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(54) Title: YELLOW ANIONIC DISAZO DYES

(57) Abstract: The present invention relates to novel yellow anionic dyes, a process for their preparation, certain novel intermediates necessary for their preparation and the use of these dyes for dyeing natural or synthetic materials, in particular, paper.

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YELLOW ANIONIC DISAZO DYES

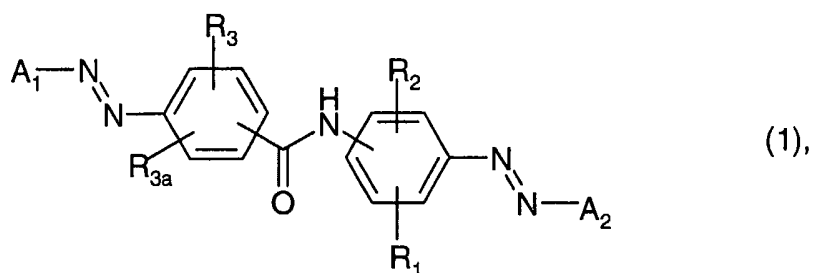
The present invention relates to novel yellow anionic dyes, a process for their preparation, certain novel intermediates necessary for their preparation and the use of these dyes for dyeing natural or synthetic materials, in particular, paper.

The use of diaminobenzanilides as building blocks for the synthesis of bisazo dyes and the advantages thereof has been described in *Dyes and Pigments*, 17, 297-302 (1991). On this basis, a number of bisazo orange and yellow dyes containing pyrazolones and phenolic derivatives as coupling components have been described, for example, in DE 818,669, DE 845,084, DE 2,362,995, GB 28,569, US 2,228,321 and in JP 51-11817, whilst further symmetrical bisazo dyes containing 1-phenyl-5-amino pyrazoles have also been reported in US 5,545,725, whilst US 2,544,087 discloses certain bis-acetoacetanilide derivatives.

However, a requirement exists to provide further anionic dyes especially of neutral or greenish yellow shades, which dyes exhibit excellent degrees of exhaustion with high colour strength, whilst being sufficiently water-soluble to provide stable aqueous formulations without the need for large quantities of solubilizers. Furthermore, dyings obtained should exhibit high degrees of bleed- and light-fastness, be even- or top-sided and be readily bleachable.

Surprisingly, it has now been found that certain bisazo dyes based on diaminobenzanilides exhibit excellent effects with respect to the desired properties.

Accordingly, the invention relates to compounds of the formula



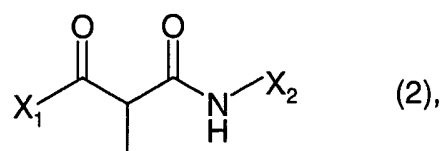
in which

R₁ represents hydrogen, substituted or unsubstituted C₁-C₈alkyl, substituted or unsubstituted C₁-C₈alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ and R_{3a} each, independently of the other, represent hydrogen, a C₁-C₄alkyl group, which may be substituted or unsubstituted, halogen, hydroxy, substituted or unsubstituted C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl and each of the residues

A₁ and A₂, independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

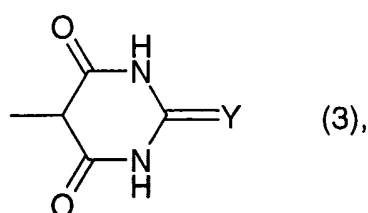


in which

X₁ represents C₁-C₄alkyl, or phenyl which is unsubstituted or monosubstituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and

X₂ represents phenyl which is unsubstituted, mono-, di- or trisubstituted by one or two SO₃H, SO₂NHC₁-C₄alkyl groups which alkyl groups may be substituted, SO₂C₁-C₄alkyl, C₁-C₄substituted or unsubstituted alkyl, hydroxy, C₁-C₄alkoxy, halogen, CF₃, NH₂, NHCOC₁-C₄alkyl, NHCOOC₁-C₄alkyl, NHCONHC₁-C₄alkyl, CO₂H, CONHC₁-C₄alkyl or NO₂; a 1- or 2-naphthyl residue which is unsubstituted or substituted by one or two SO₃H, SO₂NHC₁-C₄alkyl, carboxy, CONHC₁-C₄alkyl, carboxyC₁-C₄alkyl or carboxyaryl groups or a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated and be further substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and which may be attached to the NH-atom in formula (2) either via the hetero- or benzo-nucleus, in the case of benzannelated heterocycles;

a derivative of barbituric acid of the formula



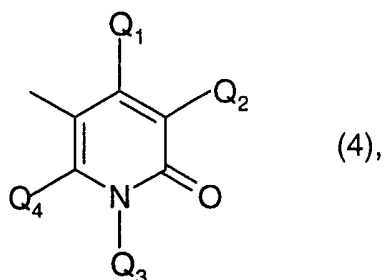
in which

- 3 -

Y represents O, NCN or NCONH₂;

a 2,4,6-triaminopyrimidine;

a pyridone derivative of the formula



in which

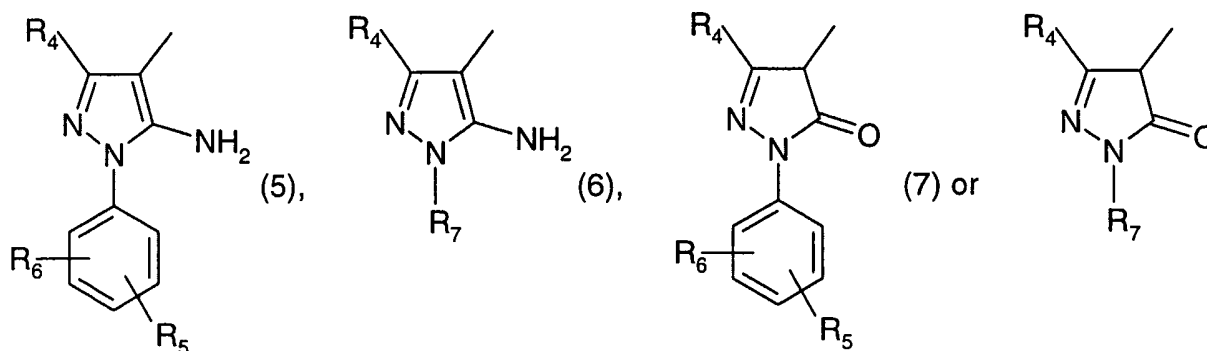
Q₁ represents hydrogen, hydroxy, C₁-C₂alkyl, hydroxyethyl, 2-(C₁-C₂alkoxy)alkyl, C₁-C₂alkoxy, COOH, CONH₂ or COO C₁-C₂alkyl,

Q₂ represents hydrogen, CN, CONH₂, halogen, SO₃H or C₁-C₂alkyl which is unsubstituted or substituted by hydroxy, phenyl or SO₃H,

Q₃ represents hydrogen, phenyl, C₁-C₂alkylphenyl, cyclohexyl or C₁-C₄alkyl which is unsubstituted or substituted by hydroxy, CN, C₁-C₂alkoxy or SO₃H and

Q₄ represents hydrogen or hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



in which

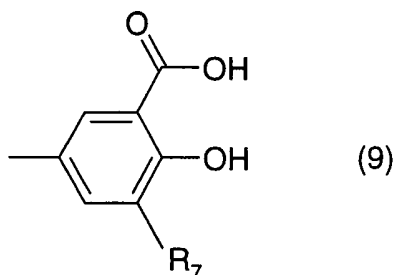
R₄ represents hydrogen, substituted or unsubstituted C₁-C₄alkyl, C₂-C₄alkenyl, NHCO C₁-C₄alkyl or CO₂H, each

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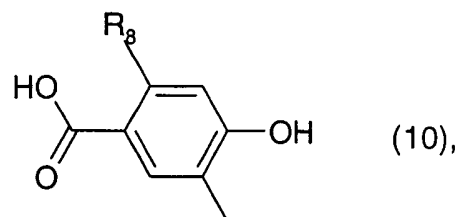
R_5 and R_6 , independently of the other, represent hydrogen, halogen, C_1 - C_4 alkyl, SO_3H or CO_2H and

R_7 represents hydrogen or C_1 - C_4 alkyl;

a benzoic acid derivative of formula



or

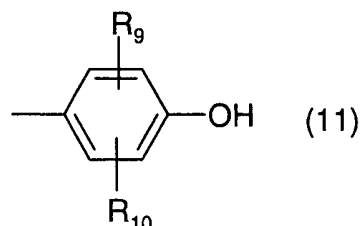


in which

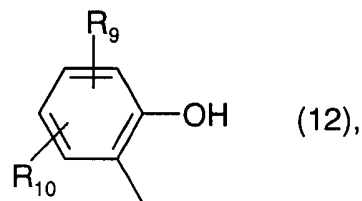
R_7 represents hydrogen or C_1 - C_4 alkyl and

R_8 represents hydrogen or hydroxy or

A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula



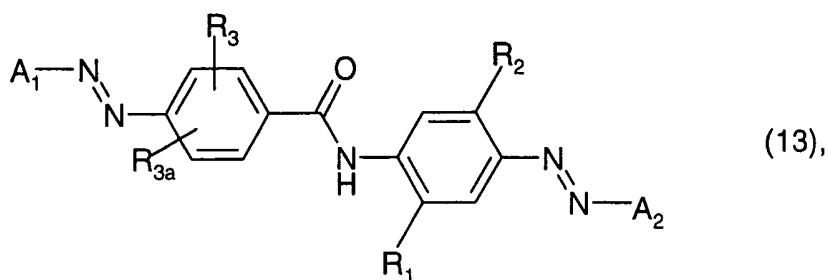
or



in which

R_9 and R_{10} , each one independently of the other, represent hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen, NH_2 , $NHCO$ C_1 - C_4 alkyl, NO_2 , SO_3H , CO_2C_1 - C_4 alkyl or $CONHC_1$ - C_4 alkyl groups,

with the proviso that in compounds of formula



if

R_1 , R_2 , R_3 and R_{3a} each, independently of the others, are hydrogen or SO_3H , then

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A_1 and A_2 are not both a 1-phenyl or 1-sulphophenyl-3-methyl-5-aminopyrazole residue,
or, if

R_1 , R_2 , R_3 and R_{3a} represent hydrogen and

A_1 is a residue of formula (9) in which

R_7 represents hydrogen or methyl, then

A_2 does not represent a 1-phenyl or 1-sulphophenyl-3-methyl- or 3-carboxy pyrazol-5-one
residue

or, if

R_1 , R_3 and R_{3a} are hydrogen and R_2 is SO_3H and one of

A_1 and A_2 represents a 1-sulphophenyl-3-methyl pyrazol-5-one residue, then the other is not
a residue of formula (11) in which both

R_9 and R_{10} are hydrogen, or if

A_1 represents a 1-nitrophenyl-, a 1-phenyl- or an unsubstituted 3-methyl pyrazol-5-one
residue,

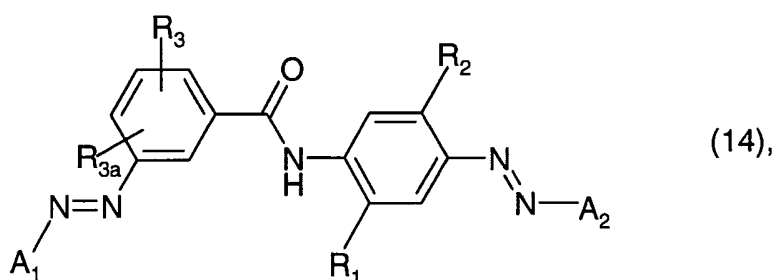
A_2 is not a residue of formula (9) in which R_7 represents hydrogen, or if

R_1 , R_3 and R_{3a} represent hydrogen, R_2 is CO_2H and

A_1 represents a residue of formula (9), in which R_7 is hydrogen,

A_2 is not a residue of formula (2) or formula (7);

in compounds of the formula

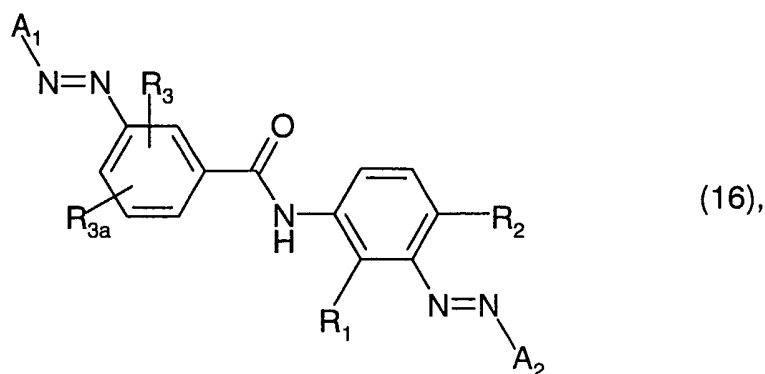


if

R_2 represents CO_2H , R_3 represents hydroxy or methoxy and R_{3a} represents hydrogen,

A_1 and A_2 do not represent residues of formulae (2) or (7) and,

in compounds of the formula



if

R_2 represents SO_3H and R_3 and R_{3a} both represent hydrogen
 A_1 and A_2 are not both 2,4-dihydroxyphenyl.

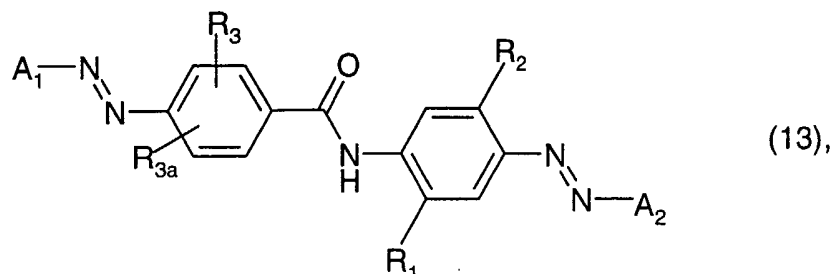
In one preferred aspect of the invention, the compounds of formula (1), contain a total number of two, three or four SO_3H and/or CO_2H groups. These sulphonic and/or carboxylic acid groups may be represented either, as written, in the form of the free acid or in the salt form, SO_3M and/or CO_2M . M is preferably one equivalent of a colourless cation, typically lithium, sodium, potassium, ammonium or the protonated form of a C_4 - C_{12} trialkylamine, C_4 - C_{12} diamine, C_2 - C_{12} alkanolamine or of a polyglycol amine, conveniently, triethanolamine triglycol ether, or mixtures of such cationic species.

M as a protonated C_4 - C_{12} trialkylamine may, for example, be a protonated N-ethyl-dimethylamine, N,N-diethylmethylamine, tri-n-propylamine, tri-n-butylamine, tri-isobutylamine, and, preferably, triethylamine or triisopropylamine.

M as a protonated C_4 - C_{12} diamine may, for example, be ethylenediamine, or 1,3-diaminopropane, in which one or both nitrogen atoms are additionally substituted by one or two C_1 - C_4 alkyl radicals, preferably methyl or ethyl radicals. M is preferably an N,N-dialkylethylenediamine or N,N-dialkyl-1,3-diaminopropane. Illustrative examples are: N-ethylethylenediamine, N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N-diethylethylenediamine, 3-dimethylamino-1-propylamine or 3-diethylamino-1-propylamine.

M as a protonated C_2 - C_{12} alkanolamine may be the protonated form of a monoalkanolamine, dialkanolamine, monoalkanolmonoalkylamine, monoalkanoldialkylamine, dialkanolalkylamine or trialkanolamine or a mixture of different protonated alkanolamines. Illustrative examples are: protonated 2-aminoethanol, bis(2-hydroxyethyl)amine, N-(2-hydroxyethyl)dimethylamine, N-(2-hydroxyethyl)diethylamine, N,N-bis(2-hydroxyethyl)ethylamine or tris(2-hydroxyethyl)-amine.

One further preferred class of compounds of formula (1) is that of the formula



in which

R_1 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or SO_3H ,

R_2 represents SO_3H or CO_2H ,

R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

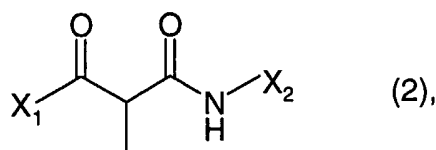
R_{3a} represents hydrogen or NH_2 and

A_1 and A_2 are as defined above.

More preferably, however, in the above compounds of formula (13),

R_3 and R_{3a} both represent hydrogen and

A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X_1 represents C_1 - C_4 alkyl, and

X_2 represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO_3H , C_1 - C_4 alkyl, hydroxy, C_1 - C_4 alkoxy, halogen or CO_2H ;

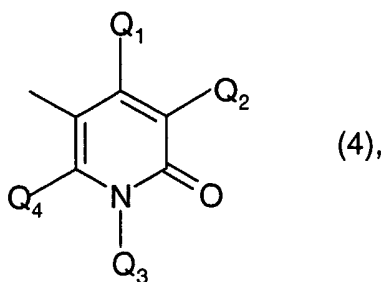
barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

a pyridone derivative of the formula

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in which

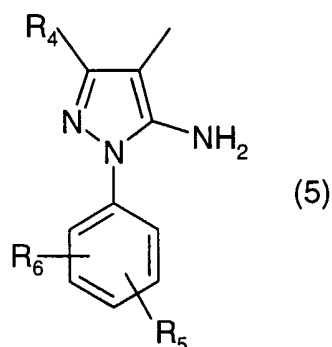
Q₁ represents C₁-C₂alkyl,

Q₂ represents CN, CONH₂ or CH₂SO₃H,

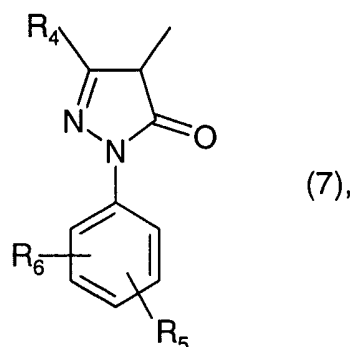
Q₃ represents C₁-C₂alkyl and

Q₄ represents hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



or



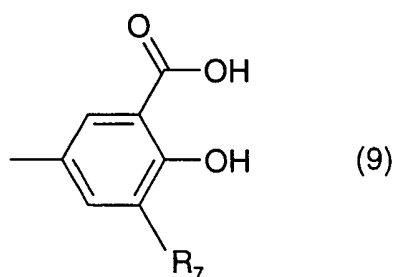
in which

R₄ represents C₁-C₄alkyl or CO₂H,

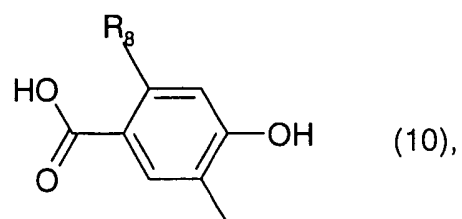
R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H and

R₆ represents hydrogen;

a benzoic acid derivative of formula



or

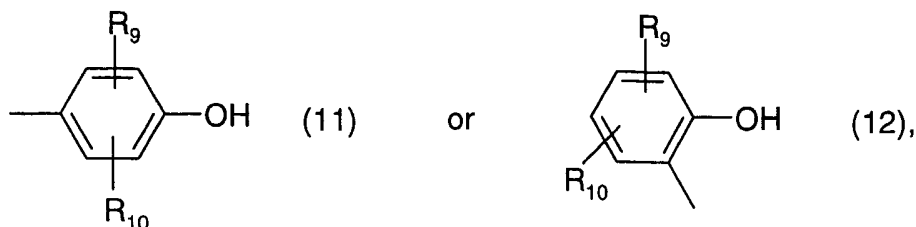


in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula



in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and

R₁₀ represents hydrogen.

