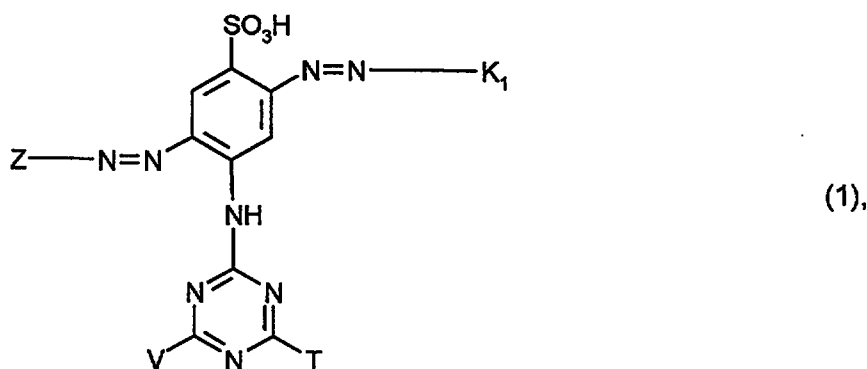


Azo dye mixtures and their use

The present invention relates to mixtures of azo dyes which are particularly suitable for dyeing or printing naturally occurring or synthetic polyamide fibre materials and give dyeings or prints with good all-round properties by these processes.

The present invention thus relates to dye mixtures comprising

(a) a compound of the formula



in which K_1 is a naphthyl radical which is unsubstituted or further substituted by hydroxyl, amino, $N-C_1-C_4$ alkylamino, C_2-C_4 alkanoylamino, benzoylamino, sulfo or a radical of the formula $-SO_2-Y$,

Z is the radical of a diazo component of the benzene or naphthalene series which contains at least one fibre-reactive radical of the formula

- $SO_2 - Y$ (3a),
- $CONH - (CH_2)_m - SO_2 - Y$ (3b),
- $CONH - (CH_2)_{m1} - O - (CH_2)_m - SO_2 - Y$ (3c),
- $(O)_p - (CH_2)_q - CONH - (CH_2)_m - SO_2 - Y$ (3d),
- $NH - CO - CHX - CH_2X$ (3e) or
- $NH - CO - CX = CH_2$ (3f),

Y is vinyl or a radical $-CH_2-CH_2-U$ and U is a leaving group,

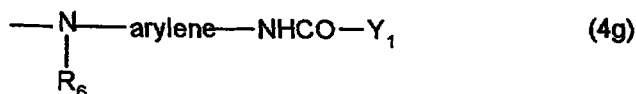
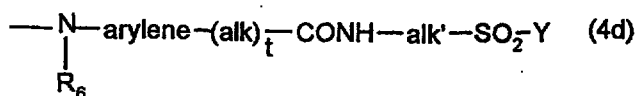
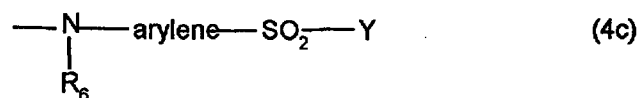
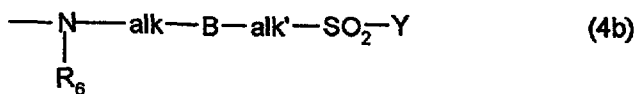
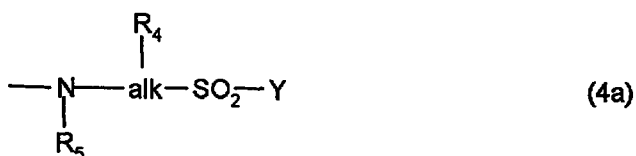
X is chlorine or bromine,

p is the number 0 or 1 and

m, m1 and q independently of one another are each an integer from 1 to 6,

T is chlorine, fluorine, bromine, 3-carboxypyridin-1-yl or 3-carbamoylpyridin-1-yl,

V is defined independently as T or is a non-reactive radical from the group consisting of hydroxyl, C₁-C₄alkoxy, phenoxy, C₁-C₄alkylthio, morpholino and substituted or unsubstituted amino, or is a reactive radical of the formula



R₄ is hydrogen, hydroxyl, sulfo, sulfato, carboxyl, cyano, halogen, C₁-C₄alkoxycarbonyl, carbamoyl or a group -SO₂-Y,

in which Y is as defined above,

R₅ is hydrogen, C₁-C₄alkyl which is unsubstituted or substituted by hydroxyl, sulfo, sulfato,

carboxy or cyano, or a radical $\begin{array}{c} R_4 \\ | \\ \text{---alk---SO}_2\text{---Y} \end{array}$,

in which R₄ and Y are each as defined above,

R₆ is hydrogen or C₁-C₄alkyl,

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

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

Y₁ is a group -CHX-CH₂X or -CX=CH₂,

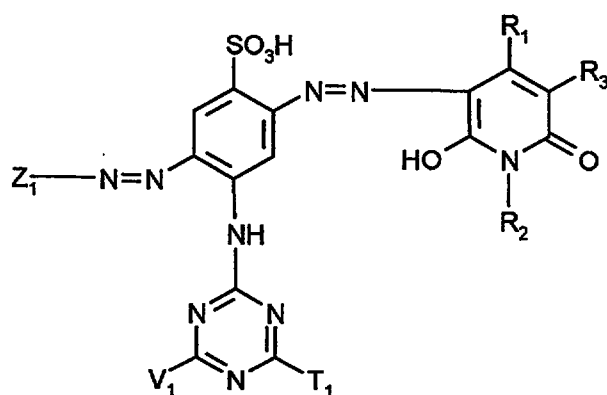
in which X is as defined above,

B is a radical -O- or -NR₆-,

in which R₆ is as defined above, and

t is the number 0 or 1, and

(b) a compound of the formula



(2),

in which R₁ and R₂ independently of one another are each C₁-C₄alkyl,

R₃ is carbamoyl, sulfomethyl or cyano, and

T₁ is defined independently as above for T,

V₁ is defined independently as above for V, and

Z₁ is defined independently as above for Z.

C₁-C₄alkyl is to be understood here as meaning generally methyl, ethyl, n- or iso-propyl or n-, iso-, sec.- or tert-butyl. C₁-C₄alkoxy is generally methoxy, ethoxy, n- or iso-propoxy and n-, iso-, sec.- or tert-butoxy. Halogen is generally, for example, fluorine, bromine or, in particular, chlorine. Examples of C₂-C₄alkanoylamino are acetylamino or propionylamino.

C₁-C₄alkoxycarbonyl is generally methoxycarbonyl, ethoxycarbonyl, n- or isopropoxycarbonyl and n-, iso-, sec.- or tert-butoxycarbonyl. Examples of C₁-C₄alkylthio are methylthio or ethylthio. Examples of N-C₁-C₄alkylamino are N-methylamino, N-ethylamino, N-(n-propyl)- or N-(iso-propyl)-amino or N-(n-butyl)-, N-(iso-butyl)-, N-(sec-butyl)- or N-(tert-butyl)-amino.

K₁ in formula (1) is preferably a 1- or 2-naphthyl radical, which is further substituted by 1 to 4 identical or different radicals from the group consisting of hydroxyl, amino, N-methyl- or N-ethylamino, acetylamino, benzoylamino and sulfo. K₁ is particularly preferably a 1-naphthyl radical which carries 1 to 4 identical or different radicals from the group consisting of hydroxyl, amino and sulfo. K₁ is particularly preferably the 2-amino-6-sulfo-8-hydroxy-1-naphthyl- or 2-amino-8-hydroxy-3,6-disulfo-1-naphthyl radical.

Z in formula (1) is a phenyl or naphthyl radical which, in addition to fibre-reactive radicals of the formulae (3a) to (3f), can have the substituents customary in organic dyes. Such substituents are, for example, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, sulfo, hydroxyl or carboxyl.

In a -CH₂-CH₂-U radical Y, the leaving group U can be, for example, -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, OPO₃H₂, -OCO-C₆H₅, OSO₂-C₁-C₄alkyl or -OSO₂-N(C₁-C₄alkyl)₂. U is preferably a group of the formula -Cl, -OSO₃H, -SSO₃H, -OCO-CH₃, -OCO-C₆H₅ or -OPO₃H₂, in particular -Cl or -OSO₃H, and particularly preferably -OSO₃H.

