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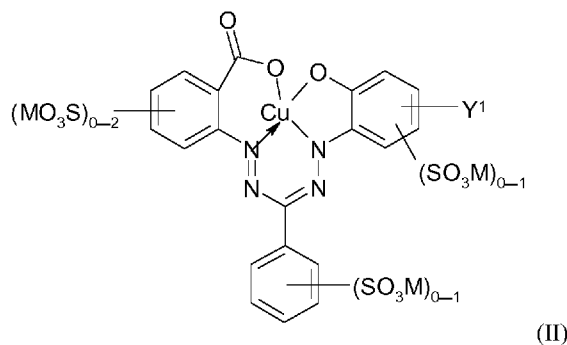
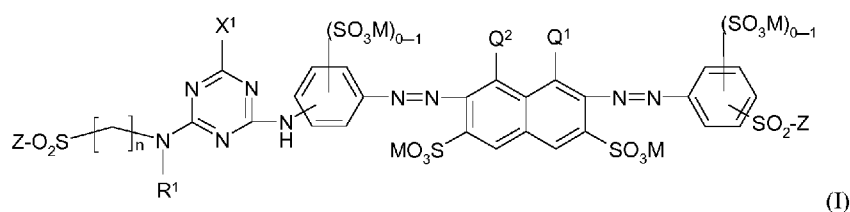
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(54) Title: BLUE AND NAVY FIBRE REACTIVE DYE MIXTURES



(57) Abstract: Dye mixtures comprising dyes of formula (I) and (II) process for the production thereof and use of said mixtures.



Blue and navy fibre reactive dye mixtures

The present invention relates to the use of mixtures of fibre reactive formazan dyes with fibre reactive azo dyes and their use for the dyeing of hydroxyl- and carboxamide-containing material

5 in blue and navy shades.

Fibre reactive formazan dyes are of interest due to their potential to produce neutral to greenish blue dyeings with high fastness to light. However, they often possess certain performance limitations, such as deficient build-up of colour to deeper shades and low resistance to oxidative agents.

10

These performance limitations can partly be overcome in some cases by the use of mixtures of fibre reactive formazan dyes with selected other fibre reactive azo dyes. Such mixtures make it possible, for example, to achieve neutral to greenish Navy shades with high light and perspiration-light fastness, good resistance to washing in the presence of modern oxidative detergents, and good colour constancy in different light sources. The use of such mixtures (as described for example in WO 2005/090485, JP 2001098183 A, JP 3405135 B2) can give dyeings with superior fastness properties to existing mono-molecular fibre reactive Navy dyes (described for example in CN 102504582 A or EP 0568876).

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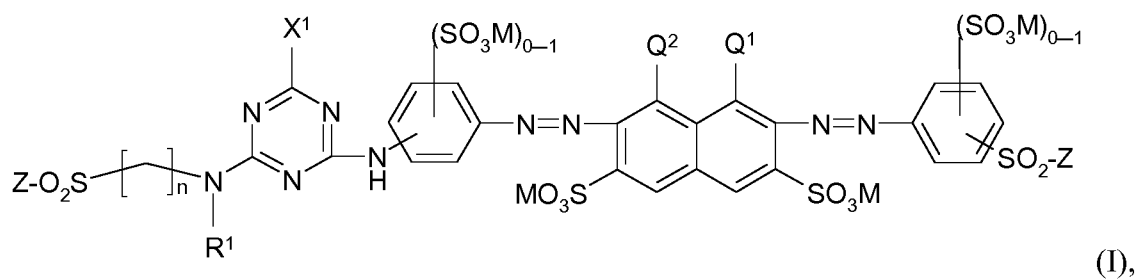
Due to developing consumer requirements there is still a need for new dyestuffs with even better build-up and levelness, high light- and oxidative fastness, especially peroxide and NO_x (moist) fastness.

25

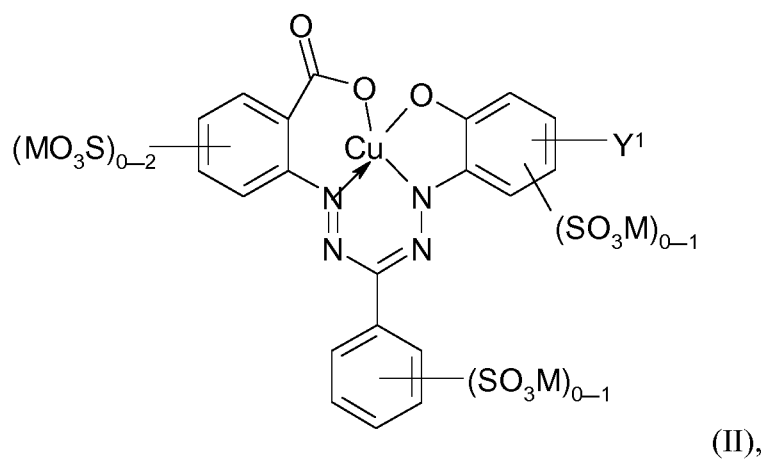
Surprisingly it was now found, that combinations of specific Formazane dyes with special types of azo Navy dyes have these required properties in a very high degree.

The present invention is thus directed to a dye mixture comprising at least one dye of formula

(I)



and at least one dye of formula (II)

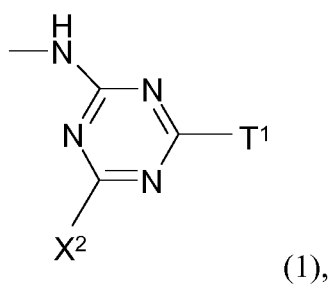


5 wherein independent from each other

Q^1 is OH and Q^2 is NH_2 or Q^1 is NH_2 and Q^2 is OH,

X^1 is Cl or F,

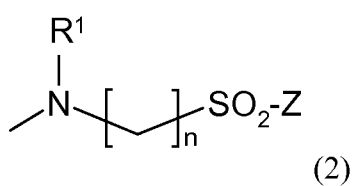
Y^1 is $-SO_2-Z$ or a group of formula (1)



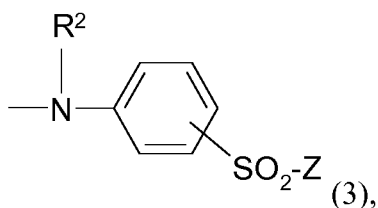
10 wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or



wherein independent from each other

R^1 is methyl, ethyl or phenyl,

R^2 is H, methyl or ethyl,

5 n is 2 or 3,

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

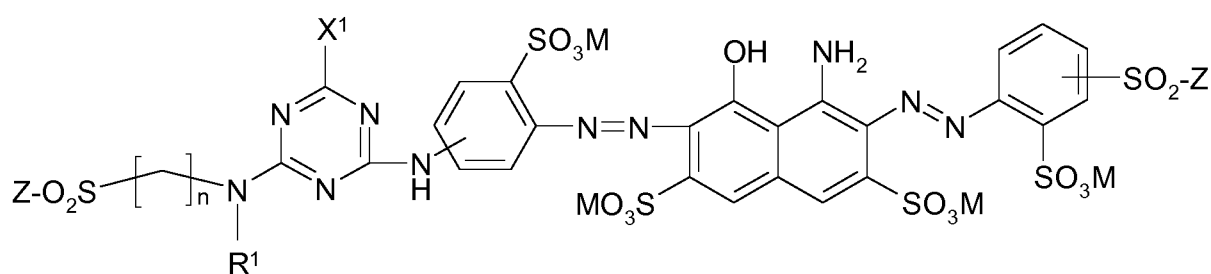
wherein G is a group that is removable under alkaline conditions and

M is H, an alkali metal or one equivalent of an alkaline earth metal.

10 The dyes of formulae (I) and (II) are known or can be prepared according to methods known per se. Dyes of formula (I) are described, for example, in CN 102504582 A and EP 0 568 876. Dyes of formula (II) are described, for example, in US 4,336,190 and US 4,754,023.

A group that is removable under alkaline conditions is e.g. $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{M}$, $-\text{OPO}_3\text{M}_2$,
 15 $-\text{O}-\text{CO}-\text{CH}_3$, $-\text{O}-\text{CO}-\text{C}_6\text{H}_5$.

