

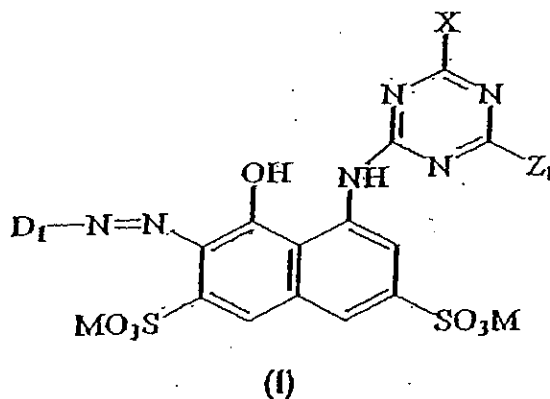
Orange- and scarlet-colored mixtures of reactive dyes.

The present invention relates to the technical field of fiber-reactive dyes.

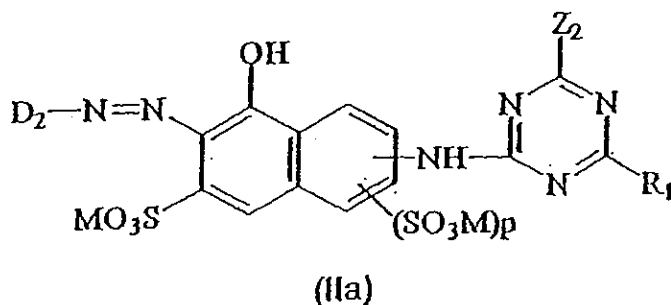
EP-A 681007 discloses reactive dye mixtures capable of dyeing hydroxyl- and/or carboxamido-containing fiber materials in brilliant orange to red shades. However, these mixtures have application defects, especially with regard to the hiding of chafe marks.

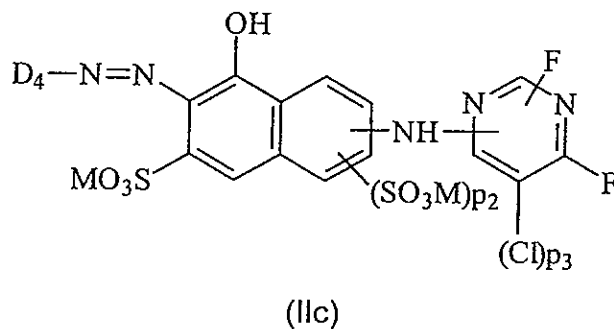
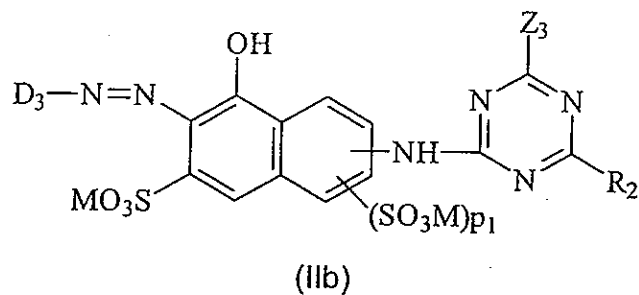
The present invention, then, provides reactive dye mixtures which have improved properties compared with prior art mixtures.

Accordingly, the present invention relates to an orange-or scarlet-colored dye mixture including one or more of the dyes of the general formula (I)



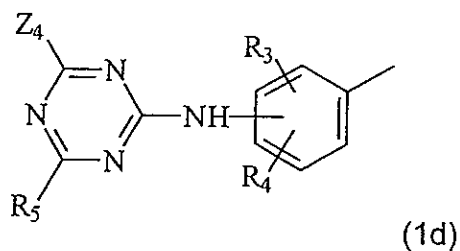
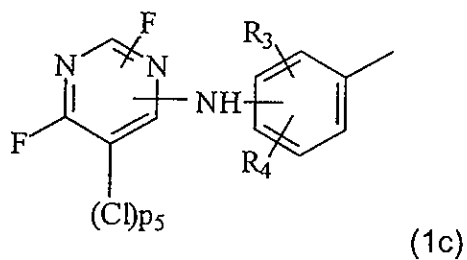
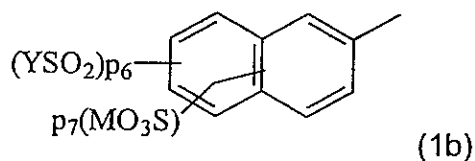
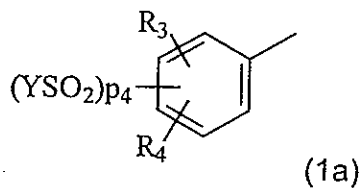
and one or more of the dyes of the general formulae (IIa), (IIb), and (IIc), and the -NH group in (IIa) and (IIb) in position 3 on the hydroxynaphthalene radical.





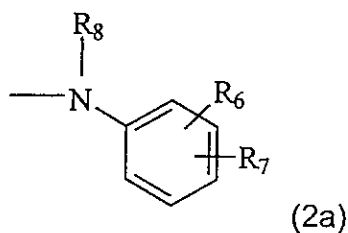
where

D₁ and D₂ are independently a group of the general formulae (1a), (1b), (1c) or (1d)



where

- R³ is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxyl;
 R⁴ is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo;
 R⁵ is hydroxyl, phenoxy, morpholino, a group of the general formula (2a)

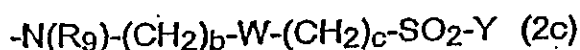


where

R^6 is hydrogen, methyl, ethyl, methoxy, ethoxy, hydroxyl, sulfo, carboxyl or a group $-(CH_2)_a-SO_2-Y$, where a is 0, 1, 2 or 3 and Y is as defined hereinbelow;

R^7 is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo and

R^8 is hydrogen, methyl, ethyl or β -sulfoethyl, or a group of the general formula (2b) or (2c)



where

R_9 is hydrogen, phenyl, phenyl substituted by 1 or 2 substituents selected from the group consisting of methyl, ethyl, methoxy, ethoxy, sulfo and carboxyl, (C_1-C_4) -alkyl or a group of the formula $-(CH_2)_b-W-(CH_2)_c-SO_2-Y$;

b is 0, 1, 2 or 3;

c is 2 or 3; and

Y is as defined hereinbelow;

Z_4 is chlorine or fluorine;

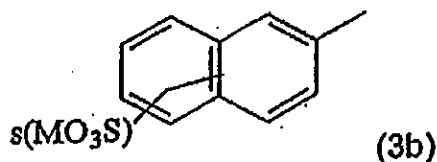
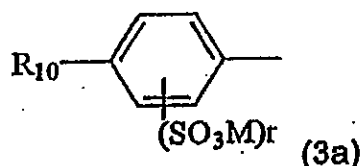
Y is vinyl or is ethyl which in the β -position contains a substituent which is eliminable by alkali to leave a vinyl group;

p_4, p_5 are independently 0 or 1; p_6 is 1; and

p_7 is 0, 1 or 2;

and M is as defined hereinbelow;

D_3 and D_4 are independently a group of the general formulae (3a) or (3b)



where

R_{10} is hydrogen, methyl, ethyl, methoxy or ethoxy;

r is 1 or 2; and

s is 1, 2 or 3;

and M is as defined hereinbelow;

Z₁ is chlorine or fluorine;

X is hydroxyl, morpholino, a group of the general formulae (2a), (2b) or (2c) or else, if Z₁ is chlorine, may also be chlorine;

Z₂ and Z₃ are independently chlorine or fluorine;

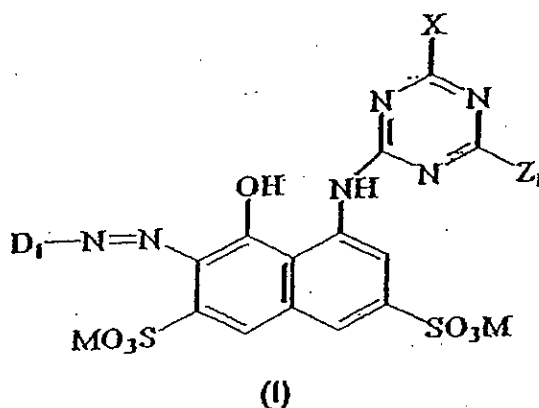
R₁ is hydroxyl, phenoxy, morpholino or a group of the general formula (2a) and, if Z₂ is chlorine, may also be chlorine;

R₂ is a group of the general formulae (2a), (2b) or (2c);

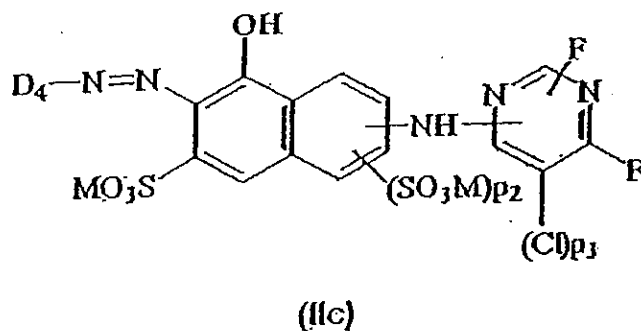
M is hydrogen or an alkali metal; and

p, p₁, p₂ and p₃ are independently 0 or 1.