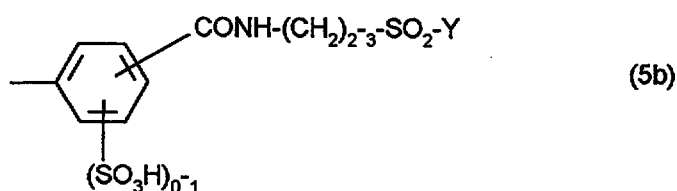
Y is preferably vinyl, β-chloroethyl, β-sulfatoethyl, β-thiosulfatoethyl, β-acetoxyethyl, β-phenoxyethyl or β-phosphatoethyl, and particularly preferably β-sulfatoethyl or vinyl.

X is preferably bromine.

m and m₁ independently of one another are each preferably the number 2, 3 or 4, particularly preferably the number 2 or 3, and especially preferably the number 2. p is preferably the number 0, and q is preferably the number 1, 2 or 3, and particularly preferably the number 1 or 2.

Z is preferably a phenyl radical which carries a fibre-reactive radical of the formula (3a) or (3b) and is further unsubstituted or substituted by sulfo, methyl, methoxy, chlorine, hydroxyl or methoxy, or is a 1- or 2-naphthyl radical which carries a fibre-reactive radical of the formula (3a) and is further unsubstituted or substituted by sulfo.

A preferred embodiment of the present invention relates to compounds of the formula (1) in which Z is a fibre-reactive radical of the formula



and Y is vinyl or β -sulfoethyl.

T is preferably fluorine or chlorine, and particularly preferably chlorine.

A non-reactive substituted or unsubstituted amino radical V can be, for example, amino; N-C₁-C₄alkylamino or N,N-di-C₁-C₄alkylamino, in which the alkyl can in each case be substituted, for example by sulfo, sulfato, hydroxyl, carboxyl or phenyl; cyclohexylamino; phenylamino or naphthylamino, in which the phenyl or naphthyl can in each case be substituted, for example by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen; or N-C₁-C₄alkyl-N-phenylamino, in which the alkyl and phenyl can be unsubstituted or substituted as described above.

Examples of suitable non-reactive amino radicals V are amino, methylamino, ethylamino, β -hydroxyethylamino, N,N-di- β -hydroxyethylamino, β -sulfoethylamino, cyclohexylamino, o-, m- or p-methylphenylamino, o-, m- or p-methoxyphenylamino, o-, m- or p-sulfophenylamino, 2,4- or 2,5-disulfophenylamino, o-carboxyphenylamino, 1- or 2-naphthylamino, 3,6,8-

trisulfonaphthylamino, 1,6-disulfonaphthylamino, N-ethyl-N-phenylamino, N-methyl-N-phenylamino, N- β -sulfoethyl-N-phenylamino, or N- β -hydroxyethyl-N-phenylamino.

A non-reactive amino radical V is preferably amino, N-mono- or N,N-di-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, cyclohexylamino, phenyl amino or naphthyl amino which is unsubstituted or substituted by methyl, methoxy, carboxyl or sulfo or N-C₁-C₂alkyl-N-phenylamino, and particularly preferably amino, N-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato or mono- or disulfophenylamino.

Preferred non-reactive C₁-C₄alkoxy radicals V are methoxy and iso-propoxy, and preferred non-reactive C₁-C₄alkylthio radicals V are methylthio and ethylthio.

One group of preferred non-reactive radicals V comprises hydroxyl, C₁-C₄alkoxy, morpholino and amino; N-C₁-C₄alkylamino or N,N-di-C₁-C₄alkylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl, and cyclohexylamino; phenylamino or naphthylamino which is unsubstituted or substituted in the phenyl or naphthyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, and N-C₁-C₄alkyl-N-phenylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl and/or substituted in the phenyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen.

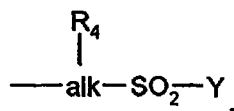
One group of particularly preferred non-reactive radicals V comprises hydroxyl, methoxy, iso-propoxy, morpholino, amino, N-mono- or N,N-di-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, cyclohexylamino, phenylamino or naphthylamino which is unsubstituted or substituted by methyl, methoxy, carboxyl or sulfo, and N-C₁-C₂-alkyl-N-phenylamino.

In a reactive radical V of the formulae (4a) - (4g), alk and alk' independently of one another are each, for example, methylene, 1,2-ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexylene or branched isomers thereof. alk and alk' independently of one another are each preferably a C₁-C₄alkylene radical, and particularly preferably an ethylene or propylene radical.

arylene is preferably a 1,3- or 1,4-phenylene radical which is unsubstituted or substituted by sulfo, methyl, methoxy or carboxyl, and in particular an unsubstituted 1,3- or 1,4-phenylene radical.

R₄ is particularly preferably hydrogen.

R₅ is particularly preferably hydrogen, C₁-C₄alkyl or a radical of the formula



in which R₄, Y and alk are in each case as defined and preferred above. R₅ is particularly preferably hydrogen, methyl or ethyl.

R₆ is preferably hydrogen, methyl or ethyl, and particularly preferably hydrogen.

The variable B is preferably -NH- or -O-, and particularly preferably -O-.

The variable t is preferably the number 0.

Preferred reactive radicals of the formulae (4a) to (4g) are those in which

R₄, R₅ and R₆ are each hydrogen,

B is the radical -NH- or -O-,

alk and alk' independently of one another are each ethylene or propylene,

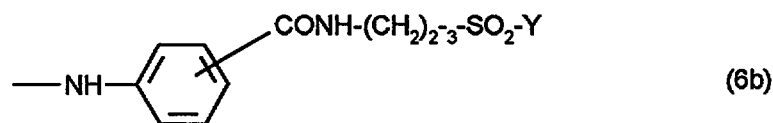
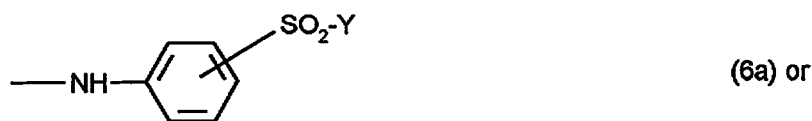
arylene is phenylene which is unsubstituted or substituted by methyl, methoxy, carboxyl or sulfo,

Y is vinyl or β-sulfatoethyl,

Y₁ is -CHBr-CH₂Br or -CBr=CH₂ and

t is the number 0.

A reactive radical V is particularly preferably a group of the formula



in which Y is as defined and preferred above.

In the formula (2),

Z₁ is independently as defined and preferred above for Z,

T₁ is independently as defined and preferred above for T and

V₁ is independently as defined and preferred above for V.

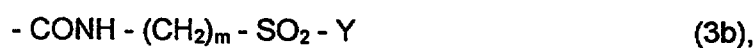
R₁ is preferably methyl, R₂ is preferably ethyl and R₃ is preferably carbamoyl or sulfomethyl.

A preferred embodiment of the present invention relates to dye mixtures comprising

(a) a compound of the formula (1) defined above in which

K₁ is a 1- or 2-naphthyl radical which is further substituted by 1 to 4 identical or different radicals from the group consisting of hydroxyl, amino, N-methyl- or N-ethylamino, acetylamino, benzoylamino and sulfo,

Z is a phenyl radical which carries a fibre-reactive radical of the formula



in which Y is vinyl or β-sulfatoethyl and

m is the number 2 or 3,

and is further unsubstituted or substituted by sulfo, methyl, methoxy, chlorine, hydroxyl or methoxy, or is a 1- or 2-naphthyl radical which carries a fibre-reactive radical of the formula (3a) as defined above and is further unsubstituted or substituted by sulfo,

T is fluorine or chlorine and

V is hydroxyl, C₁-C₄alkoxy, morpholino or amino; N-C₁-C₄alkylamino or N,N-di-C₁-C₄-alkylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl, or cyclohexylamino; phenylamino or naphthylamino which is unsubstituted or substituted in the phenyl or naphthyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, or N-C₁-C₄alkyl-N-phenylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl and/or in the phenyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, and

(b) a compound of the formula (2) defined above, in which

R₁ and R₂ independently of one another are each C₁-C₄alkyl,

R₃ is carbamoyl or sulfomethyl and

T₁ is defined independently as for T above,

V₁ is defined independently as for V above and

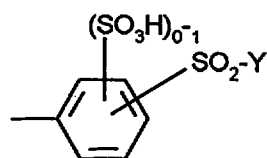
Z₁ is defined independently as for Z above.

