_{1c}, where Y_{1c} is hydrogen, CN or $CONH_2$. Most preferably it is Y_{1d}, where Y_{1d} is hydrogen or CN, of which hydrogen is most preferred.

Y is preferably Y_a, where Y_a is O or N-Y_{1a}; more preferably it is Y_b, where Y_b is O or N-Y_{1b}; even more preferably it is Y_c, where Y_c is O or N-Y_{1c}; most preferably it is Y_d, where Y_d is O or N-Y_{1d}.

Each of R_{20} and R_{21} is preferably R_{20a} and R_{21a}, where each of R_{20a} and R_{21a} is independently hydrogen, methyl, ethyl, phenyl-C_{1-2}alkyl or phenyl, the phenyl groups of which are unsubstituted or substituted by one or two groups selected from chlorine, methyl, methoxy, COOM and SO_3M, or in case where Y is N-Y_1 in which Y_1 is hydrogen, one of R_{20a} and R_{21a} has also a significance additionally given for Y_{1a}. More preferably each of R_{20} and R_{21} is R_{20b} and R_{21b}, where each of R_{20b} and R_{21b} is

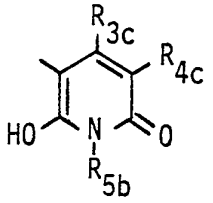
independently hydrogen, methyl, ethyl, phenyl or benzyl or in case where Y is N-Y_1 in which Y_1 is hydrogen, one of R_{20b} and R_{21b} has a significance additionally given for Y_{1b}. Most preferably R_{20} and R_{21} are hydrogen.

The group (a) is preferably (a_1) of the formula



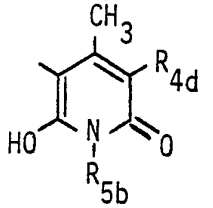
(a_1) ;

more preferably (a_2) of the formula



(a_2) ;

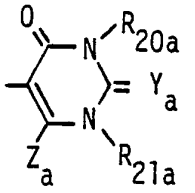
most preferably (a_3) of the formula



(a_3) ,

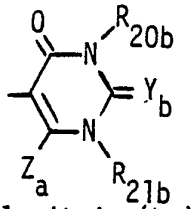
in which R_{5b} especially is hydrogen.

The group (b) is preferably (b_1) of the formula



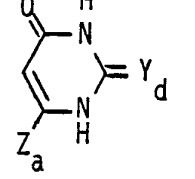
(b_1) ;

more preferably it is (b_2) of the formula



(b_2) ;

most preferably it is (b_3) of the formula



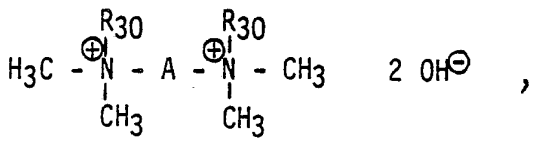
(b_3) .

K is preferably K_1, where K_1 is one of the groups (a_1) or (b_1). More preferably it is K_2, where K_2 is one of the groups (a_2) or (b_2). Even more preferably it is K_3, where K_3 is one of the groups (a_3) or (b_3). Most preferably K is K_4, where K_4 is a group (a_3).

A compound of formula I according to the invention is in free acid form, in alkali metal or unsubstituted or substituted ammonium salt form or in mixed salt form, or may form an internal salt. Any substituted ammonium cation present as M or M_1 may be derived from a primary, secondary or tertiary amine. For example, the following amines are suitable:- mono-, di- or trimethyl-, -ethyl-, -propyl- or -butyl-amine; mono-, di- or triethanol-, -propanol- or isopropanol-amine; N-methyl-N-hydroxyethylamine, N-methyl-N,N-di(hydroxyethyl)amine, N-ethyl-N-hydroxyethoxyethyl-amine, morpholine, piperidine, piperazine, hydroxyethylmorpholine, hydroxyethylpiperazine, aminoethylpiperazine; ethylenediamine, hexamethylenediamine; dimethylaminopropylamine, diethylamino-propylamine, diethylene glycol amine, diglycol amine and 3-meth-oxypropylamine.

Also suitable as amines are polyglycol amines. They can be prepared for example by reacting ammonia, alkyl- or hydroxyalkyl-amine with alkylene oxides.

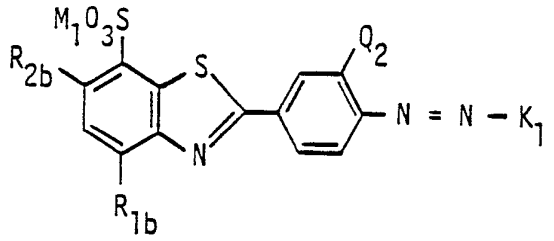
Any substituted ammonium ion may also be a quaternary ammonium ion (especially when M_1) derived from ammonium compounds which preferably contain one or two quaternary ammonium ions. Examples are tetramethyl-, tetraethyl-, trimethylethyl-, benzyl-diethylmethyl-, trimethylphenyl-, trimethylbenzyl-, triethylcyclo-hexyl-, trimethylhydroxyethyl- and tetrahydroxyethyl - ammonium-hydroxide as well as N,N-dimethylpiperidinium hydroxide, or compounds corresponding to the formula



,

in which each R_{30} is independently methyl, ethyl, hydroxyethyl or 2- or 3-hydroxypropyl and A is C_{1-4}alkylene or $-CH_2CH_2N(CH_3)CH_2CH_2-$.

Preferred compounds correspond to formula Ia



Ia

in which R_{1b}, R_{2b}, Q_2, M_1 and K_1 are as defined above with the provisos that

(ii) when in a compound of formula Ia

(1) K_1 is a group (b_1), in which Y_a is O,

(2) R_{2b} is other than COOM,

(3) Q_2 is hydrogen or SO_3M_1,

and (1) to (3) occur simultaneously,

then at least one of M_1 is a quaternary ammonium cation as defined above;

(iii) when in a compound of formula Ia in which K_1 is a group (b_1)

(1) the diazo component radical is defined as follows: R_{1b} is hydrogen, R_{2b} is methyl and Q_2 is hydrogen,

(2) each of R_{20a} and R_{21a} is hydrogen,

(3) Y_a is N-Y_{1a}, in which Y_{1a} is hydrogen,

and (1) to (3) occur simultaneously,

then M_1 has a significance other than hydrogen or sodium.

Even more preferred are compounds of formula Ia, in which

1) K_1 is K_2;

2) K_1 is K_3;

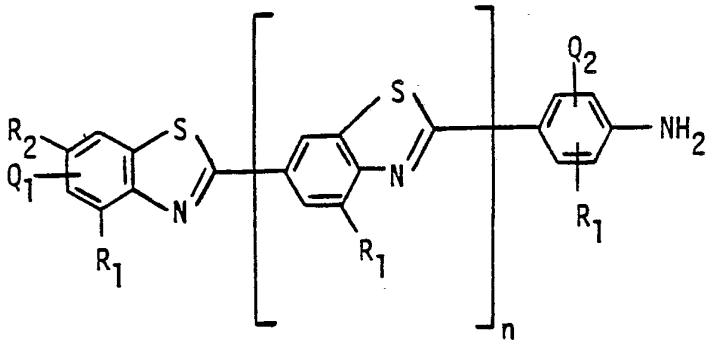
3) R_{1b} is R_{1c};

4) R_{1b} is hydrogen;

5) R_{2b} is methyl;

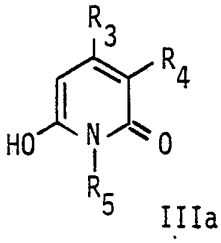
6) those of 2) to 5), in which K_1 is K_4.

The compounds of formula I can be prepared in accordance with known methods reacting the diazonium salt of an amine of formula II,

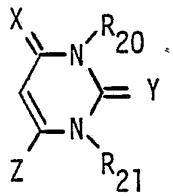


II

in which R_1, R_2, Q_1, Q_2 and n are as defined above,
or a mixture thereof
with a compound which in one of the possible tautomeric forms corresponds to formula IIIa or IIIb,



IIIa



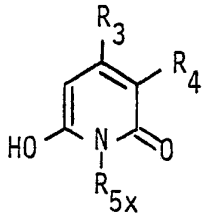
IIIb

in which R_3, R_4, R_5, R_{20}, R_{21}, X, Y and Z are as defined above.

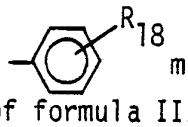
The starting compounds of formula II, diazo components of the 2-phenyl-benzthiazole series, are either known or may be prepared analogously to known processes, for example according to M. Schubert, Annalen 558, 10 (1947).
Diazo components of formula II for example are as follows:-
2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid
2-(4'-aminophenyl)-6-methylbenzthiazole-5-sulphonic acid
2-(4'-aminophenyl)-6-methylbenzthiazole-3',7-disulphonic acid
2-(4'-aminophenyl)-6-carboxybenzthiazole-7-sulphonic acid
2-(4'-amino-3'-methyl-5'-sulphophenyl)-4,6-dimethyl-benzthiazole -7-sulphonic acid
2-(4'-amino-3'-methylphenyl)-4,6-dimethyl-benzthiazole-7-sulphonic acid
2-(4'-aminophenyl)-6-methylbenzthiazole
primuline base.