In another aspect of the present invention, there is provided an orange- or scarlet-colored dye mixture of a dye having the general formula (I)



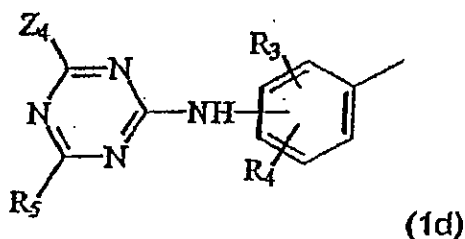
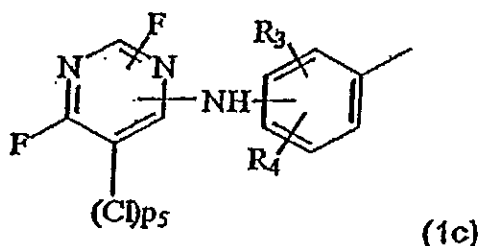
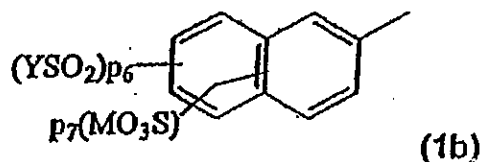
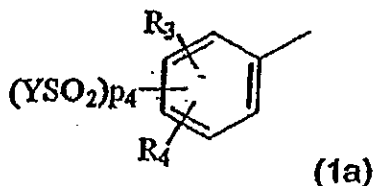
and a dye having the general formula (IIc)



wherein,

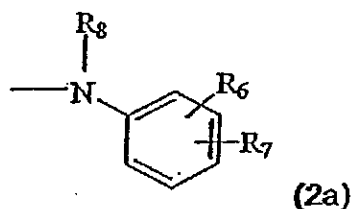
4a

D₁ is independently a group of the general formulae (1a), (1b), (1c) or (1d)



where

- R³ is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxyl;
 R⁴ is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo;
 R⁵ is hydroxyl, phenoxy, morpholino, a group of the general formula (2a)



where

- R⁶ is hydrogen, methyl, ethyl, methoxy, ethoxy, hydroxyl, sulfo, carboxyl or a group -(CH₂)_a-SO₂-Y, where a is 0, 1, 2 or 3 and Y is as defined hereinbelow;
 R⁷ is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo and
 R⁸ is hydrogen, methyl, ethyl or β-sulfoethyl, or a group of the general formula (2b) or (2c)



where

- R₉ is hydrogen, phenyl, phenyl substituted by 1 or 2 substituents selected from the group consisting of methyl, ethyl, methoxy, ethoxy, sulfo and carboxyl, (C₁-C₄)-alkyl or a group of the formula

4b

$$-(CH_2)_b-W-(CH_2)_c-SO_2-Y;$$

b is 0, 1, 2 or 3;

c is 2 or 3; and

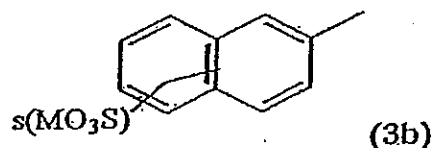
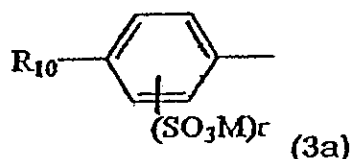
Y is as defined hereinbelow;

Z₄ is chlorine or fluorine;

Y is vinyl or is ethyl which in the β-position contains a substituent which is eliminable by alkali to leave a vinyl group;

p₄, p₅ are independently 0 or 1; p₆ is 1; andp₇ is 0, 1 or 2;

and M is as defined hereinbelow;

D₃ and D₄ are independently a group of the general formulae (3a) or (3b)

where

R₁₀ is hydrogen, methyl, ethyl, methoxy or ethoxy;

r is 1 or 2; and

s is 1, 2 or 3;

and M is as defined hereinbelow;

is chlorine or fluorine;

is hydroxyl, morpholino, a group of the general formulae (2a), (2b) or (2c) or else, if Z₁ is chlorine, may also be chlorine;and Z₃ are independently chlorine or fluorine;

is hydroxyl, phenoxy, morpholino or a group of the general formula (2a) and, if

Z₂ is chlorine, may also be chlorine;

is a group of the general formulae (2a), (2b) or (2c);

is hydrogen or an alkali metal; and

p₁, p₂ and p₃ are independently 0 or 1.

Dye mixtures according to the invention may include just one of the dyes of the general formulae (IIa), (IIb) or (IIc), but may also include two or else all three. In addition, a plurality of each of the dyes of the general formulae (IIa), (IIb) or (IIc) may be present. Dye mixtures according to the invention preferably include the dye or dyes of the general formula (I) in a fraction of 95 to 25% by weight and the dye or dyes of the general formulae (II) in a fraction of 5 to 75% by weight, each percentage being based on the total amount of the dyes of the general formulae (I) and (II). Particularly preferably dye mixtures according to the invention include the dye or dyes of the general formula (I) in a fraction of 90 to 50% by weight and the dye or dyes of the general formulae (II) in a fraction of 10 to 50% by weight. Particular preference is further given to dye mixtures according to the invention which include the dye or dyes of the general formula (I) in a fraction of 85 to 55% by weight and the dye or dyes of the general formulae (II) in a fraction of 15 to 45% by weight.

The individual symbols in the general formulae mentioned above and similarly in the general formulae mentioned hereinbelow, including those symbols which have the same designation within a general formula, may have meanings in the context of their definition which are identical to or different from each other.

Examples of alkali-eliminable substituents in the β -position of ethyl Y are halogen atoms, such as bromine and chlorine, ester groups of organic carboxylic and sulfonic acids, as of alkylcarboxylic acids, substituted or unsubstituted benzenecarboxylic acids and substituted or unsubstituted benzenesulfonic acids, such as alkanoyloxy of 2 to 5 carbon atoms, especially acetyloxy, benzoyloxy, sulfobenzoyloxy, phenylsulfonyloxy and toluylsulfonyloxy; further acidic ester groups of inorganic acids, as of phosphoric acid, sulfuric acid and thiosulfuric acid (phosphato, sulfato and thiosulfato groups), similarly dialkylamino groups having alkyl groups of 1 to 4

carbon atoms each, such as dimethylamino and diethylamino. Y is preferably β -sulfatoethyl, β -chloroethyl or vinyl, particularly preferably β -sulfatoethyl or vinyl.

The dyes of the general formulae (I) and (II) may have the same chromophore, but differ with regard to the structure of the fiber-reactive groups $-\text{SO}_2\text{-Y}$. More particularly, dye mixtures according to the invention may include dyes of the same chromophore conforming to the general formula (I) and dyes of the same chromophore conforming to one of the general formulae (II) where the fiber-reactive groups $-\text{SO}_2\text{-Y}$ are partly vinylsulfonyl groups and partly ethyl which contains in the β -position a substituent which is eliminable by means of alkali to leave a vinyl group, for example β -chloroethylsulfonyl or thiosulfatoethylsulfonyl or preferably β -sulfatoethylsulfonyl groups. If the dye mixtures include the respective dye components in the form of a vinylsulfonyl dye, then the fraction of the respective vinylsulfonyl dye to the respective β -ethyl-substituted dye is up to about 30 mol%, based on the respective dye chromophore.

Preference here is given to those dye mixtures according to the invention in which the fraction of vinylsulfonyl dyes relative to β -ethyl-substituted dyes is in a molar ratio between 5:95 and 30:70.

The groups "sulfo", "carboxyl", "thiosulfato", "phosphato" and "sulfato" include not only their acid form but also their salt form. Accordingly, sulfo groups are groups conforming to the general formula $-\text{SO}_3\text{M}$, carboxyl groups are groups conforming to the general formula $-\text{COOM}$, thiosulfato groups are groups conforming to the general formula $-\text{S-SO}_3\text{M}$, phosphato groups are groups conforming to the general formula $-\text{OPO}_3\text{M}_2$ and sulfato groups are groups conforming to the general formula $-\text{OSO}_3\text{M}$, each of which M is as defined above. Alkali metal M is particularly lithium, sodium and potassium. M is particularly preferably hydrogen and sodium.

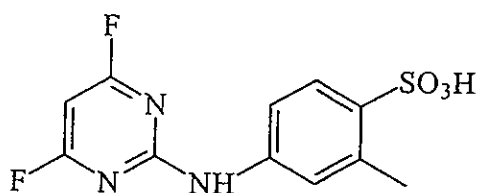
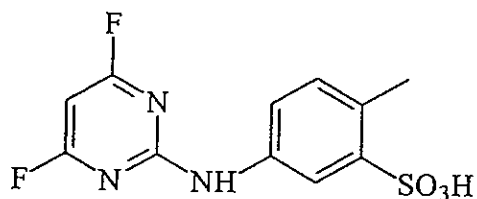
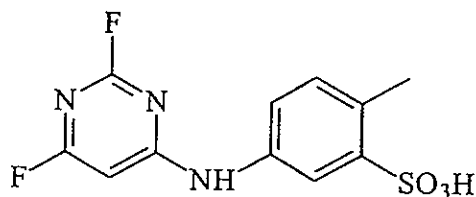
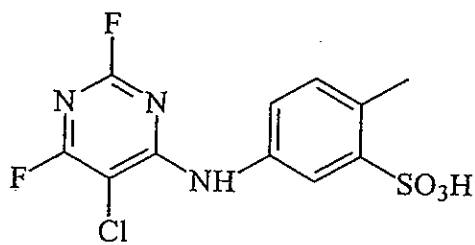
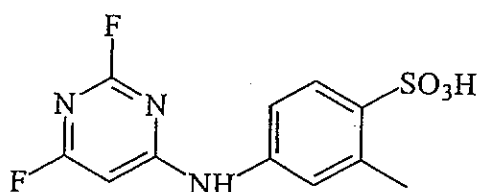
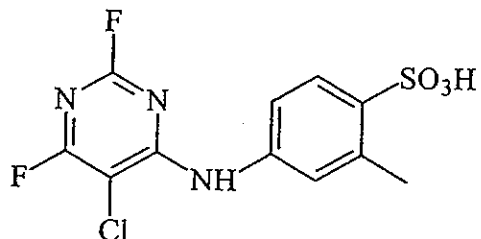
(C₁-C₄)-Alkyl R₉ may be straight-chain or branched and is in particular methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

Groups of the general formulae (1a) and (1b) are for example 3-(β -sulfatoethylsulfonyl)phenyl, 4-(β -sulfatoethylsulfonyl)phenyl, 2-methyl-5-methoxy-4-(β -sulfatoethylsulfonyl)phenyl, 2-methoxy-5-(β -sulfatoethylsulfonyl)-phenyl, 2,5-dimethoxy-4-(β -sulfatoethylsulfonyl)phenyl, 1-sulfo-6-(β -sulfatoethylsulfonyl)naphth-2-yl, 6-sulfo-8-(β -sulfatoethylsulfonyl)naphth-2-yl, 8-sulfo-6-(β -sulfatoethylsulfonyl)naphth-2-yl and their vinylsulfonyl and β -thiosulfatoethylsulfonyl derivatives, and also 1,5-disulfonaphth-2-yl, 1-sulfonaphth-2-yl,