A particularly preferred embodiment of the present invention relates to dye mixtures comprising

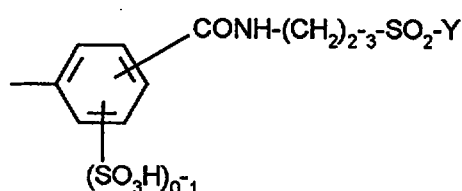
(a) a compound of the formula (1) defined above, in which

K₁ is a 1-naphthyl radical which is further substituted by 1 to 4 identical or different radicals from the group consisting of hydroxyl, amino and sulfo,

Z is a fibre-reactive radical of the formula



(5a) or



(5b)

and Y is vinyl or β-sulfatoethyl,

T is fluorine or chlorine and

V is amino, N-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or mono- or disulfophenylamino, and

(b) a compound of the formula (2) defined above, in which

R₁ is methyl,

R₂ is ethyl and

R₃ is carbamoyl or sulfomethyl, and

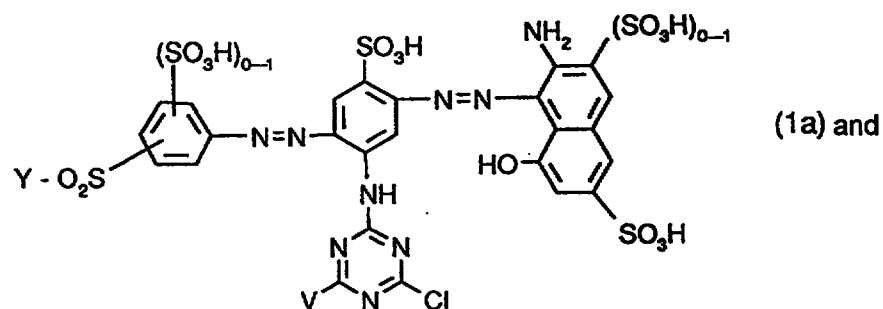
T₁ is defined independently as for T above,

V₁ is defined independently as for V above and

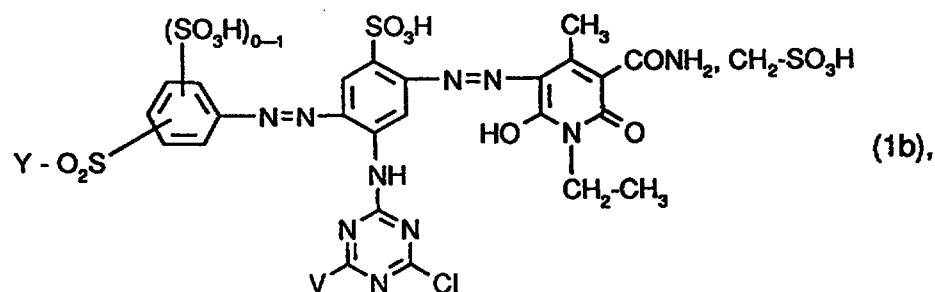
Z₁ is defined independently as for Z above.

An especially preferred embodiment of the present invention relates to dye mixtures comprising

(a) a compound of the formula



(b) a compound of the formula



in which Y is vinyl or β-sulfatoethyl and

V is amino, N-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or mono- or disulfophenylamino.

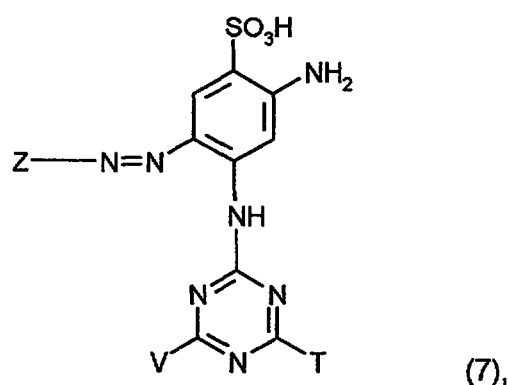
The compounds of the formulae (1) and (2) are known in some cases from EP-A-647683 or can be prepared analogously to these compounds. The compounds of the formula (2) defined above in which

T₁ is halogen and

V₁ is β-sulfoethylamino or β-hydroxyethylamino and

R₁, R₂, R₃ and Z₁ are each as defined and preferred above, are novel and the invention also relates to these compounds.

The compounds of the formulae (1) and (2) can be synthesized, for example, by diazotizing a compound of the formula

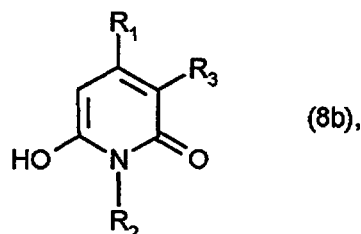


in which V, T and Z are each as defined above,

in a manner known per se, for example with sodium nitrite in a hydrochloric acid medium, and coupling the diazotization product with a coupling component of the formula

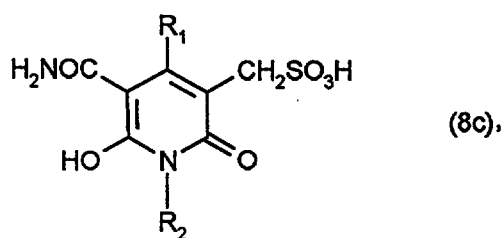


or



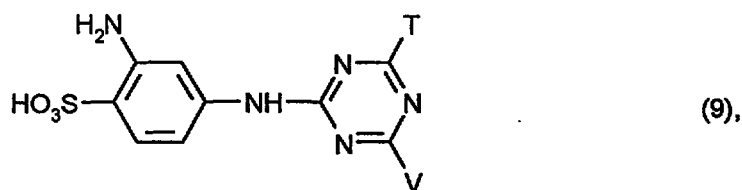
in which K, R₁, R₂ and R₃ are each as defined above.

For the preparation of compounds of the formula (2) in which R₃ is sulfomethyl, it may prove advantageous to employ in the process, instead of the coupling component of the formula (8b), a coupling component of the formula



in which R_1 and R_2 are each as defined above.

The compounds of the formula (7) can be prepared, for example, by diazotizing a compound of the formula $Z-NH_2$ and coupling the diazotization product to a compound of the formula



in which T , V and Z are each as defined above.

The dyes of the formulae (1) and (2) used according to the invention each contain at least one sulfo group and preferably in each case 1 to 3 sulfo groups which are each present either in the form of the free sulfo acid or, preferably, as a salt thereof, for example as the sodium, lithium, potassium or ammonium salt or as the salt of an organic amine, for example as the triethanolammonium salt. The dyes of the formulae (1) and (2) and therefore also the dye mixtures as a rule comprise further additives, for example sodium chloride or dextrine.

The dyes of the formulae (1) and (2) are present in the dye mixture, for example in a weight ratio of 25:1 to 1:1, preferably 20:1 to 1:1, and particularly preferably 10:1 to 1.5:1.

The dye mixtures according to the invention can be prepared, for example, by mixing the individual dyes. This mixing process is carried out, for example, in suitable mills, for example ball or pinned disc mills, and in kneaders or mixers.

Dye mixtures comprising in each case a compound of the formulae (1) and (2) in which T and T₁, V and V₁ and Z and Z₁ are in each case identical can advantageously also be obtained by mixed synthesis, i.e. by reacting a compound of the formula (7) defined above with a mixture of coupling components of the formulae (8a) and (8b) or (8c) defined above.

The invention also relates to a process for dyeing or printing fibre materials containing hydroxyl groups or nitrogen with the dye mixtures according to the invention.