Most preferred compounds of formula (13) are those in which

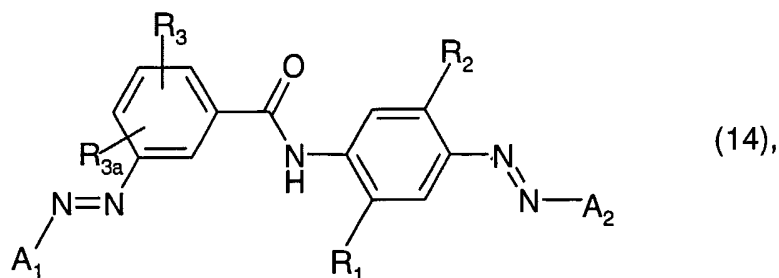
R₁ represents hydrogen, C₁-C₄alkoxy, especially methoxy, or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ and R_{3a} both represent hydrogen and the coupling component A₁ is derived from an acetoacetylated amine of formula (2), barbituric acid or cyanimino barbituric acid, a pyridone derivative of formula (4) in which Q₁ represents methyl, Q₂ is CN, CONH₂ or CH₂SO₃H, Q₃ is ethyl or methyl and Q₄ is hydroxy, a compound of formula (5) or (7) in which R₄ represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and

R₆ represents hydrogen, or from salicylic acid and the coupling component A₂ is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X₁ preferably represents methyl and X₂ preferably represents phenyl, which is monosubstituted by SO₃H or trisubstituted by SO₃H, methyl and methoxy or A₂ is derived from a pyridone derivative of formula (4) in which Q₁ represents methyl, Q₂ is CN, CONH₂ or CH₂SO₃H, Q₃ is ethyl and Q₄ is hydroxy or from an aminopyrazole of formula (5) in which R₄ represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and R₆ represents hydrogen.

A second preferred class of compounds of formula (1) is that of the formula



in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

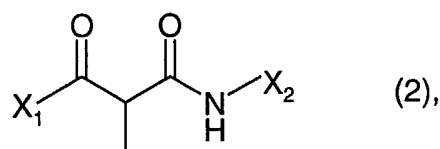
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined for formula (1) above.

More preferably, however, in the above compounds of formula (14)

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of
an acetoacetylated amine of the formula



in which

X₁ represents C₁-C₄alkyl, and

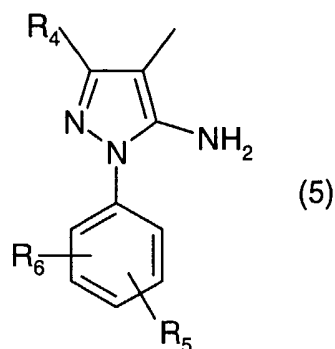
X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

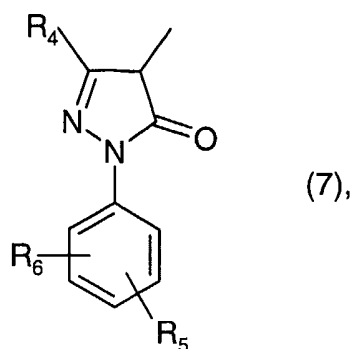
2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula



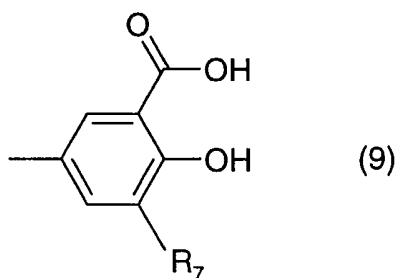
or



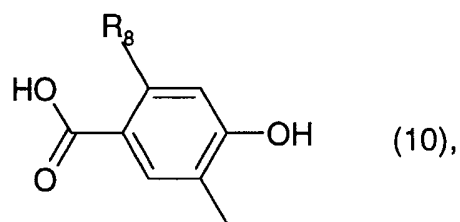
in which

R₄ represents C₁-C₄alkyl or CO₂H,R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H andR₆ represents hydrogen;

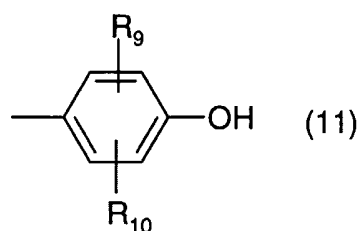
a benzoic acid derivative of formula



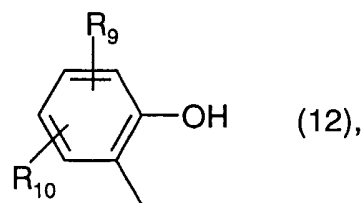
or



in which

R₇ represents hydrogen or C₁-C₄alkyl andR₈ represents hydrogen or hydroxy orA₁ and A₂, each one independently of the other, represent a phenol residue of the formula

or



in which

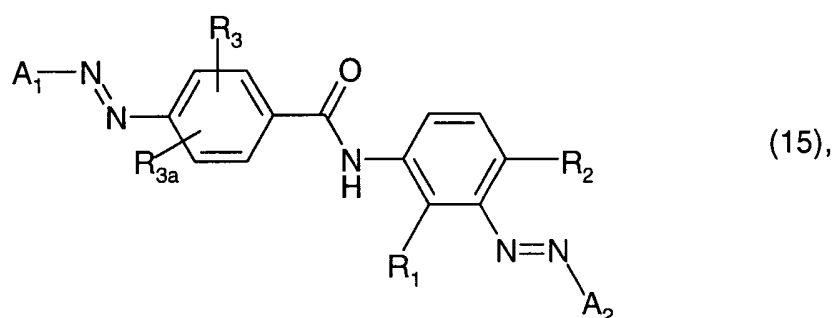
R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H andR₁₀ represents hydrogen.

Most preferred compounds of formula (14) are those in which

R₁ represents hydrogen, C₁-C₄alkoxy, especially methoxy, or SO₃H,R₂ represents SO₃H or CO₂H,

R_3 and R_{3a} both represent hydrogen and the coupling component A_1 is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid, 2,4,6-triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen or from salicylic acid, methyl salicylic acid, phenol or methyl phenol and the coupling component A_2 is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X_1 preferably represents methyl and X_2 preferably represents phenyl, which is monosubstituted by SO_3H or, especially, trisubstituted by SO_3H , methyl and methoxy or A_2 is derived from an aminopyrazole of formula (5) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen.

A third preferred class of compounds of formula (1) is that of formula



in which

R_1 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or SO_3H ,

R_2 represents SO_3H or CO_2H ,

R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH_2 and

A_1 and A_2 are as defined for formula (1) above.

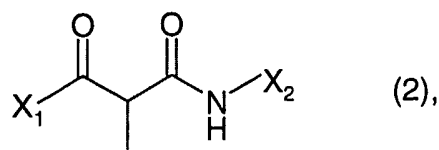
More preferably, however, in the above compounds of formula (15)

R_3 and R_{3a} both represent hydrogen and

A_1 and A_2 , each one independently of the other, is derived from a coupling component

selected from the group consisting of
an acetoacetylated amine of the formula

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in which

X_1 represents C_1 - C_4 alkyl, and

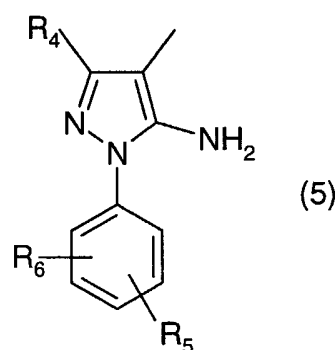
X_2 represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO_3H , C_1 - C_4 alkyl, hydroxy, C_1 - C_4 alkoxy, halogen or CO_2H ;

barbituric acid or cyanoiminobarbituric acid;

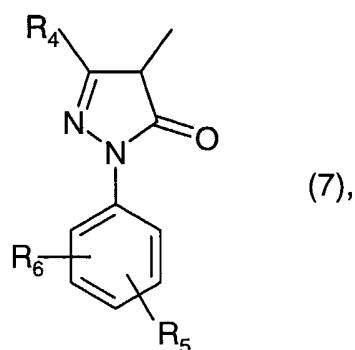
2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula



or



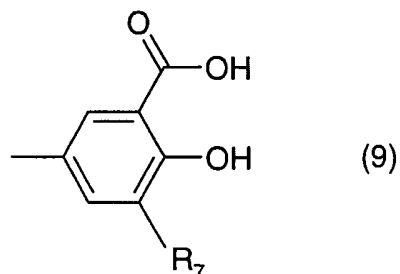
in which

R_4 represents C_1 - C_4 alkyl or CO_2H ,

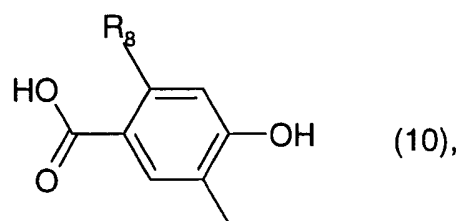
R_5 represents hydrogen, halogen, C_1 - C_4 alkyl, SO_3H or CO_2H and

R_6 represents hydrogen;

a benzoic acid derivative of formula



or

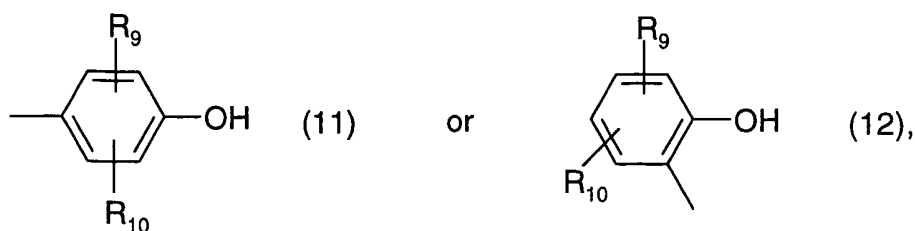


in which

R_7 represents hydrogen or C_1 - C_4 alkyl and

R_8 represents hydrogen or hydroxy or

A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula



in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and

R₁₀ represents hydrogen.

Most preferred compounds of formula (15) are those in which

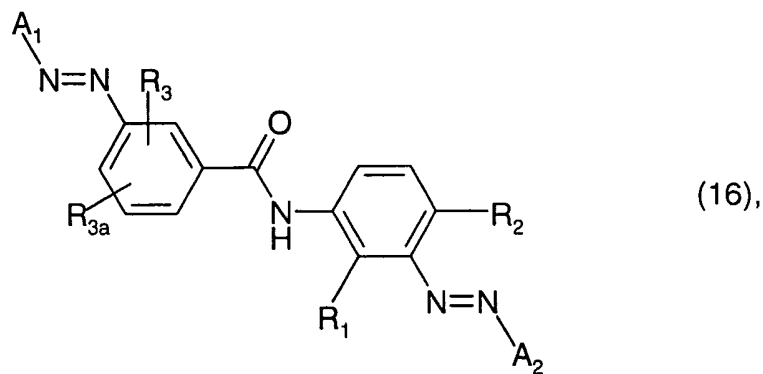
R₁ represents hydrogen or C₁-C₄alkoxy, especially hydrogen,

R₂ represents SO₃H or CO₂H, especially SO₃H,

R₃ and R_{3a} both represent hydrogen and the coupling component A₁ is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid, triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R₄ represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and

R₆ represents hydrogen or from salicylic acid, methyl salicylic acid, phenol or methyl phenol and the coupling component A₂ is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X₁ preferably represents methyl and X₂ preferably represents phenyl, which is monosubstituted by SO₃H or, especially, trisubstituted by SO₃H, methyl and methoxy or A₂ is derived from an aminopyrazole of formula (5) in which R₄ represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and R₆ represents hydrogen.

A fourth preferred class of compounds of formula (1) is that of formula



- 15 -

in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

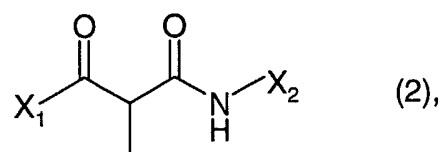
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined for formula (1) above.

More preferably, however, in the above compounds of formula (16),

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

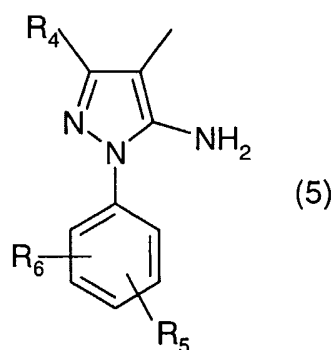
X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H; barbituric acid or cyanoiminobarbituric acid;

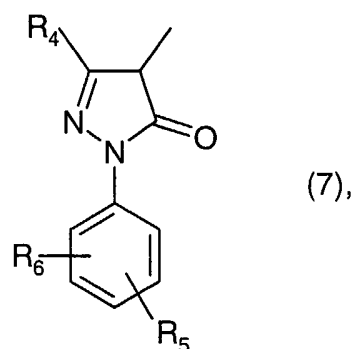
2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula



or



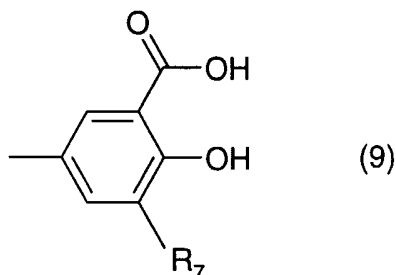
in which

R₄ represents C₁-C₄alkyl or CO₂H,

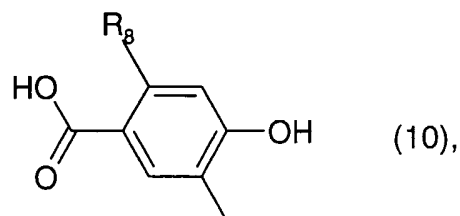
R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H and

R₆ represents hydrogen;

a benzoic acid derivative of formula



or

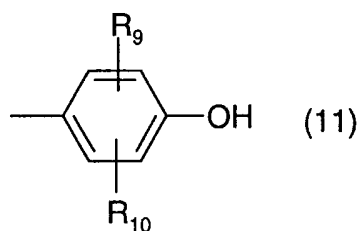


in which

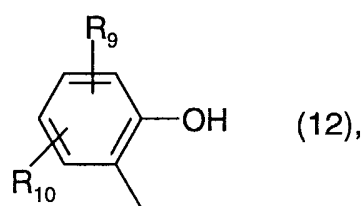
R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula



or



in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and

R₁₀ represents hydrogen.

Most preferred compounds of formula (16) are those in which

R₁ represents hydrogen or C₁-C₄alkoxy, especially hydrogen,

R₂ represents SO₃H or CO₂H, especially SO₃H,

R₃ and R_{3a} both represent hydrogen and the coupling component A₁ is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid,

2,4,6-triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R₄ represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and

R₆ represents hydrogen or from salicylic acid, methyl salicylic acid, phenol or methyl phenol and the coupling component A₂ is derived from an acetoacetylated amine of

formula (2), whereby, in formula (2), X₁ preferably represents methyl and X₂ preferably represents phenyl, which is monosubstituted by SO₃H or, especially, trisubstituted by SO₃H, methyl and methoxy or A₂ is derived from an aminopyrazole of formula (5) in which R₄

represents C₁-C₄alkyl, especially methyl, R₅ represents hydrogen or SO₃H and R₆ represents hydrogen.

Within the scope of the definitions of the above formulae and radicals (1) to (16), a C₁-C₈alkyl radical may be branched or unbranched, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl or 2-ethylhexyl.

Similarly, C₁-C₈alkoxy may be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy, t-butoxy, 2-ethylbutoxy, n-pentoxy, isopentoxy, 1-methylpentoxy, 1,3-dimethylbutoxy, n-hexyloxy, 1-methylhexyloxy, n-heptyloxy, isoheptyloxy, 1,1,3,3-tetramethylbutoxy, 1-methylheptyloxy, 3-methylheptyloxy, n-octyloxy or 2-ethylhexyloxy

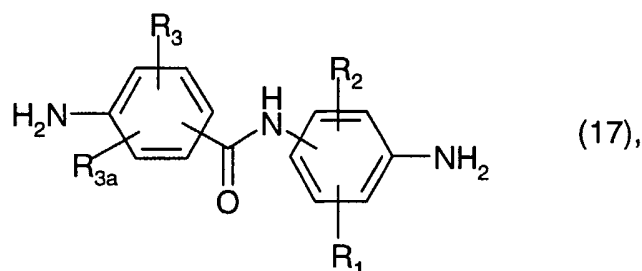
When such alkyl or alkoxy radicals are substituted, appropriate substituents may typically include one or two hydroxy, SO₃H, carboxy, C₁-C₄alkoxy, hydroxy-substituted C₁-C₄alkoxy, phenyl or phenoxy groups. Suitable radicals of this type may include hydroxyethyl, 1-hydroxyisopropyl, ethoxymethyl, 2-hydroxyethoxypentyl, benzyl, 1-phenylethyl, 2-phenylethyl, 1-methyl-2-phenylethyl, 1-isobutyl-3-phenylpropyl or 1-methyl-2-phenoxyethyl.

Halogen in the above formulae and radicals is iodine, bromine, fluorine or, especially, chlorine.

Where, in the derivatives of formulae (4) and (5), R₄ represents C₂-C₄alkenyl, this may, for example, be ethenyl, n-propenyl, isopropenyl, n-butenyl or isobutenyl.

Where, in the acetoacetylated amines of formula (2), X₂ represents a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated, these may be, for example, oxazol-2-yl, thiazol-2-yl, benzoxazol-2-, 5-, or 6-yl, benzothiazol-2-, 5- or 6-yl, benzimidazolone-5-yl, pyrid-2, 3- or 4-yl, quinolin-2-, 4-, 5- or 6-yl or 1,3,5-triazin-2-yl radicals.

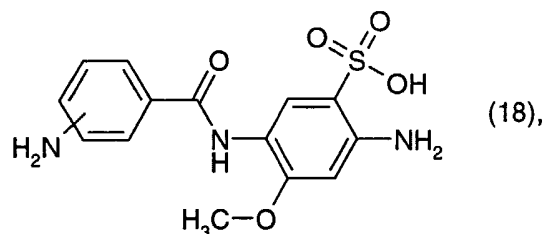
The dyes of formula (1) of the invention may be prepared by known methods, for example by tetrazotisation of a diaminobenzanilide derivative of the formula



in which R_1 , R_2 , R_3 and R_{3a} are as defined for formula (1), and sequential coupling with a coupling component of the formula A_1H or A_2H , followed by coupling with a coupling component of the formula A_2H or A_1H , A_2 and A_1 being as defined for formula (1).

Such sequential coupling reactions have been described previously (see, for example, US 5,545,725). However, it is advantageous to perform the initial coupling reaction at a pH value of between 2 and 5, especially between 2.5 and 4, whilst the subsequent coupling reaction is performed at a pH value of between 5 and 9, preferably between 6 and 8.

The coupling components A_1H and A_2H are known compounds or may be prepared by known methods, whilst some of the diaminobenzanilides of formula (14) are novel. Consequently, a further aspect of the invention is a compound of the formula



preferably 4,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid or 3,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid, a process for the preparation thereof, by reaction of 2-methoxy-4-nitroaniline-5-sulphonic acid with the appropriate nitrobenzoyl halide, preferably m- or p-nitrobenzoyl chloride, followed by reduction of the resulting dinitrobenzanilide by known methods and also the use of the compound (18) for the preparation of the appropriate compound of formula (1).

The dyes of the invention may be used to dye natural or synthetic materials, for example, cellulosic materials, carbonamide group containing materials such as polyamides, leather or

glass fibres, but are particularly useful for dyeing paper. They are preferably used as a solid or liquid commercial form.

The pulverulent or granular form of the dye is used particularly in batchwise pulp dyeing where the dye mixture, customarily in the form of a stock solution, is added in the pulper, in the beater or in the mixing chest. Preference is here given to using dye preparations which as well as the dye, may further include extenders, for example urea as solubilizer, dextrin, Glauber salt, sodium chloride and also dispersants, dustproofing agents and sequestrants, such as tetrasodium phosphate.

The present invention accordingly further provides solid dye preparations for dyeing paper comprising a compound of the formula (1) and, optionally, further auxiliaries.

In recent years, the use of concentrated aqueous solutions of dyes has gained importance because of the advantages possessed by such solutions when compared with dyes in powder form. The use of solutions avoids the difficulties associated with dust formation and releases the user from the time-consuming and frequently difficult dissolving of the dye powder in water. The use of concentrated solutions was also prompted by the development of continuous dyeing processes for paper, since it is convenient in these processes to meter the solution directly into the pulp stream or to add it at some other suitable point of the paper-making process.

The present invention accordingly further provides aqueous solutions, preferably concentrated solutions, for dyeing paper, comprising a compound of the formula (1), preferably in a concentration of from 5 to 30% by weight. Due to their excellent solubility in water, the dyes of formula (1) are particularly suitable for the preparation of such solutions.