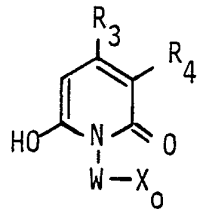
The coupling components, compounds of formula IIIa, are either known or may be prepared in accordance with known methods. Such preparation processes for example are described in: The Chemistry of Heterocyclic Compounds, Pyridine and its Derivatives, Parts I-IV; Interscience Publishers Inc. 1960-1964; furthermore in: Berichte der Deutschen Chemischen Gesellschaft 29, (1896), page 655; and in patent references, such as DE-OS 19 64 690; 20 22 817; 21 18 945; 21 23 061; 21 41 449; 21 50 598; 21 50 772; 21 50 817; 21 62 612; 23 49 709; 27 05 562; etc.

Compounds of formula IIIax,

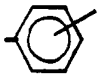


IIIax

in which R_{5x} is C_{1-6}alkylene-E_1 or the group  may be prepared for example by reacting a compound of formula IIIay,



IIIay

in which W is C_{1-6}alkylene or a group  or ,

wherein R_{31} is $-NHCOR_{12}-$, $-SO_2NHR_{12}-$ or $-CONHR_{12}-$, and X_o is a functional group, preferably a group which can be split off as an anion, with the amino compound E_1-H.

The coupling components, compounds of formula IIIb, are either known or may be prepared in accordance with known methods from known starting compounds. Such preparation processes for example are described in: The Chemistry of Heterocyclic Compounds, The Pyrimidines, Interscience Publishers 1962; furthermore in numerous patent references such as, US-PS 2,673,204 or DE-PS 134,984; 158,591; 165,692; 186,456, etc.

Diazotisation and coupling reactions may be effected in accordance with known methods. For diazotisation, the amines or amine mixtures are advantageously dissolved in an aqueous alkali or made into a paste therein, and mixed with a 5-10% molar excess sodium nitrite. Diazotisation conveniently is carried out in a medium containing a mineral acid, preferably hydrochloric acid, at 0-20°C. Coupling conveniently is carried out at pH 3-10, preferably 4-8. Optionally, a quaternary ammonium compound is added using at least an equimolar amount which is sufficient to neutralise one sulphonic acid group.

The resultant compound of formula I may be used in form of the solution as obtained; however, this solution may also be converted into a solid by spray-drying. Furthermore, the conventional method of isolation used for dyestuffs, salting out of the solution, filtering off and drying, is also suitable.

The type of cations present in a compound of formula I may be influenced in different ways depending on the preparation process. One possibility consists in filtering off the diazonium salt which is obtained in the above process, and washing it with water. The solid diazonium compound is then added to an aqueous slurry or solution of the coupling component, which contains a basic salt, lithium-, sodium-, potassium-, ammonium-hydroxide, one or more organic amines or a quaternary ammonium compound. Another method consists in converting the compound of formula I, which is obtained by diazotisation and coupling and is isolated in the sodium salt form, into the free acid by using a mineral acid, preferably hydrochloric acid, then filtering and washing with water; the compound is subsequently neutralised and thus converted into the desired alkali salt or ammonium salt. Any type of mixed salt form may be obtained by effecting partial conversion into the free acid and/or by step-wise neutralisation.
The salt-changing method, conversion of one salt form into another, can also be used.

If diazotisation takes place using alkyl nitrites, dinitrogen trioxide or mixtures of nitric oxide and oxygen instead of alkali nitrite, it is possible to produce solutions of the end products which are free from metal ions. If desired, corresponding salts may be obtained by adding a base which yields cations or by adding an amine.

The compounds according to the invention in form of their water-soluble salts are useful for dyeing or printing hydroxy group or nitrogen containing organic substrates. For example, they are suitable for dyeing or printing fibres, threads or textiles produced therefrom, which consist of or contain cellulose materials, such as cotton, in accordance with known methods; cotton is preferably dyed by the exhaust method, for example from a long or short liquor, at room temperature to boiling temperatures. Printing is effected by means of impregnation with a printing paste which is prepared by known methods.
The compounds of formula I are especially suited for dyeing or printing paper in accordance with known methods, e.g. for the preparation of sized or unsized paper dyed in the stock. They may also be used for dyeing paper by the dipping process. Furthermore, the new dyestuffs can be used for dyeing or printing leather, preferably chrometanned types of leather, in accordance with known methods. The dyeings and prints obtained (especially those on paper) have good fastness to usage.

The compounds of formula I may be used as such or may also be used in the form of dyeing preparations, which are preferably used for dyeing paper. Suitable liquid, preferably aqueous, concentrated dyeing preparations may be made in accordance with known methods, advantageously by dissolving in suitable solvents, optionally adding an adjuvant, e.g. a hydrotropic compound or a stabiliser. The possibility of producing such stable, aqueous-concentrated preparations in the course of dyestuff synthesis without intermediate isolation of the dyestuff is particularly advantageous. In this process, coupling takes place for example in the presence of appropriate amines and in particular in the presence of quaternary ammonium hydroxides which serve to introduce corres-

ponding cations as defined above, and optionally in the presence of further hydrotropic adjuvants.

Suitable hydrotropic adjuvants are for example low molecular weight amides, lactones, alcohols, glycols or polyols, low molecular weight ethers or hydroxyalkylation products, as well as nitriles or esters; among these the following compounds are preferably used:- Methanol, ethanol, propanol; ethylene-, propylene-, diethylene-, thiodiethylene- and dipropylene-glycol; butanediol; ß-hydroxypropionitrile, pentamethylene glycol, ethylene gycol monoethyl- and -propylether, ethylene diglycol monoethylether, triethylene glycol monobutylether, butyl polyglycol, formamide, dimethylformamide, pyrrolidone, N-methylpyrrolidone, glycol acetate, butyrolactone, urea and ε-caprolactam.

Hydrotropic compounds are described e.g. by H. Rath and S. Müller, in Melliand Textilberichte 40, 707 (1959) or by E.H. Daruwalla in K. Venkataraman, The Chemistry of Synthetic Dyes, Vol. VIII, pages 86-92 (1974).

The additional content of a hydrotropic compound further improves the stability on storage of the dyestuff preparation, and the solubility of the dyestuff employed.

An example of a suitable liquid dye preparation is (all parts are by weight):-

100 parts of a compound of formula I in water-soluble salt form

1-100, preferably 1-10 parts of an inorganic salt,

100-800 parts of water,

0-500 parts of one of the hydrotropic compounds as defined above.

Depending on the salt form used, the liquid dye preparation may be a suspension or is preferably a true solution. The preparations are stable and can be stored for a long period of time.

Similarly, the compounds of formula I may be made into solid, preferably granulated dyeing preparations in accordance with known methods, advantageously by granulating as described in French Patent Specification No. 1.581.900.

A suitable granulate preparation comprises (all parts are by weight):-

100 parts of a compound of formula I in water-soluble salt form,

1-100, preferably 1-10 parts of an inorganic salt,

0-800 parts of a standardising agent (preferably non-ionic, such as starch, dextrin, sugar, glucose and urea).

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

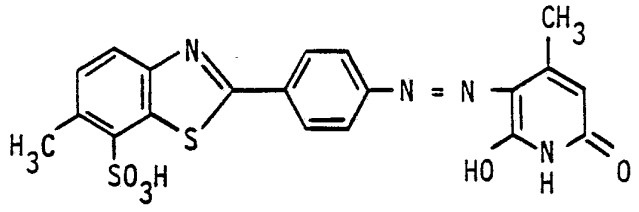
Depending on the cation mixture present, the dyestuffs of formula I possess good solubility properties, particularly good solubility in cold water. Furthermore, when used in paper-making, they colour the waste water only to a slight extent or not at all. They do not mottle on paper and are substantially insensitive to filling material and pH over wide ranges. They are only slightly inclined to give two-sided dyeing on paper. The dyeings on paper have good light fastness properties, after a long-term exposure to light, the shade alters tone-in-tone. The dyed papers also have very good wet fastness properties, they are fast not only to water, but also to milk, fruit juices, sweetened mineral water and tonic water, and in addition they show good alcohol fastness properties.

The dyestuffs have good substantivity, i.e. they exhaust practically quantitatively, and show good build-up; they can be added to the paper pulp directly, i.e. without previously dissolving, as a dry powder or granulate, without reducing the brilliance or the yield of colour. It is advantageous to use the genuine solutions of the dyestuffs as given above, which are stable, of low viscosity and thus capable of being accurately measured out. Fibre materials which contain mechanical wood pulp are dyed in good, even quality with the dyestuffs of the present invention. The dyed paper is both oxidatively and reductively bleachable, which is important for the recycling of waste paper.

The following examples further serve to illustrate the invention. In the examples, all parts are by weight or volume, and the percentages are by weight; the temperatures are given in degrees centigrade.