Fibre materials are, for example, the naturally occurring cellulosic fibres, such as cotton, linen, jute or hemp, and modified cellulosic fibres, such as cellulose or regenerated cellulose. The dye mixtures according to the invention are particularly suitable for dyeing or printing naturally occurring polyamide fibre materials, for example silk or wool, synthetic polyamide fibre materials, for example nylon 6 or nylon 6.6, or wool and synthetic polyamide blend fabrics. The dye mixtures according to the invention are particularly suitable for dyeing or printing naturally occurring polyamide fibre materials, and here in particular wool or wool which has been chlorinated or given a machine-washable treatment.

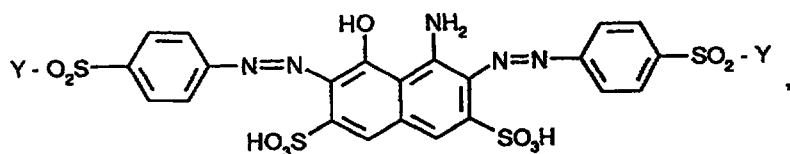
The textile fibre material mentioned can be present here in widely varying processing forms, for example as fibre, yarn, flocks, woven fabric or knitted fabric.

The dye mixtures according to the invention are suitable for the customary dyeing and printing processes and can be applied to and fixed on the fibre material in many different ways, in particular in the form of aqueous dye solutions or dye printing pastes. They are suitable both for the exhaust method and for pad dyeing, in which the goods are impregnated with aqueous dye solutions, which may contain salts, and the dyes are fixed after an alkali treatment or in the presence of alkali, where appropriate under the action of heat. The dye mixtures according to the invention are also suitable for the cold pad-batch method, in which the dye is applied on the padder together with the alkali and then fixed by storage at room temperature for several hours.

Naturally occurring and synthetic polyamide fibre materials, in particular wool, are preferably dyed by the exhaust method at a pH of about 3 to 7, in particular 3 to 5, and at temperatures of, for example, 70 to 120°C, in particular 90 to 105°C.

In addition to water and the dyes of the formulae (1) and (2), the dye liquors or printing pastes can comprise further additives, for example shading dyes, salts, buffer substances, wetting agents, antifoams, levelling agents or agents which influence the properties of the textile material, for example softeners, additives for flameproofing treatment or soil-, water- and oil-repellant agents, as well as water-softening agents and naturally occurring or synthetic thickeners, for example alginates or cellulose ethers, all of which are known per se.

Dye mixtures which have proved advantageous are, for example, those comprising 90 to 25 % by weight, and preferably 90 to 50 % by weight, of a dye mixture comprising one compound each of the formulae (1) and (2) defined above and 10-75 % by weight, and preferably 10 to 50 % by weight, in each case based on the total solid dye formulation, of a dye of the formula



in which Y is as defined and preferred above.

The dye mixtures according to the invention produce level dyeings and prints with good all-round properties, in particular good fastness to washing, rubbing, wet processing, wet rubbing and light. The dye mixtures according to the invention are furthermore distinguished by a uniform colour build-up, good uptake properties and high degrees of fixing. Furthermore, the otherwise customary after-treatment of the dyeings and prints with so-called fixing agents can be omitted with the dye mixtures according to the invention.

In the following examples, parts are by weight. The temperatures are degrees Celsius. Parts by weight and parts by volume bear the same relationship to one another as the gram to the cubic centimetre.

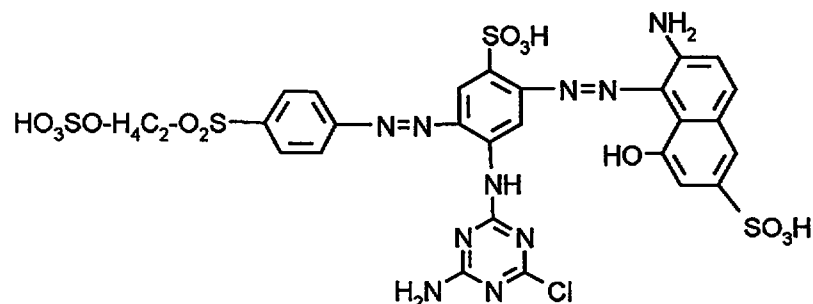
Example 1: 10 g of woollen fabric are dyed in a laboratory dyeing apparatus with the following liquor:

0.2g of sodium acetate

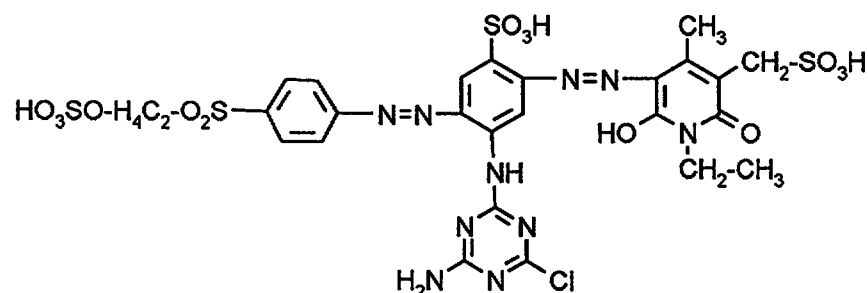
0.5g of 80% acetic acid

0.2g of a commercially available levelling agent (Albegal B®)

0.3 g of a dye mixture comprising 80 % by weight of the dye of the formula



and 20 % by weight of the dye of the formula



and 200 ml of water.

The pH of the liquor is 4.5. The textile is treated in the dye liquor at 40°C for 5 minutes, the liquor is then heated to the boiling temperature (98°C) at a heating-up rate of 1°/minute, and dyeing is carried out at this temperature for 90 minutes. After the liquor has cooled to 80°C, the dyeing is rinsed and finished in the customary manner. A black dyeing which is level over the fibre and surface and has good fastness properties is obtained.

Example 2: 10g of a woollen tricot treated to superwash standard by the Hercoset process is dyed in a laboratory dyeing apparatus with the following liquor:

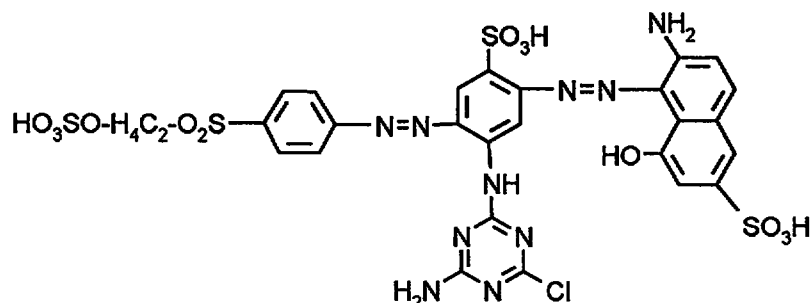
0.2g of sodium acetate

0.5g of 80% acetic acid

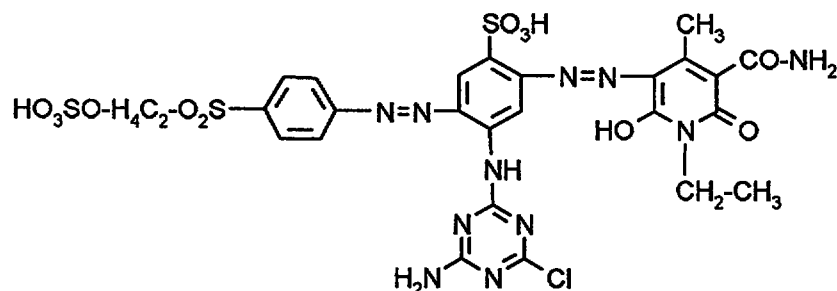
0.5g of Glauber's salt

0.2g of a commercially available levelling agent (Albegal B®)

0.4 g of a dye mixture comprising 75 % by weight of the dye of the formula



and 25 % by weight of the dye of the formula



and 200 ml of water.