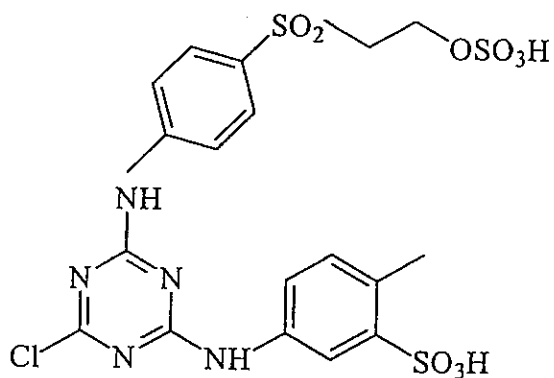
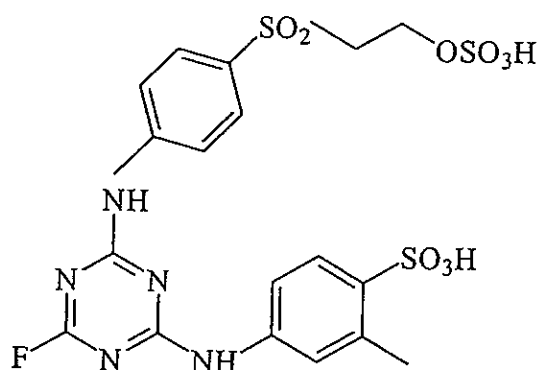
4-methyl-2-sulfophenyl and 2-sulfophenyl. Preference is given to 4-methyl-2-sulfophenyl,

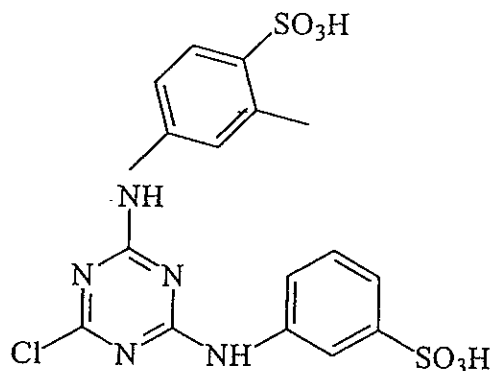
4-(β -sulfatoethylsulfonyl)phenyl, 1,5-disulfonaphth-2-yl, 1-sulfonaphth-2-yl and 1-sulfo-6-(β -sulfatoethylsulfonyl)naphth-2-yl.

Groups of the general formula (1c) conform for example to the formulae



Groups of the general formula (1d) conform for example to the formulae

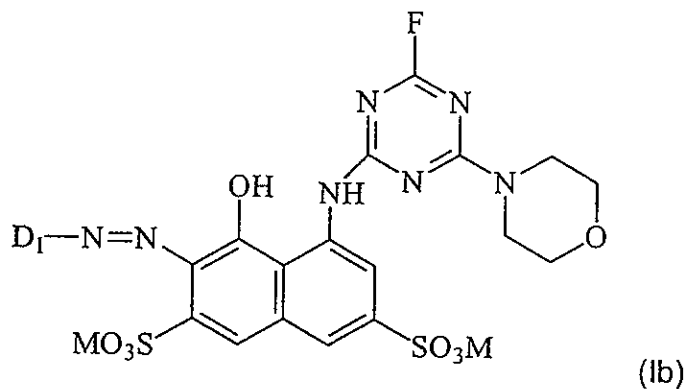
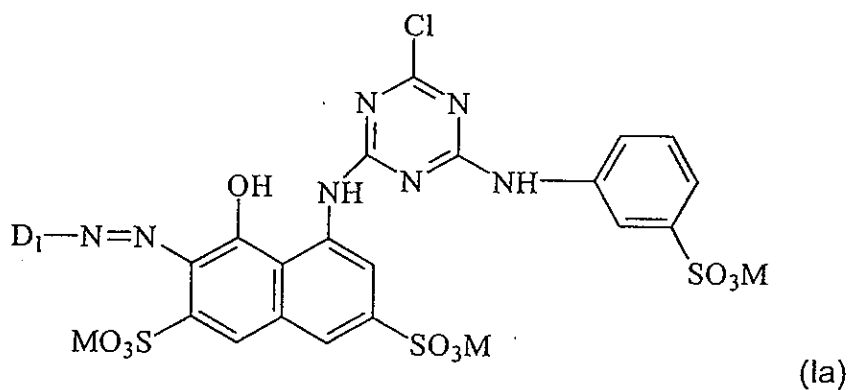




Radicals of the general formulae (2a), (2b) and (2c) are for example γ -(β -sulfatoethylsulfonyl)propylamino, N-methyl-N-[β -(β' -sulfatoethylsulfonyl)ethyl]-amino, 3-sulfophenylamino, 2,5-disulfophenylamino, 2-sulfophenylamino, 3-(β -sulfatoethylsulfonyl)phenylamino, 4-(β -sulfatoethylsulfonyl)phenylamino, N-methylaniline and N-ethylaniline.

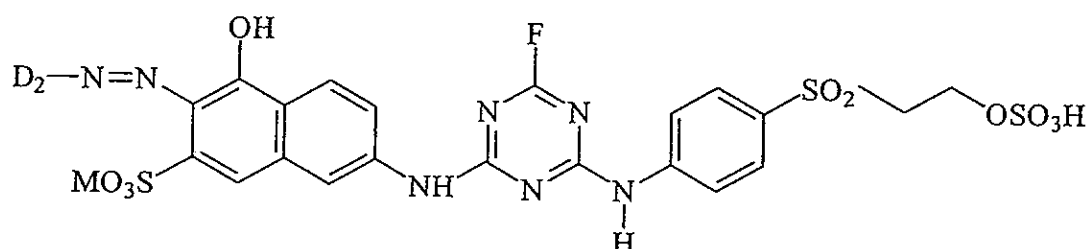
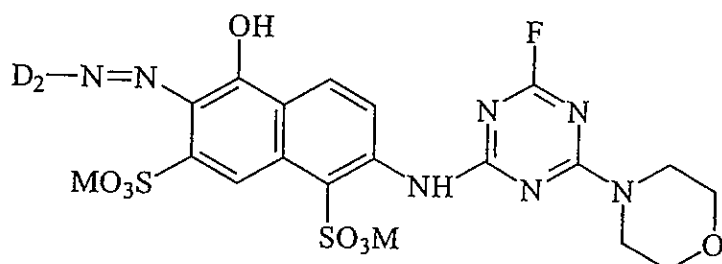
In the general formulae (IIa), (IIb) and (IIc), the -NH- group is preferably in position 3 on the 8-hydroxynaphthalene radical. In the general formula (IIc), p_2 is preferably zero.

Preferred dyes of the general formula (I) are those of the general formulae (Ia) and (Ib)

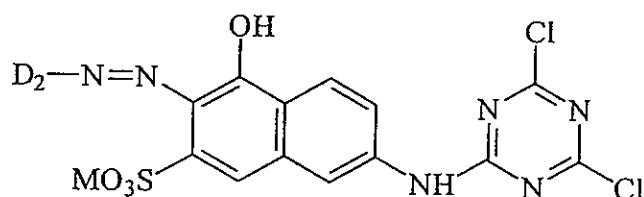


where D_1 and M are each as defined above.

Preferred dyes of the general formula (IIa) have the formula



or



where D_2 is as defined above.

Preferred dyes of the general formulae (IIb) and (IIc) are those wherein D_3 and D_4 are each 2-sulfo-4-methylphenyl, 2-sulfo-4-methoxyphenyl, 2,5-disulfo-4-methoxyphenyl or 1,5-disulfonaphth-2-yl, p_1 is 1, the sulfo group is in position 4 on the 8-naphthol radical, the triazinyl or pyrimidinyl group is in position 2 or 3, especially position 3, on the 8-naphthol radical, Z_3 is chlorine and especially fluorine and R_2 is a group of the general formula (2b) where R_9 is methyl and b is 2.

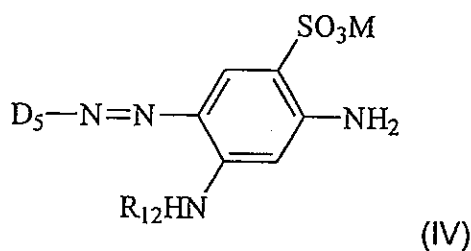
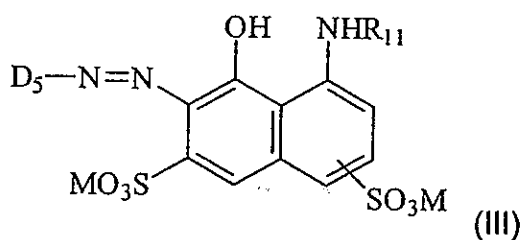
Preference is given to dye mixtures of the invention including one or more dyes of the general formula (I) where D_1 is one of the groups of the formulae (1a) and (1b) and one or more dyes of the general formula (IIa) where D_2 is 3- or 4-(vinylsulfonyl)-phenyl or 3 or 4-(β -sulfatoethylsulfonyl)phenyl, Z_2 is chlorine and R_1 is chlorine or 3-sulfophenylamino, subject to the proviso that when not only vinylsulfonyl but also

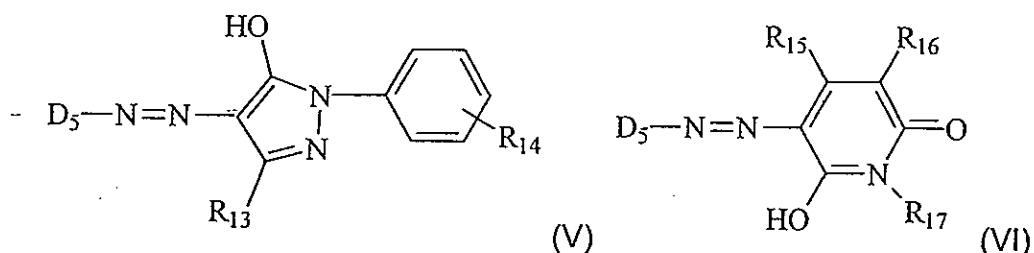
β -sulfatoethylsulfonyl groups are present in the dye mixtures the molar ratio between the vinylsulfonyl fractions and the β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.

Preference is further given to dye mixtures of the invention including one or more dyes of the general formula (I) of the above-indicated, especially preferred, meaning and one or more dyes of the general formula (IIc) where D_4 is 1,5-disulfonaphth-2-yl or 4-methyl-2-sulfophenyl, p_3 is 1, subject to the proviso that when not only vinylsulfonyl but also β -chloroethylsulfonyl or β -sulfatoethylsulfonyl groups are present in the dye mixtures the molar ratio between the vinylsulfonyl fractions and the β -chloroethylsulfonyl or β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.