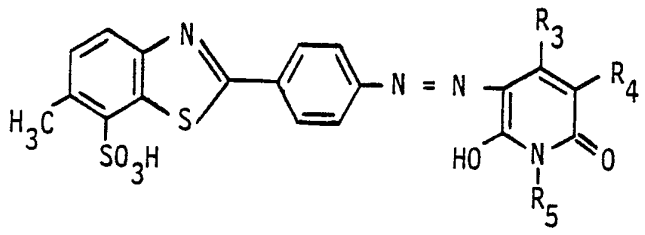
Example 1

6.4 Parts of 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are stirred into 100 parts of water, and dissolved by adding 5.1 parts of 30% sodium hydroxide solution. 6 Parts of 4N sodium nitrite solution are added, and the solution is poured whilst stirring into a preparation of 200 parts of ice and 7 parts of 30% hydrochloric acid. A yellow diazo suspension is obtained. After stirring for three hours, whereby the temperature may increase to 20°, any excess nitrous acid is decomposed by adding a small amount of sulphamic acid. Then, 3.3 parts of 4-methyl-6-hydroxypyridone-(2) are added to the diazo suspension, and 10 parts of sodium carbonate are subsequently sprinkled in. Coupling commences immediately, whereby an orange suspension is obtained. After about one hour coupling is complete. 10 parts of 30% sodium hydroxide solution are added, and the dyestuff thus formed goes totally into solution. By sprinkling in 20% by volume of sodium chloride, the dyestuff can be completely salted out. After drying, the dyestuff corresponding to the formula



is obtained in form of a powder. It dyes paper a brilliant neutral-yellow shade. The paper dyeings have very good light and wet fastness properties.

By a method analogous to that of Example 1 further heterocyclic monoazo compounds can be prepared from appropriate starting compounds. They correspond to formula (A),



(A)

in which the symbols are defined in Table 1 below.

In the last column of this Table 1 and also of the following Tables 2 and 3 the shade of the obtained paper dyeings is given whereby

a is neutral-yellow

b is reddish-yellow and

c is orange.

The paper dyeings made with the dyestuffs in Tables 1 to 3 in conventional manner have good light and wet fastness properties.

Table 1 / Compounds of formula (A)

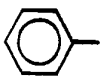
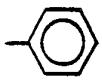
Ex. No.	R_3	R_4	R_5	shade on paper
2	CH_3	CN	H	c
3		CN	H	c
4	CH_3	CN		c
5	do.	CN	$-CH_2$ 	c
6	do.	CN	-NH 	c
7	do.	CN	$-C_2H_5$	c
8	do.	CN	$-CH_2COOC_2H_5$	c

Table 1 (continued)

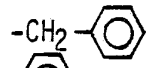
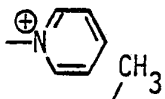
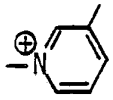
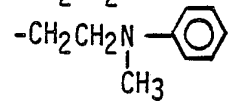
Ex. No.	R_3	R_4	R_5	shade on paper
9	CH_3	CN	$-CH_2COOH$	c
10	do.	CN	$-CH_2CH_2SO_3H$	c
11	do.	CN	$-CH_2CH_2OSO_3H$	c
12	CH_2SO_3H	CN	H	c
13	do.	H	H	b
14	CH_3	$CONH_2$	H	b
15	do.	do.	$-C_2H_5$	b
16	do.	$COCH_3$	H	b
17	do.	Cl		b
18	do.	Cl		b
19	do.	Cl	$-C_2H_5$	b
20	do.	H	do.	a
21	NH_2	CN	H	a
22	do.	$CONH_2$	H	a
23	do.	$COOC_2H_5$	H	a
24	CH_3		H	c
25	do.		H	c
26	OH	H	H	c
27	COOH	H	H	b
28	CH_3	CN	$-CH_2CH_2OH$	c
29	do.	CN		c
30	do.	CN	$-CH_2CH_2OCH_3$	c
31	do.	$NHCOCH_3$	$-C_2H_5$	b
32	do.	NH_2	do.	b
33	do.	$NHCOCH_3$	H	a

Table 1 (continued)

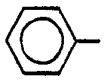
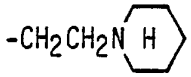
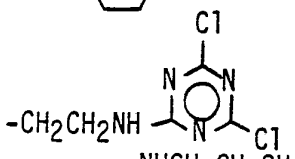
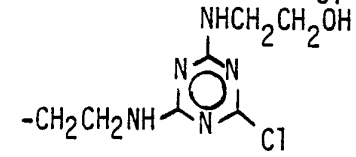
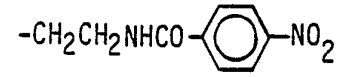
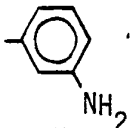
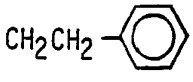
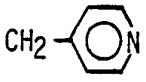
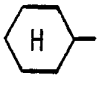
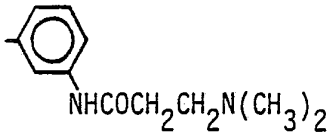
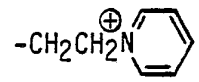
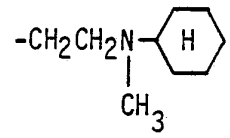
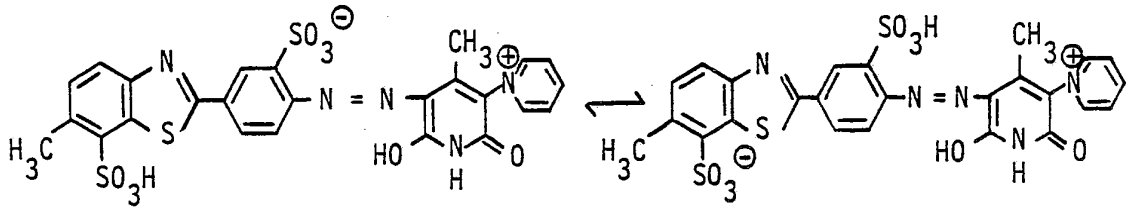
Ex. No.	R_3	R_4	R_5	shade on paper
34		H	H	a
35	CH_3	H	$-(CH_2)_3N(CH_3)_2$	a
36	do.	H		a
37	CH_2CH_2OH	CN		c
38	$CH_2CH_2OC_2H_5$	CN		c
39	CH_3	CN		c
40	do.	CN		c
41	do.	CN	$-N(C_2H_5)_2$	c
42	do.	SO_3H	$-C_2H_5$	a
43	do.	CH_2SO_3H	do.	a
44	do.	CN	$-CH_2CH_2NH_2$	c
45	do.	CN		c
46	do.	CN		c
47		CN	H	c
48		CN	H	c
49	OCH_3	H	$-(CH_2)_2N(C_2H_5)_2$	a
50		CN	H	c

Table 1 (continued)

Ex. No.	R_3	R_4	R_5	shade on paper
51	CH_3	$CH_2NHCOCH_2N(CH_3)_2$	$-C_2H_5$	a
52	do.	CN		c
53	do.	CN	$-(CH_2)_3N(C_2H_5)_2$	c
54	do.	H	$-CH_2CH_2\overset{\oplus}{N}(CH_3)_3$	a
55	do.	CN		a
56	do.	H		a

Example 57

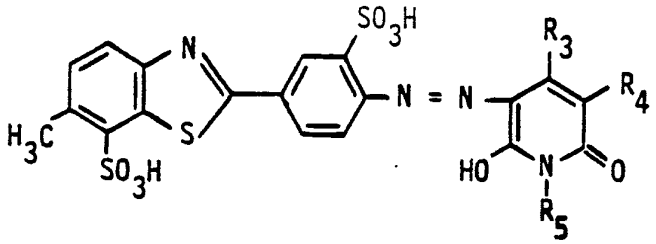
12 Parts of 2-(4'amino-3'-sulphophenyl)-6-methylbenzthiazole-7-sulphonic acid are dissolved in 200 parts of water. 100 Parts of ice are added, followed by 7.5 parts of 30% hydrochloric acid. Subsequently, at 0° 8 parts of 4N sodium nitrite solution are added dropwise. A yellow diazo solution is obtained which is stirred for two hours. 8 Parts of 6-hydroxy-4-methylpyridonyl-(3)-pyridinium chloride are then added. The pH is adjusted to 8 by adding 20 parts of sodium carbonate. Coupling commences immediately, and an orange suspension is formed. This suspension is stirred for four hours, afterwards the precipitated dyestuff is filtered off. After drying, a readily soluble dyestuff powder is obtained containing the dyestuff which, in the possible tautomeric forms, corresponds to one of the given formulae:



This dyestuff dyes paper a brilliant reddish-yellow shade. The paper dyeings obtained have good light and wet fastness properties.

Examples 58-71

By a method analogous to that of Example 57 further compounds may be prepared using appropriate starting compounds. They correspond to formula (B),



(B)

in which the symbols are defined in Table 2 below.

Table 2 / Compounds of formula (B)

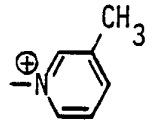
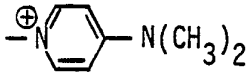
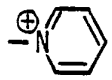
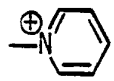
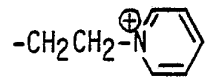
Ex. No.	R_3	R_4	R_5	shade on paper
58	CH_3	H	H	a
59	do.	CN	H	c
60	do.		H	b
61	do.		H	c
62	do.		$-(CH_2)_3N(CH_3)_2$	c
63	do.	CN	do.	c
64	do.		$-CH_2CH_2NH_2$	c
65	do.	CN	$-CH_2CH_2\overset{\oplus}{N}(CH_3)_3$	c
66	NH_2	CN	H	b

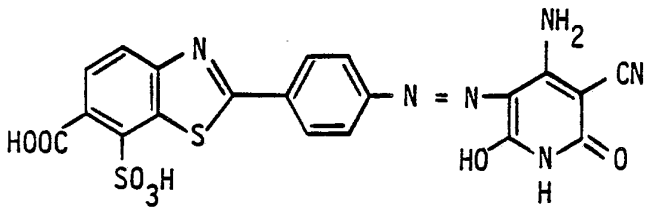
Table 2 (continued)

Ex. No.	R_3	R_4	R_5	shade on paper
67	CH_3	CN		c
68	do.	H	do.	a
69	do.	H	$-CH_2CH_3$	a
70	NH_2	CN	do.	b
71	CH_3	H	$-CH_2CH_2NH_2$	a

Example 72

7 Parts of 2-(4'-aminophenyl)-6-carboxybenzthiazole-7-sulphonic acid are stirred into 40 parts of water and dissolved with 4 parts of 30% sodium hydroxide solution. 5.5 Parts of 4N sodium nitrite solution are added, and this mixture is poured into a preparation consisting of 100 parts of ice and 10 parts of 30% hydrochloric acid whilst stirring. A light yellow diazo suspension is formed.