The concentrated solutions preferably contain a low level of inorganic salts, which may be achieved, if necessary, by known methods, for example reverse osmosis.

The solutions may include further auxiliaries, for example solubilizers such as ϵ -caprolactam or urea, organic solvents, for example glycols, polyethylene glycols, dimethyl sulphoxide, N-methylpyrrolidone, acetamide, alkanolamines or polyglycolamines, which is a still further aspect of the invention.

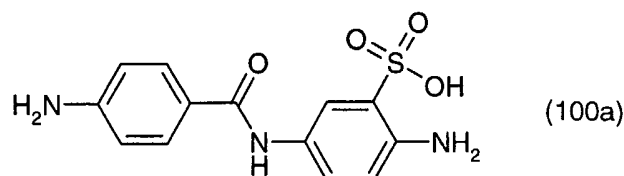
In addition, the aqueous dye solutions of the present invention may be applied to paper by use of the so-called spraying technique.

The novel dyes of the invention dye paper in predominantly yellow shades with excellent degrees of exhaustion with high colour strength, whilst being sufficiently water-soluble to provide stable aqueous formulations without the need for large quantities of solubilizers. Furthermore, dyings obtained exhibit high degrees of bleed- and light-fastness, are even- or top-sided and readily bleachable.

Furthermore, as a result of their high colour strength and water solubility, the novel dyes of the invention are suitable for use in the ink-jet printing method.

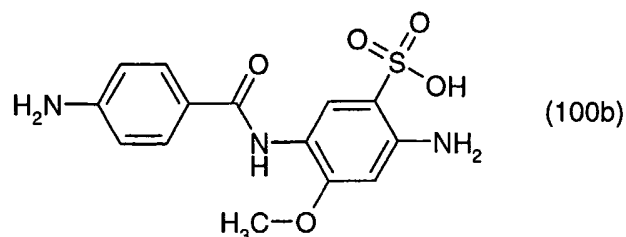
Consequently, one further aspect of the invention is paper which is dyed with a compound of the formula (1), either in the form of a solid dye preparation, or an aqueous solution, as described above.

The following Examples serve to illustrate the invention without intending to be restrictive in nature. Parts and percentages are by weight unless otherwise stated.

Synthesis of Intermediate Diaminobenzanilides**Example 1**

73.5g of p-phenylenediamine 2-sulphonic acid are added to 300g of water and, after addition of approximately 40g of sodium carbonate, the violet suspension is stirred until solution results. The pH is adjusted to 7.5 by addition of concentrated hydrochloric acid and a solution of 78g of p-nitrobenzoyl chloride in 100ml of acetone then added slowly at 25-32°C, the pH being maintained at 6.7-7.0 by addition of 2N aqueous sodium hydroxide. After stirring for a further 1.5 hours, 210ml of water are added and the pH adjusted to 4.0 by addition of 22ml of concentrated hydrochloric acid. The readily stirrable suspension is filtered at room temperature and washed with 200ml of water. The filter cake is then stirred in water at 50°C, filtered hot and dried to yield 75g of 4'-amino-4-nitrobenzanilide 3-sulphonic acid.

A mixture of 1300g of water, 46.2g of iron filings and 5.8g of ammonium chloride is heated to boiling with vigorous stirring and then treated with 55g of 4'-amino-4-nitrobenzanilide 3-sulphonic acid, obtained as described above. The resulting suspension is stirred for a further 1 hour at 95-100°C and, subsequently, cooled to room temperature. The suspension is filtered hot and the filtrate stirred with 5g of Hyflo Carcel™ for 30 minutes at room temperature. After filtering, the pH of the hot filtrate is adjusted to 2.0 by addition of 18g of concentrated hydrochloric acid and the white precipitate filtered and dried. There are obtained 39g of 4,4'-diaminobenzanilide 5'-sulphonic acid of formula (100a).

Example 2

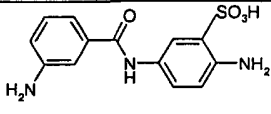
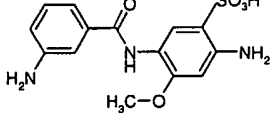
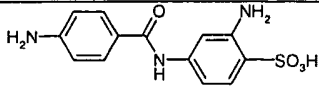
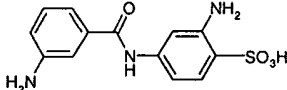
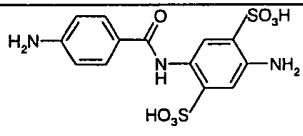
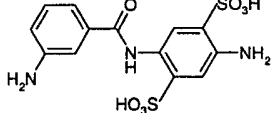
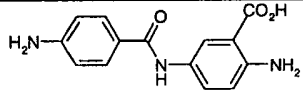
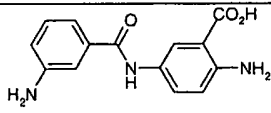
74.5g of 2-methoxy-4-nitroaniline 5-sulphonic acid are added to 300g of water and, after addition of approximately 30g of sodium carbonate, the yellowish orange suspension is stirred until solution results. The pH is adjusted to 7.0 by addition of concentrated hydrochloric acid and a solution of 60g of p-nitrobenzoyl chloride in 75ml of acetone then added slowly below 28°C, the pH being maintained at 6.7-7.0 by addition of 2N aqueous sodium hydroxide. After stirring for a further 2 hours, 650g of water are added and the pH adjusted to 4.0 by addition of 2N aqueous hydrochloric acid. The readily stirrable suspension is filtered, the filter cake washed with 200g of water and sucked dry. There are obtained 391g of damp filter cake, which is used directly for the next step.

A mixture of 1000g of water, 60g of iron filings and 7.6g of ammonium chloride is heated to boiling with vigorous stirring and then treated with 145g of the damp filter cake, obtained as described above. The resulting suspension is stirred for a further 2 hours at 90-95°C and, subsequently, 700g of water are added. The suspension is filtered hot and the filtrate stirred with 10g of Hyflo Supercel™ for 30 minutes at 85°C. After filtering, the pH of the hot filtrate is adjusted to 3.8 by addition of 24g of concentrated hydrochloric acid and the white precipitate filtered and dried. There are obtained 34.3g of 4,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b).

Examples 3-10

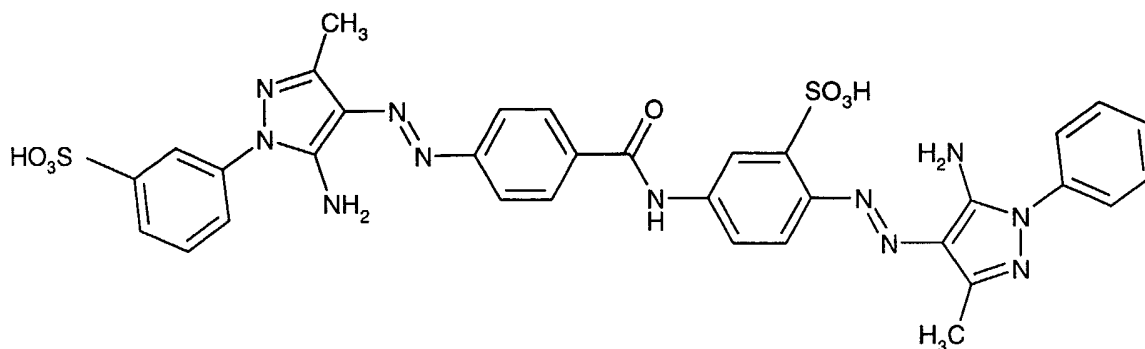
By following the procedure described in Examples 1 or 2, employing appropriate starting materials, the following benzanilides may be obtained, as summarized in Table 1 below.

Table 1

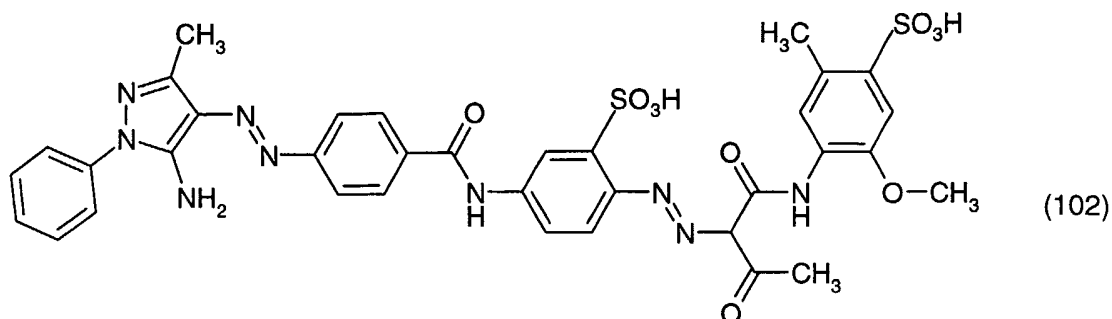
Example Nr.	Compound Nr	Formula
3	(100c)	
4	(100d)	
5	(100e)	
6	(100f)	
7	(100g)	
8	(100h)	
9	(100i)	
10	(100j)	

Synthesis of Dyes

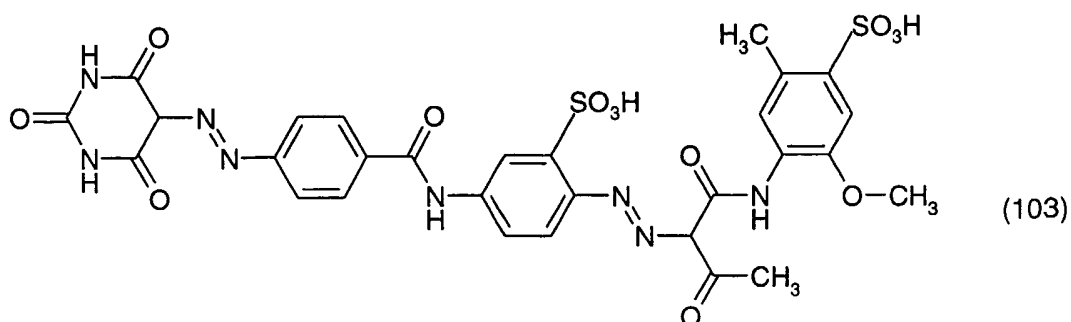
Example 11



3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with a total of 2.4g of 5-amino-3-methyl-1-(3-sulphophenyl) pyrazole, in portions, at 5°C, the pH being maintained at 3.6-4.0 by addition of a total of 13.7ml of 2N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 70 minutes, to a solution of 1.7g of 5-amino-3-methyl-1-phenyl pyrazole dissolved in 50g of water and 50g of dimethyl formamide, the pH being maintained at 6.5 by addition of a total of 11.9ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1.5 hours at room temperature, 50ml of isopropanol and 30g of sodium chloride are added, the mixture stirred for 1 hour and the resulting yellowish brown suspension filtered. After drying, there are obtained 6.7g of the compound of formula (101).

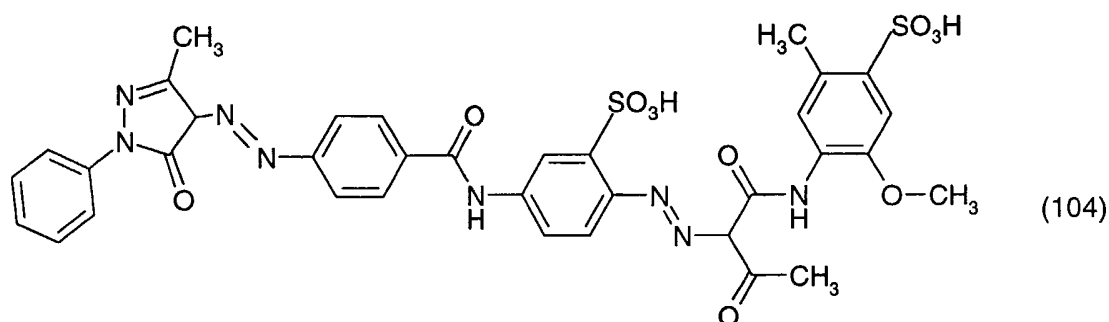
Example 12

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with 1.75g of 5-amino-3-methyl-1-phenyl pyrazole and reaction continued for 2.5 hours at 5°C, the pH being maintained at 3.8-4.0 by addition of a total of 15.9ml of 2N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 2.5 hours, to a solution of 3.0g of 3-acetoacetyl-amino-4-methoxy toluene 6-sulphonic acid dissolved in 50g of water and 50g of dimethyl formamide, the pH being maintained at 6.8 by addition of a total of 7ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1.5 hours at 30-35°C, 75ml of isopropanol and 45g of sodium chloride are added and the resulting yellow suspension filtered. After drying, there are obtained 6.8g of the compound of formula (102).

Example 13

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with 1.2g of barbituric acid. The pH is raised to 2.5 and then maintained at 2.3-2.5 over a period of 3 hours by addition of a total of 5.1ml of 4N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 1.5 hours, to a solution of 3.5g of 3-acetoacetylamino-4-methoxy toluene 6-sulphonic acid dissolved in 100g of water, the pH being maintained at 6.5 by addition of a total of 5.4ml of 4N aqueous sodium hydroxide solution. After stirring for a further 2.5 hours at room temperature, 75ml of isopropanol and 15g of sodium chloride are added and, after stirring briefly at room temperature, the resulting yellowish red suspension is filtered. After drying, there are obtained 7.1g of the compound of formula (103).

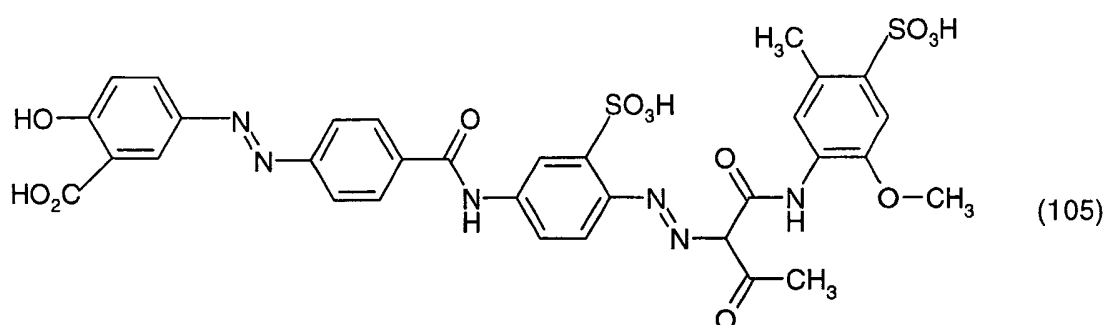
Example 14



3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is filtered and the moist presscake suspended in 110ml of water. 1.75g of 3-methyl-1-phenyl pyrazo-2-one are added and the pH raised to 3.7. By the addition of a total of 2.5ml of 4N aqueous sodium hydroxide solution, the pH is maintained at 3.5-4.0, whilst the temperature is raised stepwise from 10°C to 30°C. After stirring for a total of 3.5 hours the coupling reaction is complete. To the resulting monoazo suspension are then added 50g of dimethyl formamide followed by 3.5g of 3-acetoacetylamino-4-methoxy toluene

6-sulphonic acid. The pH is adjusted to 7.0-7.5 and maintained at this value by addition of a further 2.7ml of 4N aqueous sodium hydroxide solution. After stirring for a further 2 hours at room temperature, 20g of sodium chloride are added, the mixture stirred for 1 hour at room temperature and the resulting yellow suspension filtered. After drying, there are obtained 5.5g of the compound of formula (104).

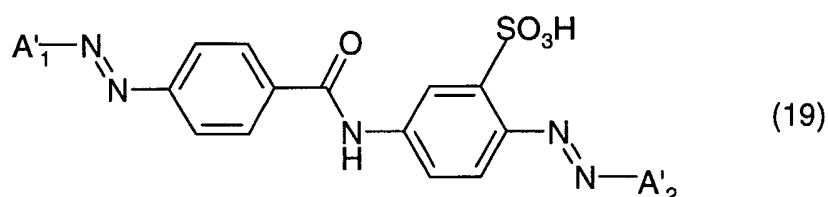
Example 15



3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5^oC over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is filtered and the moist presscake suspended in 110ml of water. 1.4g of salicylic acid are added and the pH raised to 3.0-3.3. By the addition of a total of 4.9ml of 2N aqueous sodium hydroxide solution, the pH is maintained at 3.0-3.5. After stirring for a total of 2.5 hours at room temperature the coupling reaction is complete. To the resulting monoazo suspension are then added 3.5g of 3-acetoacetylamino-4-methoxy toluene 6-sulphonic acid. The pH is adjusted to 6.5 and maintained at this value by addition of a further 4.9ml of 2N aqueous sodium hydroxide solution. After stirring for a total of 3.5 hours at room temperature, 10g of sodium chloride and 15ml of isopropanol are added, the pH increased to 8.5 and the resulting yellowish brown suspension filtered. After drying, there are obtained 5.2g of the compound of formula (105).

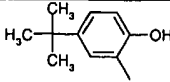
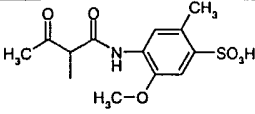
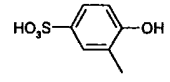
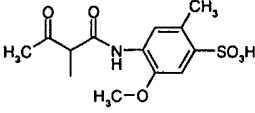
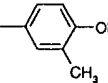
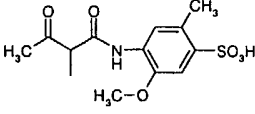
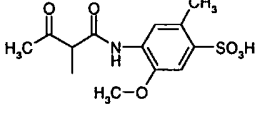
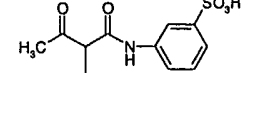
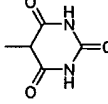
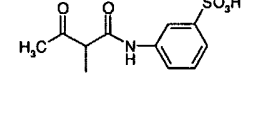
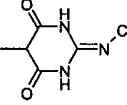
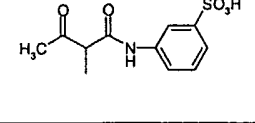
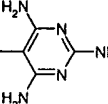
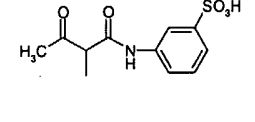
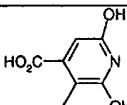
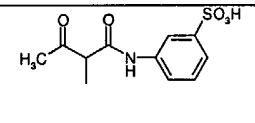
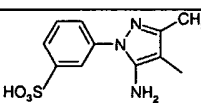
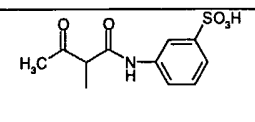
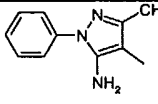
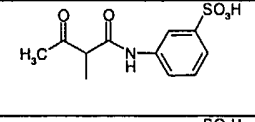
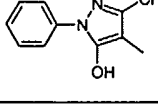
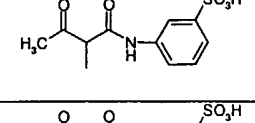
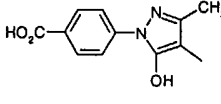
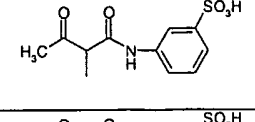
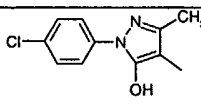
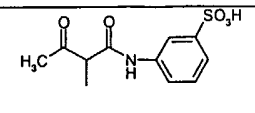
Examples 16-116

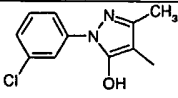
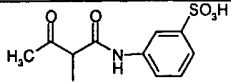
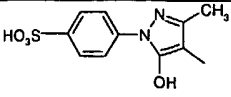
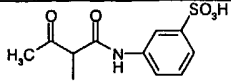
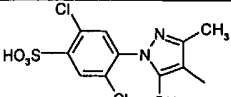
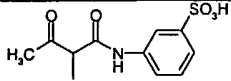
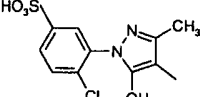
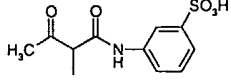
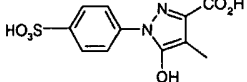
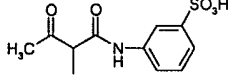
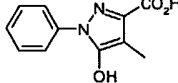
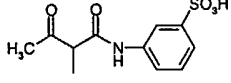
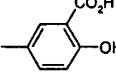
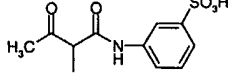
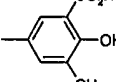
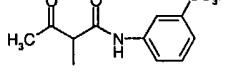
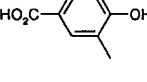
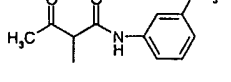
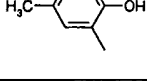
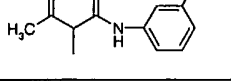
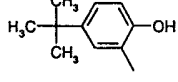
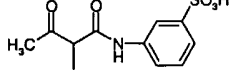
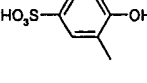
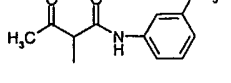
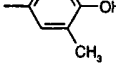
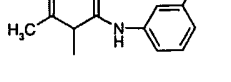
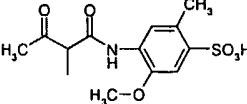
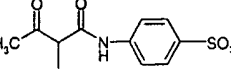
By proceeding in an analogous manner to that described in Examples 11-15, but utilizing the appropriate coupling components, compounds of formula (19) are obtained, as summarized in the following Table 2.