Preference is also given to dye mixtures of the invention which include one or more dyes of the general formula (1) of the abovementioned, especially preferred, meaning and one or more dyes of the general formula (IIb) where D_3 is 2-sulfo-4-methylphenyl, 2-sulfo-4-methoxyphenyl or 1,5-disulfonaphth-2-yl, Z_3 is fluorine and R_2 is γ -(β -sulfatoethylsulfonyl)propylamino, N-methyl- β -(β' -sulfatoethylsulfonyl)-ethylamino or 4-(β -sulfatoethylsulfonyl)phenylamino, subject to the proviso that when not only vinylsulfonyl but also β -sulfatoethylsulfonyl groups are present in the dye mixtures, the molar ratio between the vinylsulfonyl fractions and the β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.

The dye mixtures of the invention may additionally be shaded with a yellow or red dye in amounts of up to 10% by weight, preferably up to 5% by weight. Such known dyes are for example monoazo dyes conforming to the general formulae (III), (IV), (V) and (VI)





where

D^5 is 3-(β -sulfatoethylsulfonyl)phenyl, 4-(β -sulfatoethylsulfonyl)phenyl, 3-vinylsulfonylphenyl, 4-vinylsulfonylphenyl, 2-methoxy-5-(β -sulfatoethylsulfonyl)phenyl or 2-methoxy-5-vinylsulfonylphenyl;

M is as defined above;

R^{11} is acetyl, benzoyl, 4,6-di-cyanamido-1,3,5-triazin-2-yl, 4-cyanamido-6-(sulfophenylamino)-1,3,5-triazin-2-yl, 4-(N-morpholino)-6-(sulfophenylamino)-1,3,5-triazin-2-yl or 4-(N-morpholino)-6-(sulfophenylamino)-1,3,5-triazin-2-yl which is substituted by methyl or methoxy in the benzene nucleus;

R^{12} is acetyl, carbamoyl, 4,6-di-cyanamido-1,3,5-triazin-2-yl, 4-cyanamido-6-(sulfophenylamino)-1,3,5-triazin-2-yl, 4-(N-morpholino)-6-(sulfophenylamino)-1,3,5-triazin-2-yl or 4-(N-morpholino)-6-(sulfophenylamino)-1,3,5-triazin-2-yl which is substituted by methyl or methoxy in the benzene nucleus,

R^{13} is methyl or carboxyl;

R^{14} is sulfo, β -chloroethylsulfonyl or β -sulfatoethylsulfonyl;

R^{15} is hydrogen or methyl;

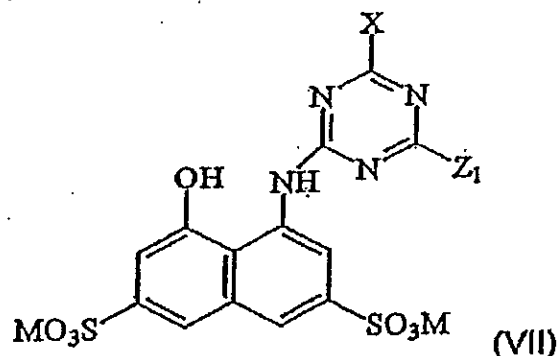
R^{16} is hydrogen, cyano, carbamoyl, carboxyl or sulfomethyl; and

R^{17} is methyl, ethyl or β -sulfoethyl.

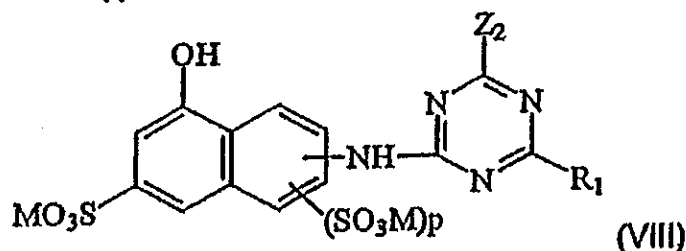
The dye mixtures of the invention may be present as preparations in solid or liquid (dissolved) form. They generally include the electrolyte salts customary in the case of water-soluble and especially fiber-reactive dyes, such as sodium chloride, potassium chloride and sodium sulfate, and may further include the auxiliaries customary in commercial dyes, such as buffer substances capable of setting a pH in aqueous solution between 3 and 7, such as sodium acetate, sodium borate, sodium bicarbonate, sodium dihydrogenphosphate and disodium hydrogenphosphate, small amounts of siccatives or, if they are present in liquid, aqueous solution (including the presence of thickeners of the type customary in print pastes), they may also include substances which ensure a long life for these preparations, for example mold preventatives.

Generally the dye mixtures are present as dye powders containing 10 to 80% by weight, based on the dye powder or preparation, of an electrolyte salt which is also known as a standardized agent. These dye powders may additionally include the aforementioned buffer substances in a total amount of up to 5%, based on the dye powder. If the dye mixtures of the invention are present in aqueous solution, then these aqueous solutions contain the mixtures of the invention in an amount between 0.1 and 55% by weight, typically between 5 and 50% by weight, and the electrolyte salt content of these aqueous solutions is preferably below 10% by weight, based on the aqueous solution. The aqueous solutions (liquid preparations) include the aforementioned buffer substances in an amount which is typically within the range from 0.1 to 5% by weight, preferably within the range from 0.3 to 2% by weight.

The dye mixtures of the invention are preparable in a conventional manner, for example by mechanically mixing the individual dyes in the requisite fractions or, if D_1 is equal to D_2 , by synthesis by means of the customary diazotization and coupling reactions using appropriate mixtures of the diazo and coupling components in the requisite fractions and in a manner familiar to the person skilled in the art. In an example of a possible procedure, aqueous solutions of mixtures of two appropriate coupling components, for instance a compound of the general formula (VII)



where M, X and Z_1 are each as defined above, as coupling component of the dyes of the general formula (I) and a compound of the general formula (VIII)



where M, R₁, Z₂ and p are each as defined above, and aqueous solutions or suspensions of the diazo components of the general formula D₁-NH₂ equal to D₂-NH₂, where D₁ and D₂, respectively, are each as defined above, are reacted (coupled) with each other in the appropriate proportions at a pH between 3 and 7. The resulting dye mixture may be isolated from the solution in a conventional manner, for example by salting out with an electrolyte salt, such as sodium chloride, potassium chloride or lithium chloride, or by spray drying.

When the dye mixtures of the invention are prepared by mechanically mixing the individual dyes, it is customary for any necessary standardizing, dustproofing or other auxiliary agents typical in dyeing technology or the dye preparations used for this purpose to be added during the mixing.

Dye mixtures in which the dye chromophores, as well as a β -chloroethylsulfonyl or β -thiosulfatoethylsulfonyl or β -sulfatoethylsulfonyl group, additionally include for example fractions containing vinylsulfonyl groups, as well as by the abovementioned method involving the use of appropriate vinylsulfonyl starting anilines, may also be prepared by reacting the dye mixture in which Y is a β -chloroethyl or β -thiosulfatoethyl or β -sulfatoethyl radical with an amount of alkali sufficient for only a portion of these groups and converting a portion of the β -substituted ethylsulfonyl groups mentioned into vinylsulfonyl groups. This measure is carried out according to generally known methods for converting β -substituted ethylsulfonyl groups into vinylsulfonyl.

The dye mixtures of the invention comprising the dyes of the formulae (I) and (II) dye hydroxyl- and/or carboxamido-containing fiber materials by the application and fixing methods extensively described in the art for fiber-reactive dyes in orange to scarlet-colored shades with good color buildup and good washoff properties with regard to unfixed dye portions. Moreover, the dyeings obtained are readily dischargeable and the dye mixtures of the invention are very useful as combination dyes in combination dyeings with other dyes.

The present invention therefore also provides for the use of the dye mixtures of the invention for dyeing (including printing and combination dyeing) hydroxyl- and/or carboxamido-containing fiber materials, or rather processes for dyeing such fiber materials using a dye mixture according to the invention by applying it in dissolved form to the substrate and fixing the dyes on the fiber by the action of an alkaline agent or by heat or by both measures.

Hydroxyl-containing materials are natural or synthetic hydroxyl-containing materials, for example cellulose fiber materials, including in the form of paper, or regenerated cellulose products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton, but other vegetable fibers as well, such as linen, hemp, jute and ramie fibers. Examples of regenerated cellulose fibers are staple viscose and filament viscose.

Examples of carboxamido-containing materials are synthetic and natural polyamides and polyurethanes, especially in the form of fibers, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11 and nylon-4.

The dye mixtures of the invention are used according to generally known methods for dyeing and printing fiber materials as per the known application techniques for fiber-reactive dyes. Since the dyes in the dye mixtures of the invention are highly compatible with each other, the dye mixtures of the invention can also be employed with advantage in exhaust dyeing processes. Applied in this way by exhaust dyeing processes for example to cellulose fibers from a long liquor at temperatures between 40 and 105°C, if appropriate at temperatures up to 130°C under superatmospheric pressure, and in the presence or absence of customary dyeing assistants with the use of acid-binding agents and, if appropriate neutral salts such as sodium chloride or sodium sulfate, they produce dyeings in very good color yields and with excellent color buildup and on-tone hue. One possible procedure is to introduce the material into the warm bath, and to gradually heat the bath to the desired dyeing temperature and to complete the dyeing process at that temperature. The neutral salts which accelerate the exhaustion of the dyes may also, if appropriate, not be added to the bath until the actual dyeing temperature has been reached.

Similarly, the customary printing processes for cellulose fibers, which can be carried out in single phase, for example by printing with a print paste which includes sodium bicarbonate or some other acid-binding agent as well as the colorant and subsequent steaming at 100 to 103°C, or in two phases, for example by printing with the neutral or weakly acidic print paste containing the colorant and subsequently fixing either by passing the printed material through a hot electrolyte-containing alkaline bath or by overpadding with an alkaline electrolyte-containing padding liquor with subsequent batching of this treated material or subsequent steaming or subsequent treatment with dry heat, produce strong prints with well defined contours and a clear white ground. The outcome of the prints is not greatly affected by variations in the fixing conditions. The degrees of fixation obtained with the dye

mixtures of the invention are very high not only in dyeing but also in printing. When fixing by means of dry heat as per the customary thermofix processes, hot air at 120 to 200°C is used. In addition to the customary steam at 101 to 103°C it is also possible to use superheated steam and high-pressure steam at temperatures of up to 160°C.