The pH of the liquor is 4.7. The textile material is treated in the dye liquor at 40°C for 5 minutes and the liquor is then heated to 60°C at a heating-up rate of 1°/minute and kept at 60°C for 20 minutes. It is then heated to the boiling temperature (98°C) at 1°/minute and dyeing is carried out at this temperature for 90 minutes. After cooling, the textile material is treated in a fresh liquor comprising 5 g/l of sodium bicarbonate at 80°C and pH 8.3 for 20 minutes. It is then rinsed in the customary manner and 1 % formic acid, based on the fibre weight, is added to the last rinsing bath for acidification. A black dyeing which is level over the fibre and surface and has good fastness properties is obtained.

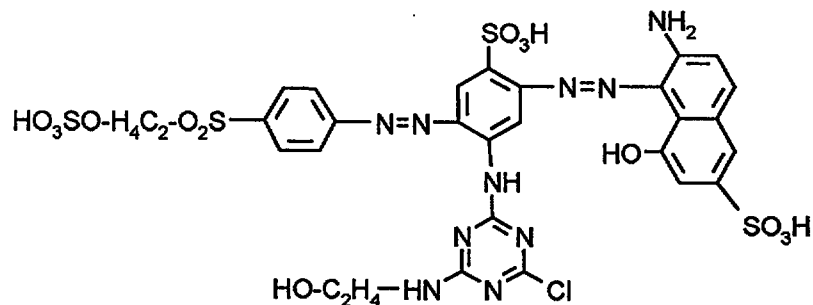
Example 3: 5 g of loose wool are dyed in a laboratory dyeing apparatus with the following liquor:

0.2 g of sodium acetate

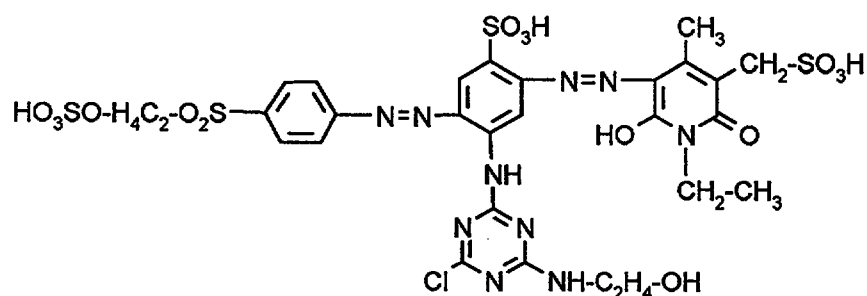
0.5 g of 80 % acetic acid

0.2 g of a commercially available levelling agent (Albegal B®)

105 mg of a dye mixture comprising 75 parts of the dye of the formula



and 25 parts of the dye of the formula



and 400 ml of water.

The pH of the liquor is 4.7. The material is treated in the dye liquor at 40°C for 5 minutes, the liquor is then heated to the boiling temperature (98°C) at a heating-up rate of 1°C/minute, and dyeing is carried out at this temperature for 90 minutes. After cooling the liquor to 80°C, the dyeing is rinsed and finished in the customary manner. A black dyeing which is level over the fibre and surface and has good fastness properties is obtained.

Example 4: 1 kg of woollen worsted yarn in the form of a cheese is pretreated in a circulating apparatus at 40°C for 10 minutes with a liquor comprising

9 l of water,

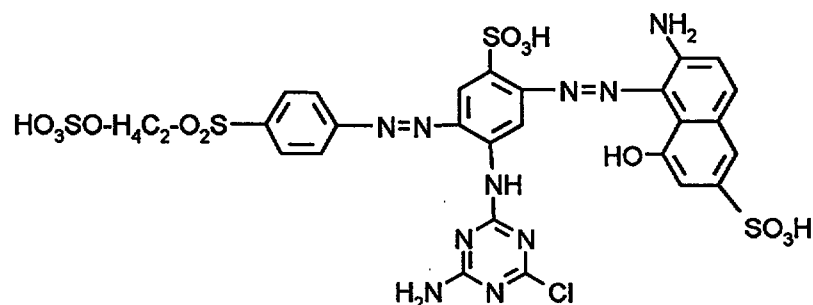
9 g of ammonium acetate,

37 ml of 80 % acetic acid,

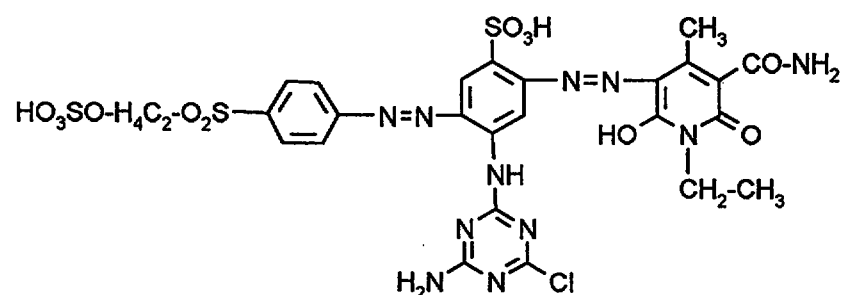
9 g of a nonionic wetting agent (Albegal FFA®), and

20 g of a commercially available levelling agent (Albegal B®).

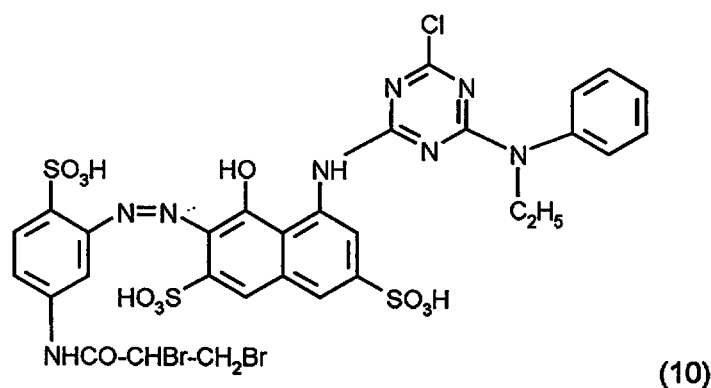
The pH of the liquor is 4.65. After addition of a solution which comprises 24 g of the dye of the formula



6 g of the dye of the formula



and 1 g of the dye of the formula



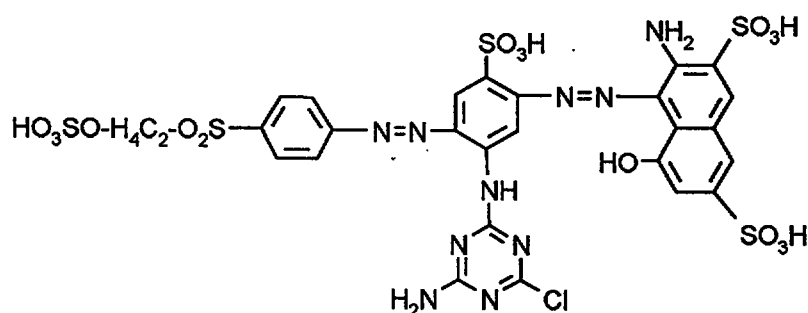
(10)

the yarn is treated in the dye liquor at 40°C for 5 minutes and the liquor is then heated to 70°C with a heating-up rate of 1°C/minute and kept at 70°C for 15 minutes. It is then heated to the boiling temperature (98°C) at 1°/minute and dyeing is carried out at this temperature

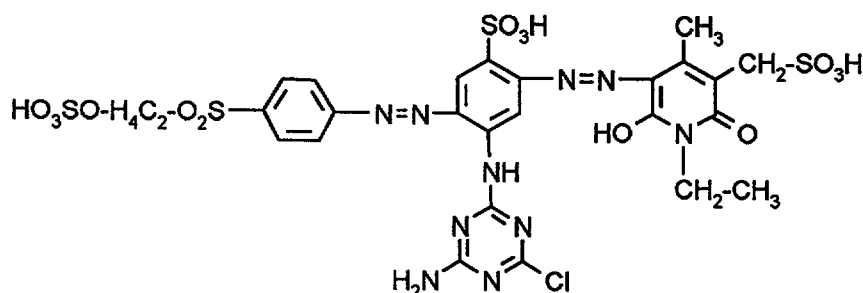
for 90 minutes. After cooling, the textile material is treated at 80°C for 20 minutes in a fresh liquor brought to pH 8.5 with 35 g of 35 % ammonia. It is then rinsed in the customary manner and 1 % of formic acid, based on the fibre weight, is added to the last rinsing bath for acidification. A black dyeing which is level over the fibre and surface and has good fastness properties is obtained.