Of course there exist preferred versions and a dye mixture as described above, comprising at least one dye of formula (Ia)



20 (Ia)

wherein independent from each other

X^1 is Cl or F,

R^1 is methyl, ethyl or phenyl,

n is 2 or 3,

25 Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

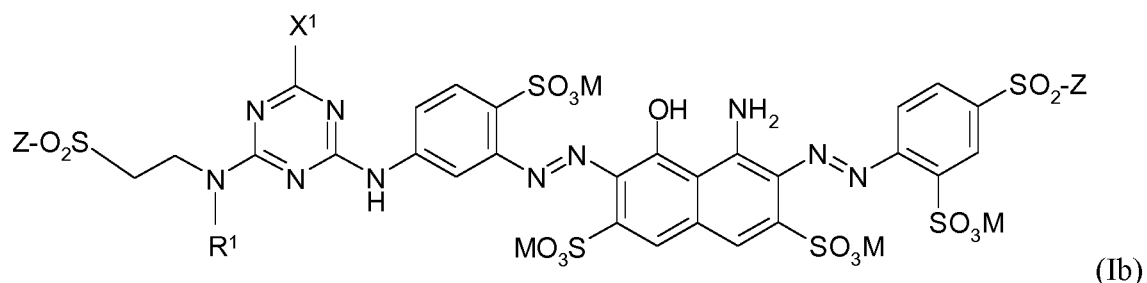
wherein

G is -Cl, -Br, -F, -OSO₃M or -OPO₃M₂ and

M is H, Na, K or Li

is preferred.

- 5 More preferred is a dye mixture as described above, comprising at least one dye of formula (Ib)



wherein independent from each other

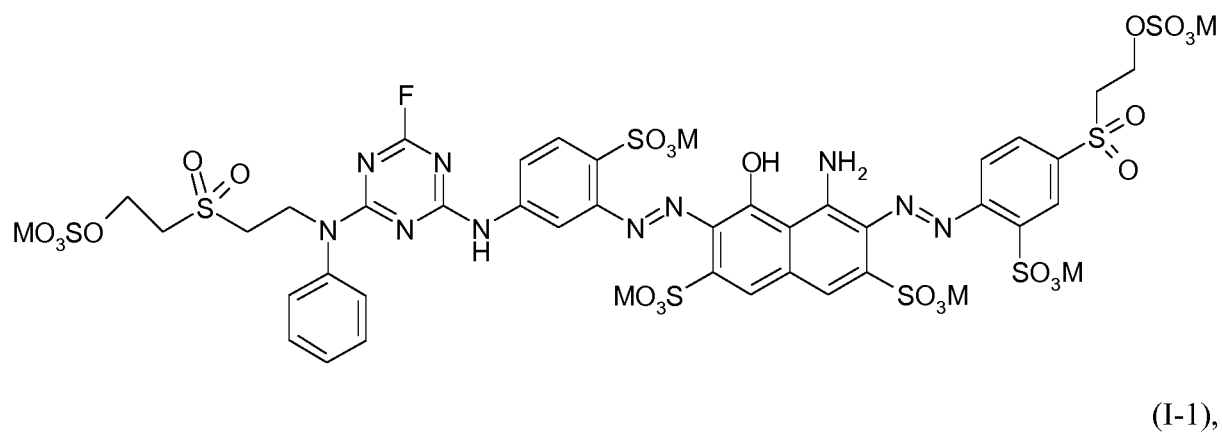
X¹ is Cl or F,

R¹ is methyl, ethyl or phenyl,

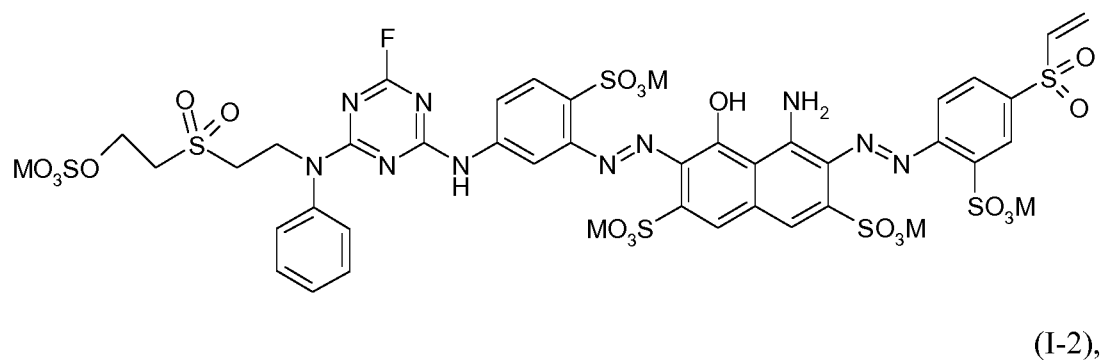
- 10 Z is -CH=CH₂ or a -CH₂-CH₂-OSO₃M and

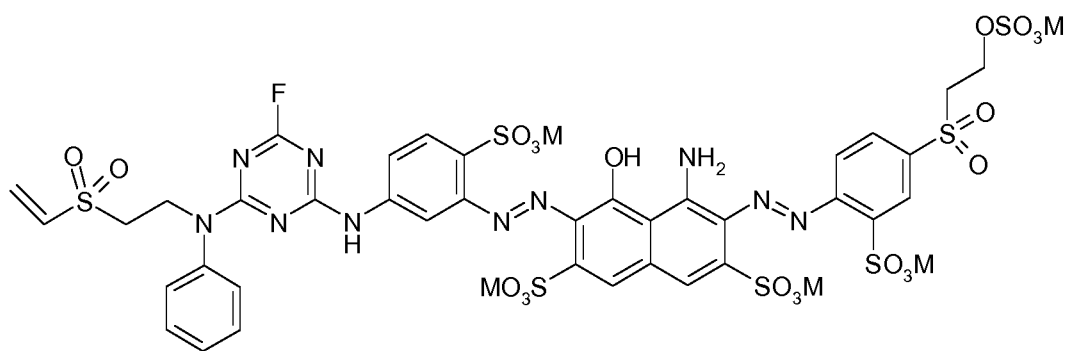
M is H or Na.

Even more preferred is a dye mixture as described above, comprising at least one dye selected from the list consisting of:

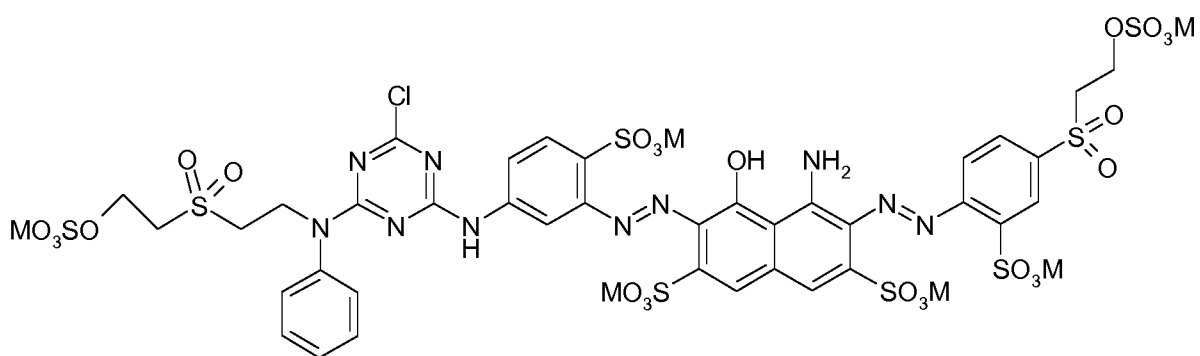


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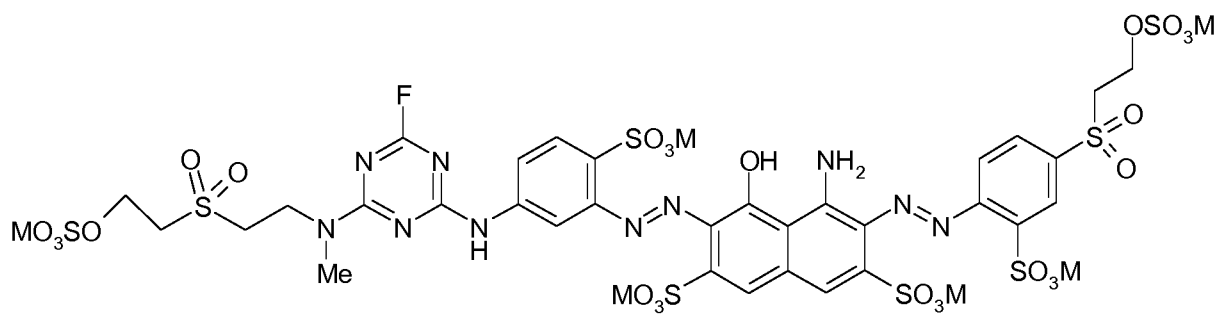