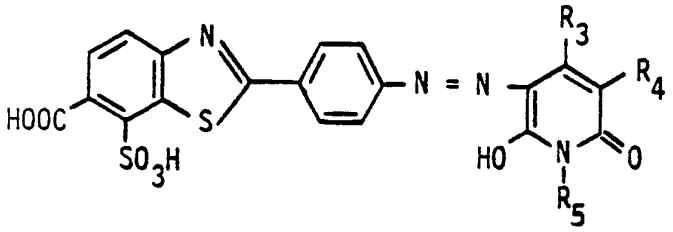
After stirring for one hour, the excess nitrous acid is decomposed by adding sulphamic acid. 4 Parts of 4-amino-3-cyano-6-hydroxypyridone-(2) are added, and then 10 parts of sodium carbonate are sprinkled in. Coupling commences, and a brownish-orange suspension is obtained. After two hours coupling is complete. Subsequently, 20 parts of 30% sodium hydroxide solution are added dropwise, and the mixture is heated to 70°; the resultant dyestuff thus goes into solution. It is salted out by sprinkling in 40 parts of sodium chloride, filtered off and dried. An orange-red powder is obtained which contains the dyestuff having the formula



This dyestuff dyes paper a brilliant reddish-yellow shade. The obtained paper dyeings show notably good light and wet fastness properties.

Examples 73-89

By a method analogous to that described in Example 72 further compounds can be prepared from appropriate starting compounds. They correspond to formula (C),



(C)

in which the symbols are defined in Table 3 below.

Table 3 / Compounds of formula (C)

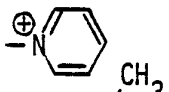
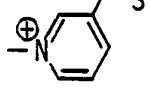
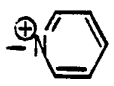
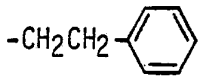
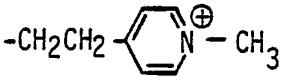
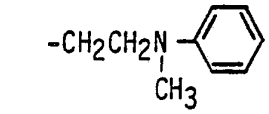
Ex. No.	R_3	R_4	R_5	shade on paper
73	CH_3	H	H	b
74	do.	CN	H	c
75	do.	$CONH_2$	H	b
76	do.	H	$-CH_2CH_3$	b
77	do.		H	c
78	do.		H	c
79	do.		$-(CH_2)_3N(CH_3)_2$	c
80	do.	CN	do.	c

Table 3 (continued)

Ex. No.	R_3	R_4	R_5	shade on paper
81		CN		c
82	CH_3	CN	do.	c
83	do.	$COCH_3$	H	b
84	do.	Br	$-CH_2CH_3$	b
85	NH_2	CN	do.	b
86	CH_3	H	$-CH_2CH_2OH$	a
87	do.	H		a
88	do.	H	$-(CH_2)_3N(CH_3)_2$	a
89	do.	H	$-(CH_2)_3\overset{\oplus}{N}(CH_3)_3$	a

In accordance with the reaction and isolation conditions as described the compounds of Examples 1 to 89 are obtained in the sodium salt form provided that no internal salt is formed. They may, depending on the reaction and isolation conditions, or by reacting the sodium salts in accordance with known methods also be obtained in free acid form or in other salt forms containing one or more cations indicated in the description.

Example 90

6.4 Parts 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are diazotised in accordance with the method described in Example 1. The mixture is stirred for three hours and then filtered. The well-pressed filter cake is made into a paste in ice water; this paste is adjusted to 40 parts with ice water. 3.3 Parts of 4-methyl-6-hydroxypyridone-(2) are added followed by 8 parts of triethanolamine. Coupling commences whereby an orange-red mixture is obtained. During coupling, a further 30 parts of ice are added portionwise. After one hour 8 parts of urea are added,

then the mixture is heated to 50° whereby a solution is obtained. This solution is ready for use, it contains the dyestuff of Example 1 in the triethanolammonium salt form.

Example 91

The dyestuff prepared according to the method given in Example 1 is stirred into 200 parts of water prior to drying, and is mixed with 20 parts of 30% hydrochloric acid. After having stirred for a longer time, the dyestuff in the free acid form is filtered off and is added into a mixture consisting of 8 parts of diglycol amine and 5 parts ethylene glycol. The dyestuff dissolves whilst releasing heat. This solution is adjusted to 90 parts by adding water to give a dyestuff solution which is storage-stable and ready for use.

Example 92

If in Example 91 2 parts of monoethanolamine and 15 parts of urea are used instead of a mixture of diglycol amine and ethylene glycol a liquid dyestuff preparation is obtained which is stable on storage and has good dyeing properties.

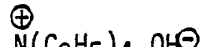
Also suitable amines instead of monoethanolamine are diethanolamine, monoisopropanolamine or diisopropanolamine.

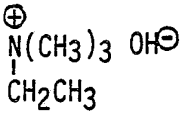
Example 93

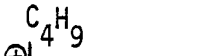
If in Example 90 5 parts of tetramethylammonium hydroxide are used instead of triethanolamine a liquid dyestuff preparation is obtained which is ready for use. By employing tetramethylammonium hydroxide there is no need for adding a further solubilising agent.

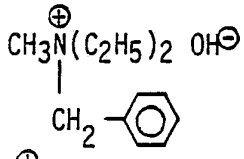
Instead of tetramethylammonium hydroxide equimolar amounts of the following quaternary ammonium hydroxides may be used to produce liquid storage-stable preparations of the dyestuff of Example 1.

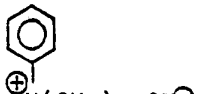
Examples 93a to 93x

93a: 

93 b: 

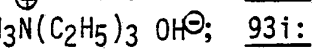
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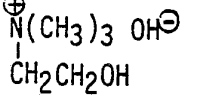
93d: 

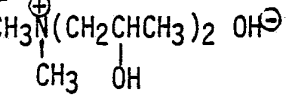
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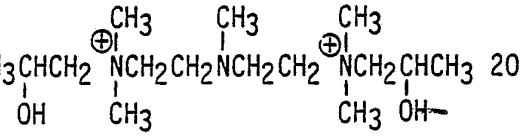
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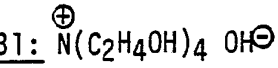
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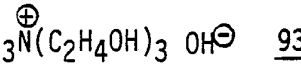
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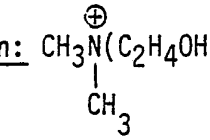
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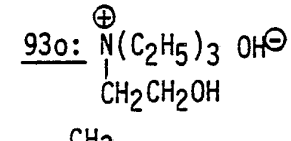
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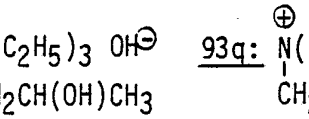
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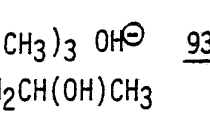
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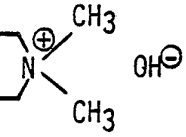
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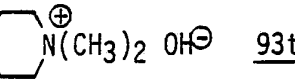
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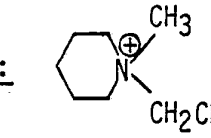
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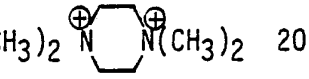
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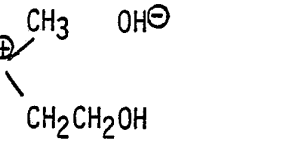
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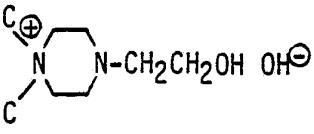
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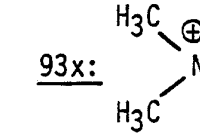
93s: 

93t: 

93u: 

93v: 

93w: 

93x: 

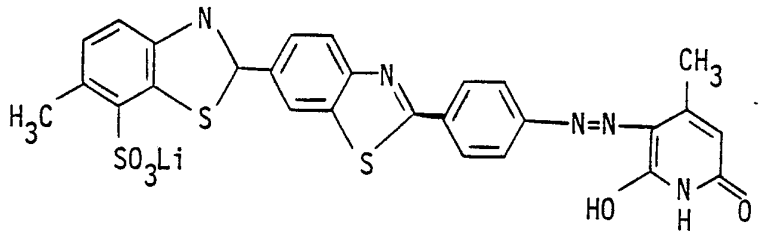
Example 94

If lithium hydroxide solution is used instead of the amine or amine mixture employed in one of Examples 90 to 93, a liquid aqueous dye preparation is obtained which contains the dyestuff according to Example 1 in the lithium salt form.