Example 5: The procedure described in Example 4 is repeated, but 4 % by weight, based on the textile material, of a commercially available wool-protecting agent (Irgasol HTW®) is additionally added to the dye liquor, dyeing is carried out at 105°C and the dyeing time is shortened to 45 minutes. A black dyeing which is level over the fibre and surface and has good fastness properties is likewise obtained.

Example 6: The procedure described in Example 1 is repeated using as the dye 500 mg of a mixture of 85 parts of the dye of the formula

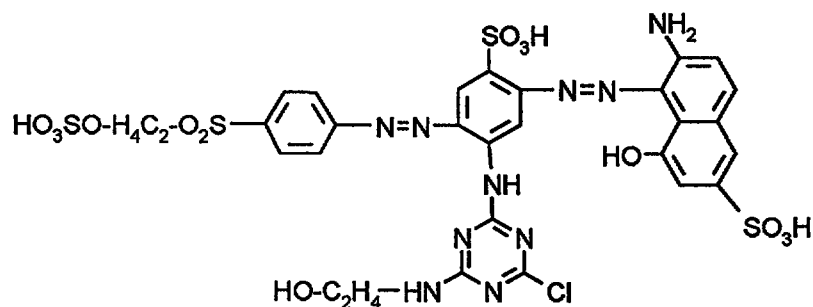


and 15 parts of the dye of the formula

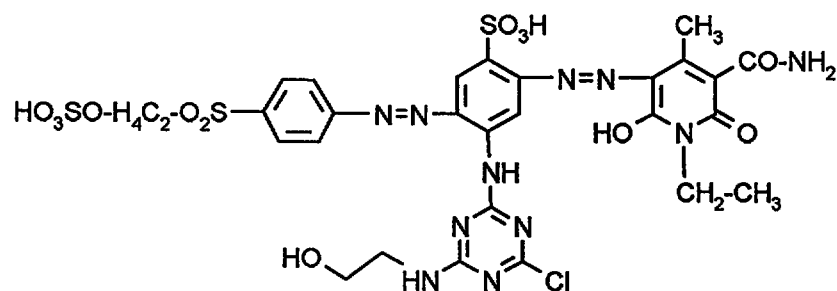


A black dyeing which is level over the fibre and surface and has good fastness properties is likewise obtained.

Example 7: The procedure described in Example 1 is repeated using as the dye 350 mg of a mixture of 65 parts of the dye of the formula

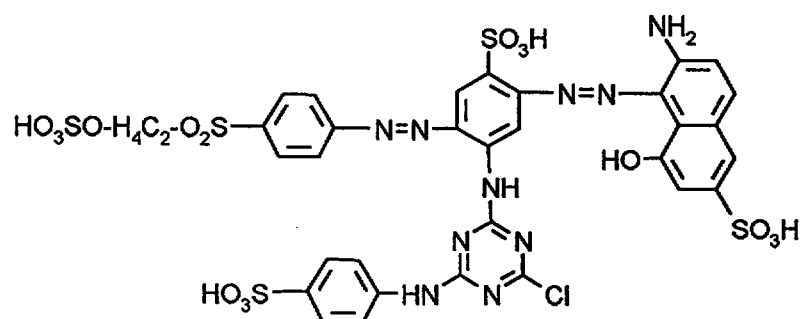


and 35 parts of the dye of the formula

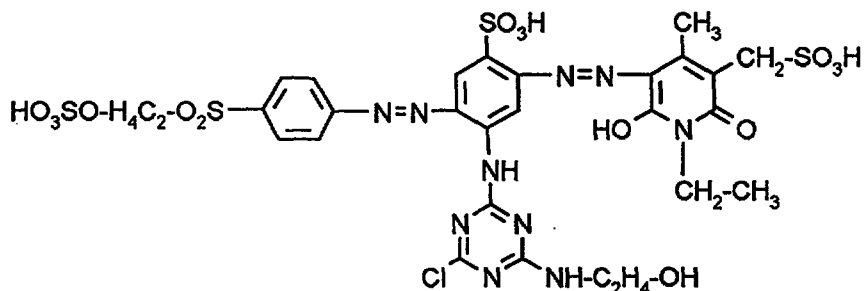


A black dyeing which is level over the fibre and surface and has good fastness properties is likewise obtained.

Example 8: The procedure described in Example 1 is repeated using as the dye 400 mg of a mixture of 70 parts of the dye of the formula

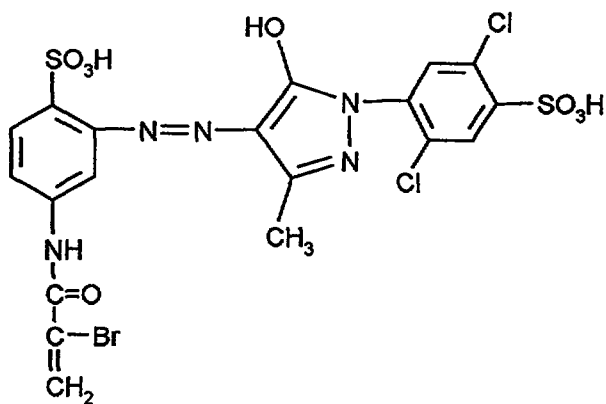


and 30 parts of the dye of the formula



A black dyeing which is level over the fibre and surface and has good fastness properties is likewise obtained.

Example 9: The procedure described in Example 4 is repeated using, instead of the shading dye of the formula (10), 1.25 g of the dye of the formula



A black dyeing which is level over the fibre and surface and has good fastness properties is likewise obtained

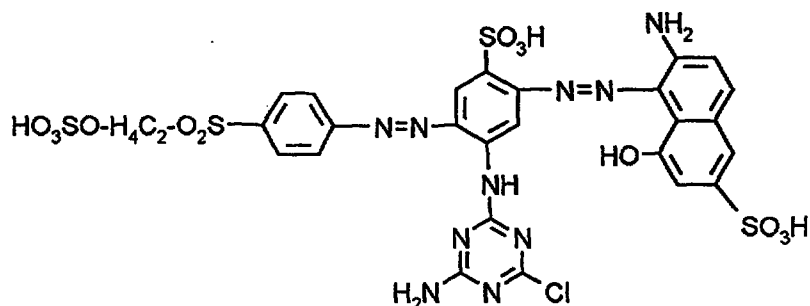
Example 10: 10 g of a woollen tricot treated to superwash standard by the Hercoset process is dyed in a laboratory dyeing apparatus with the following liquor:

- 0.2 g of sodium acetate
- 0.5 g of 80 % acetic acid
- 0.5 g of Glauber's salt

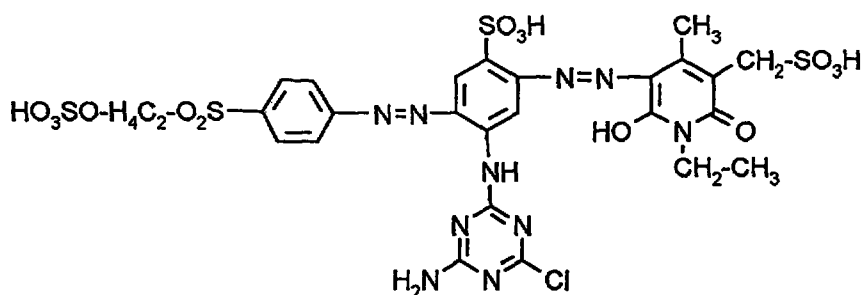
0.2 g of a commercially available levelling agent (Albegal B®)

0.4 g of a dye mixture comprising

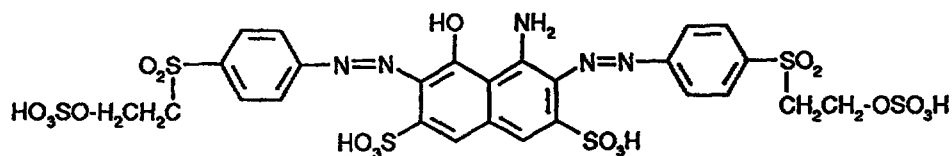
45 % by weight of the dye of the formula



15 % by weight of the dye of the formula



and 40 % by weight of the dye of the formula



and 200 ml of water.