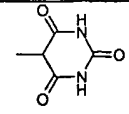
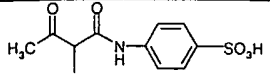
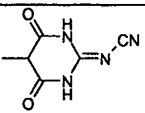
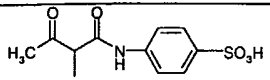
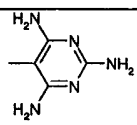
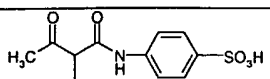
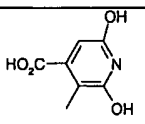
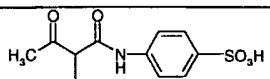
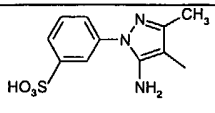
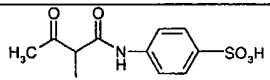
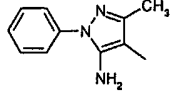
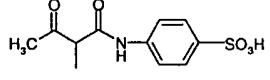
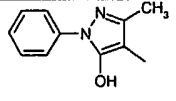
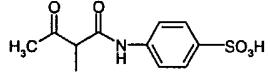
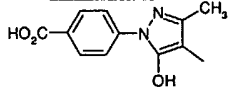
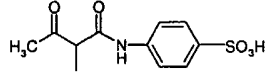
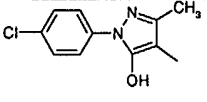
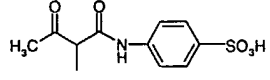
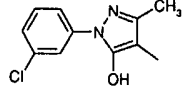
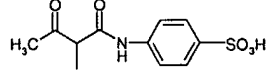
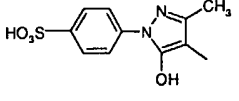
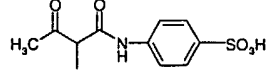
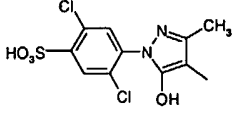
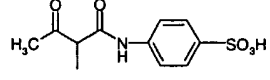
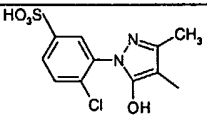
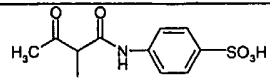
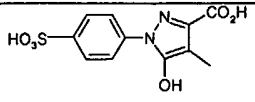
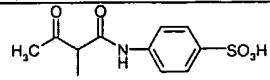
Table 2

Example Nr.	Compound Nr.	A ₁	A ₂
16	(106)		
17	(107)		
18	(108)		
19	(109)		
20	(110)		
21	(111)		
22	(112)		

23	(113)		
24	(114)		
25	(115)		
26	(116)		
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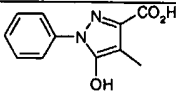
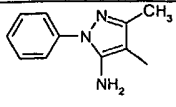
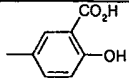
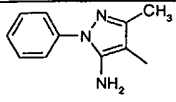
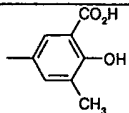
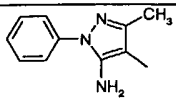
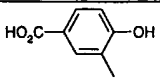
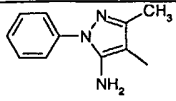
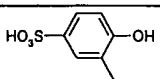
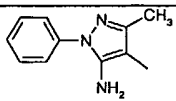
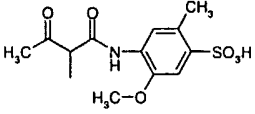
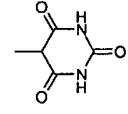
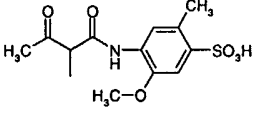
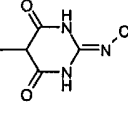
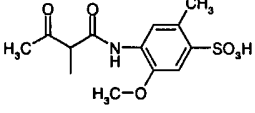
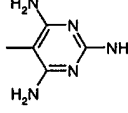
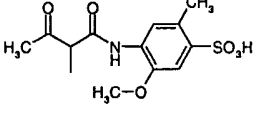
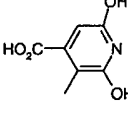
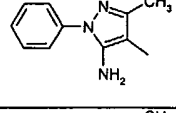
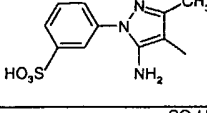
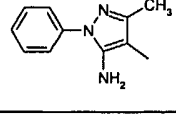
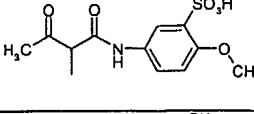
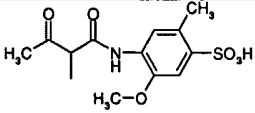
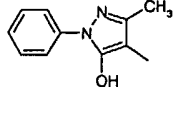
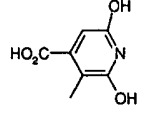
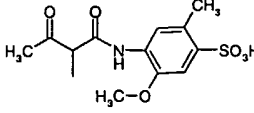
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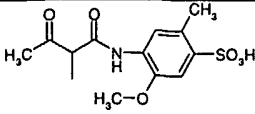
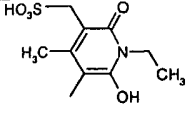
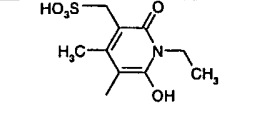
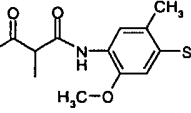
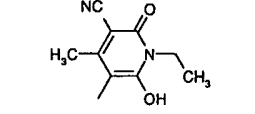
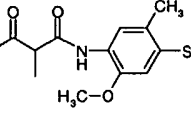
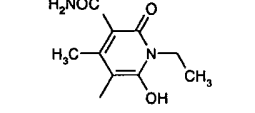
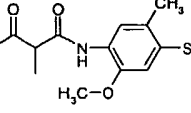
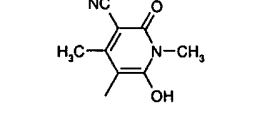
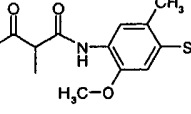
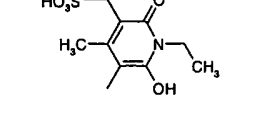
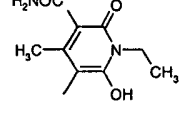
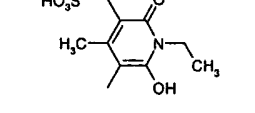
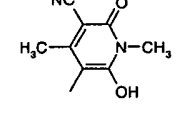
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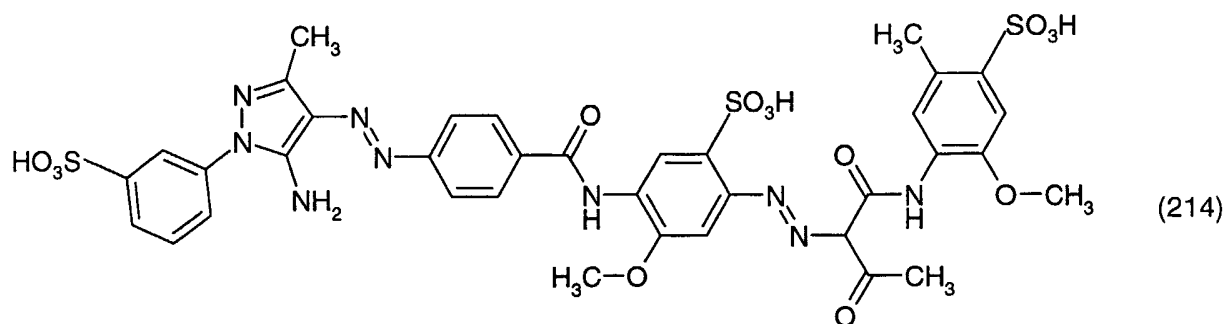
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76	(166)		
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84	(174)		
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89	(179)		

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100	(190)		
101	(191)		
102	(192)		
103	(193)		

104	(194)		
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106	(196)		
107	(197)		
108	(198)		
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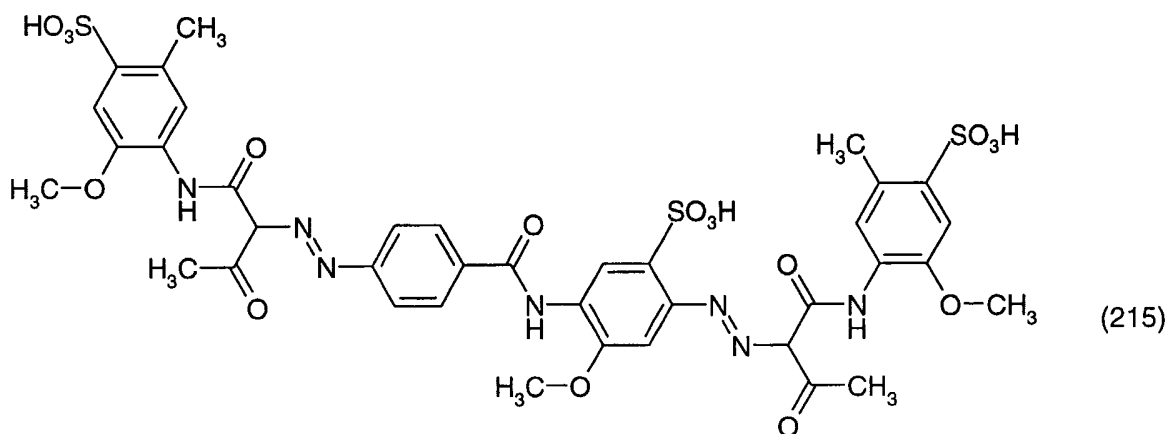
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121	(211)		
122	(212)		
123	(213)		

Example 124

4.5g of 4,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed

by addition of 0.8ml of 2N aqueous sulphamic acid solution. The resulting yellow suspension is diluted with 60g of water and treated with 2.9g of 5-amino-3-methyl-1-(3-sulphophenyl) pyrazole at 5°C, the pH being initially raised to 3.5 and maintained at 3.0-3.5 by the addition of a total of 27.4ml of 2N aqueous sodium hydroxide solution. After stirring for 2.5 hours the initial coupling reaction is completed. The resulting monoazo suspension is slowly added to a solution of 4.0g of 3-acetacetyl-amino-4-methoxytoluene 6-sulphonic acid in 50g of dimethylformamide over 2.5 hours at 30°C, the pH being maintained at 6.8-7.0 by addition of a total of 7.3ml of 4N aqueous sodium hydroxide solution. After stirring for 1.5 hours at 30°C, 35g of sodium chloride and 50g of isopropanol are added, the mixture stirred over night and the precipitated solids filtered. After drying, there are obtained 10.2g of the compound of formula (214).

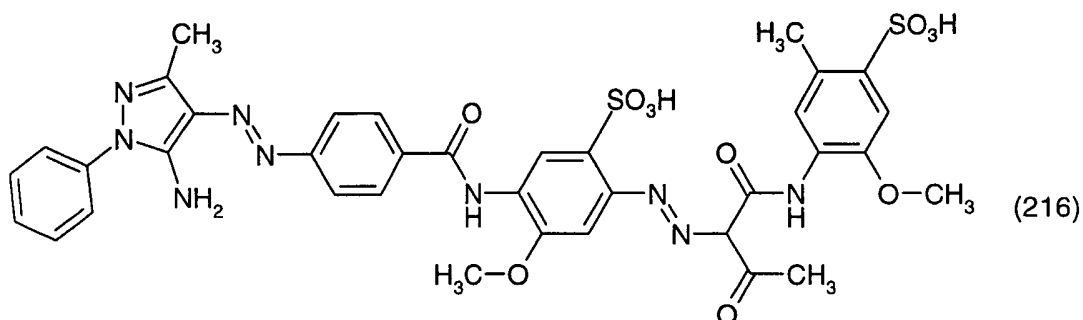
Example 125



4.5g of 4,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed by addition of 0.8ml of 2N aqueous sulphamic acid solution. The resulting yellow suspension is added to a solution of 7.7g of 3-acetyl-amino-4-methoxytoluene 6-sulphonic acid in 100g of water over 30 minutes at 5°C, the pH being of which is initially adjusted to 3.8 and is maintained at 3.8-4.0 by the addition of a total of 22.6ml of 2N aqueous sodium hydroxide solution. Subsequently, the pH is raised to 6.8-7.4 by addition of a further 10.1ml of 2N aqueous sodium hydroxide solution and the temperature increased to 25-40°C. After stirring

for a total of 3 hours, 45g of potassium chloride and 50g of isopropanol are added and the precipitated solids filtered. After drying, there are obtained 12.9g of the compound of formula (215).

Example 126



2.1g of 4,4'-diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed by addition of 2N aqueous sulphamic acid solution. The resulting yellow solution is treated with 0.9g of 5-amino-3-methyl-1-phenyl pyrazole at 5°C, the pH being initially raised to 3.0 and maintained at 2.5-3.0 by the addition of a total of 3.1ml of 4N aqueous sodium hydroxide solution. After stirring for 2.5 hours and slowly warming to 20°C, the initial coupling reaction is completed. To the resulting monoazo suspension are added 1.7g of 3-acetacetylamino-4-methoxytoluene 6-sulphonic acid, the pH raised to 6.5 and maintained at 6.0-7.5 by addition of a total of 2.2ml of 4N aqueous sodium hydroxide solution. After stirring for 3 hours at 20-40°C reaction is complete and the precipitated solids are filtered. After drying, there are obtained 5.4g of the compound of formula (216).

Examples 127-198

By proceeding in an analogous manner to that described in Examples 124-126, but utilizing the appropriate coupling components, compounds of formula (20) are obtained, as summarized in the following Table 3.

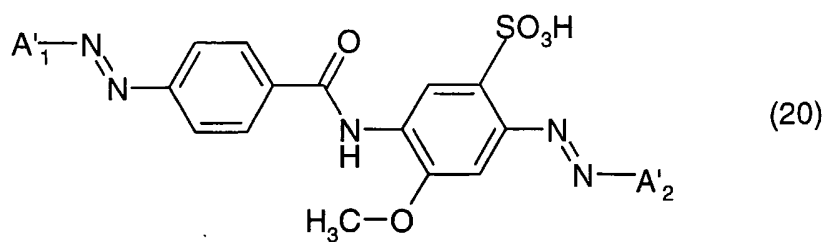
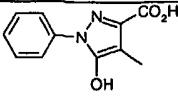
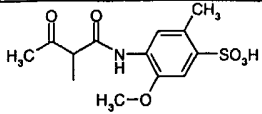
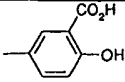
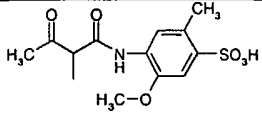
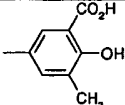
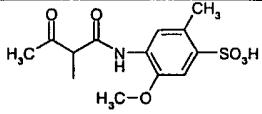
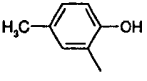
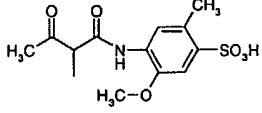
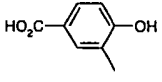
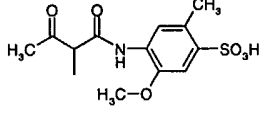
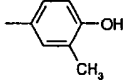
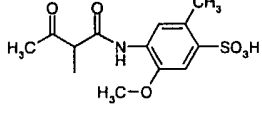
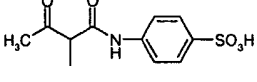
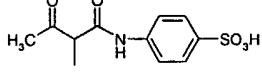
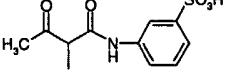
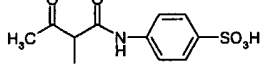
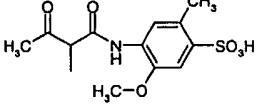
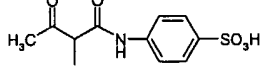
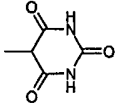
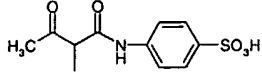
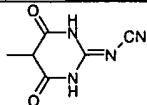
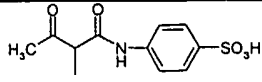
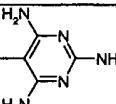
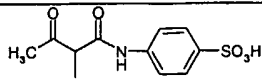
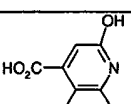
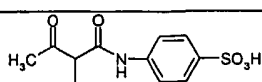
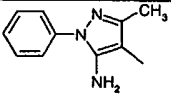
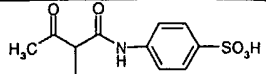
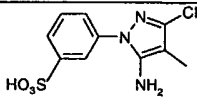
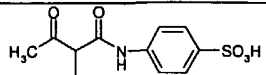
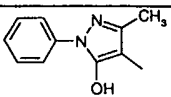
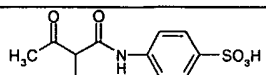
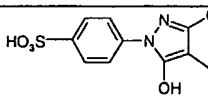
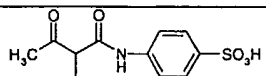
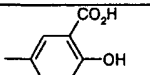
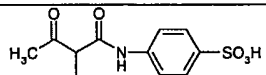
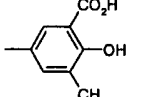
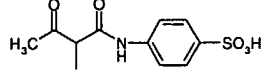
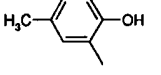
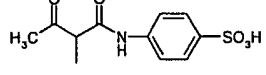
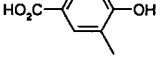
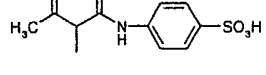
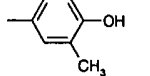
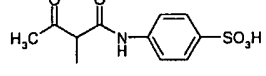
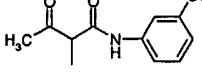
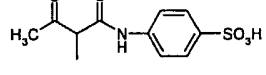
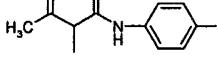
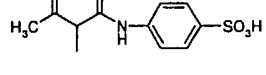
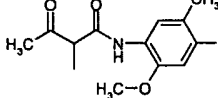
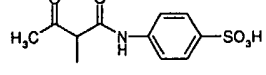
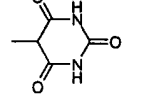
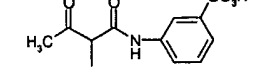
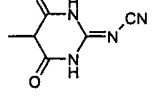
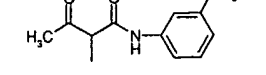
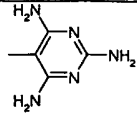
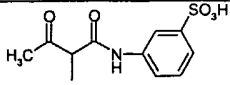
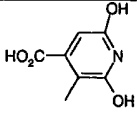
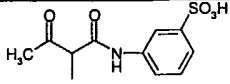
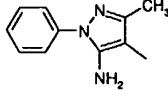
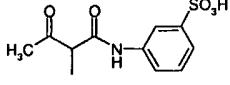
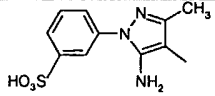
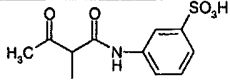
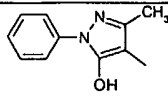
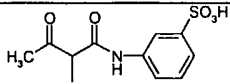
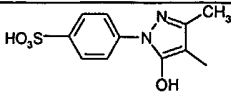
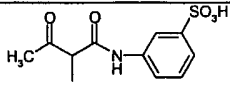
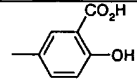
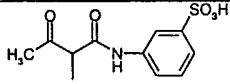
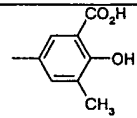
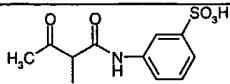
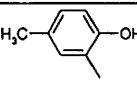
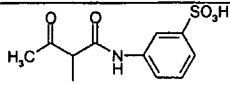
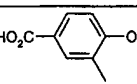
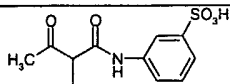
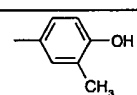
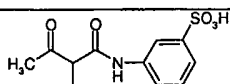
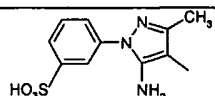
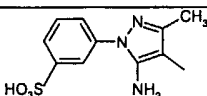
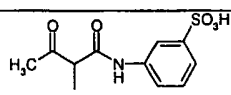
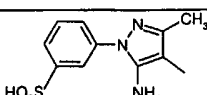
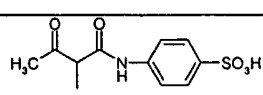
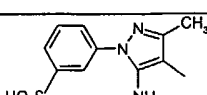