The acid-binding agents which effect the fixation of the dyes of the cellulose fibers include for example water-soluble basic salts of the alkali metals and the alkaline earth metals of inorganic or organic acids and likewise compounds which release alkali when hot.

The alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids are particularly useful, preferred alkali metal compounds being the sodium and potassium compounds. Such acid-binding agents include for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate and disodium hydrogenphosphate.

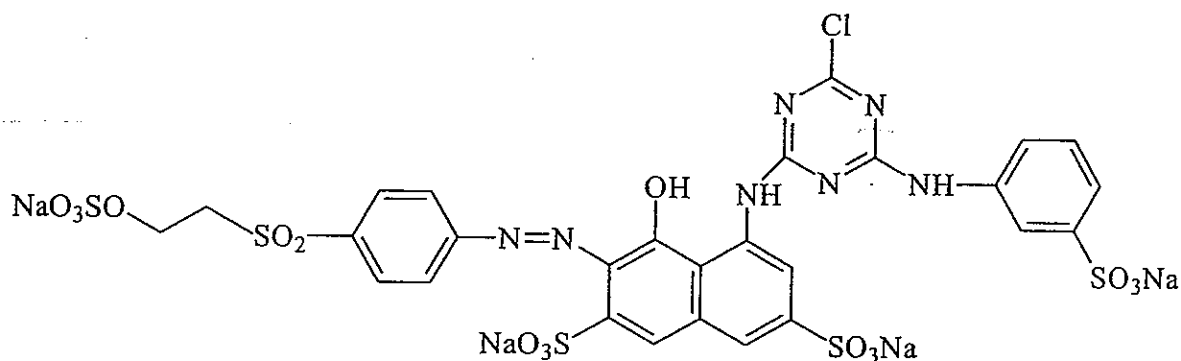
Treating the dyes of the dye mixtures of the invention with the acid-binding agents with or without heating binds the dyes chemically to the cellulose fiber. Cellulose dyeings in particular, following the customary aftertreatment of rinsing to remove unfixed dye portions, exhibit very good wet fastnesses, in particular since such unfixed dye portions are easily washed off on account of their good solubility in cold water.

Dyeings on polyurethane and polyamide fibers are customarily carried out from an acidic medium. For instance, the dyebath may include acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate in order to obtain the desired pH. To achieve useful levelness for the dyeing, it is advisable to add customary leveling aids, for example based on a reaction product of cyanuric chloride with three times the molar amount of an aminobenzenesulfonic acid or aminonaphthalenesulfonic acid or based on a reaction product of for example stearylamine with ethylene oxide. Generally the material to be dyed is introduced into the bath at a temperature of about 40°C, agitated therein for some time, then the dyebath is adjusted to the desired weakly acidic pH, preferably weakly acetic acid, and the actual dyeing is carried out at a temperature of between 60 and 98°C. However, the dyeings can also be carried out at boiling point or at temperatures of up to 120°C (under pressure).

The examples hereinbelow illustrate the invention. Parts and percentages are by weight, unless otherwise stated. Parts by weight relate to parts by volume as the kilogram relates to the liter.

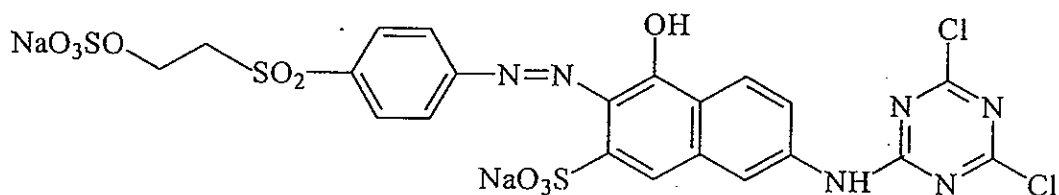
Example 1

440 parts of an electrolyte-containing dye powder which contains the red azo dye of the formula (A)



(A)

in a fraction of 68% are mixed with 72.6 parts of an electrolyte-containing dye powder which contains the orange monoazo dye of the formula (B)



(B)

in a fraction of 50% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fibers, for example, dyeings and prints in deep orange shades.

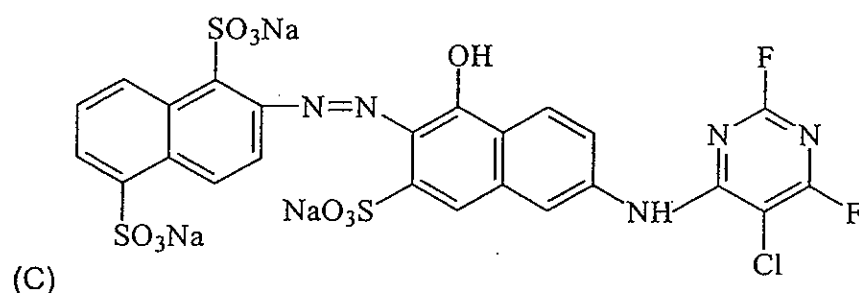
Example 2

A dye mixture according to the invention is prepared by adjusting a suspension of 288 parts of 4-(β -sulfatoethylsulfonyl)aniline in 250 parts of water to a pH of 4.5 to 5 with about 59 parts of sodium carbonate, diazotizing the aniline compound with 186 parts by volume of a 38% strength aqueous sodium nitrite solution following addition of 234 parts by volume of 30% strength aqueous hydrochloric acid and 400 parts of ice, adding 242 parts of 1-N-(2'-(3''-sulfophenylamino)-4'-chloro-1',3',5'-triazin-6'-yl)amino-8-hydroxy-3,6-disulfonaphthalene, 232 parts of 6-(4,6-dichlorotriazin-2-yl)amino-1-hydroxy-naphthalene-3-sulfonic acid, setting a pH of 5 to 6 by means of sodium carbonate, and conducting the coupling reaction at 20°C and within this pH

range to obtain a dye solution which includes the dyes of the formulae (A) and (B) mentioned in Example 1 in a ratio of 40:60. This dye solution may be adjusted to a pH of 4.5 by addition of 5 parts of sodium phosphate buffer. By further diluting with water or by evaporating the solution, this liquid dye mixture may then be standardized to the desired strength for a liquid preparation, which in a conventional manner is used either directly, if appropriate after addition of the corresponding amount of an alkaline agent, as dyebath or dyeing liquor or may be used to prepare a dyebath or dyeing liquor. This dye mixture provides deep orange dyeings.

Example 3

750 parts of an electrolyte-containing dye powder which contains the red azo dye of the formula (A) indicated in Example 1 in a fraction of 68% are mixed with 250 parts of an electrolyte-containing dye powder which contains the orange monoazo dye of the formula (C)



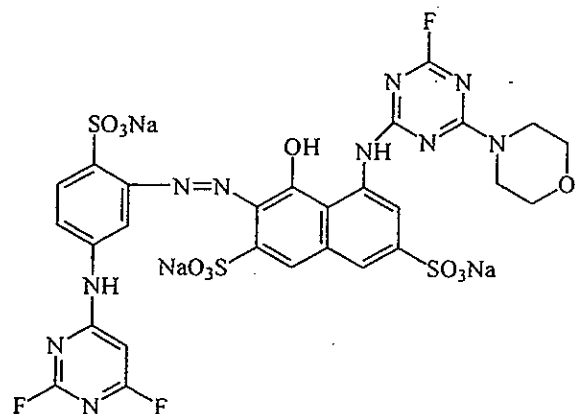
in a fraction of 56% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fiber materials, for example, strong dyeings and prints in deep orange shades.

Example 4

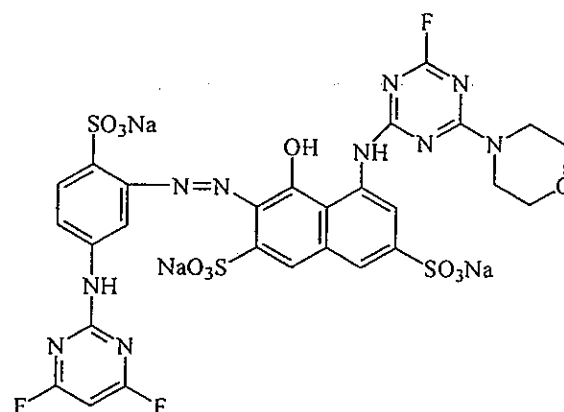
300 parts of an electrolyte-containing dye powder which contains the red azo dye of the formula (A) indicated in Example 1 in a fraction of 68% are mixed with 700 parts of an electrolyte-containing dye powder which contains the orange monoazo dye of the formula (C) in a fraction of 56% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fiber materials, for example, strong dyeings and prints in deep scarlet shades.

Example 5

152.6 parts of an electrolyte-containing dye powder which contains the red azo dye of the formula (Da) in a fraction of 39% and the red azo dye (Db) in a fraction of 11%



(Da)

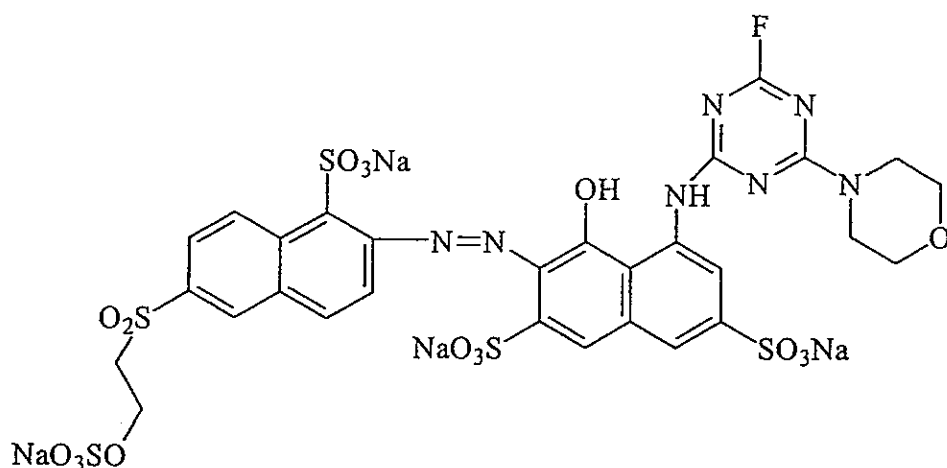


(Db)

are mixed with 29.0 parts of an electrolyte-containing dye powder which contains the orange monoazo dye of the formula (C) indicated in Example 3 in a fraction of 56% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fiber materials, for example, dyeings and prints in deep scarlet shades.