By a method analogous to that described in one of Examples 90 to 94 the dyestuffs of Examples 2 to 89 may also be converted into liquid aqueous dyeing preparations showing high stability on storage.

Example 95

A mixture consisting of 9.5 parts of primulin base, 1.4 parts of potassium hydroxide, 40 parts of water and 4.3 parts 5N sodium nitrite solution is added to a mixture of 5 parts of hydrochloric acid and 20 parts of ice whilst stirring. Stirring is effected for a further two hours at 20°. The diazonium salt which precipitates is filtered off and washed with water. The diazonium salt together with 3 parts of 4-methyl-6-hydroxypyridone-(2) is suspended in a small quantity of water. To this suspension a 10% lithium hydroxide solution is added to adjust the pH at 8. After stirring for one hour, 20 parts of urea are added. The solution thus obtained is ready for use, it contains the dyestuff of the formula

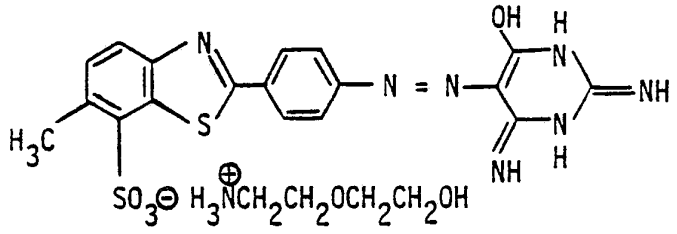


which has notably good properties with respect to substantivity. This dyestuff solution dyes paper a brilliant golden-yellow shade.

Example 96

6.4 Parts of 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are stirred into 100 parts of water; and dissolved by adding 5.1 parts of 30% sodium hydroxide solution. To this solution 6 parts of 4N sodium nitrite solution are added, and the resultant mixture is poured into a preparation consisting of 200 parts of ice and 7 parts of 30% hydrochloric acid. A yellow diazo suspension is obtained. After stirring for three hours any excess

nitrous acid is decomposed by the addition of a small quantitiy of sulphamic acid. The precipitation thus formed which contains the diazonium salt of the above mentional amino compound is filtered off and washed with water acid-free. This diazonium salt together with 2.7 parts of 2,4-diamino-6-hydroxypyrimidine is suspended in a small amount of water, then 20 parts of diethylene glycol amine are added. Coupling commences whereby an orange-coloured mass is produced. After coupling is complete, 10 parts of ethylene glycol and 20 parts of urea are added followed by the addition of water to adjust to a volume of 140 parts. The mixture is heated to 40°, and a clear dyestuff solution of low viscosity is formed. This dyeing preparation is ready for use and storage-stable for several months. It contains the dyestuff in the salt form corresponding to the formula

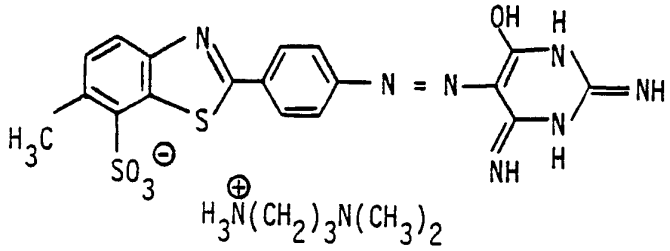


This dyestuff dyes paper a brilliant neutral-yellow shade. The paper dyeings have very good wet fastness properties. The back water of these dyeings is approximately colourless.

Example 97

6.4 Parts of 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are diazotised according to the method given in Example 96 and coupled with 2,4-diamino-6-hydroxypyrimidine in the presence of sodium carbonate. Then 15 parts of 30% hydrochloric acid are added. Stirring is effected for three hours at 40°. The precipitation is filtered off and washed with water until it is acid-free. The press cake thus obtained is added into a preparation consisting of 30 parts of water and 30 parts of dimethylaminopropylamine. A clear dyestuff solution is obtained which is

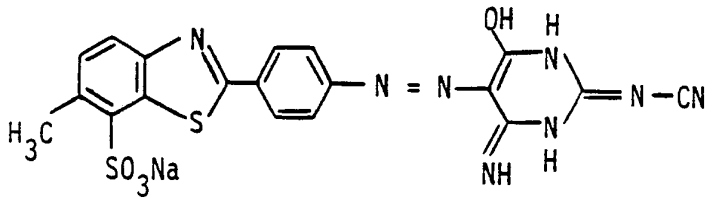
stable on storage for several months. It contains the dyestuff in the probable salt form corresponding to the formula



which dyes paper a brilliant neutral-yellow shade.

Example 98

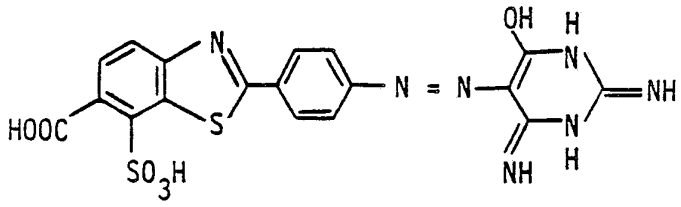
6.4 Parts of 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are diazotised according to the method described in Example 96 and coupled with 3.3 parts of 2-cyanimino-4-amino-6-hydroxypyrimidine in the presence of sodium carbonate. The thus obtained suspension is filtered, and the residue is dried. The dyestuff corresponding to the formula



is obtained in form of a powder. It dyes paper a brilliant reddish-yellow shade. The paper dyeings have notably good wet fastness properties; the back water is colourless.

Example 99

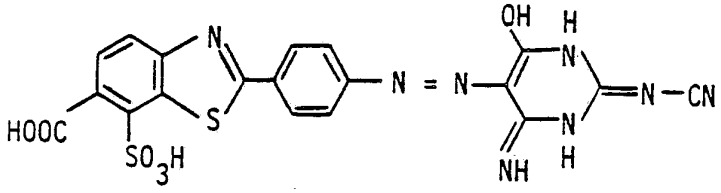
7 Parts of 2-(4'-aminophenyl)-6-carboxybenzthiazole-7-sulphonic acid are diazotised according to the method described in Example 96. To the resultant diazonium salt 2.7 parts of 2,4-diamino-6-hydroxypyrimidine are added, and coupling is effected in the presence of lithium hydroxide. After coupling is complete, the dyestuff which precipitates is filtered off and dried. The dyestuff corresponding to the formula



is obtained in the lithium salt form. It dyes paper a brilliant neutral-yellow shade. The wet fastness properties of these paper dyeings are notably good; the back water is colourless.

Example 100

If in Example 99 4.5 parts of 2-cyanimino-4-amino-6-hydroxypyrimidine are employed instead of 2.7 parts of 2,4-diamino-6-hydroxypyrimidine the lithium salt of the dyestuff corresponding to the formula

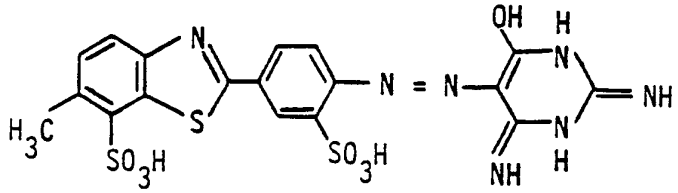


is obtained. It dyes paper a brilliant reddish-yellow shade. The wet fastness properties of these paper dyeings and their properties with respect to back water coloration are very good.

Example 101

8 Parts of 2-(4'-aminophenyl)-6-methylbenzthiazole-3',7-disulphonic acid are dissolved in 100 parts of water whilst stirring and then 7 parts of 30% hydrochloric acid are added. To this solution which is cooled to 5° 6 parts of 4N sodium nitrite solution are added. Any excess nitrous acid in the diazo solution thus obtained is decomposed by the addition of sulphamic acid. Subsequently, 2.7 parts of 2,4-diamino-6-hydroxypyrimidine are added. Coupling commences when by the addition of sodium carbonate the pH

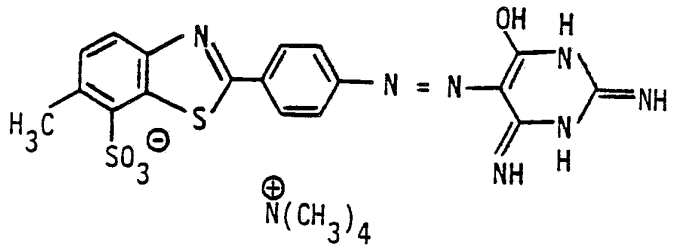
is adjusted to an alkaline range. An orange-coloured suspension is obtained. After coupling is complete, 20 parts of 30% hydrochloric acid are added, and then the strongly acidic suspension is filtered off and washed with water. The obtained press cake is added into a preparation consisting of 200 parts of water and 15 parts of lithium hydroxide. The mixture is heated to 70° whereby a solution is obtained. After cooling down, the dyestuff corresponding to the formula



cristallizes in form of the lithium salt. It dyes paper a neutral-yellow shade. The resultant back water is colourless. These paper dyeings have notably good wet fastness properties.