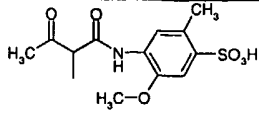
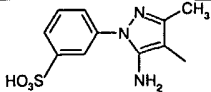
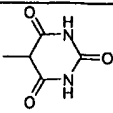
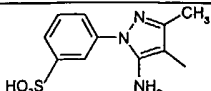
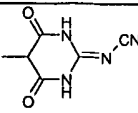
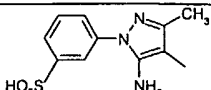
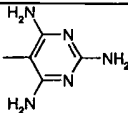
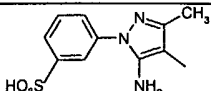
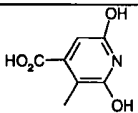
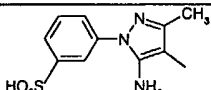
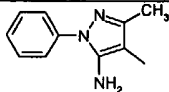
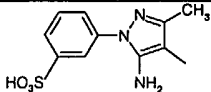
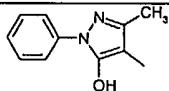
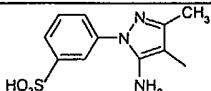
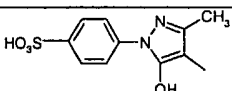
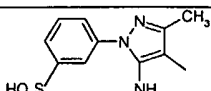
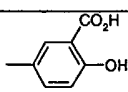
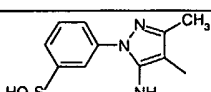
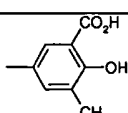
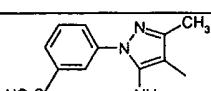
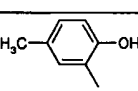
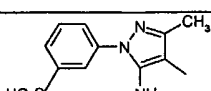
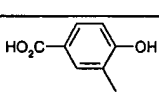
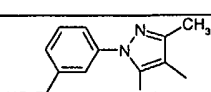
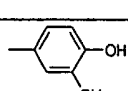
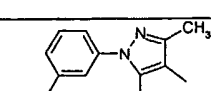
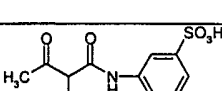
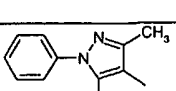
Table 3

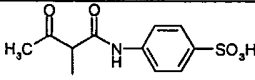
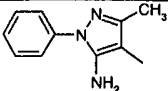
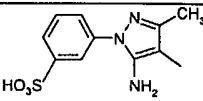
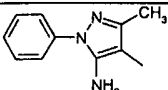
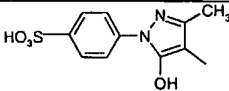
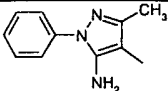
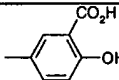
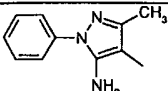
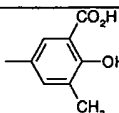
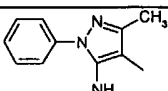
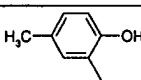
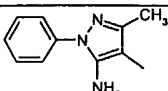
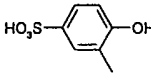
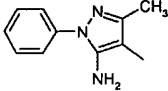
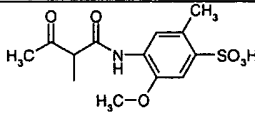
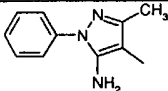
Example Nr.	Compound Nr.	A' ₁	A' ₂
127	(217)		
128	(218)		
129	(219)		
130	(220)		
131	(221)		
132	(222)		
133	(223)		
134	(224)		
135	(225)		

136	(226)		
137	(227)		
138	(228)		
139	(229)		
140	(230)		
141	(231)		
142	(232)		
143	(233)		
144	(234)		
145	(235)		
146	(236)		
147	(237)		
148	(238)		

149	(239)		
150	(240)		
151	(241)		
152	(242)		
153	(243)		
154	(244)		
155	(245)		
156	(246)		
157	(247)		
158	(248)		
159	(249)		
160	(250)		
161	(251)		
162	(252)		

163	(253)		
164	(254)		
165	(255)		
166	(256)		
167	(257)		
168	(258)		
169	(259)		
170	(260)		
171	(261)		
172	(262)		
173	(263)		
174	(264)		
175	(265)		
176	(266)		

177	(267)		
178	(268)		
179	(269)		
180	(270)		
181	(271)		
182	(272)		
183	(273)		
184	(274)		
185	(275)		
186	(276)		
187	(277)		
188	(278)		
189	(279)		
190	(280)		

191	(281)		
192	(282)		
193	(283)		
194	(284)		
195	(285)		
196	(286)		
197	(287)		
198	(288)		

Examples 199-217

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100c) and utilizing the appropriate coupling components, compounds of formula (21) are obtained, as summarized in the following Table 4.

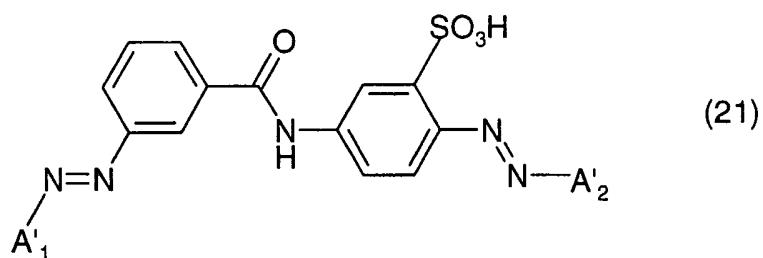
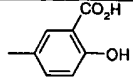
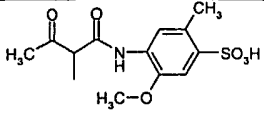
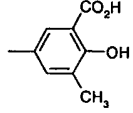
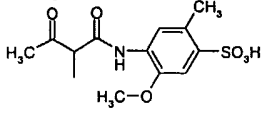
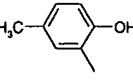
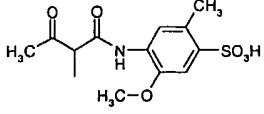
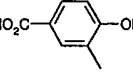
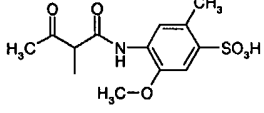
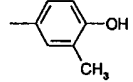
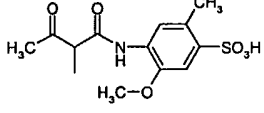
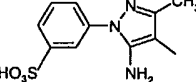
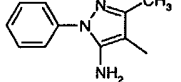
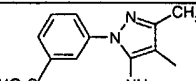
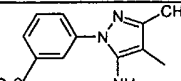
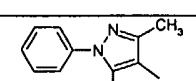
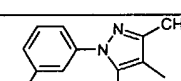


Table 4

Example Nr.	Compound Nr.	A ₁	A ₂
199	(289)		
200	(290)		
201	(291)		
202	(292)		
203	(293)		
204	(294)		
205	(295)		
206	(296)		
207	(297)		
208	(298)		
209	(299)		

210	(300)		
211	(301)		
212	(302)		
213	(303)		
214	(304)		
215	(305)		
216	(306)		
217	(307)		

Examples 218-236

By proceeding in an analogous manner to that described in Examples 124-126, but replacing the compound of formula (100b) by the compound of formula (100d) and utilizing the appropriate coupling components, compounds of formula (22) are obtained, as summarized in the following Table 5.

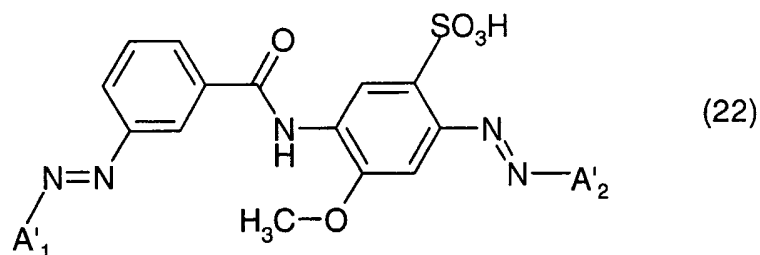
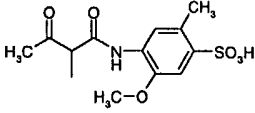
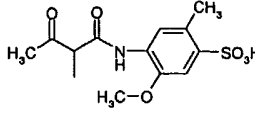
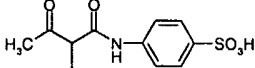
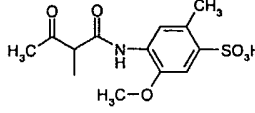
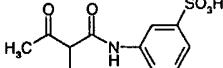
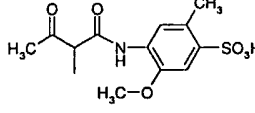
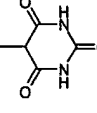
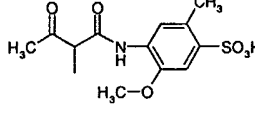
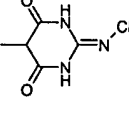
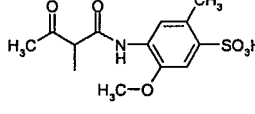
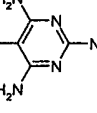
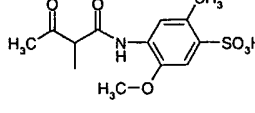
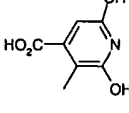
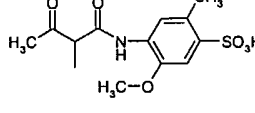
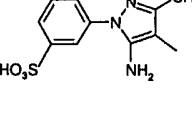
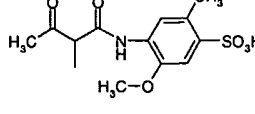
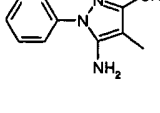
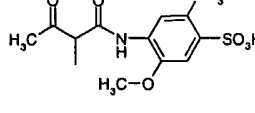
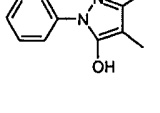
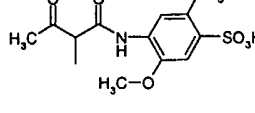
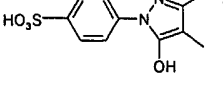
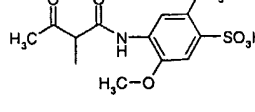
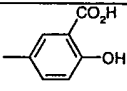
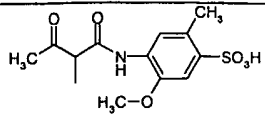
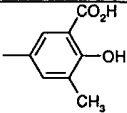
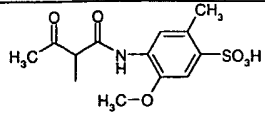
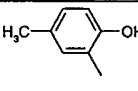
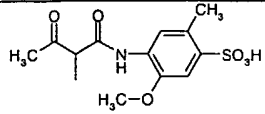
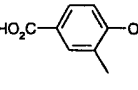
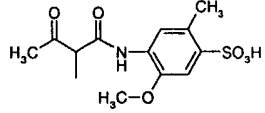
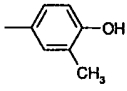
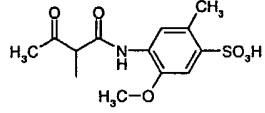
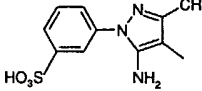
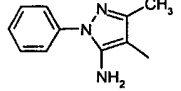
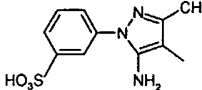
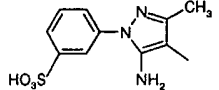
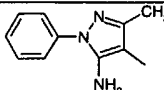
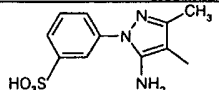


Table 5

Example Nr.	Compound Nr.	A' ₁	A' ₂
218	(308)		
219	(309)		
220	(310)		
221	(311)		
222	(312)		
223	(313)		
224	(314)		
225	(315)		
226	(316)		
227	(317)		
228	(318)		

229	(319)		
230	(320)		
231	(321)		
232	(322)		
233	(323)		
234	(324)		
235	(325)		
236	(326)		

Examples 237-255

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100e) and utilizing the appropriate coupling components, compounds of formula (23) are obtained, as summarized in the following Table 6.

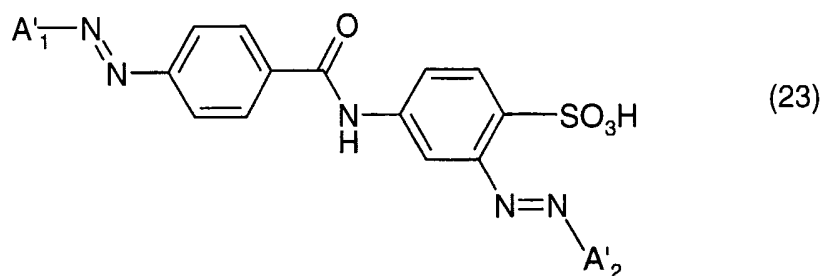
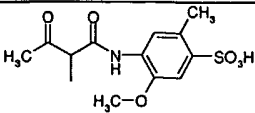
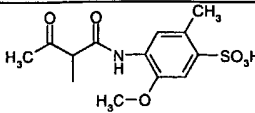
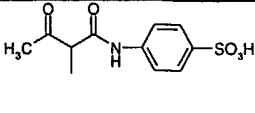
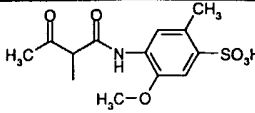
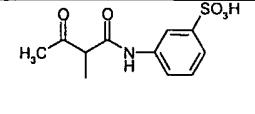
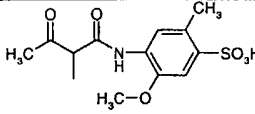
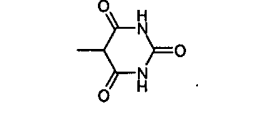
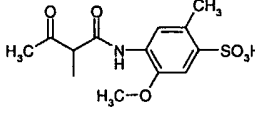
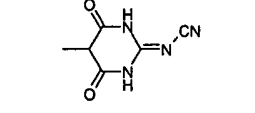
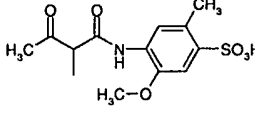
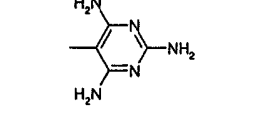
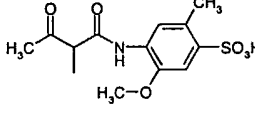
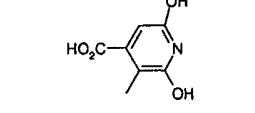
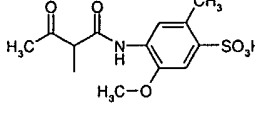
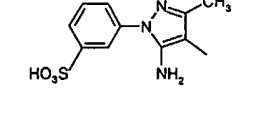
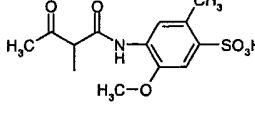
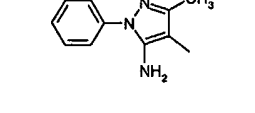
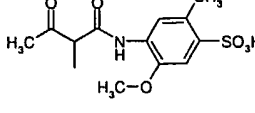
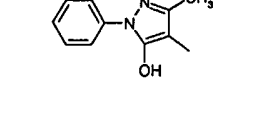
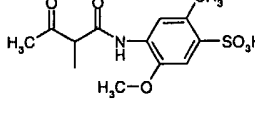
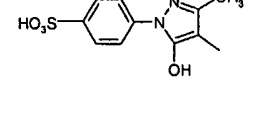
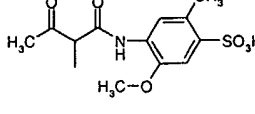
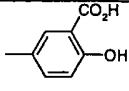
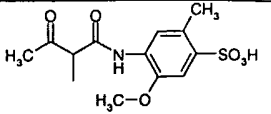
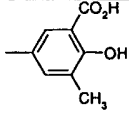
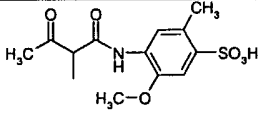
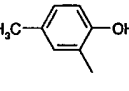
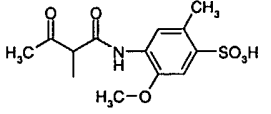
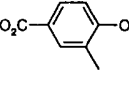
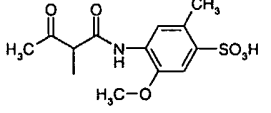
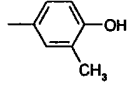
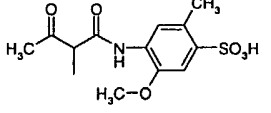
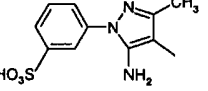
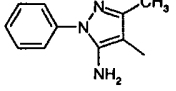
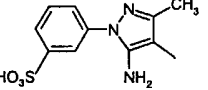
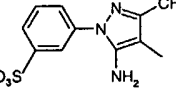
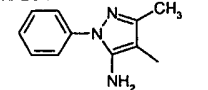
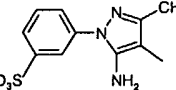


Table 6

Example Nr.	Compound Nr.	A ₁	A ₂
237	(327)		
238	(328)		
239	(329)		
240	(330)		
241	(331)		
242	(332)		
243	(333)		
244	(334)		
245	(335)		
246	(336)		
247	(337)		

248	(338)		
249	(339)		
250	(340)		
251	(341)		
252	(342)		
253	(343)		
254	(344)		
255	(345)		

Examples 256-274

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100f) and utilizing the appropriate coupling components, compounds of formula (24) are obtained, as summarized in the following Table 7.