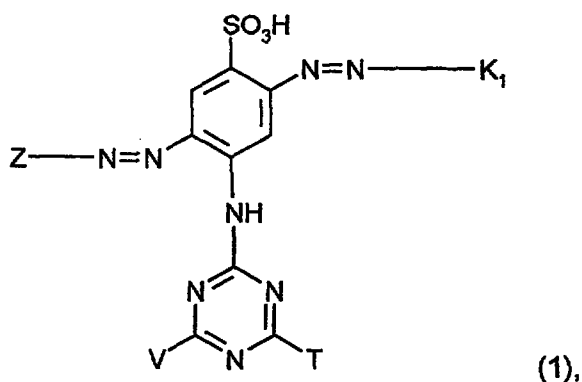
The pH of the liquor is 4.7. The textile material is treated in the dye liquor at 40°C for 5 minutes and the liquor is then heated to 60°C at a heating-up rate of 1°/minute and kept at 60°C for 20 minutes. It is then heated to the boiling temperature (98°C) at 1°/minute and dyeing is carried out at this temperature for 90 minutes. After cooling, the textile material is treated in a fresh liquor comprising 5 g/l of sodium bicarbonate at 80°C and at pH 8.3 for 20 minutes. (Alternatively, the treatment can be carried out with ammonia, sodium carbonate or

sodium hydroxide solution, in each case at a pH of 7.5 to 9). The dyeing is rinsed in the customary manner and 1 % of formic acid, based on the fibre weight, is added to the last rinsing bath for acidification. A black dyeing which is level over the fibre and surface and has good fastness properties is obtained.



WHAT IS CLAIMED IS:

1. A dye mixture comprising
- (a) a compound of the formula



in which K_1 is a naphthyl radical which is unsubstituted or further substituted by hydroxyl, amino, N-C₁-C₄alkylamino, C₂-C₄alkanoylamino, benzoylamino, sulfo or a radical of the formula -SO₂-Y,

Z is the radical of a diazo component of the benzene or naphthalene series which contains at least one fibre-reactive radical of the formula

- | | |
|---|---------|
| - SO ₂ - Y | (3a), |
| - CONH - (CH ₂) _m - SO ₂ - Y | (3b), |
| - CONH - (CH ₂) _{m1} - O - (CH ₂) _m - SO ₂ - Y | (3c), |
| - (O) _p - (CH ₂) _q - CONH - (CH ₂) _m - SO ₂ - Y | (3d), |
| - NH - CO - CHX - CH ₂ X | (3e) or |
| - NH - CO - CX = CH ₂ | (3f), |

Y is vinyl or a radical -CH₂-CH₂-U

and U is a leaving group,

X is chlorine or bromine,

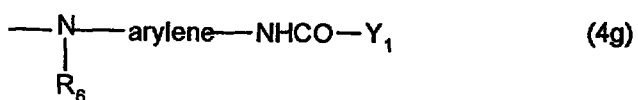
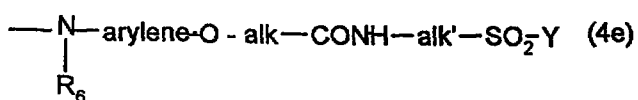
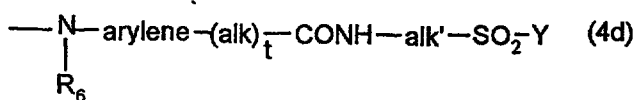
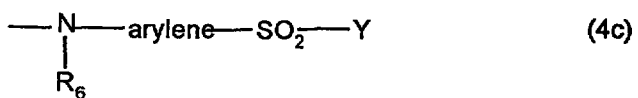
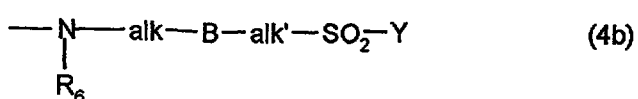
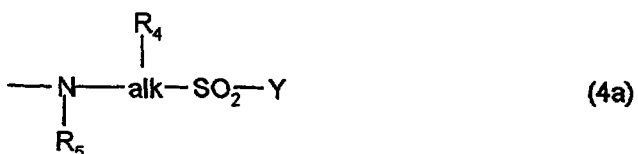
p is the number 0 or 1 and

m, m₁ and q independently of one another are each an integer from 1 to 6,

T is chlorine, fluorine, bromine, 3-carboxypyridin-1-yl or 3-carbamoylpyridin-1-yl,



V is defined independently as T or is a non-reactive radical from the group consisting of hydroxyl, C₁-C₄alkoxy, phenoxy, C₁-C₄alkylthio, morpholino and substituted or unsubstituted amino, or is a reactive radical of the formula



R₄ is hydrogen, hydroxyl, sulfo, sulfato, carboxyl, cyano, halogen, C₁-C₄alkoxycarbonyl, carbamoyl or a group -SO₂-Y,

in which Y is as defined above,

R₅ is hydrogen, C₁-C₄alkyl which is unsubstituted or substituted by hydroxyl, sulfo, sulfato,

carboxy or cyano, or a radical $\begin{array}{c} \text{R}_4 \\ | \\ \text{---alk---SO}_2\text{---Y} \end{array}$,



in which R_4 and Y are each as defined above,

R_6 is hydrogen or C_1 - C_4 alkyl,

alk and alk' independently of one another are each C_1 - C_6 alkylene,

arylene is a phenylene or naphthylene radical which is unsubstituted or substituted by sulfo, carboxyl, hydroxyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen,

Y_1 is a group $-CHX-CH_2X$ or $-CX=CH_2$,

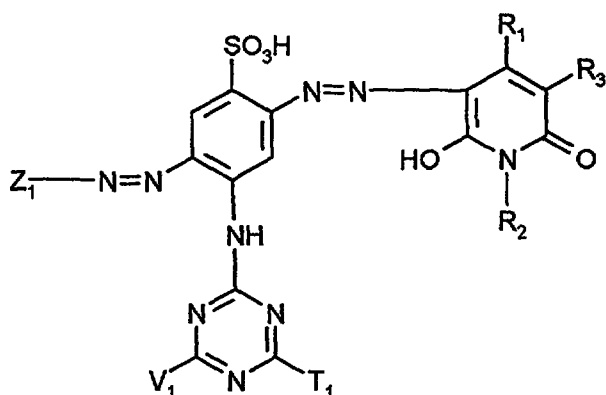
in which X is as defined above,

B is a radical $-O-$ or $-NR_6$,

in which R_6 is as defined above, and

t is the number 0 or 1, and

(b) a compound of the formula



(2),

in which R_1 and R_2 independently of one another are each C_1 - C_4 alkyl,

R_3 is carbamoyl, sulfomethyl or cyano, and

T_1 is defined independently as above for T ,

V_1 is defined independently as above for V , and

Z_1 is defined independently as above for Z .

2. A dye mixture according to claim 1, in which

K_1 in formula (1) is a 1- or 2-naphthyl radical which is further substituted by 1 to 4 identical or different radicals selected from the group consisting of hydroxyl, amino, N-methyl- or N-ethylamino, acetylamino, benzoylamino and sulfo.