Example 6

110 parts of an electrolyte-containing dye powder which contains the red azo dye of the formula (E)

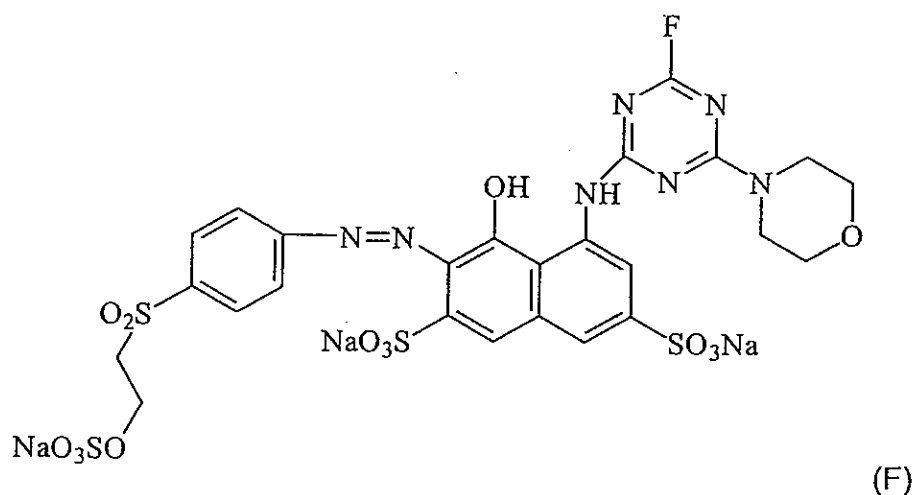


(E)

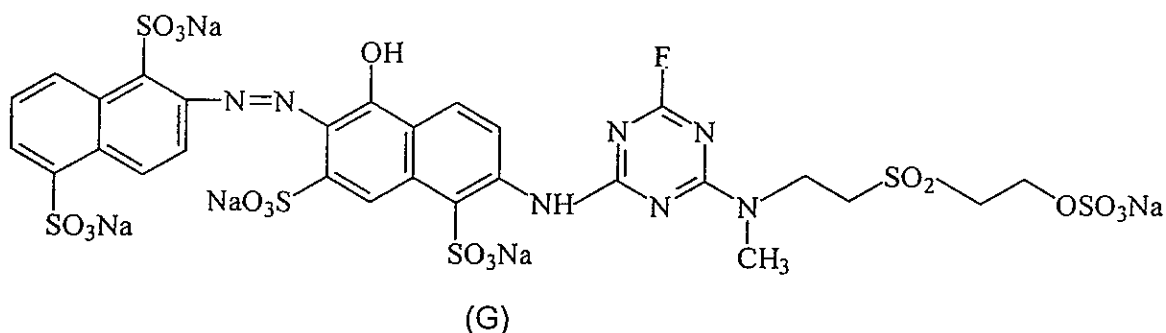
in a fraction of 50% are mixed with 21.8 parts of an electrolyte-containing dye powder which contains the orange monoazo dye of the formula (C) indicated in Example 3 in a fraction of 50% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fiber materials, for example, dyeings and prints in deep orange shades.

Example 7

270 parts of an electrolyte-containing dye powder which contains the red dye of formula (F)



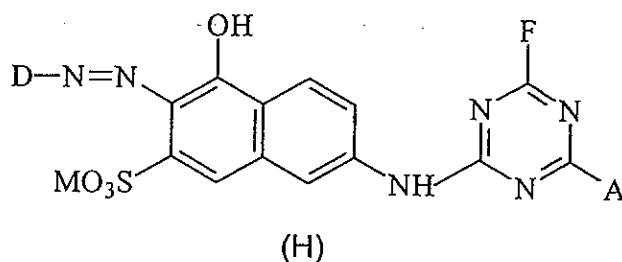
in a fraction of 50% are mixed with 72.6 parts of an electrolyte-containing dye powder which contains the orange dye of the formula (G)



in a fraction of 50% in a mechanical mixer. The resulting dye mixture of the invention, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produces on cellulose fibers, for example, dyeings and prints in deep scarlet shades.

Examples 8 to 18

The table examples hereinbelow describe further dye mixtures according to the invention comprising the dye of the formula (A) and a dye conforming to the general formula (H)



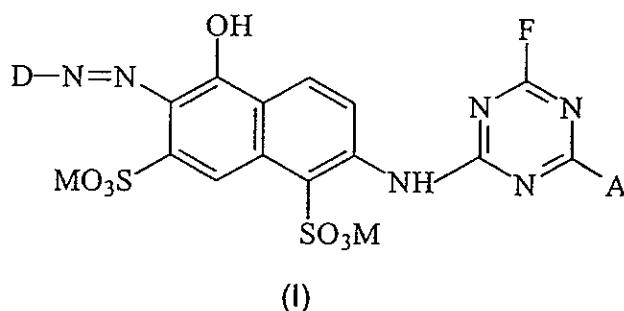
where M is as defined above and D and A are each as defined in the respective table example. These dye mixtures, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produce on the fiber materials mentioned in the description, for example, cellulose fiber materials, strong level dyeings having the hue indicated in the particular table example for cotton.

Ex.	Dye of formula (H)		Ratio of (A):(H) in mixture in % by weight	Hue
	D	A		
8	1,5-disulfonaphth-2-yl	γ -(β' -sulfatoethylsulfonyl)propylamino	75 : 25	scarlet
9	ditto	ditto	50 : 50	orange
10	ditto	ditto	65 : 35	reddish orange
11	ditto	N-phenyl-N-[β -(β' -sulfatoethylsulfonyl)-ethyl]amino	55 : 45	orange
12	4-methyl-2-sulfophenyl	ditto	70 : 30	scarlet
13	ditto	N-(methyl)-N-[β -(β' -sulfatoethylsulfonyl)-ethyl]amino	60 : 40	orange
14	ditto	ditto	75 : 25	scarlet
15	1,5-disulfonaphth-2-yl	4-(β -sulfatoethylsulfonyl)phenylamino	60 : 40	orange

Ex.	Dye of formula (H)		Ratio of (A):(H) in mixture in % by weight	Hue
	D	A		
16	ditto	ditto	65 : 35	scarlet
17	ditto	?	60 : 40	orange
18	ditto	ditto	50 : 50	orange

Examples 19 to 29

The table examples hereinbelow describe further dye mixtures according to the invention comprising the dye of the formula (A) and a dye conforming to the general formula (I)



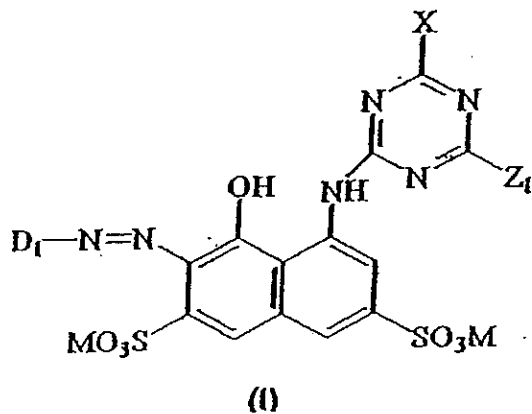
where M is as defined above and D and A are each as defined in the respective table example. These dye mixtures, when employed according to the application and fixing methods customary in the art for fiber-reactive dyes, produce on the fiber materials mentioned in the description, for example, cellulose fiber materials, strong level dyeings having the hue indicated in the particular table example for cotton.

Ex.	Dye of formula (I)		Ratio of (A):(I) in mixture in % by weight	Hue
	D	A		
19	1,5-disulfonaphth-2-yl	N-methyl-N-(β -(β 'sulfatoethylsulfonyl)ethyl)amino	60 : 40	orange
20	4-methyl-2-sulfophenyl	ditto	75 : 25	scarlet

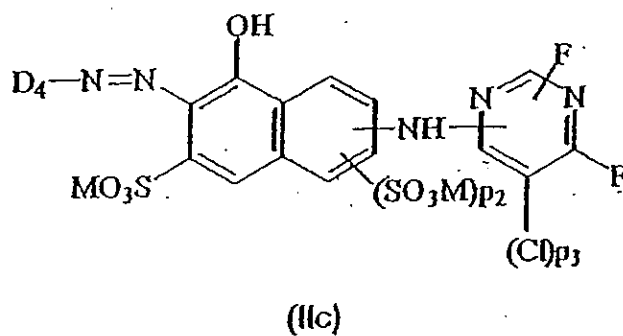
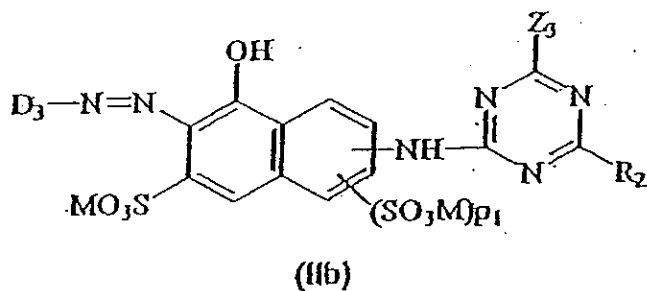
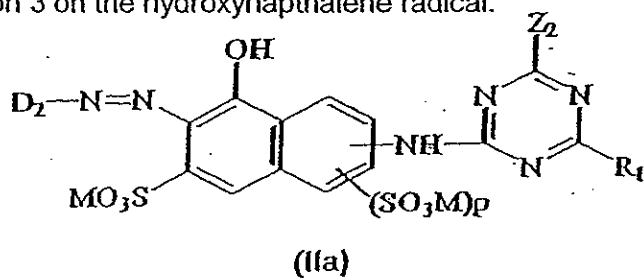
Ex.	Dye of formula (I)		Ratio of (A):(I) in mixture in % by weight	Hue
	D	A		
21	4-methoxy-2-sulfophenyl	ditto	60 : 40	orange
22	ditto	ditto	75 : 25	scarlet
23	1-sulfo-6-(β -sulfatoethylsulfonyl)naphth-2-yl	morpholino	60 : 40	orange
24	ditto	ditto	70 : 30	scarlet
25	ditto	N-methyl-(β -(β' -sulfatoethylsulfonyl)-ethyl)amino	60 : 40	orange
26	ditto	ditto	75 : 25	scarlet
27	1,5-disulfonaphth-2-yl	bis-N,N-(β -vinylsulfonyl)ethyl)amino	65 : 35	reddish orange
28	ditto	ditto	75 : 25	scarlet
29	ditto	3-(β -sulfatoethylsulfonyl)phenylamino	60 : 40	orange