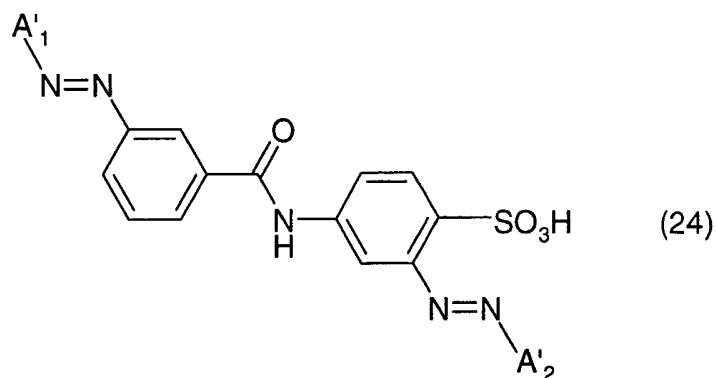
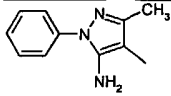
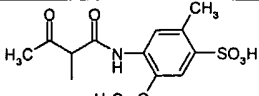
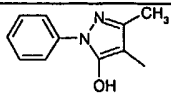
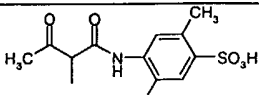
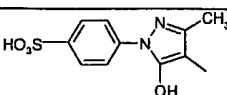
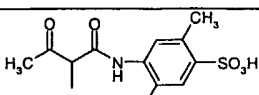
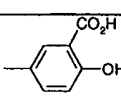
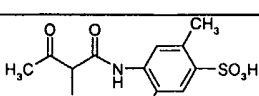
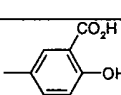
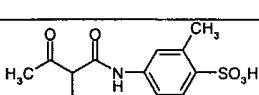
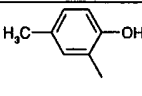
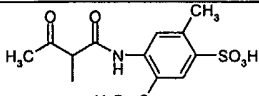
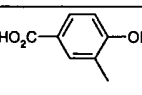
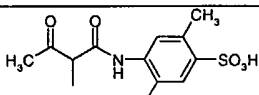
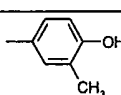
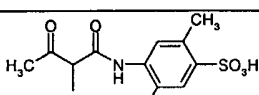
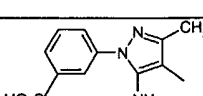
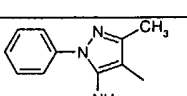
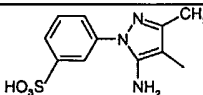
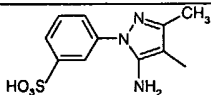
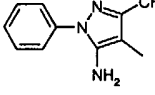
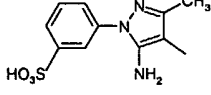


Table 7

Example Nr.	Compound Nr.	A ₁	A ₂
256	(346)		
257	(347)		
258	(348)		
259	(349)		
260	(350)		
261	(351)		
262	(352)		
263	(353)		

264	(354)		
265	(355)		
266	(356)		
267	(357)		
268	(358)		
269	(359)		
270	(360)		
271	(361)		
272	(362)		
273	(363)		
274	(364)		

Examples 275-286

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100g) and utilizing the

appropriate coupling components, compounds of formula (25) are obtained, as summarized in the following Table 8.

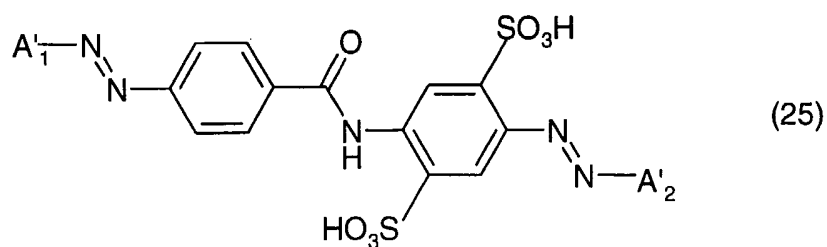
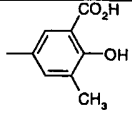
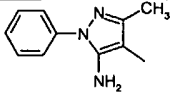
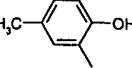
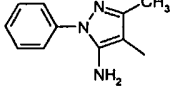
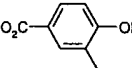
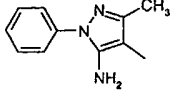
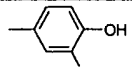
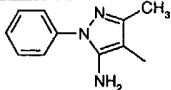


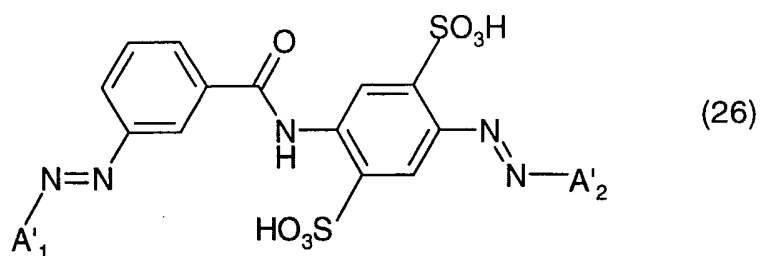
Table 8

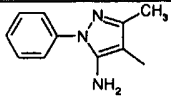
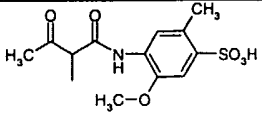
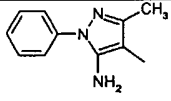
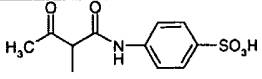
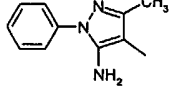
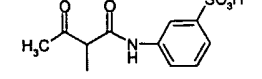
Example Nr.	Compound Nr.	A' ₁	A' ₂
275	(365)		
276	(366)		
277	(367)		
278	(368)		
279	(369)		
280	(370)		
281	(371)		
282	(372)		

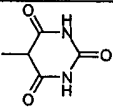
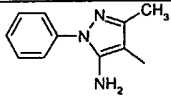
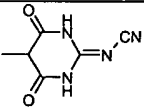
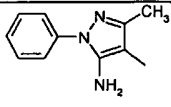
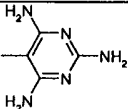
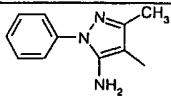
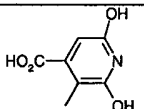
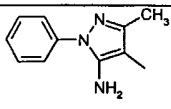
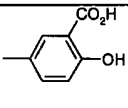
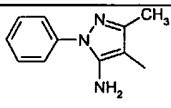
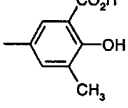
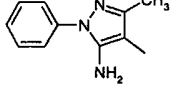
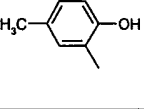
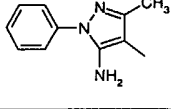
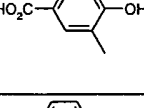
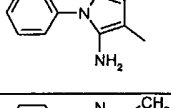
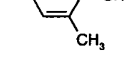
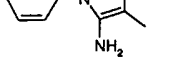
283	(373)		
284	(374)		
285	(375)		
286	(376)		

Examples 287-298

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100h) and utilizing the appropriate coupling components, compounds of formula (26) are obtained, as summarized in the following Table 9.

Table 9

Example Nr.	Compound Nr.	A' ₁	A' ₂
287	(377)		
288	(378)		
289	(379)		

290	(380)		
291	(381)		
292	(382)		
293	(383)		
294	(384)		
295	(385)		
296	(386)		
297	(387)		
298	(388)		

Examples 299-365

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100i) and utilizing the appropriate coupling components, compounds of formula (27) are obtained, as summarized in the following Table 10.

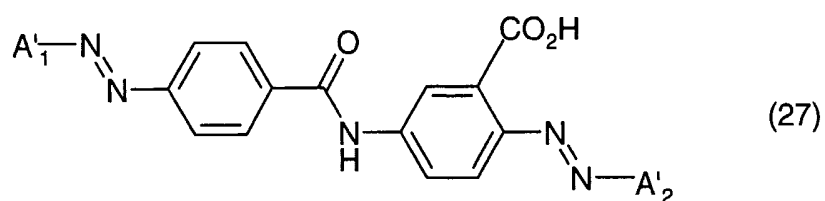
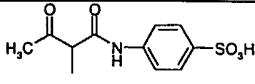
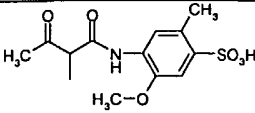
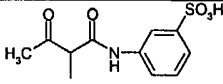
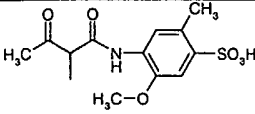
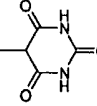
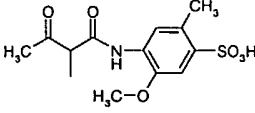
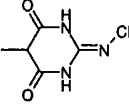
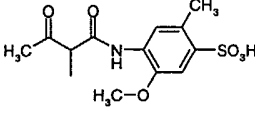
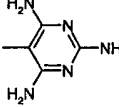
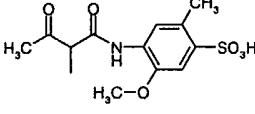
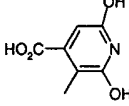
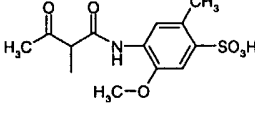
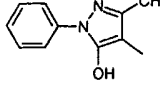
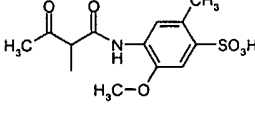
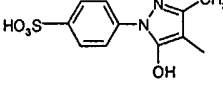
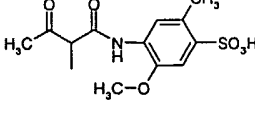
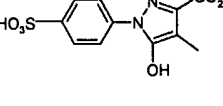
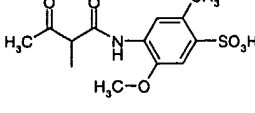
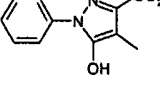
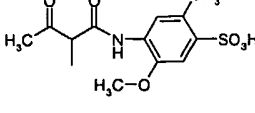
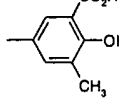
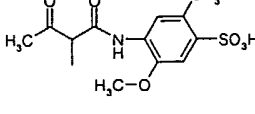
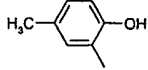
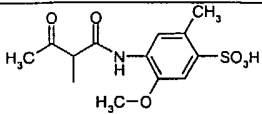
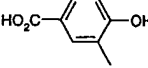
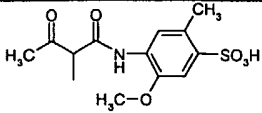
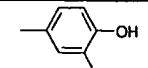
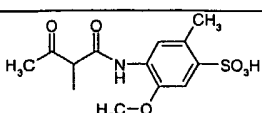
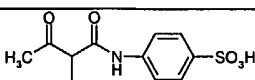
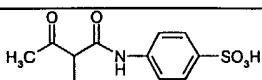
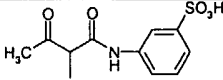
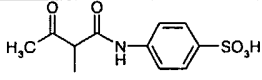
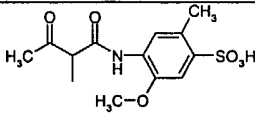
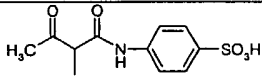
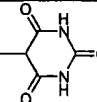
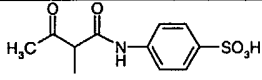
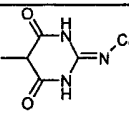
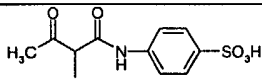
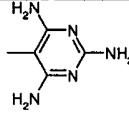
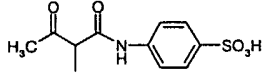
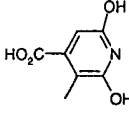
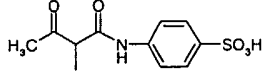
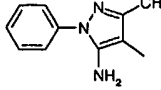
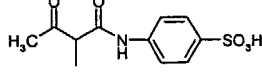
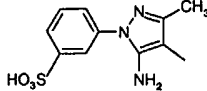
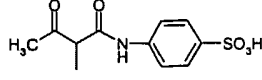
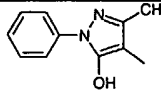
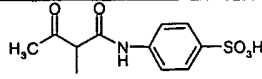
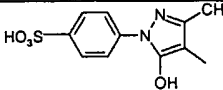
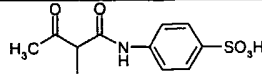
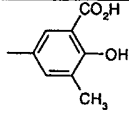
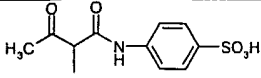
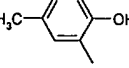
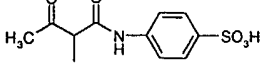
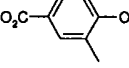
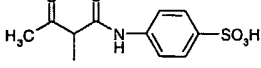
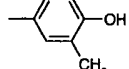
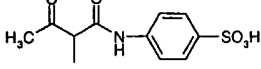
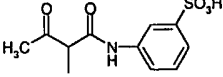
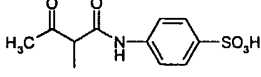
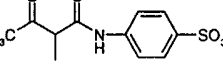
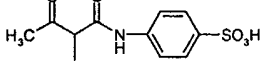
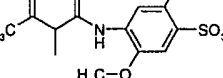
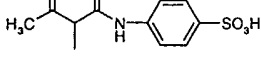

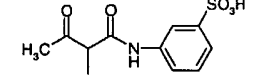
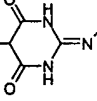
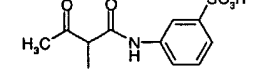
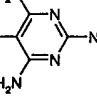
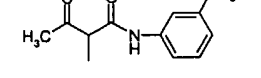

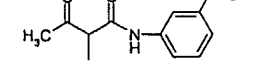
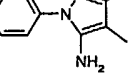
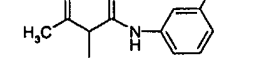
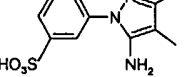
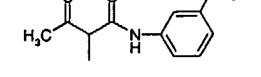
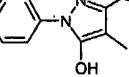
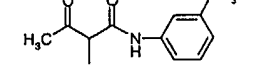


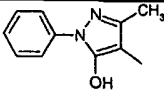
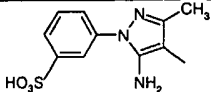
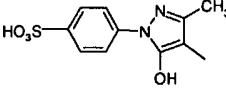
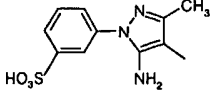
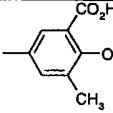
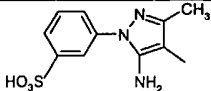
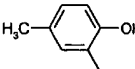
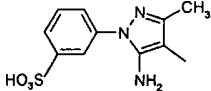
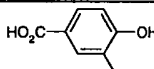
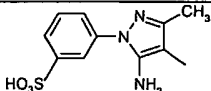
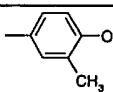
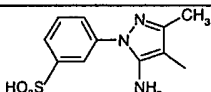
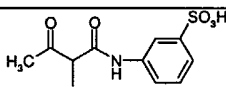
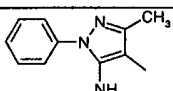
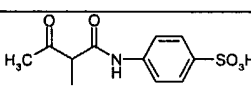
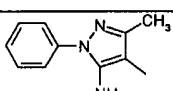
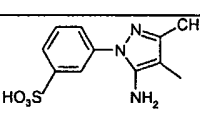
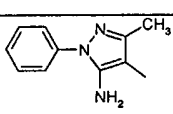
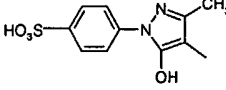
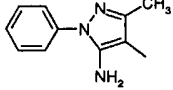
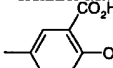
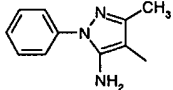
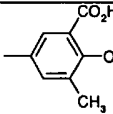
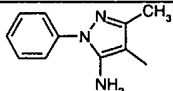
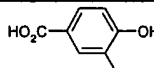
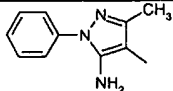
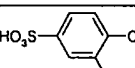
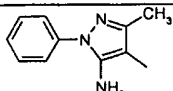
Table 10

Example Nr.	Compound Nr.	A' ₁	A' ₂
299	(389)		
300	(390)		
301	(391)		
302	(392)		
303	(393)		
304	(394)		
305	(395)		
306	(396)		
307	(397)		
308	(398)		
309	(399)		

310	(340)		
311	(401)		
312	(402)		
313	(403)		
314	(404)		
315	(405)		
316	(406)		
317	(407)		
318	(408)		
319	(409)		
320	(410)		
321	(411)		
322	(412)		
323	(413)		

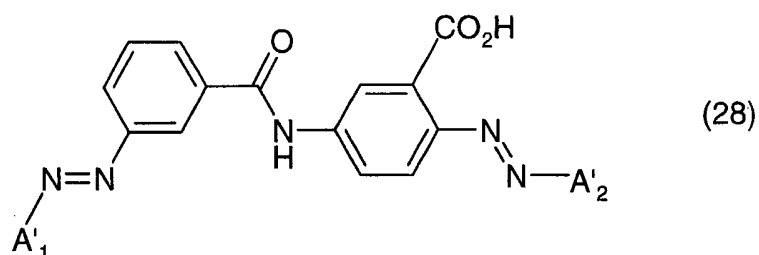
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325	(415)		
326	(416)		
327	(417)		
328	(418)		
329	(419)		
330	(420)		
331	(421)		
332	(422)		
333	(423)		
334	(424)		
335	(425)		
336	(426)		
337	(427)		

338	(428)		
339	(429)		
340	(430)		
341	(431)		
342	(432)		
343	(433)		
344	(434)		
345	(435)		
346	(436)		
347	(437)		
348	(438)		
349	(439)		
350	(440)		
351	(441)		

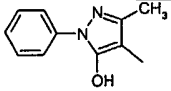
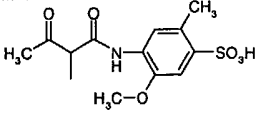
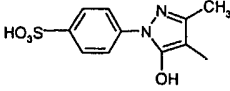
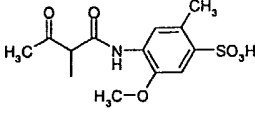
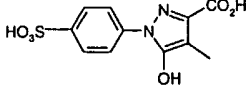
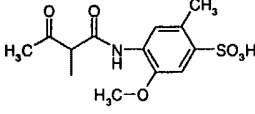
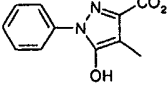
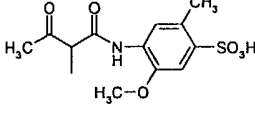
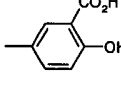
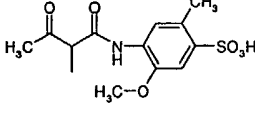
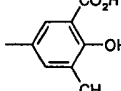
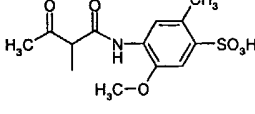
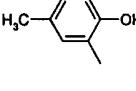
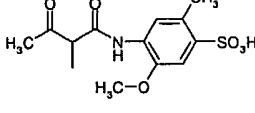
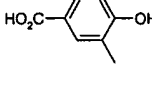
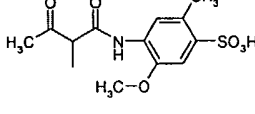
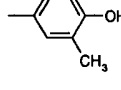
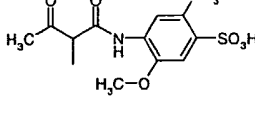
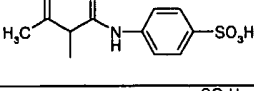
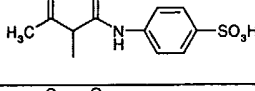
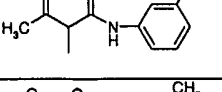
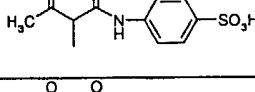
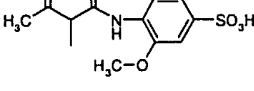
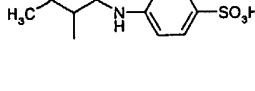
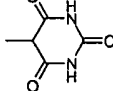
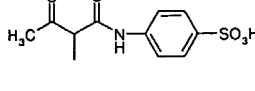
352	(442)		
353	(443)		
354	(444)		
355	(445)		
356	(446)		
357	(447)		
358	(448)		
359	(449)		
360	(450)		
361	(451)		
362	(452)		
363	(453)		
364	(454)		
365	(455)		

Examples 366-436

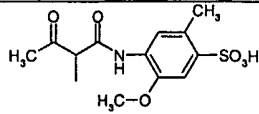
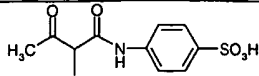
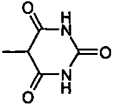
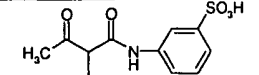
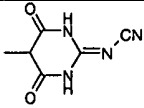
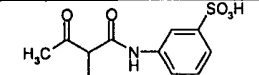
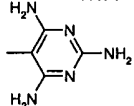
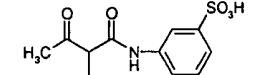
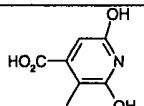
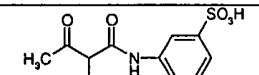
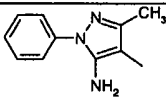
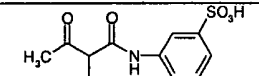
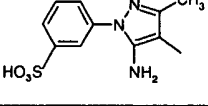
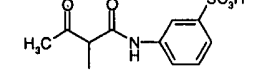
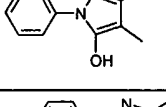
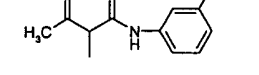
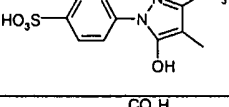
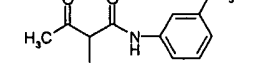
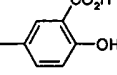
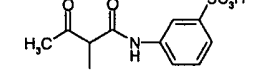
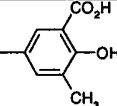
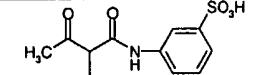
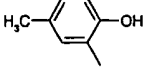
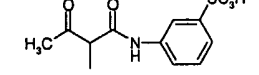
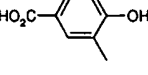
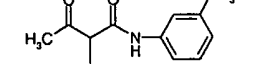
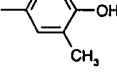
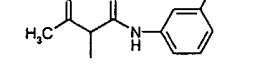
By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100J) and utilizing the appropriate coupling components, compounds of formula (28) are obtained, as summarized in the following Table 11.