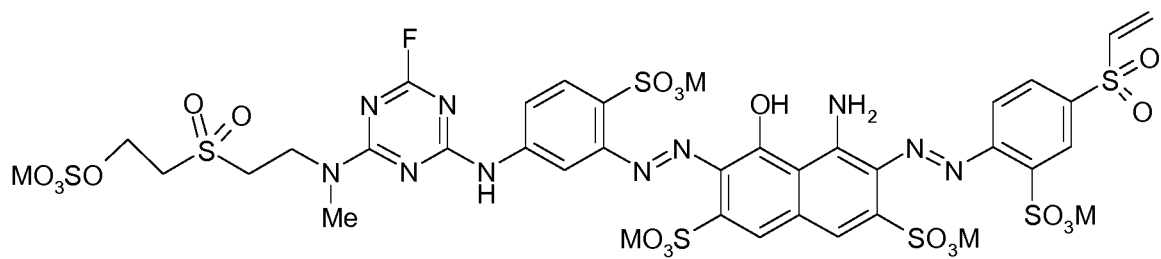
(I-3),



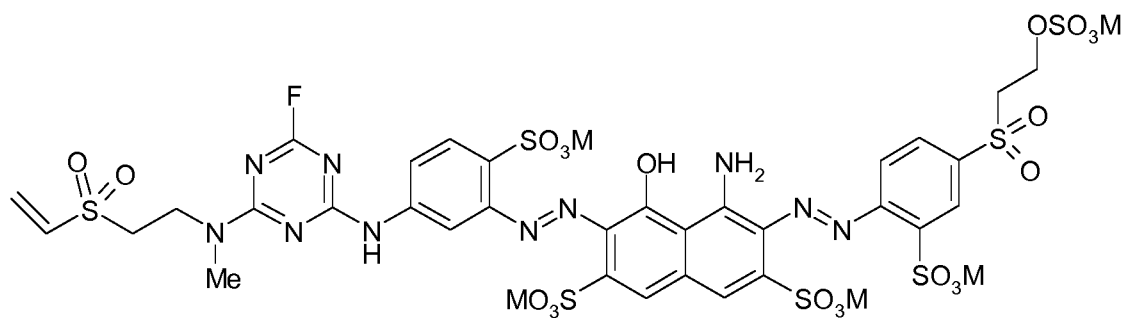
(I-4),



(I-5),

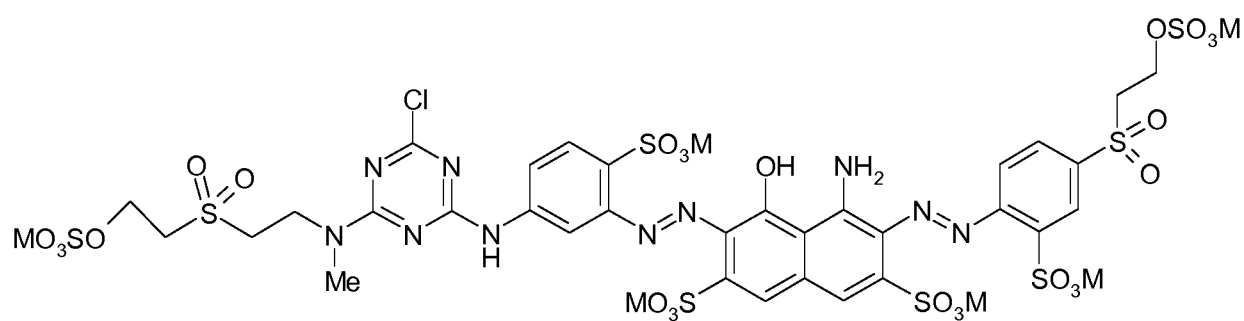


(I-6),



(I-7)

and



(I-8),

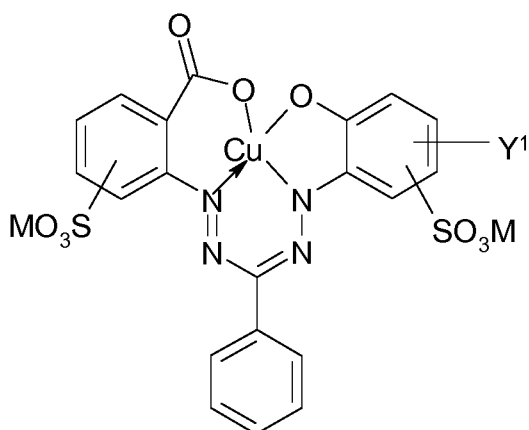
5

wherein

M is H or Na.

10

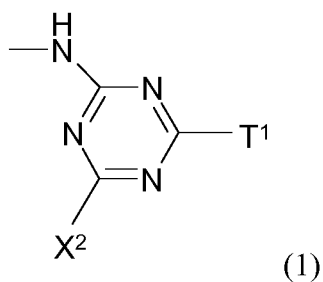
Also regarding the selection of the dyes of formula (II) there exist preferred versions and a dye mixture as described above, comprising at least one dye of formula (IIa)



(IIa)

wherein

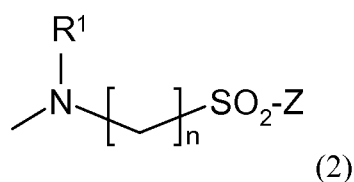
Y¹ is -SO₂-Z or a group of the formula (1)



wherein

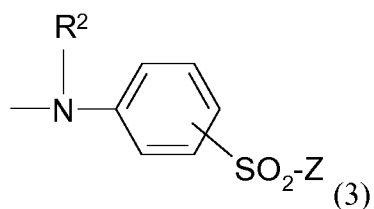
X^2 is Cl or F,

T^1 is a group of formula



wherein R^1 is methyl, ethyl or phenyl,

or



wherein R^2 is H, methyl or ethyl,

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical,

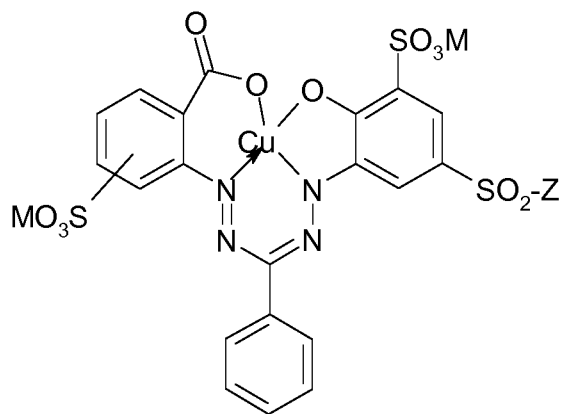
wherein G is $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{M}$ or $-\text{OPO}_3\text{M}_2$

n is 2 or 3 and

M is H, Na, K or Li

is preferred.

More preferred is a dye mixture as described above, comprising at least one dye of formula (IIb)



(IIb)

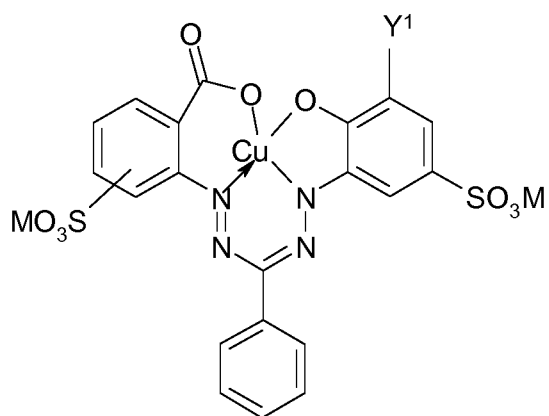
wherein independent from each other

Z is $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

M is H or Na.