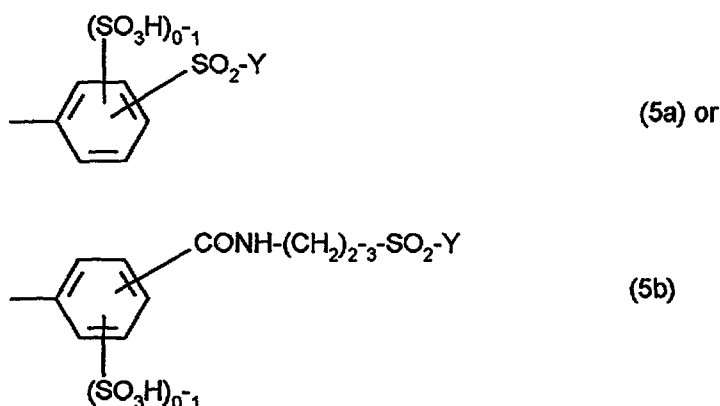
3. A dye mixture according to claim 1 or 2, in which



K₁ is a 1-naphthyl radical which carries 1 to 4 identical or different radicals selected from the group consisting of hydroxyl, amino and sulfo.

4. A dye mixture according to any one of claims 1 to 3, in which Z and Z₁ independently of one another are each a phenyl radical, which carries a fibre-reactive radical of the formula (3a) or (3b) defined in claim 1 and is further unsubstituted or substituted by sulfo, methyl, methoxy, chlorine, hydroxyl or methoxy, or are a 1- or 2-naphthyl radical which carries a fibre-reactive radical of the formula (3a) defined in claim 1 and is further unsubstituted or substituted by sulfo.

5. A dye mixture according to any one of claims 1 to 4, in which Z and Z₁ independently of one another are each a fibre-reactive radical of the formula



in which Y is vinyl or β-sulfatoethyl.

6. A dye mixture according to any one of claims 1 to 5, in which T and T₁ independently of one another are each fluorine or chlorine, and preferably each chlorine.

7. A dye mixture according to any one of claims 1 to 6, in which V and V₁ independently of one another are each hydroxyl, C₁-C₄alkoxy, morpholino or amino; N-C₁-C₄alkylamino or N,N-di-C₁-C₄alkylamino, which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl, or cyclohexylamino; phenylamino or naphthylamino which is unsubstituted or substituted in the phenyl or



naphthyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, or N-C₁-C₄alkyl-N-phenylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl and/or substituted in the phenyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen.

8. A dye mixture according to any one of claims 1 to 7, in which V and V₁ independently of one another are each amino, N-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or mono- or disulfophenylamino.

9. A dye mixture according to claim 1, which comprises

(a) a compound of the formula (1) defined in claim 1 in which

K₁ is a 1- or 2-naphthyl radical which is further substituted by 1 to 4 identical or different radicals selected from the group consisting of hydroxyl, amino, N-methyl- or N-ethylamino, acetylamino, benzoylamino and sulfo,

Z is a phenyl radical which carries a fibre-reactive radical of the formula



in which Y is vinyl or β -sulfatoethyl and

m is the number 2 or 3,

and is further unsubstituted or substituted by sulfo, methyl, methoxy, chlorine, hydroxyl or methoxy, or is a 1- or 2-naphthyl radical which carries a fibre-reactive radical of the formula (3a) as defined above and is further unsubstituted or substituted by sulfo,

T is fluorine or chlorine and

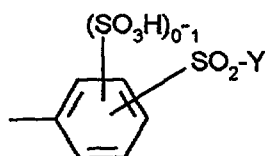
V is hydroxyl, C₁-C₄alkoxy, morpholino or amino; N-C₁-C₄alkylamino or N,N-di-C₁-C₄alkylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxyl or phenyl, or cyclohexylamino; phenylamino or naphthylamino which is unsubstituted or substituted in the phenyl or naphthyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, or N-C₁-C₄alkyl-N-phenylamino which is unsubstituted or substituted in the alkyl part by sulfo, sulfato, hydroxyl, carboxy or phenyl and/or in the phenyl part by C₁-C₄alkyl, C₁-C₄alkoxy, amino, C₂-C₄alkanoylamino, carboxyl, sulfo or halogen, and



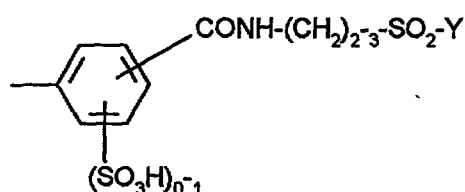
(b) a compound of the formula (2) defined in claim 1, in which
 R_1 and R_2 independently of one another are each C_1-C_4 alkyl,
 R_3 is carbamoyl or sulfomethyl and
 T_1 is defined independently as for T above,
 V_1 is defined independently as for V above and
 Z_1 is defined independently as for Z above.

10. A dye mixture according to claim 1, which comprises

(a) a compound of the formula (1) defined in claim 1, in which
 K_1 is a 1-naphthyl radical which is further substituted by 1 to 4 identical or different radicals
from the group consisting of hydroxyl, amino and sulfo,
Z is a fibre-reactive radical of the formula



(5a) or



(5b)

and Y is vinyl or β -sulfatoethyl,

T is fluorine or chlorine and

V is amino, $N-C_1-C_2$ alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or mono- or disulfophenylamino, and

(b) a compound of the formula (2) defined in claim 1, in which

R_1 is methyl,

R_2 is ethyl and

R_3 is carbamoyl or sulfomethyl, and

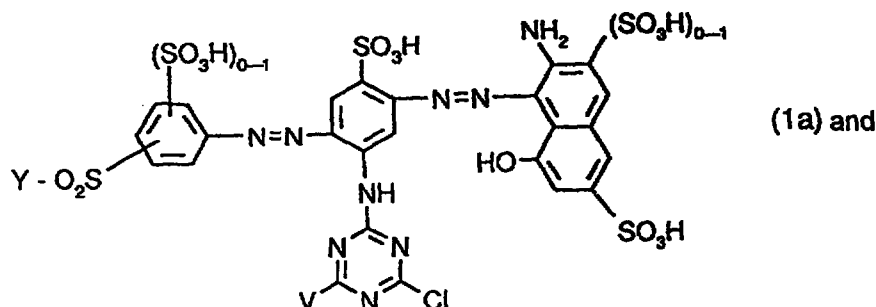
T_1 is defined independently as for T above,

V_1 is defined independently as for V above and

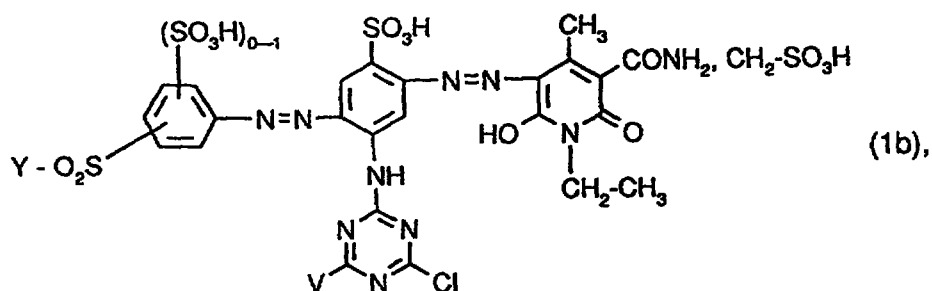
Z_1 is defined independently as for Z above.



11. A dye mixture according to claim 1, which comprises
(a) a compound of the formula



- (b) a compound of the formula



in which Y is vinyl or β -sulfatoethyl and

V is amino, N-C₁-C₂alkylamino which is unsubstituted or substituted by hydroxyl, sulfo or sulfato, or mono- or disulfophenylamino.

12. A dye mixture according to any one of claims 1 to 11, which comprises the compounds of the formula (1) and (2) in a weight ratio of 25:1 to 1:1, and preferably 10:1 to 1.5:1.

13. A process for dyeing or printing fibre material containing hydroxyl groups or nitrogen, which comprises bringing these fibre materials into contact with a dye mixture according to any one of claims 1 to 12 in an aqueous solution.

14. The process according to claim 13 for dyeing or printing naturally occurring or synthetic polyamide fibre materials, in particular wool.



15. The use of a dye mixture according to any one of claims 1 to 12 for dyeing or printing naturally occurring or synthetic polyamide fibre materials, in particular wool.

16. A compound of the formula (2) according to claim 1, in which

T₁ is halogen and

V₁ is β -sulfoethylamino or β -hydroxyethylamino and

R₁, R₂, R₃ and Z₁ are each as defined in claim 1.