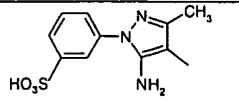
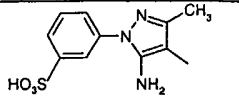
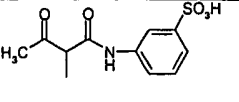
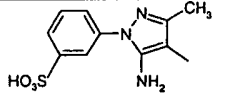
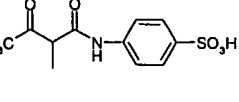
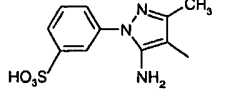
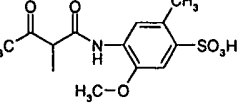
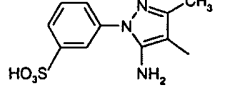
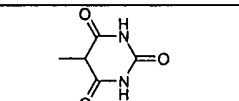
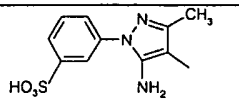
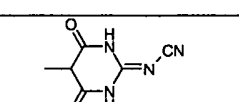
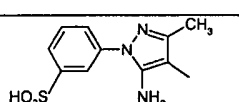
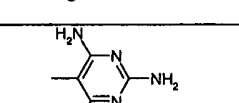
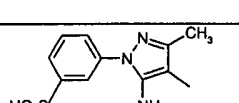
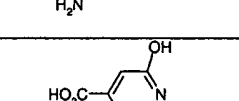
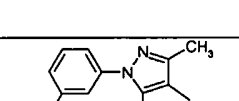
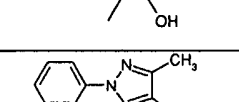
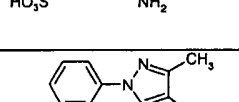
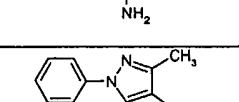
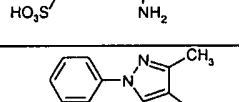
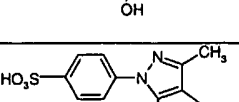
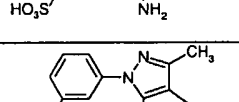
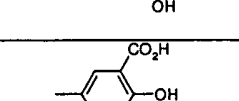
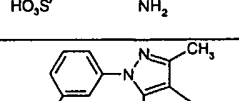
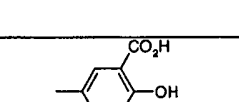
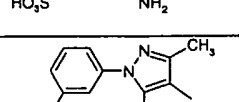
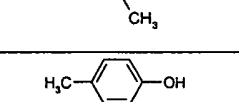
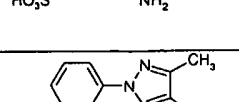
Table 11

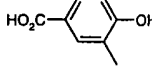
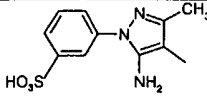
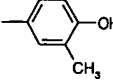
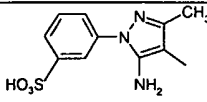
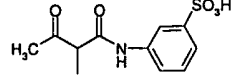
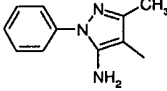
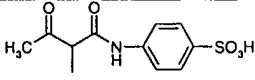
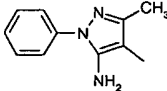
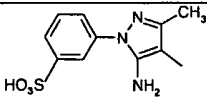
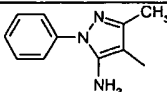
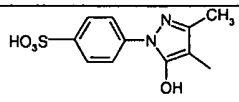
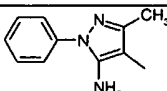
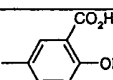
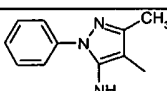
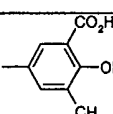
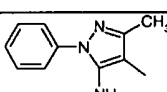
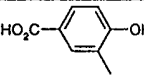
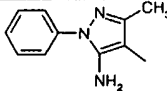
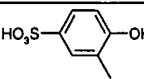
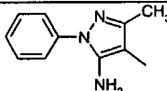
Example Nr.	Compound Nr.	A ₁	A ₂
366	(456)		
367	(457)		
368	(458)		
369	(459)		
370	(460)		
371	(461)		

372	(462)		
373	(463)		
374	(464)		
375	(465)		
376	(466)		
377	(467)		
378	(468)		
379	(469)		
380	(470)		
381	(471)		
382	(472)		
383	(473)		
384	(474)		

385	(475)		
386	(476)		
387	(477)		
388	(478)		
389	(479)		
390	(480)		
391	(481)		
392	(482)		
393	(483)		
394	(484)		
395	(485)		
396	(486)		
397	(487)		
398	(488)		

399	(489)		
400	(490)		
401	(491)		
402	(492)		
403	(493)		
404	(494)		
405	(495)		
406	(496)		
407	(497)		
408	(498)		
409	(499)		
410	(500)		
411	(501)		
412	(502)		

413	(503)		
414	(504)		
415	(505)		
416	(506)		
417	(507)		
418	(508)		
419	(509)		
420	(510)		
421	(511)		
422	(512)		
423	(513)		
424	(514)		
425	(515)		
426	(516)		

427	(517)		
428	(518)		
429	(519)		
430	(520)		
431	(521)		
432	(522)		
433	(523)		
434	(524)		
435	(525)		
436	(526)		

Application Examples

Example 437 - Unsized without filler

A mixture consisting of 50% long fibre spruce sulphite bleached and 50% short fibre beech sulphite bleached fibres is suspended in deionised water, as a 2% suspension, and refined and beaten to 22°SR (Schopper Riegler). After dewatering by means of a centrifuge and testing for dry weight, the equivalent to 10g of dry fibre are placed in a beaker and made up to a volume of 500ml with tap water. After stirring for 1 hour, 0.42%, based on the weight of dry fibre, of compound (101) as a 5g/l aqueous solution are added to the furnish suspension

and stirring continued for a further 15 minutes. The suspension is made up to 700ml with water and from 300ml of the resulting suspension a hand sheet is produced using a Lhomargy sheet former. After drying on a cylinder at 90°C for 12 minutes, a greenish-yellow dyeing is obtained showing excellent bleed-fastness to water, soda and acetic acid and good light-fastness. The backwater from the dyeing is almost colourless and the degree of exhaustion amounts to 92-94%.

Examples 438-

The procedure described in Example 437 is repeated using, instead of compound (101), sufficient amounts of the appropriate dye to produce a dyeing of standard depth 0.2. The degrees of exhaustion of the respective dyes are calculated and the results summarized in Table 12 below.

Table 12

Example Nr.	Compound Nr.	Degree of Exhaustion in %
438	(102)	98
439	(103)	98
440	(104)	92-94
441	(105)	98-99
442	(106)	93-94
443	(107)	93
444	(108)	92
445	(110)	98
446	(135)	97-98
447	(151)	95
448	(157)	98-99
449	(189)	95
450	(190)	97.5
451	(200)	96.5
452	(205)	97
453	(214)	95-97

453	(216)	97-98
454	(267)	93
455	(288)	98

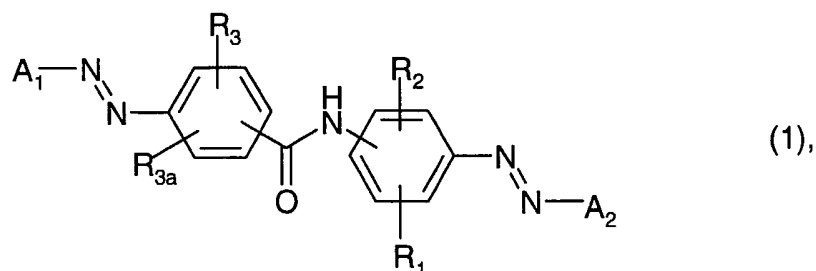
The above results clearly demonstrate the excellent degrees of exhaustion of the dyes tested, the backwater, in all cases, being almost colourless.

Example 456 – Neutral sized with filler

A mixture consisting of 50% long fibre spruce sulphite bleached and 50% short fibre beech sulphite bleached fibres is suspended in deionised water, as a 2% suspension, and refined and beaten to 35°SR (Schopper Riegler). After dewatering by means of a centrifuge and testing for dry weight, the equivalent to 10g of dry fibre and 2g of dry chalk filler are placed in a beaker and made up to a volume of 500ml with tap water. After stirring for 1 hour, 0.78%, based on the weight of dry fibre, of compound (101) as a 5g/l aqueous solution are added to the furnish suspension and stirring continued for a further 15 minutes. 2% of alkyl ketene dimer size is then added, the suspension stirred for 30 minutes, 0.05% retention aid added and the suspension stirred vigorously for a further 5 minutes. The suspension is made up to 700ml with water and from 300ml of the resulting suspension a hand sheet is produced using a Lhomargy sheet former. After drying on a cylinder at 90°C for 12 minutes, a greenish-yellow dyeing is obtained showing excellent fastness values. The backwater from the dyeing is only weakly coloured.

Claims

1. A compound of the formula



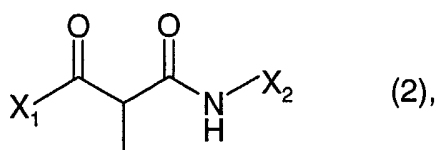
in which

R₁ represents hydrogen, substituted or unsubstituted C₁-C₈alkyl, substituted or unsubstituted C₁-C₈alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ and R_{3a} each, independently of the other, represent hydrogen, a C₁-C₄alkyl group, which may be substituted or unsubstituted, halogen, hydroxy, substituted or unsubstituted C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl and each of the residues

A₁ and A₂, independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

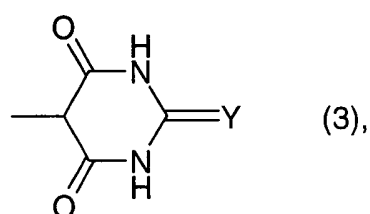
X₁ represents C₁-C₄alkyl, or phenyl which is unsubstituted or monosubstituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and

X₂ represents phenyl which is unsubstituted, mono-, di- or trisubstituted by one or two SO₃H, SO₂NHC₁-C₄alkyl groups which alkyl groups may be substituted, SO₂C₁-C₄alkyl, C₁-C₄substituted or unsubstituted alkyl, hydroxy, C₁-C₄alkoxy, halogen, CF₃, NH₂, NHCOC₁-C₄alkyl, NHCOOC₁-C₄alkyl, NHCONHC₁-C₄alkyl, CO₂H, CONHC₁-C₄alkyl or NO₂;

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a 1- or 2-naphthyl residue which is unsubstituted or substituted by one or two SO₃H, SO₂NHC₁-C₄alkyl, carboxy, CONHC₁-C₄alkyl, carboxyC₁-C₄alkyl or carboxyaryl groups or a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated and be further substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and which may be attached to the NH-atom in formula (2) either via the hetero- or benzo-nucleus, in the case of benzannelated heterocycles;

a derivative of barbituric acid of the formula

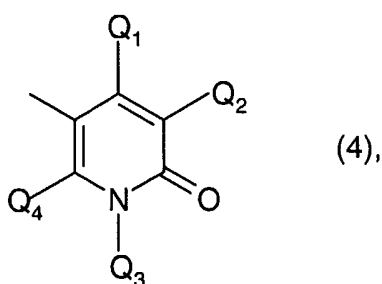


in which

Y represents O, NCN or NCONH₂;

a 2,4,6-triaminopyrimidine derivative;

a pyridone derivative of the formula



in which

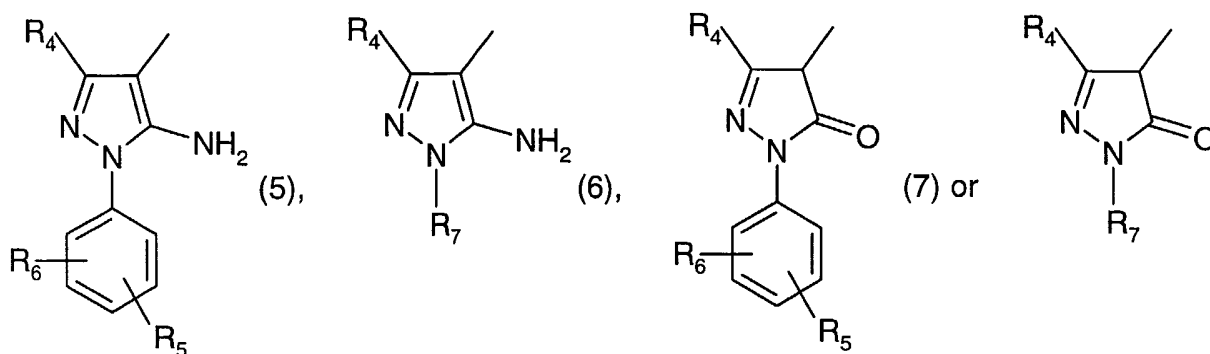
Q₁ represents hydrogen, hydroxy, C₁-C₂alkyl, hydroxyethyl, 2-(C₁-C₂alkoxy)alkyl, C₁-C₂alkoxy, COOH, CONH₂ or COOC₁-C₂alkyl,

Q₂ represents hydrogen, CN, CONH₂, halogen, SO₃H or C₁-C₂alkyl which is unsubstituted or substituted by hydroxy, phenyl or SO₃H,

Q₃ represents hydrogen, phenyl, C₁-C₂alkylphenyl, cyclohexyl or C₁-C₄alkyl which is unsubstituted or substituted by hydroxy, CN, C₁-C₂alkoxy or SO₃H and

Q₄ represents hydrogen or hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



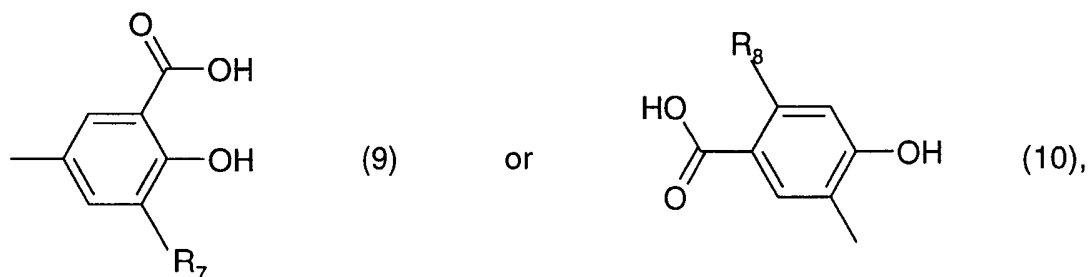
in which

R_4 represents hydrogen, substituted or unsubstituted C_1 - C_4 alkyl, C_2 - C_4 alkenyl, $NHCO$ C_1 - C_4 alkyl or CO_2H , each

R_5 and R_6 , independently of the other, represent hydrogen, halogen, C_1 - C_4 alkyl, SO_3H or CO_2H and

R_7 represents hydrogen or C_1 - C_4 alkyl;

a benzoic acid derivative of formula

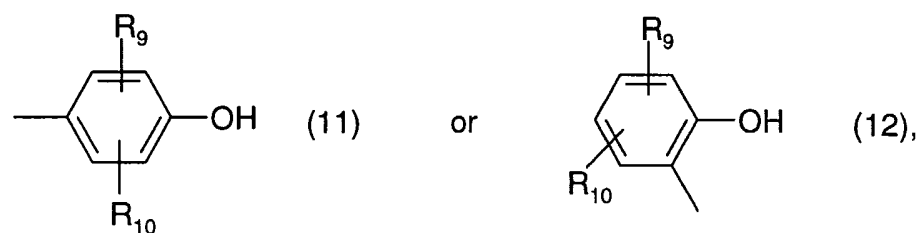


in which

R_7 represents hydrogen or C_1 - C_4 alkyl and

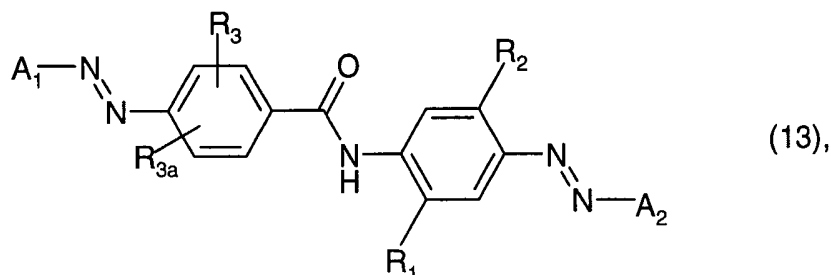
R_8 represents hydrogen or hydroxy or

A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula



in which

R_9 and R_{10} , each one independently of the other, represent hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen, NH_2 , $NHCO$ C_1 - C_4 alkyl, NO_2 , SO_3H , CO_2C_1 - C_4 alkyl or $CONHC_1$ - C_4 alkyl groups,
with the proviso that in compounds of formula



if

R_1 , R_2 , R_3 and R_{3a} each, independently of the others, are hydrogen or SO_3H , then
 A_1 and A_2 are not both a 1-phenyl or 1-sulphophenyl-3-methyl-5-aminopyrazole residue,
or, if

R_1 , R_2 , R_3 and R_{3a} represent hydrogen and

A_1 is a residue of formula (9) in which

R_7 represents hydrogen or methyl, then

A_2 does not represent a 1-phenyl or 1-sulphophenyl-3-methyl- or 3-carboxy pyrazol-5-one residue

or, if

R_1 , R_3 and R_{3a} are hydrogen and R_2 is SO_3H and one of

A_1 and A_2 represents a 1-sulphophenyl-3-methyl pyrazol-5-one residue, then the other is not a residue of formula (11) in which both

R_9 and R_{10} are hydrogen, or if

A_1 represents a 1-nitrophenyl-, a 1-phenyl- or an unsubstituted 3-methyl pyrazol-5-one residue,

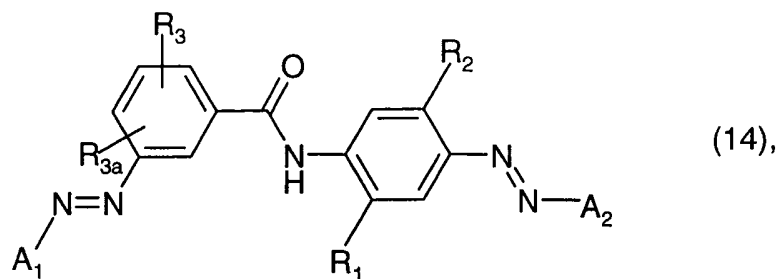
A_2 is not a residue of formula (9) in which R_7 represents hydrogen, or if

R_1 , R_3 and R_{3a} represent hydrogen, R_2 is CO_2H and

A_1 represents a residue of formula (9), in which R_7 is hydrogen,

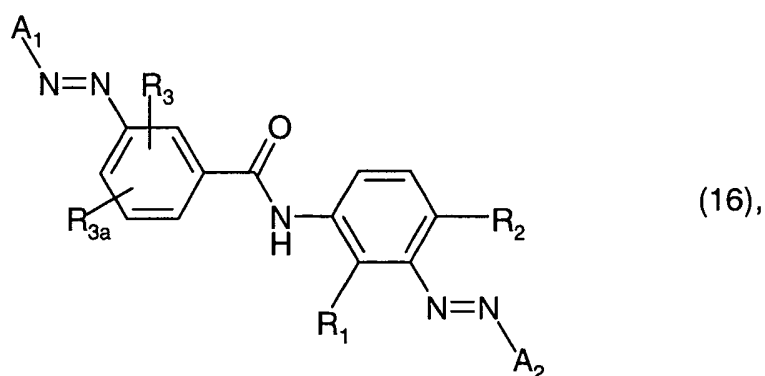
A_2 is not a residue of formula (2) or formula (7);

in compounds of the formula



if

R_2 represents CO_2H , R_3 represents hydroxy or methoxy and R_{3a} represents hydrogen, A_1 and A_2 do not represent residues of formulae (2) or (7) and, in compounds of the formula

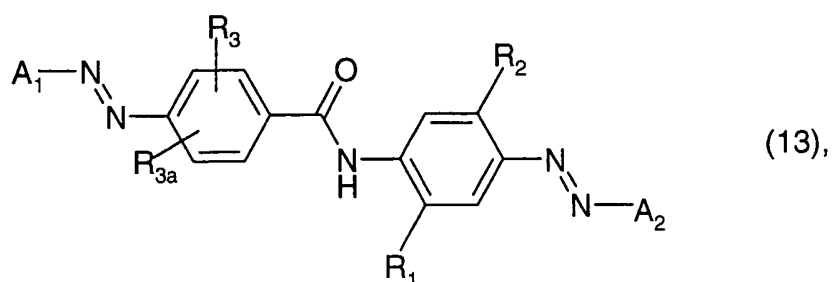


if

R_2 represents SO_3H and R_3 and R_{3a} both represent hydrogen A_1 and A_2 are not both 2,4-dihydroxyphenyl.