5

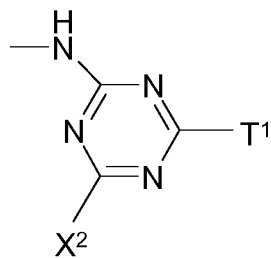
Also preferred is a dye mixture as described above, comprising at least one dye of formula (IIc)



(IIc)

wherein independent from each other

Y^1 is a group of the formula (1)



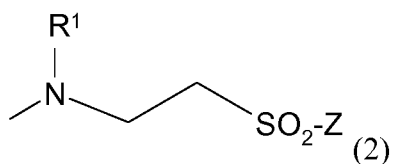
(1)

wherein independent from each other

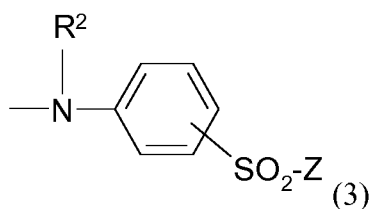
X^2 is Cl or F,

T^1 is a group of formula

10



or



wherein independent from each other

5

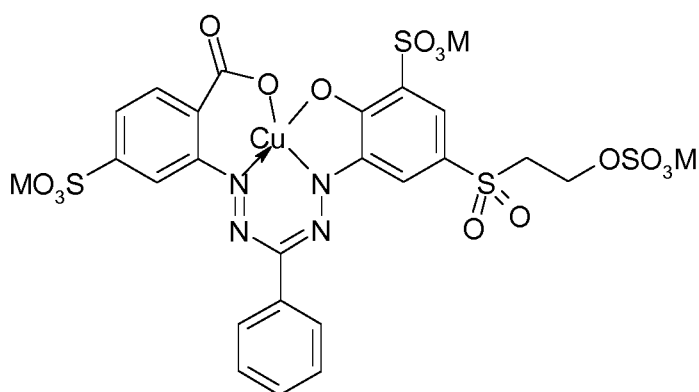
R^1 is methyl, ethyl or phenyl,

R^2 is H, methyl or ethyl,

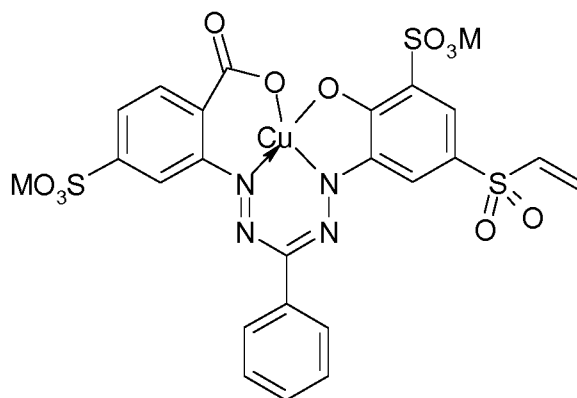
Z is $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

M is H or Na.

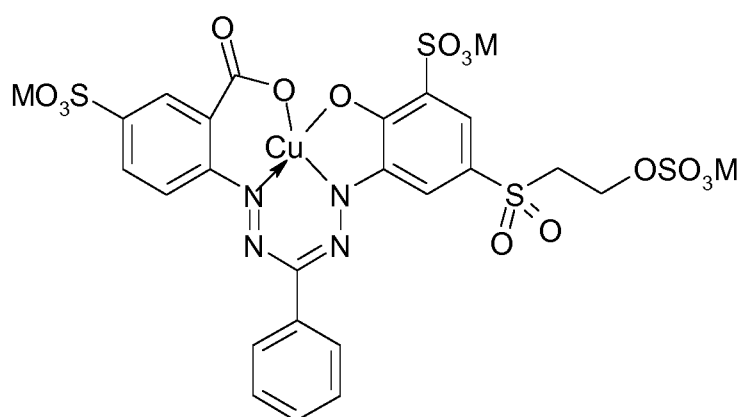
- 10 Even more preferred is a dye mixture as described above, comprising at least one dye selected from the list consisting of:



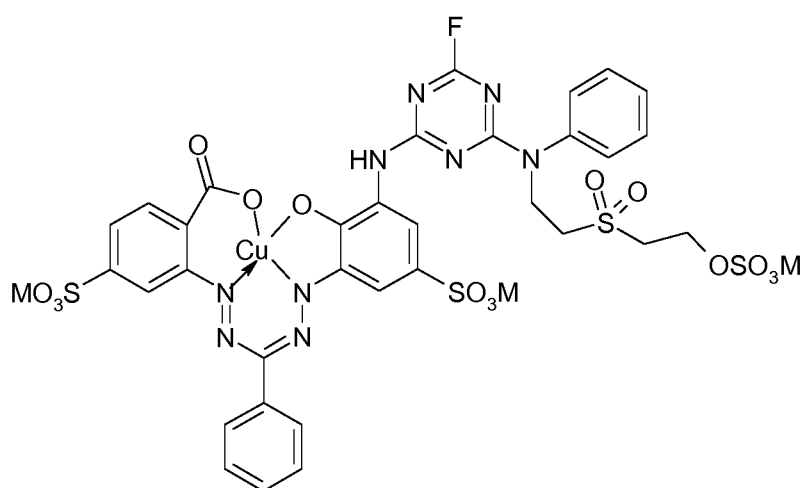
(II-1),



(II-2),

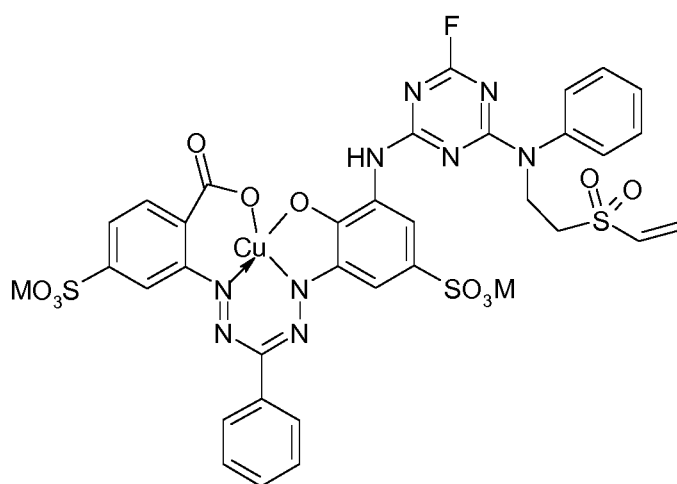


(II-3),

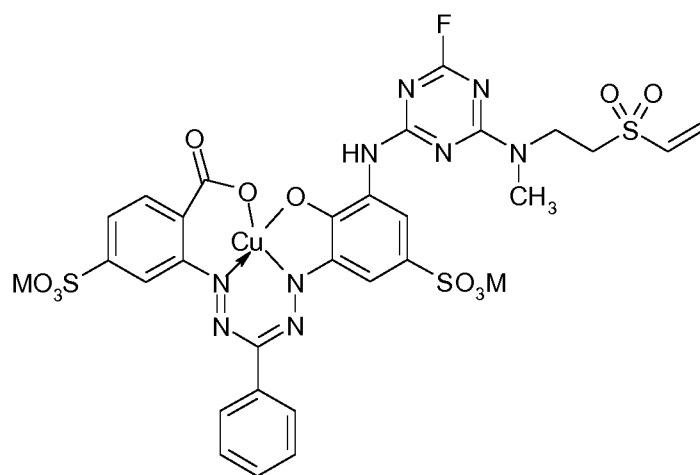
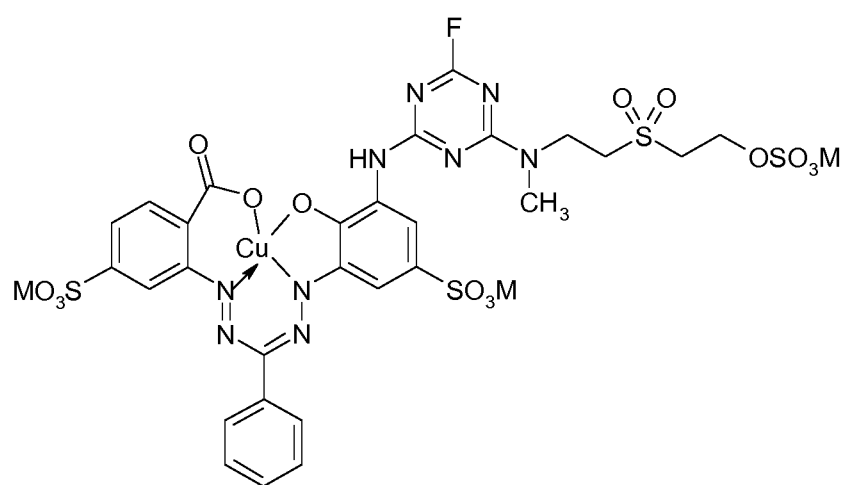
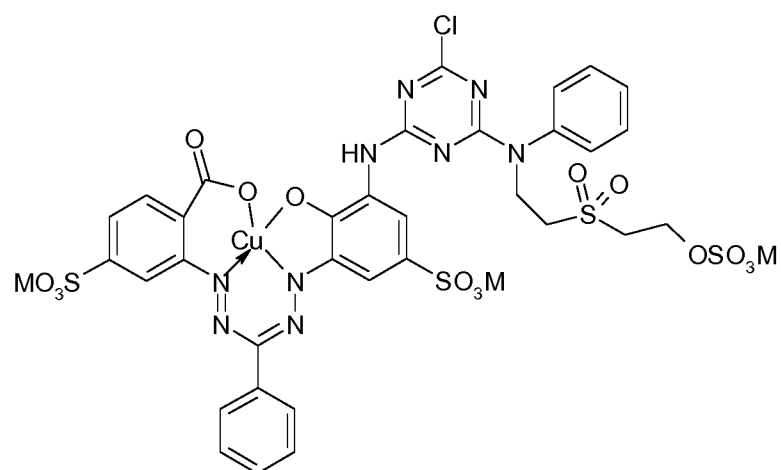