Example 102

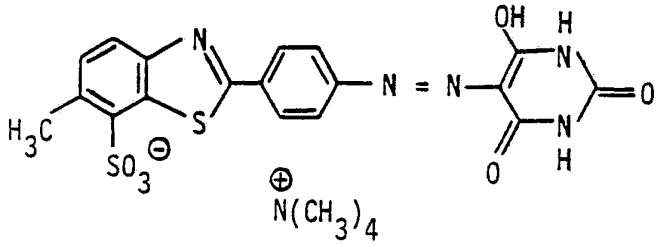
32 Parts 2-(4'-aminophenyl)-6-methylbenzthiazole-7-sulphonic acid are stirred into 300 parts of water followed by the addition of 11 parts of 30% hydrochloric acid. Then 27 parts of 4N sodium nitrite solution are slowly added dropwise, and the temperature is kept at 15-20°. After stirring for two hours, any excess nitrous acid is decomposed by adding a small amount of sulphamic acid. Subsequently, the obtained diazo suspension is added dropwise a preparation consisting of 13 parts of 2,4-diamino-6-hydroxy-pyrimidine and 125 parts of 24.5% tetramethylammonium hydroxide solution. Coupling commences immediately. After coupling is complete, the solution is filtered clear. A storage-stable dyeing preparation is obtained which is ready for use containing the dyestuff which corresponds to the formula



This preparation dyes paper a billiant neutral-yellow shade; the back water is practically colourless. The paper dyeings thus obtained have notably good dyeing properties.

Example 103

If in Example 102 13.2 parts of barbituric acid are employed instead of 13 parts of 2,4-diamino-6-hydroxypyrimidine, a storage-stable dyeing preparation is obtained containing the dyestuff in salt form which corresponds to the formula

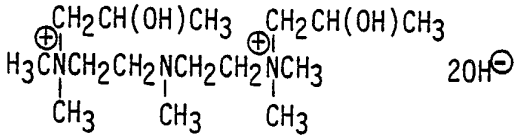


and dyes paper a yellow shade. The paper dyeings show high general fastness properties.

If in Example 102 or 103 instead of tetramethylammonium hydroxide equimolar amounts of one of the quaternary ammonium hydroxides given for Examples 93a to 93j or 93l to 93x are used, storage-stable dye preparations may be obtained which have good dyeing properties.

Example 104

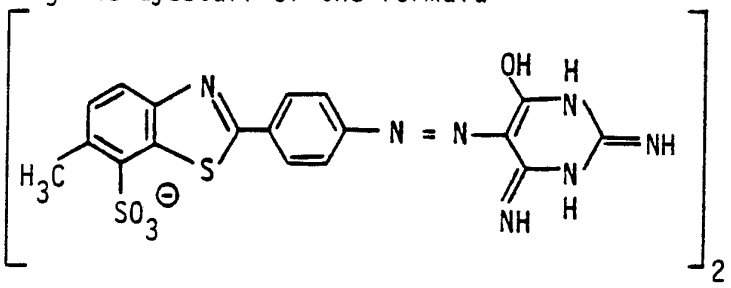
If in Example 102 instead of the tetramethylammonium hydroxide solution 33 parts of the bisquaternary ammonium hydroxide of the formula

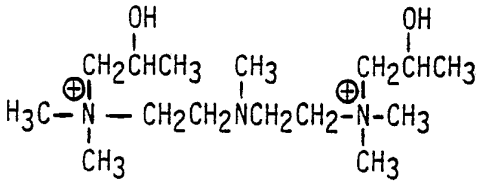


(prepared by the addition of propylene oxide to the compound of the formula

$(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$)

are used, a yellow storage-stable dye preparation is obtained containing the dyestuff of the formula





The resultant solution is a liquid of low viscosity, it is therefore easily dosable. This dyeing preparation dyes paper a brilliant neutral-yellow shade.

In the following examples the application of the compounds of this invention as well as liquid aqueous dyeing preparations thereof is illustrated.

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 a Hollander in 2000 parts of water. 0.2 Parts of the dyestuff of Example 1, 98 or 101 are sprinkled into this pulp or 1.0 parts of the liquid dyestuff preparation according to Example 92, 96 or 102 are added to this pulp. After mixing for 20 minutes, paper is produced from this pulp.

The absorbent paper obtained in this way is dyed a brilliant yellow shade (reddish-yellow shade, respectively). The waste water is practically colourless.

Application Example B

0.5 Parts of the dyestuff of Example 1, 98 or 101 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 2000 parts of water. After thorough mixing for 15 minutes, sizing takes place in the usual way with rosin size and aluminium sulphate. Paper which is produced from this material is of brilliant yellow shade (reddish-yellow shade, respectively) and has good waste water and wet fastness properties.

Application Example C

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

0.5	parts	of the dyestuff of Example 1, 98 or 101 or of the liquid dye preparation according to Example 92, 96 or 102
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 yellow (reddish-yellow) shade.

The dyestuffs or liquid dyestuff preparations of the remaining examples may also be used for dyeing paper according to Application Examples A to C.

Application Example D (leather)

100 Parts of intermediately dried chrome velours leather are agitated for one hour at 50° in a vessel with a liquor consisting

of 400 parts of water, 2 parts of 25% ammonium hydroxide solution and 0.2 parts of a conventional wetting agent. Then the liquor is run off. To the agitated still wet chrome velours leather 400 parts of water of 60° and 1 part 25% ammonium hydroxide solution are added. After the addition of 5 parts of the dyestuff of Example 1 dissolved in 200 parts of water, dyeing is effected during 90 minutes at 60°. Subsequently, 50 parts of 8% formic acid are slowly added to adjust to an acidic pH, and agitating is continued for a further 30 minutes. The leather is then rinsed, dried and prepared in the normal way giving a leather evenly dyed in a yellow tone with good light fastness properties.

Application Example E (cotton)

To a dyebath consisting of 3000 parts of demineralized water, 2 parts of sodium carbonate and 1 part of the dyestuff of Example 1, 100 parts of pre-wetted cotton fabric are added at 30°. After the addition of 10 parts of sodium sulphate, the dyebath is heated to the boil within 30 minutes whereby, at a temperature of 50° and 70°, at each of these stages a further 10 parts of sodium sulphate are added. Dyeing is continued for a further 15 minutes at the boil followed by the addition of a further 10 parts of sodium sulphate. The dyebath is then cooled down. At 50° the dyed fabric is removed from the dye liquor, rinsed with water and dried at 60°. A golden-yellow cotton dyeing is obtained having good light and wet fastness properties.

Application Example F (polyamide)

0.1 Parts of the dyestuff of Example 1 are dissolved in 300 parts of water, and 0.2 parts of ammonium sulphate are added to this solution. Then the pre-wetted textile fabric (5 parts wool gaberdine or 5 parts nylon satin) is entered into the bath which is heated to the boil during the course of 30 minutes. The water that evaporates during the dyeing process for 30 minutes is replaced, and dyeing at the boil is continued for a further 30 minutes. Finally, the dyed fabric is removed from the liquor and

rinsed with water. After drying a clear yellow polyamide dyeing is obtained having good light and wet fastness properties.

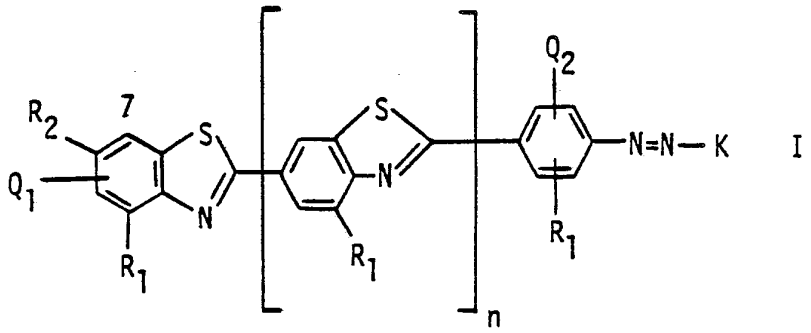
In analogous manner as described in Application Examples D to F the dyestuffs of the remaining examples may be used for dyeing. The thus obtained substrates are dyed in a yellow tone and have good fastness properties.

List of maximum absorption wavelenghts (in nanometer) for the exemplified compounds. These values were measured in 1% acetic acid solution with the exception that for the compounds of Examples 96, 97 and 102 demineralised water, and for the compounds of Examples 99-101 0.1% sodium carbonate solution was used.