What is claimed is:

1. An orange-or scarlet-colored dye mixture including one or more of the dyes of the general formula (I)

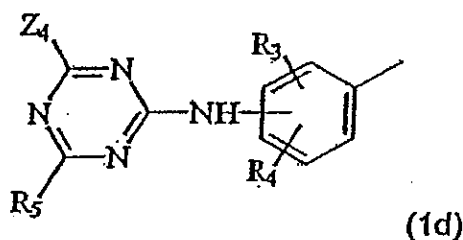
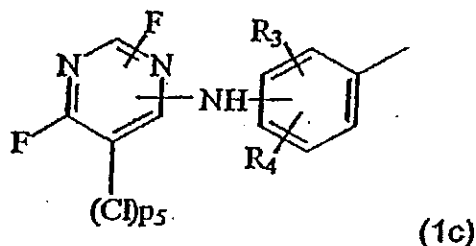
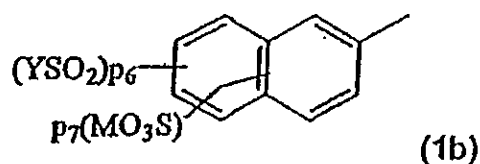
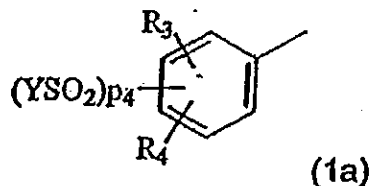


and one or more of the dyes of the general formulae (IIa), (IIb), and (IIc), and the -NH group in (IIa) and (IIb) in position 3 on the hydroxynaphthalene radical.



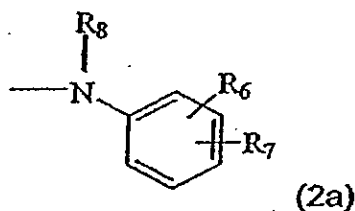
where

D₁ and D₂ are independently a group of the general formulae (1a), (1b), (1c) or (1d)



where

- R³ is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxyl;
- R⁴ is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo;
- R⁵ is hydroxyl, phenoxy, morpholino, a group of the general formula (2a)

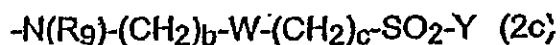
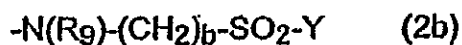


where

R⁶ is hydrogen, methyl, ethyl, methoxy, ethoxy, hydroxyl, sulfo, carboxyl or a group $-(CH_2)_a-SO_2-Y$, where a is 0, 1, 2 or 3 and Y is as defined hereinbelow;

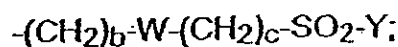
R⁷ is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo and

R⁸ is hydrogen, methyl, ethyl or β -sulfoethyl, or a group of the general formula (2b) or (2c)



where

R₉ is hydrogen, phenyl, phenyl substituted by 1 or 2 substituents selected from the group consisting of methyl, ethyl, methoxy, ethoxy, sulfo and carboxyl, (C₁-C₄)-alkyl or a group of the formula



b is 0, 1, 2 or 3;

c is 2 or 3; and

Y is as defined hereinbelow;

Z_4 is chlorine or fluorine;

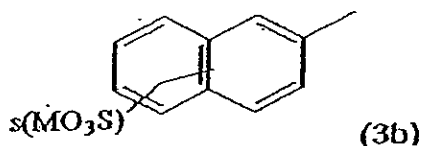
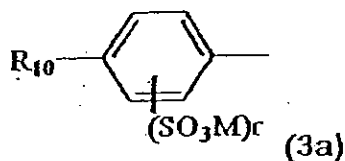
Y is vinyl or is ethyl which in the β -position contains a substituent which is eliminable by alkali to leave a vinyl group;

p_4, p_5 are independently 0 or 1; p_6 is 1; and

p_7 is 0, 1 or 2;

and M is as defined hereinbelow;

D_3 and D_4 are independently a group of the general formulae (3a) or (3b)



where

R_{10} is hydrogen, methyl, ethyl, methoxy or ethoxy;

r is 1 or 2; and

s is 1, 2 or 3;

and M is as defined hereinbelow;

Z_1 is chlorine or fluorine;

X is hydroxyl, morpholino, a group of the general formulae (2a), (2b) or (2c) or else, if Z_1 is chlorine, may also be chlorine;

Z_2 and Z_3 are independently chlorine or fluorine;

R_1 is hydroxyl, phenoxy, morpholino or a group of the general formula (2a) and, if Z_2 is chlorine, may also be chlorine;

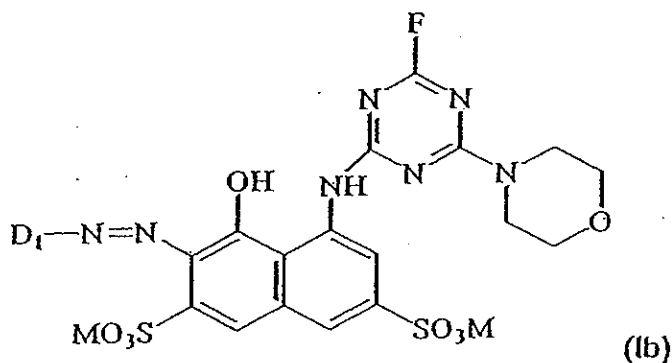
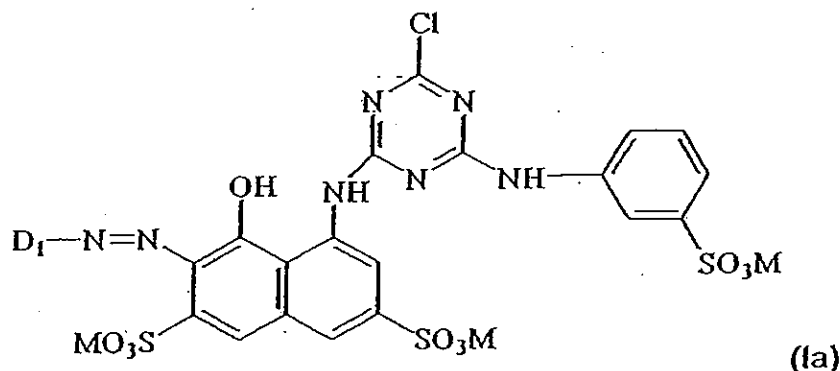
R_2 is a group of the general formulae (2a), (2b) or (2c);

M is hydrogen or an alkali metal; and

p, p_1, p_2 and p_3 are independently 0 or 1.

2. An orange-or scarlet-colored dye mixture as claimed in claim 1, including the dye or dyes of the general formula (I) in a fraction of 95 to 25% by weight and the dye or dyes of the general formula (II) in a fraction of 5 to 75% by weight, each percentage being based on the total amount of the dyes of the general formulae (I) and (II).

3. An orange-or scarlet-colored dye mixture as claimed in claim 1 and/or 2, wherein the dye of the general formula (I) conforms to the general formulae (Ia) or (Ib)



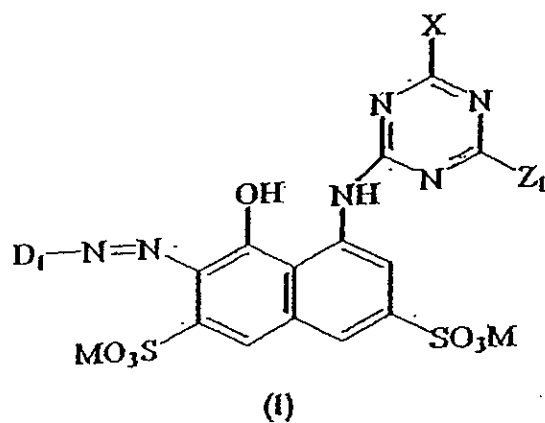
4. An orange-or scarlet dye mixture as claimed in one or more of claims 1 to 3, wherein D_1 and D_4 are each 2-sulfo-4-methylphenyl, 2-sulfo-4-methoxyphenyl, 2,5-disulfo-4-methoxyphenyl or 1,5-disulfonaphth-2-yl, p_1 is 1, the sulfo group is in position 4 on the 8-naphthol radical, the triazinyl or pyrimidinyl group is in position 2 or 3, especially position 3, on the 8-naphthol radical, Z_1 is chlorine and especially fluorine and R_2 is a group of the general formula (2b) where R_9 is methyl and b is 2.

5. An orange-or scarlet dye mixture as claimed in claim 1 and /or 2, including one or more dyes of the general formula (I) where D_1 is one of the groups of the formulae (Ia) and (Ib) and one or more dyes of the general formula (IIa) where D_2 is 3-or 4-(vinylsulfonyl)-phenyl or 3 or 4-(β -sulfatoethylsulfonyl)phenyl, Z_2 is chlorine and R_1 is chlorine or 3-sulfophenylamino, subject to the proviso that when not only vinylsulfonyl but also β -sulfatoethylsulfonyl groups are present in the dye mixture the molar ratio between the vinylsulfonyl fractions and the β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.