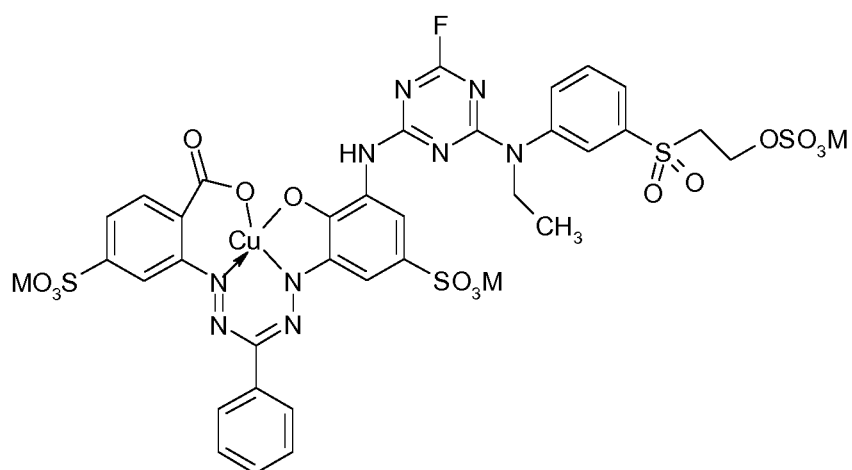
(II-4),

5

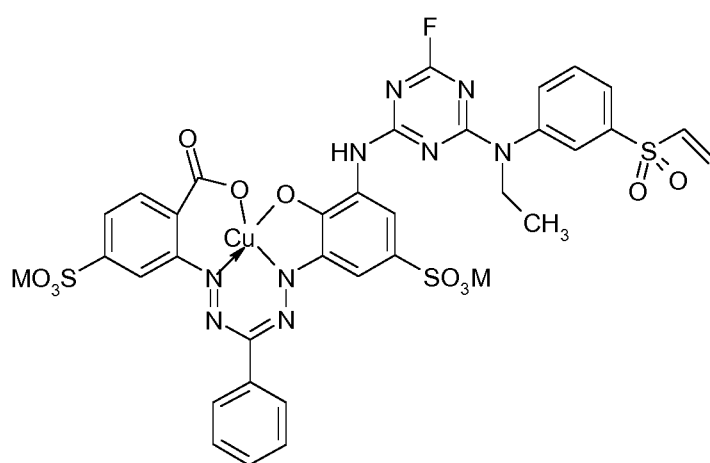


(II-5),

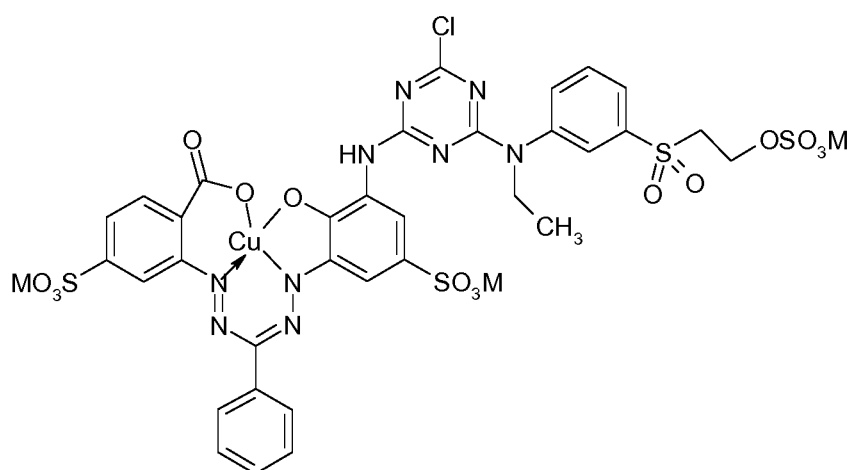




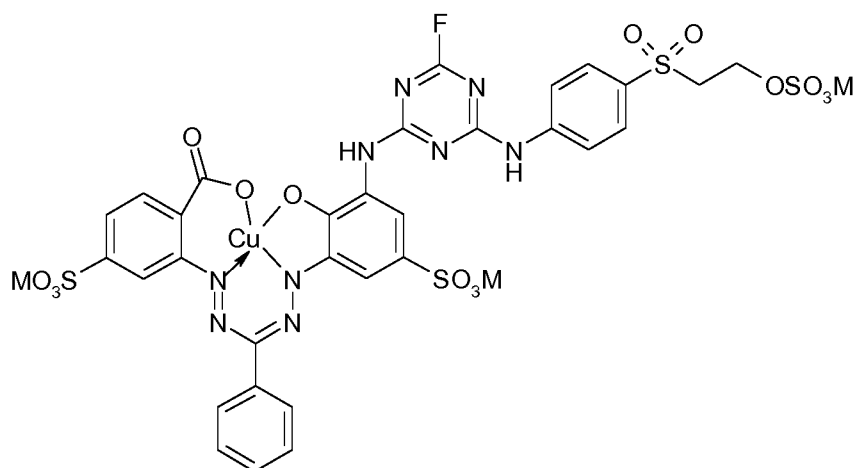
(II-9),



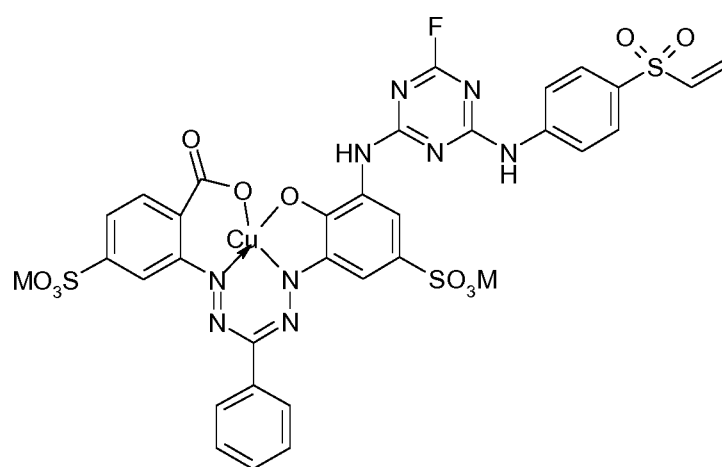
(II-10),



(II-11),

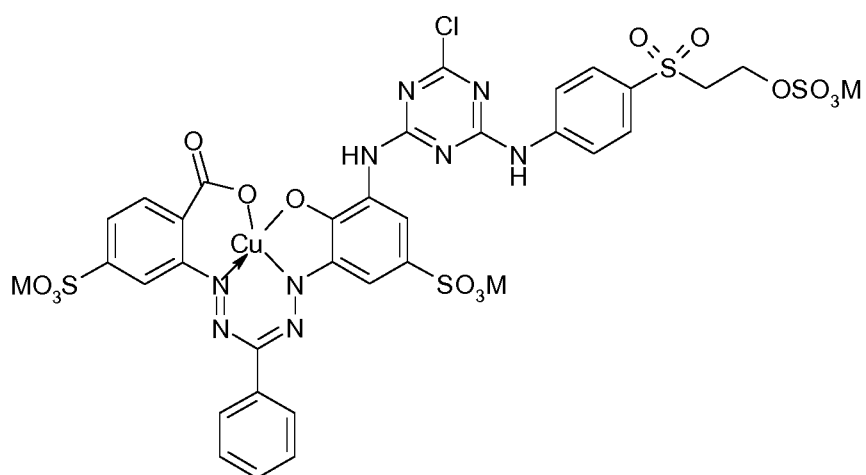


(II-12),



(II-13)

and



(II-14)

5

wherein

M is H or Na.

Combinations of preferred selections of dye(s) (I) and of dye(s) (II) are particularly preferred. Accordingly dye mixtures comprising at least one dye of formula (Ia) and at least one dye of formula (IIa) are preferred. Even more preferred are dye mixtures comprising at least one dye of formula (Ib) and at least one dye of formula (IIb) and/or (IIc). Those dye mixtures, in which
5 dyes selected from the list of dyes of formula (I-1) to (I-8) are combined with dyes selected from the list of dyes of formula (II-1) to (II-14) are particularly preferred. Within this group the most preferred dye mixtures are those, wherein at least one dye of formula (I) is selected from the list consisting of (I-1), (I-2) and (I-4) and the at least one dye of formula (II) is selected from the list consisting of (II-1), (II-4) and (II-11).

10

The most preferred dye mixtures are comprising dyes of formula:

(I-1) and (II-1), (I-1) and (II-4), (I-1) and (II-11), (I-2) and (II-1), (I-2) and (II-4), (I-2) and (II-11), (I-4) and (II-1), (I-4) and (II-4) or (I-4) and (II-11).

15 The dyes of formula (I) and (II) and also the dye mixture according to the present invention may be present as a preparation in solid or in liquid (dissolved) form. In solid form they comprise, to the extent necessary, the electrolyte salts, which are customary for water-soluble and, in particular, fiber-reactive dyes, such as sodium chloride, potassium chloride, and sodium sulfate, and may further comprise the auxiliaries that are customary in commercial dyes, such
20 as buffer substances capable of setting a pH of between 3 and 7 in aqueous solution, such as sodium acetate, sodium citrate, sodium borate, sodium hydrogencarbonate, sodium dihydrogenphosphate and disodium hydrogenphosphate, and additionally dyeing auxiliaries, antidust agents, and small amounts of siccatives. If they are present in liquid, aqueous solution (including the content of thickeners of the kind customary for print pastes), they may also
25 comprise substances which ensure a long life for these preparations, such as mold preventatives, for example.

In solid form, the dyes of the formula (I) and (II) and also the dye mixture according to the invention are typically in the form of powders or granules which contain electrolyte salts
30 (referred to generally, below, as preparations) with, where appropriate, one or more of the abovementioned auxiliaries. In the preparations the dyes are present at 20 % to 90 % by weight, based on the preparation. The buffer substances are generally present in a total amount of up to 5 % by weight, based on the preparation.

Where the dyes of the formula (I) and (II) as well as the dye mixture according to the invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, such as, for example, between 5 % and 50 % by weight, the electrolyte salt content of these aqueous solutions being preferably below 10 % by weight, based on the aqueous solution; the aqueous solutions (liquid preparations) may contain the aforementioned buffer substances in general in an amount of up to 5 % by weight, preferably up to 2 % by weight.

For the dyes as such there exist preferred ranges as well. And a dye mixture as described above, wherein the amount of dye(s) of formula (I) is 80 to 20 wt% and the amount of dye(s) of formula (II) is 20 to 80 wt% of the total weight of dyes in the mixture is preferred. More preferred is a dye mixture as described above, wherein the amount of dye(s) of formula (I) is 65 to 35 wt% and the amount of dye(s) of formula (II) is 35 to 65 wt% of the total weight of dyes in the mixture. The total weight of dyes in the mixture is 100 wt%.

The dyes of formula (I) and (II) can be isolated in conventional manner by being salted out, using common salt or potassium chloride, for example, or by spray drying or evaporation. An alternative option is to put the as-synthesized solutions, where necessary following addition of a buffer substance and if desired after concentration, to dyeing use directly, in the form of liquid preparations.

A solution for dyeing comprising a dye mixture as described above thus is another aspect of the present invention.

A process for the production of a dye mixture as described above, comprising

- a) mixing the components of the dye mixture,
 - b) homogenizing the mixture obtained in step a)
- forms yet another aspect of the present invention.

The mixtures of dyes of formula (I) and (II) according to the present invention possess valuable performance properties and can be used for dyeing and printing carboxamido- and/or hydroxyl-containing materials. Accordingly the process for dyeing or printing material, comprising contacting the material with a dye mixture as described above and/or a solution as described above forms another aspect of the present invention.

The stated materials may take the form, for example, of sheet-like structures such as paper and leather, the form of films, such as polyamide films, for example, or the form of a bulk composition, as of polyamide or polyurethane, for example. More particularly, however, they
5 take the form of fibers of the stated materials.

The mixtures of the dyes of formula (I) and (II) according to the present invention are used for dyeing and printing cellulosic fiber materials of all kinds. They are preferably also suitable for dyeing or printing polyamide fibers or blend fabrics of polyamide with cotton or with polyester
10 fibers.

It is also possible to use the dye mixture of dyes having formula (I) and (II) according to the invention to print textiles or paper by the inkjet process.

15 The use of the mixtures of formula (I) and (II) as described above for dyeing or printing carboxamido- and/or hydroxyl-containing materials forms another aspect of the present invention, and processes for dyeing or printing carboxamido- and/or hydroxyl-containing materials in conventional procedures, by using one or more dyes of the general formula (I) according to the invention as colourants forms yet another aspect of the present invention.

20 Fibers or fiber materials for the purposes of the present invention are more particularly textile fibers, which may be present as woven fabrics or as yarns or in the form of hanks or wound packages.

25 Carboxamido-containing materials are, for example, synthetic and natural polyamides and polyurethanes, more particularly in the form of fibers, examples being wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11 and nylon-4.

30 Hydroxyl-containing materials are those of natural or synthetic origin, such as, for example, cellulose fiber materials or their regenerated products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton, but also other plant fibers, such as linen, hemp, jute, and ramie fibers. Regenerated cellulose fibers are, for example, staple viscose and filament viscose.

The mixtures according to the present invention can be applied to and fixed on the stated

materials, more particularly the stated fiber materials, by the application techniques that are known for water-soluble dyes, and particularly for fiber-reactive dyes.

Wool, which has been given a non-felting or low-felting finish (cf., for example, H. Rath, Lehrbuch der Textilchemie, Springer-Verlag, 3rd edition (1972), pp. 295-299, especially wool finished by the Hercosett process (p. 298); J. Soc. Dyers and Colourists 1972, 93-99, and 1975, 33-44) can be dyed with very good fastness properties. The process of dyeing on wool takes place in a conventional dyeing procedure from an acidic medium. For example, acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate can be added to the dyebath in order to obtain the desired pH. To achieve a useful levelness in the dyeing, it is advisable to add customary levelling assistants, such as, for example, a levelling assistant based on a reaction product of cyanuric chloride with three times the molar amount of aminobenzenesulfonic acid and/or of an aminonaphthalenesulfonic acid, or one based on a reaction product of, for example, stearylamine with ethylene oxide.