Ex. No.	$\lambda_{max.}$ (nm)	Ex. No.	$\lambda_{max.}$ (nm)	Ex. No.	$\lambda_{max.}$ (nm)
1	429	29	448	65	448
2	449	30	448	66	432
3	459	31	454	69	431
4	496	32	431	72	438
5	446	33	429	73	432
6	458	34	427	74	440
7	452	35	432	75	429
8	456	36	432	76	431
9	456	37	449	77	438
10	457	38	449	78	438
11	458	39	451	79	440
12	466	40	452	80	448
13	443	41	454	81	447
14	444	42	432	83	431
15	448	43	430	84	435
16	446	44	447	90	429
17	442	45	448	91	429
18	435	46	480	92	429
19	442	47	452	93	429
20	430	48	454	94	429
21	403	57	438	96	413
22	422	58	430	97	413
23	426	59	445	98	400
24	437	60	436	99	432
25	438	61	448	100	422
26	443	62	439	101	436
27	430	63	442	102	412
28	448	64	438		

CLAIMS: -

1. A compound which, in one of the possible tautomeric forms, corresponds to formula I,



I

in which

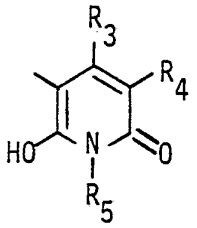
each of R_1 and R_2 is independently hydrogen, C_{1-4}alkyl, C_{1-4}alkoxy or COOM,

each of Q_1 and Q_2 is independently hydrogen or SO_3M_1,

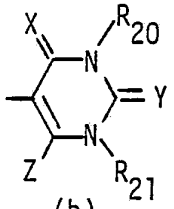
n is 0 or 1,

each of M and M_1 is independently hydrogen or a non-chromophoric cation;

K is one of the groups (a) and (b),



(a)

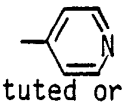


(b)

in which

R_3 is hydrogen, CN, NH_2, OH, C_{1-4}alkoxy, C_{1-4}alkyl, C_{2-4}alkyl monosubstituted by hydroxy or C_{1-4}alkoxy, C_{5-6}cycloalkyl; phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M; a saturated or unsaturated 5- or 6-membered heterocyclic ring containing one to three hetero atoms which is unsubstituted or further substituted by one to three C_{1-4}-alkyl groups and which is bound by a carbon or nitrogen atom directly or via a bridge member provided that any $\geq\overset{\oplus}{N}$ is bound via a bridge member; $-COR_6$ or $-(CH_2)_{1-3}-R_7$,

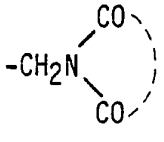
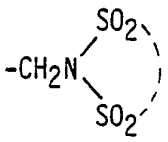
R_6 is OH, NH_2 or C_{1-4}alkoxy,

R_7 is CN, halogen, SO_3M, $-OSO_3M$, $-COR_8$ or ,

R_8 is OH, NH_2, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN or C_{1-4}alkoxy; C_{1-4}alkoxy, phenoxy, phenyl or phenyl-C_{1-4}alkyl in which the phenyl groups of the latter three groups are unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M;

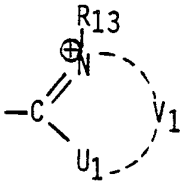
R_4 is hydrogen, CN, halogen, SO_3M, NO, NO_2, $-NR_9R_{10}$, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}alkoxy, phenyl, SO_3M or $-OSO_3M$;

$-SO_2NH_2$, $-COR_{11}$, $-CH_2NHCOR_{12}E$, a group of the formulae

 or ,

in which the carbonyl or sulphonyl groups are bound to two carbon atoms of an aromatic ring which are in ortho position to each other;

a group of the formula  in which the $\overset{\oplus}{N}$ ion is part of a 5- or 6-membered ring containing one to three hetero atoms which is further unsubstituted or substituted by one or two methyl groups or by NH_2, $-NHC_{1-4}$alkyl or $N(C_{1-4}alkyl)_2$; or a group of the formula



in which

R_{13} is hydrogen or C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}alkoxy or phenyl,

U_1 is S, -NH or $-NC_{1-4}$alkyl, and

V_1 is a group necessary to form a 5- or 6-membered ring to which ring a further 5- or 6-membered carbocyclic or heterocyclic ring containing one or two hetero atoms may be condensated,

or

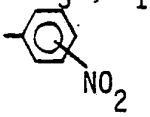
both R_3 and R_4 together form a C_3- or C_4-chain which may be part of a further 5- or 6-membered ring by two vicinal chain members,

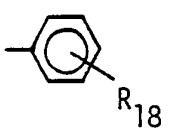
each of R_9 and R_{10} is independently hydrogen, C_{1-4}alkyl which is unsubstituted or monosubstituted by OH, halogen, CN, C_{1-4}-alkoxy or phenyl; or $-COR_{12}E$,

R_{11} is OH, NH_2, $-NHC_{1-4}$alkyl, $-N(C_{1-4}alkyl)_2$, C_{1-4}alkyl, C_{1-4}-alkoxy, phenyl or phenoxy which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, COOM and SO_3M,

R_{12} is C_{1-6}alkylene,

E is hydrogen, halogen, a protonable amine group, a quaternary ammonium group or a hydrazinium group; SO_3M or $-OSO_3M$;

R_5 is hydrogen, CN, NO_2, $-NR_{14}R_{15}$, a saturated or unsaturated 5- or 6-membered heterocyclic ring containing one or two hetero atoms which is bound by a carbon or nitrogen atom and which is further unsubstituted or substituted by up to three methyl groups or by NH_2, $-NHC_{1-4}$alkyl or $-N(C_{1-4}alkyl)_2$; C_{1-6}alkyl, C_{2-4}alkenyl, C_{2-4}alkinyl; C_{1-6}alkyl monosubstituted by OH, CN, C_{1-4}alkoxy, acetamido, $-COR_{16}$, SO_3M or $-OSO_3M$; C_{5-6}cyclo-alkyl, phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one to three groups selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, NO_2, NH_2, COOM and SO_3M; C_{1-6}alkylene-E_1, $-C_{1-6}$alkylene-NCO- or a group of the formula

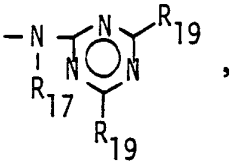


,

each of R_{14} and R_{15} is independently hydrogen, C_{1-4}alkyl, C_{1-4}-alkyl monosubstituted by OH, halogen, CN or C_{1-4}alkoxy; phenyl or phenyl substituted by one or two groups selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy,

R_{16} is OH or C_{1-4}alkoxy,

R_{17} is hydrogen or C_{1-4}alkyl,

E_1 is a protonable amine group, a quaternary ammonium group or a hydrazinium group or a group of the formula ,

R_{18} is E_2, $-NHCOR_{12}E_2$, $-SO_2NHR_{12}E_2$ or $-CONHR_{12}E_2$;

each R_{19} is independently halogen, NH_2 or an aliphatic amine group,

E_2 is a protonable amine group, a quaternary ammonium group or a hydrazinium group,

X is O or NH,

Z is OH, NH_2, methyl or ethyl,

Y is O, S or N-Y_1,

Y_1 is hydrogen, CN, $CONH_2$, C_{1-4}alkyl, C_{1-4}alkyl monosubstituted by OH, CN, halogen or C_{1-4}alkoxy; phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from halogen, C_{1-4}alkyl, C_{1-4}alkoxy, acetamido, COOM and SO_3M; 1- or 2-naphthyl; C_{1-6}alkylene-SO_3M, C_{1-6}alkylene-OSO_3M or C_{1-6}-alkylene-COOM,

each of R_{20} and R_{21} is independently hydrogen, C_{1-4}alkyl, phenyl or phenyl-C_{1-4}alkyl which phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from halogen, C_{1-4}alkyl, C_{1-4}alkoxy, COOM and SO_3M; or, provided that Y is N-Y_1 where Y_1 is hydrogen, one of R_{20} and R_{21} may also have a significance additionally given for Y_1;

with the provisos that

(i) in a compound of formula I at least one sulphonic acid group is present;

(ii) when in a compound of formula I

(1) K is a group (b), in which Y is O or S,

(2) R_2 is other than COOM,

(3) one of Q_1 and Q_2 or both Q_1 and Q_2 are SO_3M_1,

and (1) to (3) occur simultaneously,

then at least one of M_1 is a quaternary ammonium cation;

(iii) when in a compound of formula I containing as K a group (b)

(1) the diazo component radical is defined as follows:

R_1 is hydrogen, R_2 is methyl, Q_1 is SO_3M_1 in the 7-position, n is 0 and Q_2 is hydrogen,

(2) X is O or NH,

(3) each of R_{20} and R_{21} is hydrogen,

(4) Y is N-Y_1 in which Y_1 is hydrogen,

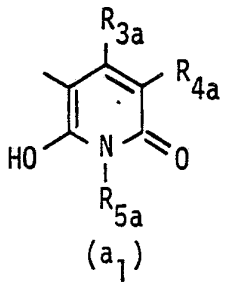
and (1) to (4) occur simultaneously,

then M_1 has a significance other than hydrogen or sodium;

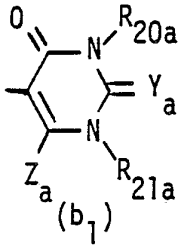
which compound of formula I is in free acid or salt form with the proviso that each sulphonic acid group as well as each protonable amine group can be present in ionized form.

2. A compound according to Claim 1, in which each R_1 is R_{1b}, where each R_{1b} is independently hydrogen, methyl, ethyl, methoxy or ethoxy; R_2 is R_{2b}, where R_{2b} is methyl, methoxy, ethoxy or COOM; n is 0, and Q_1 is SO_3M_1 in the 7-position.