2. A compound of formula (1), according to claim 1, which contains a total number of two, three or four SO_3H and/or CO_2H groups.

3. A compound of the formula



according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

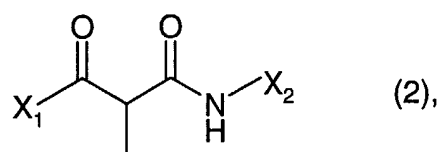
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

4. A compound of formula (13), according to claim 3, in which

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X₁ represents C₁-C₄alkyl, and

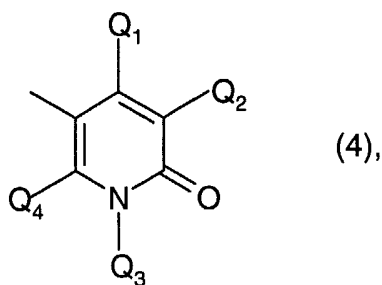
X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

a pyridone derivative of the formula



in which

Q₁ represents C₁-C₂alkyl,

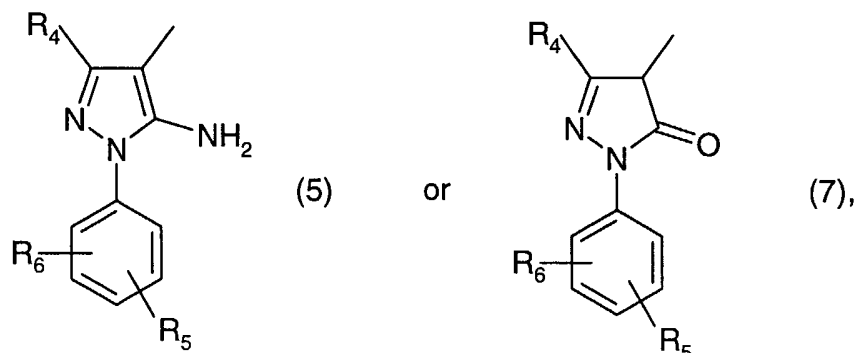
- 75 -

Q₂ represents CN, CONH₂ or CH₂SO₃H,

Q₃ represents C₁-C₂alkyl and

Q₄ represents hydroxy;

an aminopyrazole or a pyrazolone derivative of formula



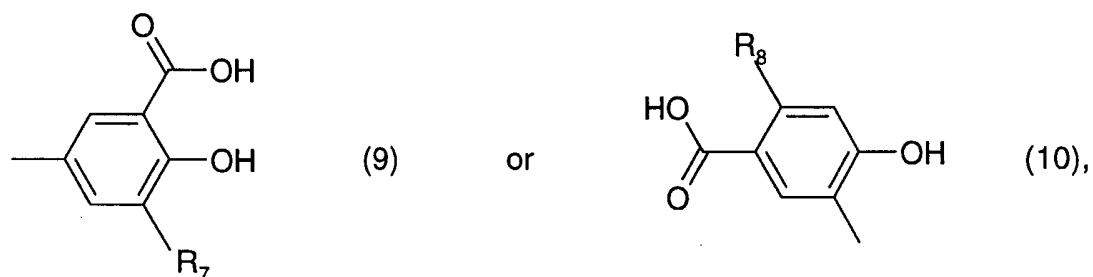
in which

R₄ represents C₁-C₄alkyl or CO₂H,

R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H and

R₆ represents hydrogen;

a benzoic acid derivative of formula

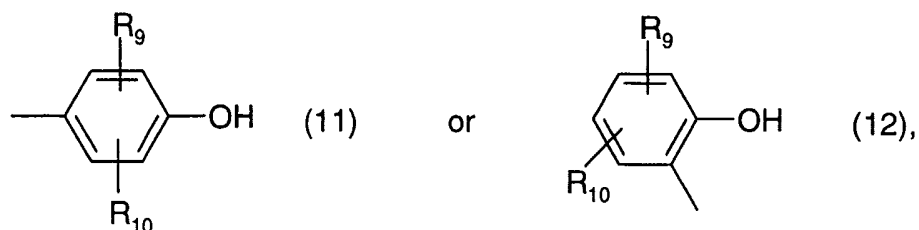


in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula

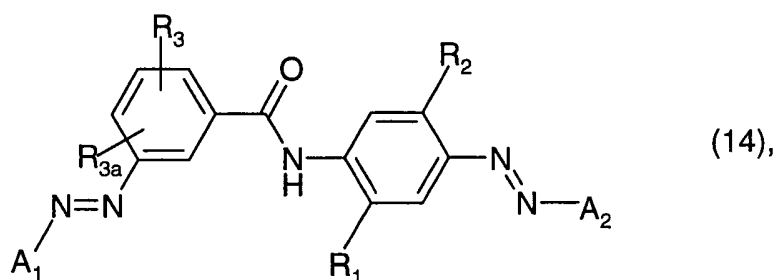


in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and

R₁₀ represents hydrogen.

5. A compound of formula



according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

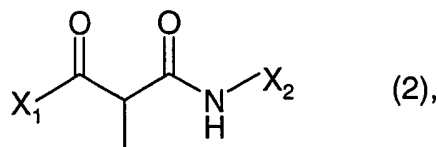
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

6. A compound of formula (14), according to claim 5, in which

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

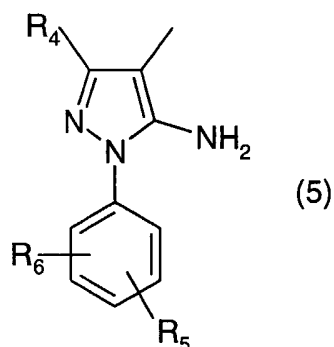
X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H; barbituric acid or cyanoiminobarbituric acid;

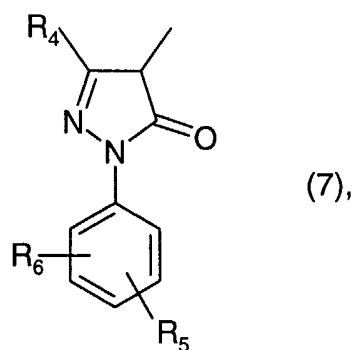
2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula



or



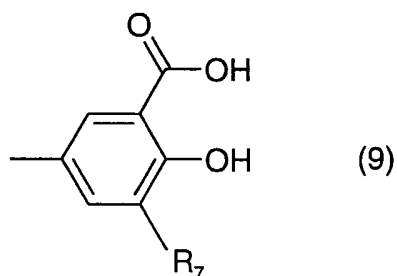
in which

R₄ represents C₁-C₄alkyl or CO₂H,

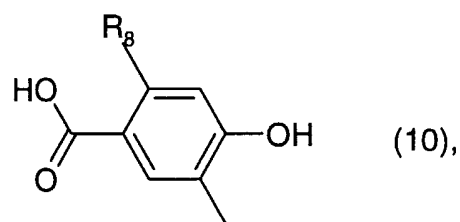
R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H and

R₆ represents hydrogen;

a benzoic acid derivative of formula



or

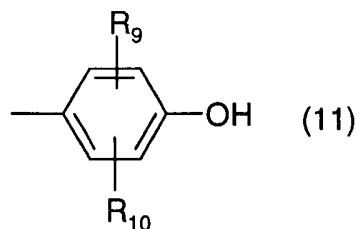


in which

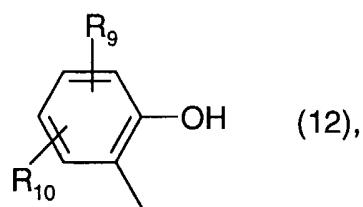
R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula



or

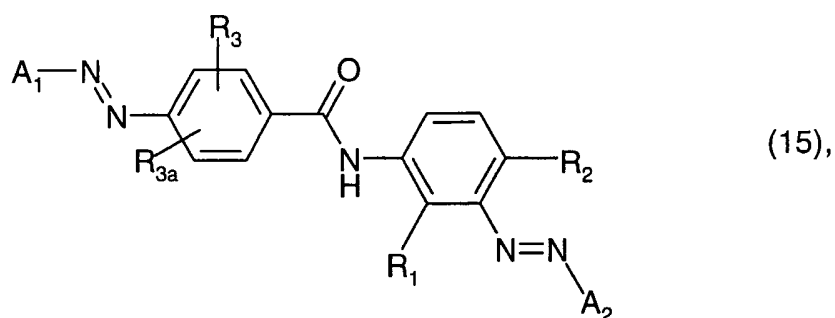


in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and

R₁₀ represents hydrogen.

7. A compound of formula



according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

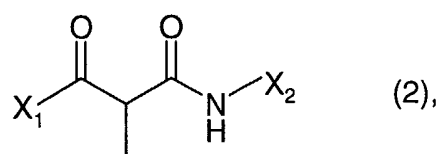
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

8. A compound of formula (15), according to claim 7, in which

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

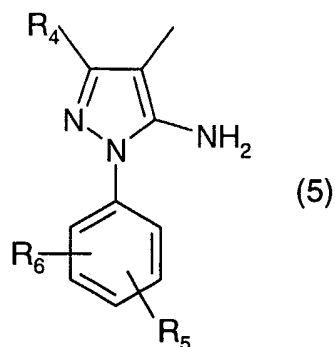
barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

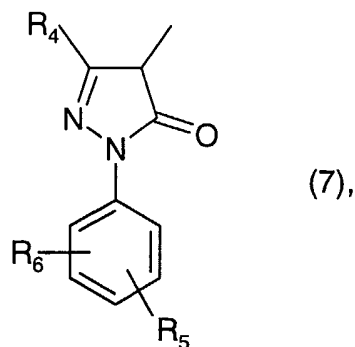
citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

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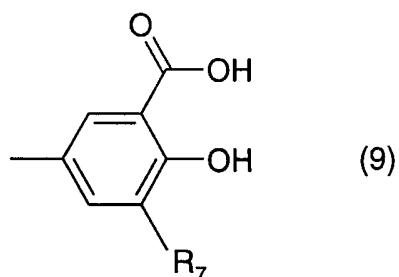
or



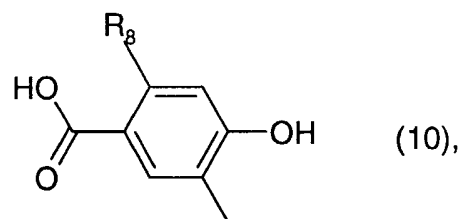
in which

R₄ represents C₁-C₄alkyl or CO₂H,R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H andR₆ represents hydrogen;

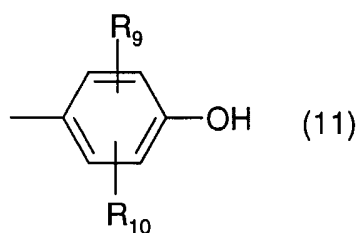
a benzoic acid derivative of formula



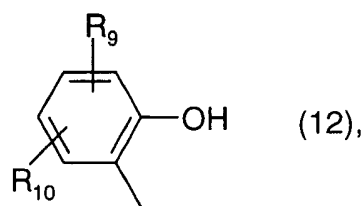
or



in which

R₇ represents hydrogen or C₁-C₄alkyl andR₈ represents hydrogen or hydroxy orA₁ and A₂, each one independently of the other, represent a phenol residue of the formula

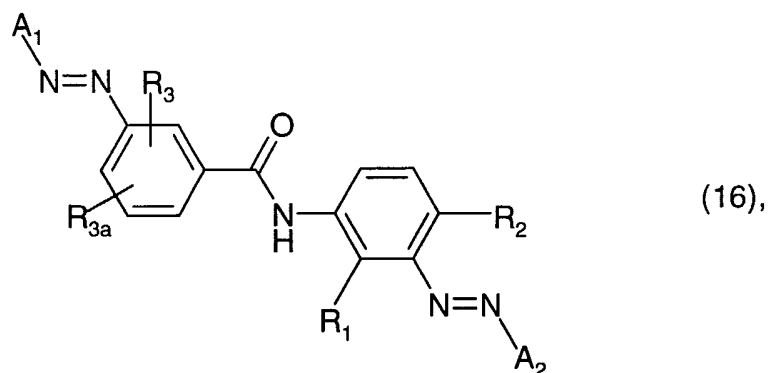
or



in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H andR₁₀ represents hydrogen.

9. A compound of formula



according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

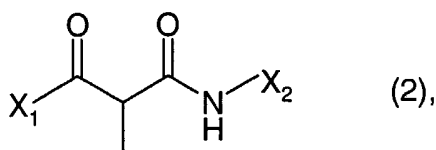
R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

10. A compound of formula (16), according to claim 9, in which

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula



in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

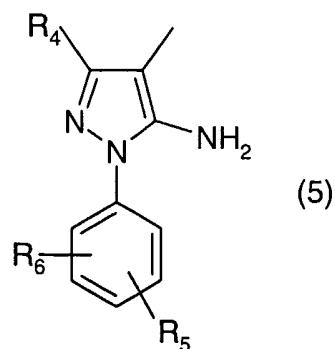
barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

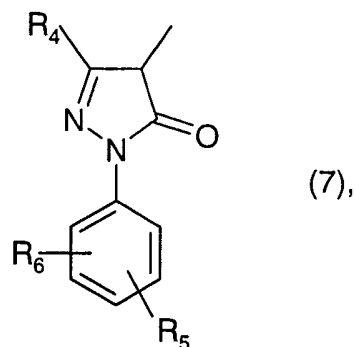
citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

- 81 -



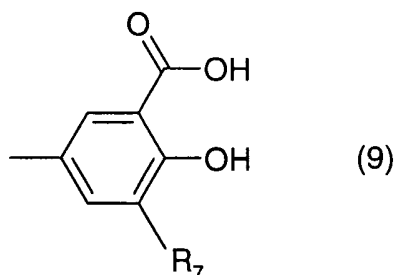
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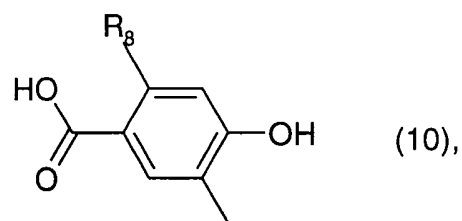
in which

R₄ represents C₁-C₄alkyl or CO₂H,R₅ represents hydrogen, halogen, C₁-C₄alkyl, SO₃H or CO₂H andR₆ represents hydrogen;

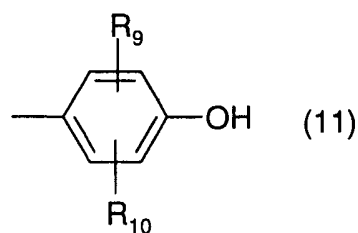
a benzoic acid derivative of formula



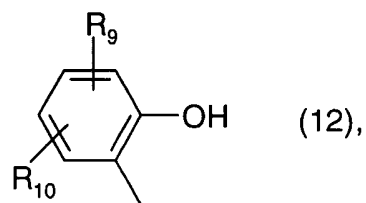
or



in which

R₇ represents hydrogen or C₁-C₄alkyl andR₈ represents hydrogen or hydroxy orA₁ and A₂, each one independently of the other, represent a phenol residue of the formula

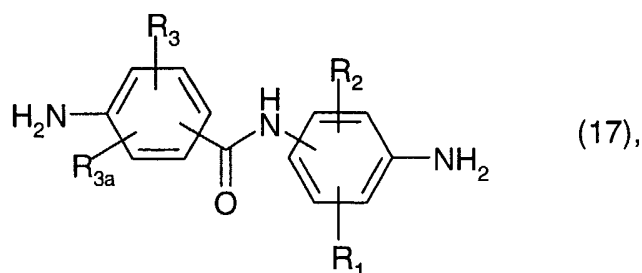
or



in which

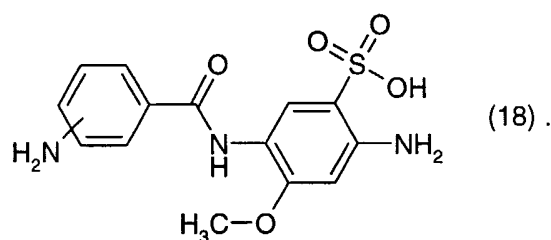
R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H andR₁₀ represents hydrogen.

11. A process for the preparation of a compound of formula (1), according to claim 1, by tetrazotisation of a diaminobenzanilide derivative of the formula



in which R_1 , R_2 , R_3 and R_{3a} are as defined in claim 1, and sequential coupling with a coupling component of the formula A_1H or A_2H , followed by coupling with a coupling component of the formula A_2H or A_1H , A_2 and A_1 being as defined in claim 1.

12. A compound of the formula



13. A process for the preparation of compound (18), according to claim 12, by reaction of 2-methoxy-4-nitroaniline-5-sulphonic acid with the appropriate nitrobenzoyl halide, followed by reduction of the resulting dinitrobenzanilide.

14. Use of the compound of formula (18), according to claim 12, for the preparation of the appropriate compound of formula (1), according to claim 1.

15. Use of the compound of formula (1), according to claim 1, for dyeing natural or synthetic materials.

16. A solid dye preparation for dyeing paper, comprising a compound of the formula (1) according to claim 1, and, optionally, further auxiliaries.

17. Aqueous solutions for dyeing paper, comprising a compound of the formula (1), according to claim 1, and, optionally, further auxiliaries.

18. Aqueous solutions according to claim 17 containing, as further auxiliaries, solubilizers and/or organic solvents.

19. Paper which is dyed with a compound of the formula (1), according to claim 1, in the form of a solid dye preparation, according to claim 16, or an aqueous solution, according to claim 17.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/05561

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B35/28 C09B35/03 C09B35/033 C09B35/023 C07C309/29
//D21H21/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 28569 A A.D. 1913 (H. LEVINSTEIN ET AL.) 11 February 1915 (1915-02-11) page 3, line 6 - line 8; claims; example III ---	1-19
Y	US 2 544 087 A (PETER HINDERMANN) 6 March 1951 (1951-03-06) Table, compounds 1,2,41 claim 6; example 2 ---	1-19
Y	US 2 228 321 A (ERNST MESSMER) 14 January 1941 (1941-01-14) Table, first two compounds claims 1,2,4; example 2 ---	1-19
	-/--	

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document but published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
O document referring to an oral disclosure, use, exhibition or other means	*&* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 12 September 2003	Date of mailing of the international search report 19/09/2003
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Ginoux, C
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INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/EP 03/05561

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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