Thus, for example, the dye mixture of the invention is preferably first subjected to the exhaust process from an acidic dyebath having a pH of about 3.5 to 5.5, with monitoring of the pH, and then, toward the end of the dyeing time, the pH is shifted into the neutral and optionally weakly alkaline range, to a pH of up to 8.5, in order, in particular, to induce the full reactive binding between the dyes of the dye mixtures of the invention and the fiber, in order to obtain high depths of colour. At the same time the fraction of dye which has not been reactively bound is removed.

The procedure described here also applies to the production of dyeings on fiber materials composed of other natural polyamides or of synthetic polyamides and polyurethanes. These materials can be dyed using the customary dyeing and printing processes that are described in the literature and known to the person skilled in the art (see, for example, H.-K. Rouette, Handbuch der Textilveredlung, Deutscher Fachverlag GmbH, Frankfurt am Main).

Besides mixtures of the general formula (I) and (II) and water, the dyeing liquors and print pastes may comprise further additives. Additives are, for example, wetting agents, antifoams, levelling agents, and agents that influence the properties of the textile material, such as softeners, flame retardant finish additives, and agents, which impart dirt, water, and oil repellency or that soften water. Print pastes in particular may also comprise natural or synthetic

thickeners, such as alginates and cellulose ethers, for example. In the dyebaths and print pastes, the amounts of dye may vary within wide limits, in accordance with the desired depth of colour. Generally speaking, a dye mixture of the formula (I) and (II) according to the present invention is present in amounts of 0.01 % to 15 % by weight, more particularly in amounts of 0.1 % to 10 % by weight, based on the dyeing goods or the print paste, respectively.

On cellulose fibers, dyeings having very good colour yields are obtained by the exhaust processes from a long liquor, using a wide variety of acid-binding agents and, where appropriate, neutral salts, such as sodium chloride or sodium sulfate. In the case of the exhaust process, it is preferred to carry out dyeing at a pH of 3 to 7, more particularly at a pH of 4 to 6. The liquor ratio may be selected within a wide range and is for example between 3 : 1 and 50 : 1, preferably between 5 : 1 and 30 : 1. Dyeing is done preferably in an aqueous bath at temperatures between 40 and 105 °C, optionally at a temperature up to 130 °C under superatmospheric pressure, and where appropriate in the presence of customary dyeing auxiliaries. The wet fastness properties of the dyed material can be enhanced by an aftertreatment to remove unfixed dye. This aftertreatment takes place more particularly at a pH of 8 to 9 and at temperatures of 75 to 80 °C.

One possible exhaust process procedure is to introduce the material into the warm bath and to gradually heat the bath to the desired temperature and complete the dyeing operation. The neutral salts, which accelerate the exhaustion of the dyes can also, if desired, not be added to the bath until the actual dyeing temperature has been reached.

The padding process on cellulose fibers likewise produces excellent colour yields and a very good colour build-up, with fixing able to take place in conventional manner by batching at room temperature or elevated temperature, at up to about 60 °C, for example, by steaming or by means of dry heat.

The customary printing processes for cellulose fibers as well, which can be carried out in one step - as for example by printing with a print paste comprising sodium bicarbonate or another acid-binding agent and by subsequent steaming at 100 to 103 °C - or in two steps - as for example by printing with a neutral or weakly acidic printing ink, followed by fixing either by passage of the printed materials through a hot, electrolyte-containing alkaline bath or by overpadding with an alkaline, electrolyte-containing padding liquor, and subsequent batching

or steaming or dry heat treatment of the alkali-overpadded material - produces strongly coloured prints with well-defined contours and a clear white ground. The outcome of the prints is affected little, if at all, by variations in the fixing conditions.

- 5 In the case of fixing by means of dry heat, in accordance with the customary thermofix processes, hot air at 120 to 200 °C is used. Besides 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.
- 10 The acid-binding agents which effect the fixation of the dyes on the cellulose fibers are, for example, water-soluble basic salts of the alkali metals and likewise alkaline earth metals of organic or inorganic acids or compounds which liberate alkali in the heat. Particularly included are the alkali metal hydroxides and alkali metal salts of weak to moderately strong organic or inorganic acids, the preferred alkali metal compounds being the sodium compounds and
- 15 potassium compounds. Examples of such acid-binding agents include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate, or mixtures thereof.
- 20 The dye mixtures comprising dyes of formula (I) and (II) according to the invention are notable in particular for high colour strengths and fixing yields and ease of wash-off of the portions not fixed on the fiber. Moreover, the dyeings and prints have good all-round fastness properties, such as high light fastness and very good wet fastnesses, such as fastness to washing, to water, to salt water, to cross-dyeing, and to perspiration, for example, and also good fastness to
- 25 pleating, hot pressing, and rubbing. They exhibit, furthermore, little tendency to stain polyamide in cotton/polyamide blend fabrics. All in all, therefore, they have an improved profile of properties relative to the dyes known from JP 47 036 838.

The present invention also provides inks for digital textile printing by the inkjet process, which

30 comprise a dye mixture of the formula (I) and (II) according to the invention.

The inks of the invention comprise a dye mixture comprising dyes of formula (I) and (II) according to the invention, in amounts, for example, of 0.1 % to 50 % by weight, preferably in amounts of 1 % to 30 % by weight, and more preferably in amounts of 1 % to 15 % by weight,

based on the total weight of the ink. It will be appreciated that the inks may also comprise mixtures of dyes of the general formula (I) according to the invention and other dyes used in textile printing.

- 5 For the use of the inks in the continuous flow process, a conductivity of 0.5 to 25 mS/m can be set by addition of electrolyte. Examples of suitable electrolyte include lithium nitrate and potassium nitrate.

10 The inks of the invention may contain organic solvents with a total content of 1 to 50 %, preferably of 5 to 30 % by weight.

Examples of suitable organic solvents include alcohols, such as methanol, ethanol, 1-propanol, isopropanol, 1-butanol, tert-butanol, pentyl alcohol, polyhydric alcohols, such as 1,2-ethanediol, 1,2,3-propanetriol, butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-propanediol, 1,3-
15 propanediol, pentanediol, 1,4-pentanediol, 1,5-pentanediol, hexanediol, D,L-1,2-hexanediol, 1,6-hexanediol, 1,2,6-hexanetriol, 1,2-octanediol, polyalkylene glycols, such as polyethylene glycol, polypropylene glycol, alkylene glycols having 2 to 8 alkylene groups, e.g.: monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, thioglycol, thiodiglycol, butyltriglycol, hexylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol monohexyl ether, triethylene glycol monomethyl ether, triethylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monobutyl ether, tetraethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, tripropylene glycol isopropyl ether, polyalkylene glycol ethers, such as polyethylene glycol monomethyl ether, polypropylene glycol glycerol ether, polyethylene glycol tridecyl ether, and polyethylene glycol nonylphenyl ether, amines, such as methylamine, ethylamine, diethylamine, triethylamine, diethylamine, dimethylamine, trimethylamine, dibutylamine, diethanolamine, triethanolamine, ethylenediamine, urea derivatives, such as urea, thiourea, N-methylurea, N,N'-dimethylurea, ethyleneurea, and 1,1,3,3-tetramethylurea, amides, such as dimethylformamide, dimethylacetamide, acetamide, N-formylethanolamine, N-acetyethanolamine, ketones or keto alcohols, such as acetone, diacetone alcohol, cyclic

ethers, such as tetrahydrofuran, dioxane, and also trimethylolethane, trimethylolpropane, 2-butoxyethanol, benzyl alcohol, gamma-butyrolactone, epsilon-caprolactam, and additionally sulfolane, methylsulfolane, 2,4-dimethylsulfolane, dimethyl sulfone, butadiene sulfone, dimethyl sulfoxide, dibutyl sulfoxide, N-cyclohexylpyrrolidone, N-methyl-2-pyrrolidone, N-ethylpyrrolidone, 2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidone, 1-(3-hydroxypropyl)-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-2-imidazolinone, 1,3-bismethoxymethylimidazolidine, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-(2-butoxyethoxy) ethanol, 2-(2-propoxyethoxy)ethanol, 1,2-dimethoxypropane, trimethoxypropane, pyridine, piperidine, ethyl acetate, ethylenediaminetetraacetate, and ethyl pentyl ether.