3. A compound according to Claim 1, in which K is K_1, where K_1 is a group (a_1) or (b_1)



(a_1)



(b_1)

in which

R_{3a} is hydrogen, CN, NH_2, OH, methyl, ethyl, hydroxyethyl, C_{1-2}alkoxyethyl, methoxy, ethoxy, cyclohexyl; phenyl or phenyl-C_{1-2}alkyl in which the phenyl group is unsubstituted or substituted by one or two groups selected from methyl, methoxy, chlorine, COOM and SO_3M; $-CH_2-\overset{\oplus}{N}$ , $-COR_{6a}$ or $-(CH_2)_{1-2}R_{7a}$,

R_{6a} is OH, NH_2, methoxy or ethoxy,

R_{7a} is CN, chlorine, SO_3M, $-OSO_3M$, $-$ or $-COR_{8a}$,

R_{8a} is OH, NH_2, methyl, ethyl, methoxy or ethoxy;

R_{4a} is hydrogen, CN, chlorine, bromine, SO_3M, $-NR_{9a}R_{10a}$, C_{1-2}alkyl, C_{1-2}alkyl monosubstituted by OH, phenyl, SO_3M or $-OSO_3M$; $-COR_{11a}$, $-CH_2NHCOR_{12a}B_2$ or a group $-\overset{\oplus}{N}<$ forming a pyridine, pyrimidine or benzimidazole ring which is further unsubstituted or monosubstituted by methyl, NH_2, $-NHCH_3$ or $-N(CH_3)_2$,

each of R_{9a} and R_{10a} is independently hydrogen, C_{1-2}-alkyl, C_{1-2}alkyl monosubstituted by OH, C_{1-2}alkoxy or phenyl, or $-COR_{12a}E_a$,

R_{12a} is C_{1-2}alkylene,

E_a is hydrogen, chlorine, a group B_2 or SO_3M,

B_2 is a group $R_{22a}R_{23a}$ or $-\overset{\oplus}{N}R_{24a}R_{25a}R_{26a}$,

each of R_{22a} and R_{23a}, independently, is hydrogen, C_{1-2}-alkyl, unbranched hydroxy-C_{2-3}alkyl or benzyl or both R_{22a} and R_{23a}, together with the N-atom to which they are attached, form a pyrrolidine, piperidine, morpholine, piperazine or N-methyl-piperazine group,

each of R_{24a} and R_{25a} has independently one of the non-cyclic or cyclic significances of R_{22a} and R_{23a} except hydrogen, and

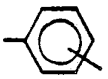
R_{26a} is methyl, ethyl or benzyl, or

R_{24a}, R_{25a} and R_{26a}, together with the N-atom to which they are attached, form a pyridinium group unsubstituted or substituted by one or two methyl groups

R_{11a} is OH, NH_2, $-NHCH_3$, $-N(CH_3)_2$, methyl, ethyl, methoxy or ethoxy;

R_{5a} is hydrogen, $-NR_{14a}R_{15a}$, phenyl, phenyl-C_{1-2}alkyl,

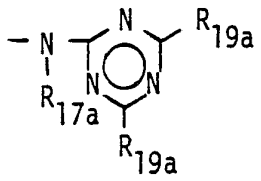
cyclohexyl; C_{1-4}alkyl, C_{1-4}alkyl monosubstituted by OH, CN, C_{1-2}alkoxy, $-COR_{16a}$, SO_3M or $-OSO_3M$;

$-C_{1-3}$alkylene-E_{1a}, $-C_{1-3}$alkylene-$N(R_{17a})CO$- or ,

each of R_{14a} and R_{15a} is independently hydrogen, methyl, ethyl or phenyl,

R_{16a} is OH, methoxy or ethoxy,

E_{1a} is B_2 or a group of the formula

,

R_{17a} is hydrogen or methyl,

each R_{19a} is independently fluorine, chlorine, NH_2, $-NHC_{1-2}$alkyl or $-N(C_{1-2}alkyl)_2$, in which the alkyl groups are unsubstituted or monosubstituted by OH, CN or C_{1-2}alkoxy,

R_{18a} is E_{2a}, $-NHCOR_{12a}E_{2a}$, $-SO_2NHR_{12a}E_{2a}$ or $-CONHR_{12a}E_{2a}$,

E_{2a} is a group B_2;

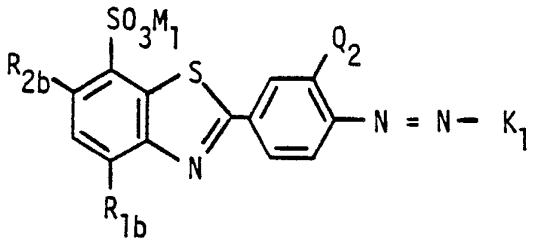
Z_a is OH or NH_2,

Y_a is O or N-Y_{1a},

Y_{1a} is hydrogen, CN, $CONH_2$, methyl, ethyl, C_{2-4}alkyl monosubstituted by OH, CN, chlorine or C_{1-2}alkoxy; phenyl or phenyl-C_{1-2}alkyl, the phenyl group of the latter two groups is unsubstituted or substituted by one or two groups selected from chlorine, methyl, methoxy, COOM and SO_3M; C_{2-4}alkylene-SO_3M, C_{2-4}alkylene-OSO_3M or C_{2-4}alkylene-COOM,

each of R_{20a} and 21_a is independently hydrogen, methyl, ethyl, phenyl-C_{1-2}alkyl or phenyl, the phenyl groups of which are unsubstituted or substituted by one or two groups selected from chlorine, methyl, methoxy, COOM and SO_3M, or in case where Y_a is N-Y_{1a} in which Y_{1a} is hydrogen, one of R_{20a} and R_{21a} also has a significance additionally given for Y_{1a}.

4. A compound according to any one of Claims 1 to 3 which compound corresponds to formula Ia,



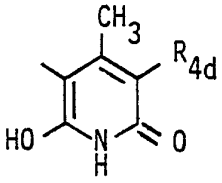
Ia

in which M_1 and Q_2 are as defined in Claim 1,
R_{1b} and R_{2b} are as defined in Claim 2, and
K_1 is as defined in Claim 3,
with the provisos that

(ii) when in a compound of formula Ia
(1) K_1 is a group (b_1), in which Y_a is O,
(2) R_{2b} is other than COOM,
(3) Q_2 is hydrogen or SO_3M_1,
and (1) to (3) occur simultaneously,
then at least one of M_1 is a quaternary ammonium cation asdefined above;

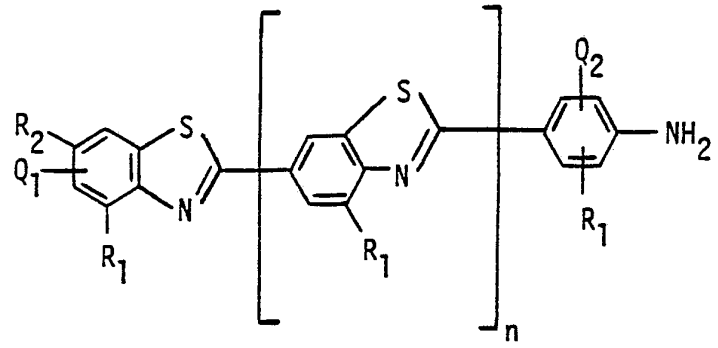
(iii) when in a compound of formula Ia in which K_1 is a group (b_1)
(1) the diazo component radical is defined as follows: R_{1b} is hydrogen, R_{2b} is methyl and Q_2 is hydrogen,
(2) each of R_{20a} and R_{21a} is hydrogen,
(3) Y_a is N-Y_{1a}, in which Y_{1a} is hydrogen,
and (1) to (3) occur simultaneously,
then M_1 has a significance other than hydrogen or sodium.

5. A compound according to Claim 4, in which K_1 is a group of the formula



wherein R_{4d} is hydrogen or cyano.

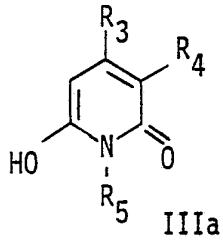
6. A process for the preparation of a compound of formula I as defined in Claim 1 comprising reacting the diazonium salt of an amine of formula II



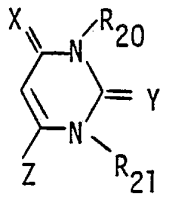
II

in which R_1, R_2, Q_1, Q_2 and n are as defined in Claim 1, or a mixture thereof

with a compound which in one of the possible tautomeric forms corresponds to formula IIIa or IIIb



IIIa



IIIb

in which R_3, R_4, R_5, R_{20}, R_{21}, X, Y and Z are as defined in Claim 1.

7. A process according to Claim 6 comprising reacting the diazonium salt of an amine of formula II with a compound of formula IIIa or IIIb in the presence of a basic salt, lithium-, sodium-, potasium-, ammonium-hydroxide, one or more organic amines or a quaternary ammonium compound.

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

9. A process for dyeing or printing comprising applying to a hydroxy group or nitrogen containing organic substrate a compound of formula I defined in Claim 1 in water-soluble salt form.

10. A process according to Claim 9 wherein said substrate is a textile consisting of or containing cellulose material, leather or paper.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 85/00491

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 09 B 29/01; C 09 B 29/36; C 09 B 44/08; D 06 P 1/02; D 21 H 3/80

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 09 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	FR, A, 2111697 (E.I. DU PONT DE NEMOURS) 9 June 1972, see claims 1,2; page 4, line 33 - page 5, line 14; page 1, line 1-23	1-4,6-10
X	DE, A, 2033281 (BASF) 20 January 1972, see claims 1-5; examples 3-50	1-7,9,10
X	FR, A, 2373586 (CIBA GEIGY) 7 July 1978, see claims 1-15	1-4,6-10
A	EP, A, 0084372 (CIBA GEIGY) 27 July 1983, see claims 1,11; page 3, lines 6-8	1,9,10
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* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28th January 1986	14 FEB 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/EP 85/00491 (SA 10807)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/02/86

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