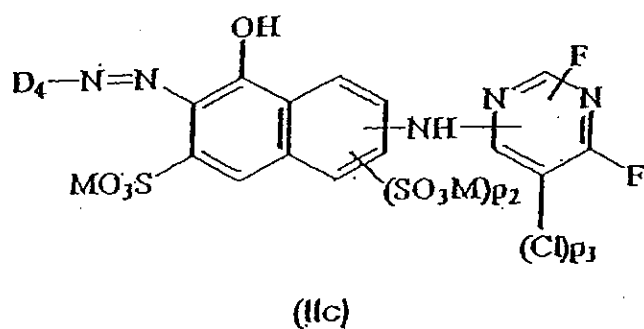
6. An orange-or scarlet dye mixture as claimed in one or more of claims 1 to 3, including one or more dyes of the general formula (IIc) where D_4 is 1,5-disulfonaphth-2-yl or 4-methyl-2-sulfophenyl, p_3 is 1, subject to the proviso that when not only vinylsulfonyl but also β -chloroethylsulfonyl or β -sulfatoethylsulfonyl groups are present in the dye mixtures the molar ratio between the vinylsulfonyl fractions and the β -chloroethylsulfonyl or β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.
7. An orange-or scarlet dye mixture as claimed in one or more of claims 1 to 3, including one or more dyes of the general formula (IIb) where D_3 is 2-sulfo-4-methylphenyl, 2-sulfo-4-methoxyphenyl or 1,5-disulfonaphth-2-yl, Z_3 is fluorine and R_2 is γ -(β -sulfatoethylsulfonyl) propylamino, N-methyl- β -(β -sulfatoethylsulfonyl) ethylamino or 4-(β -sulfatoethylsulfonyl) phenylamino, subject to the proviso that when not only vinylsulfonyl but also β -sulfatoethylsulfonyl groups are present in the dye mixtures the molar ratio between the vinylsulfonyl fractions and the β -sulfatoethylsulfonyl fractions is between 5:95 and 30:70.
8. An orange-or scarlet-colored dye mixture as claimed in one or more of claims 1 to 7, shaded with a yellow or red dye in amounts of up to 10% by weight, preferably up to 5% by weight.
9. A process for preparing a dye mixture as claimed in one or more of claims 1 to 8, which comprises dyes of the general formulae (I) and (II) being mechanically mixed in the requisite fractions or, if D_1 is equal to D_2 , being synthesized by means of the customary diazotization and coupling reactions using appropriate mixtures of the diazo and coupling components in the requisite fractions.
10. The method of using a dye mixture as claimed in one or more of claims 1 to 8 for dyeing hydroxyl- and/or carboxamido-containing fiber material.

27a

11. An orange-or scarlet-colored dye mixture of a dye having the general formula (I)



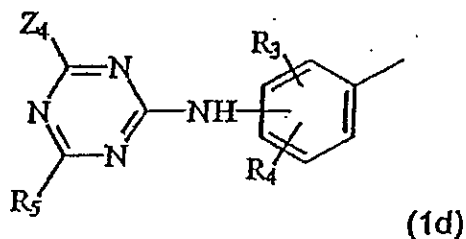
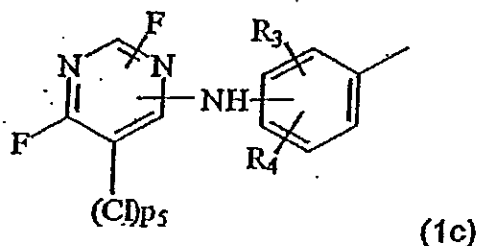
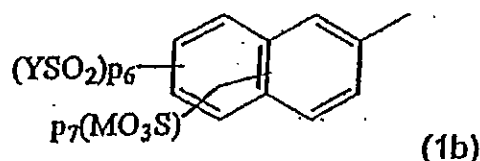
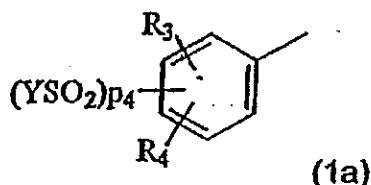
and a dye having the general formula (II.C)



wherein,

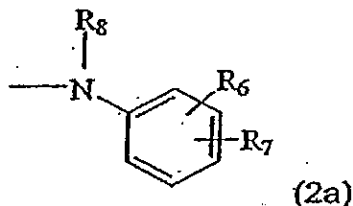
27b

D₁ is independently a group of the general formulae (1a), (1b), (1c) or (1d)



where

- R^3 is hydrogen, methyl, ethyl, methoxy, ethoxy, sulfo or carboxyl;
 R^4 is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo;
 R^5 is hydroxyl, phenoxy, morpholino, a group of the general formula (2a)

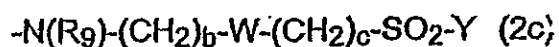


where

R^6 is hydrogen, methyl, ethyl, methoxy, ethoxy, hydroxyl, sulfo, carboxyl or a group $-(CH_2)_a-SO_2-Y$, where a is 0, 1, 2 or 3 and Y is as defined hereinbelow;

R^7 is hydrogen, methyl, ethyl, methoxy, ethoxy or sulfo and

R^8 is hydrogen, methyl, ethyl or β -sulfoethyl, or a group of the general formula (2b) or (2c)



where

R_9 is hydrogen, phenyl, phenyl substituted by 1 or 2 substituents selected from the group consisting of methyl, ethyl, methoxy, ethoxy, sulfo and carboxyl, (C_1-C_4) -alkyl or a group of the formula

27c

 $-(CH_2)_b-W-(CH_2)_c-SO_2-Y;$

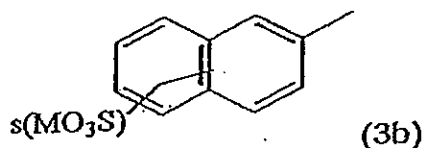
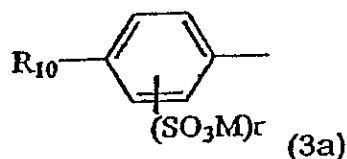
b is 0, 1, 2 or 3;

c is 2 or 3; and

Y is as defined hereinbelow;

Z₄ is chlorine or fluorine;Y is vinyl or is ethyl which in the β -position contains a substituent which is eliminable by alkali to leave a vinyl group;p₄, p₅ are independently 0 or 1; p₆ is 1; andp₇ is 0, 1 or 2;

and M is as defined hereinbelow;

D₃ and D₄ are independently a group of the general formulae (3a) or (3b)

where

R₁₀ is hydrogen, methyl, ethyl, methoxy or ethoxy;

r is 1 or 2; and

s is 1, 2 or 3;

and M is as defined hereinbelow;

is chlorine or fluorine;

is hydroxyl, morpholino, a group of the general formulae (2a), (2b) or (2c) or else, if Z₁ is chlorine, may also be chlorine;and Z₃ are independently chlorine or fluorine;

is hydroxyl, phenoxy, morpholino or a group of the general formula (2a) and, if

Z₂ is chlorine, may also be chlorine;

is a group of the general formulae (2a), (2b) or (2c);

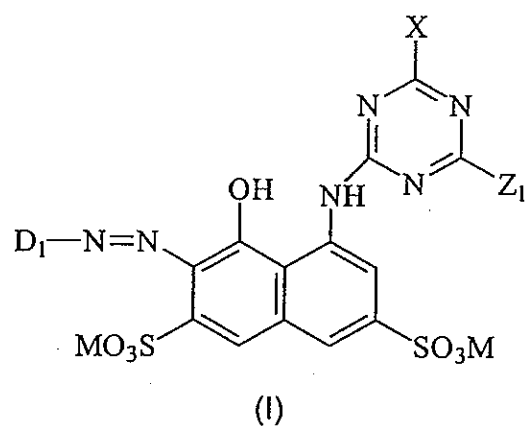
is hydrogen or an alkali metal; and

p₁, p₂ and p₃ are independently 0 or 1.

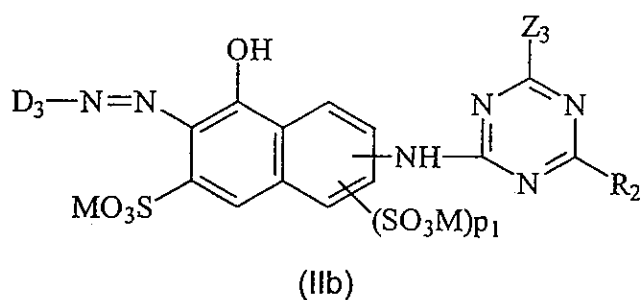
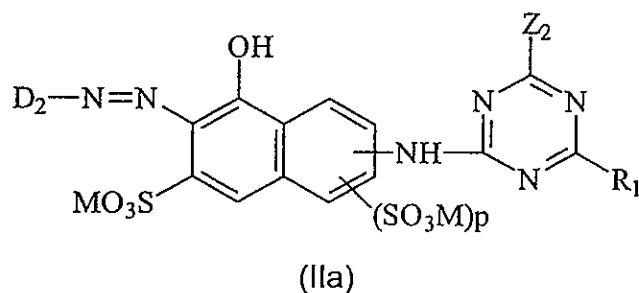
ABSTRACT

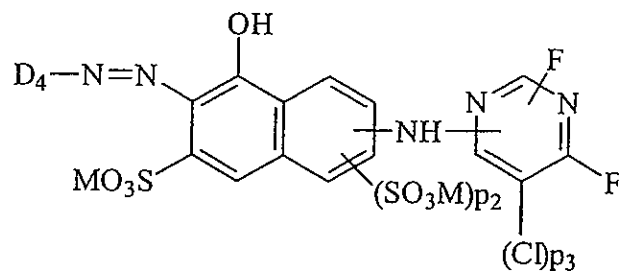
Orange- and scarlet-colored mixtures of reactive dyes

The present invention provides a dye mixture including one or more of the dyes of the general formula (I)



and one or more of the dyes of the general formulae (2a), (2b) and (2c)

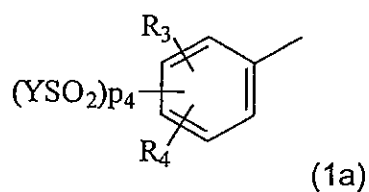




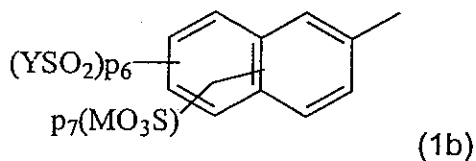
(IIc)

where

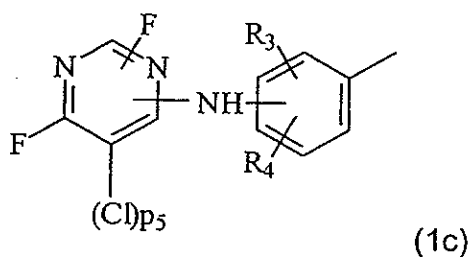
D₁ and D₂ are independently a group of the general formulae (1a), (1b), (1c) or (1d)



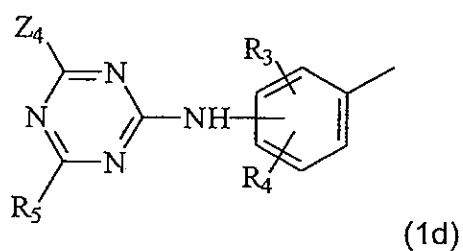
(1a)



(1b)



(1c)



(1d)

and the variable substituents are each as defined in claim 1, processes for their preparation and their use for dyeing hydroxyl- and carboxamido-containing fiber material.