The inks of the invention may further comprise the customary additives, such as, for example, viscosity moderators to set viscosities in the range from 1.5 to 40 mPas in a temperature range from 20 to 50 °C. Preferred inks have a viscosity of 1.5 to 20 mPas, and particularly preferred inks have a viscosity of 1.5 to 15 mPas.

Suitable viscosity moderators are rheological additives, examples being the following: polyvinylcaprolactam, polyvinylpyrrolidone, and also their copolymers, polyetherpolyol, associative thickeners, polyurea, polyurethane, sodium alginates, modified galactomannans, polyetherurea, polyurethane, and nonionic cellulose ethers.

As further additives the inks of the invention may include surface-active substances for setting surface tensions of 20 to 65 mN/m, which are adapted if necessary as a function of the process used (thermo or piezoelectric technology).

Examples of suitable surface-active substances include the following: surfactants of all kinds, preferably nonionic surfactants, butyldiglycol, and 1,2-hexanediol.

The inks may further comprise customary additives, such as substances for inhibiting fungal and bacterial growth, for example, in amounts of 0.01 % to 1 % by weight, based on the total weight of the ink.

The inks of the invention may be prepared in conventional manner by mixing of the components in water.

The inks of the invention are suitable for use in inkjet printing processes for printing a very wide variety of pretreated materials, such as silk, leather, wool, polyamide fibers and polyurethanes, and more particularly cellulosic fiber materials of all kinds. The printing inks of the invention are also suitable for printing pretreated hydroxyl- and/or amino-containing fibers that are present in blend fabrics; for example, mixtures of cotton, silk, wool with polyester fibers or polyamide fibers.

In contrast to conventional textile printing, where the printing ink already contains all of the fixing chemicals and thickeners for a reactive dye, it is necessary in the case of inkjet printing to apply the auxiliaries to the textile substrate in a separate pretreatment step.

The pretreatment of the textile substrate, such as, for example, cellulose fibers and regenerated cellulose fibers, and also silk and wool, takes place with an aqueous alkaline liquor prior to printing. Fixing reactive dyes requires alkali, for example sodium carbonate, sodium bicarbonate, sodium acetate, trisodium phosphate, sodium silicate, sodium hydroxide, alkali donors such as, for example, sodium chloroacetate, sodium formate, hydrotropic substances such as, for example, urea, reduction inhibitors, such as, for example, sodium nitrobenzenesulfonates, and also thickeners to prevent flowing of the motifs when the printing ink is applied, examples thereof being sodium alginates, modified polyacrylates or highly etherified galactomannans.

These pretreatment reagents are applied uniformly to the textile substrate in a defined amount, using suitable applicators, as for example with a 2- or 3-roll pad mangle, by contactless spraying technologies, by means of foam application, or with appropriately adapted inkjet technologies, and are subsequently dried.

After printing has taken place, the textile fiber material is dried at 120 to 150 °C and then fixed.

Fixing the inkjet prints produced with reactive dyes can be accomplished at room temperature, or with saturated steam, with superheated steam, with hot air, with microwaves, with infrared radiation, with laser beams or electron beams, or with other suitable energy transfer techniques.

A distinction is made between one- and two-phase fixing operations. In one-phase fixing, the chemicals needed for fixing are already on the textile substrate. In two-phase fixing, this

pretreatment is unnecessary. Fixing requires only alkali, which, following inkjet printing, is applied prior to the fixing operation, without drying in between. Further additives such as urea or thickeners are redundant.

- 5 Following the fixing operation, the print is aftertreated, which is a prerequisite for good fastness properties, high brilliance, and an impeccable white ground.

The prints produced with the inks of the invention possess high colour strength and a high fiber-dye bond stability, not only in the acidic range but also in the alkaline range, and also have good
10 light fastness and very good wet fastness properties, such as fastness to washing, water, salt water, cross-dyeing, and perspiration, and also good fastness to pleating, hot pressing, and rubbing.

The dye mixtures comprising dyes of formula (I) and (II) according to the present invention
15 furnish blue / navy blue dyeings and prints, and inkjet prints, on the materials specified.

The examples herein below serve to illustrate the invention. The parts are parts by weight and the percentages are percent by weight, unless noted otherwise. The relationship between parts by weight and parts by volume is that of the kilogram to the liter. The compounds described by
20 formula in the examples are written in the form of the sodium salts, since in general they are prepared and isolated in the form of their salts, preferably sodium salts or potassium salts, and used for dyeing in the form of their salts. The starting compounds specified in the examples below, especially the tabular examples, can be used in the synthesis in the form of the free acid or likewise in the form of their salts, preferably alkali metal salts, such as sodium salts or
25 potassium salts.

The dyes of formulae (I) and (II) are known or can be prepared according to methods known per se. Dyes of formula (I) are described, for example, in CN 102504582 A and EP0568876. Dyes of formula (II) are described, for example, in US 4336190 and US 4754023. The dye
30 mixtures were then prepared as in the following examples.

Examples:

Example 1:

53 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-3) [component (I)], and 47 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-6) [component (II)], were mixed mechanically with one another.

5

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

Example 2:

10 45 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-1) [component (I)], 35 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-1) [component (II)], and 20 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-2) [component (II)'] were mixed mechanically with one another.

15

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

Example 3:

20 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-4) [component (I)], 24 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-3) [component (I)], 30 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-1) [component (II)] and 26 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-5) [component (II)'] were mixed mechanically with one another.

25

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

30 Further mixtures are described in the following table:

Table 1:

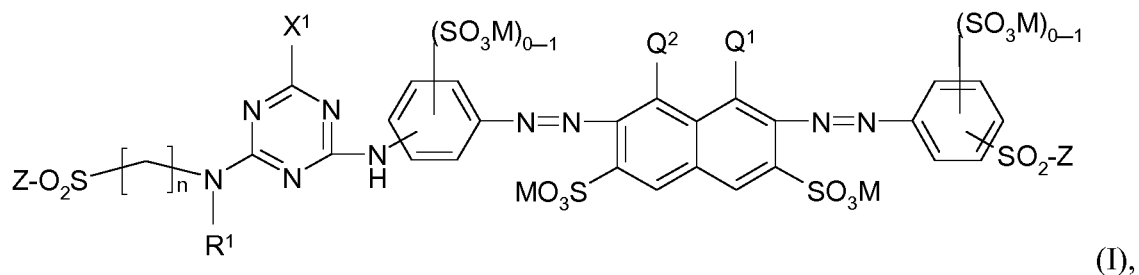
Example	(I)	wt. %	(I)'	wt. %	(II)	wt. %	(II)'	wt. %
4	I-1	39	I-2	39	II-1	22	-	

5	I-1	35	-		II-1	65	-	
6	I-1	45	-		II-1	55	-	
7	I-1	50	-		II-1	30	II-4	20
8	I-2	53	-		II-1	47	-	
9	I-2	19	I-2	19	II-1	62	-	
10	I-3	75	-		II-1	25	-	
11	I-3	56	-		II-1	44	-	
12	I-3	33	-		II-1	67	-	
13	I-4	68	-		II-1	32	-	
14	I-4	45	-		II-1	55	-	
15	I-4	30	-		II-1	70	-	
16	I-5	25	I-6	20	II-1	55	-	
17	I-6	36	-		II-1	64	-	
18	I-7	55	-		II-1	45	-	
19	I-8	60	-		II-1	40	-	
20	I-1	78	-		II-2	22	-	
21	I-1	35	-		II-2	65	-	
22	I-1	45	-		II-2	55	-	
23	I-1	80	-		II-2	10	II-4	10
24	I-1	20	-		II-2	30	II-4	50
25	I-2	72	-		II-2	28	-	
26	I-2	53	-		II-2	47	-	
27	I-3	75	-		II-2	25	-	
28	I-4	45	-		II-2	55	-	
29	I-5	45	-		II-2	55	-	
30	I-6	36	-		II-2	64	-	
31	I-7	55	-		II-2	45	-	
32	I-8	60	-		II-2	40	-	
33	I-1	25	-		II-4	75	-	
34	I-1	50	-		II-4	30	II-6	20
35	I-2	72	-		II-4	28	-	
36	I-2	38	-		II-4	62	-	

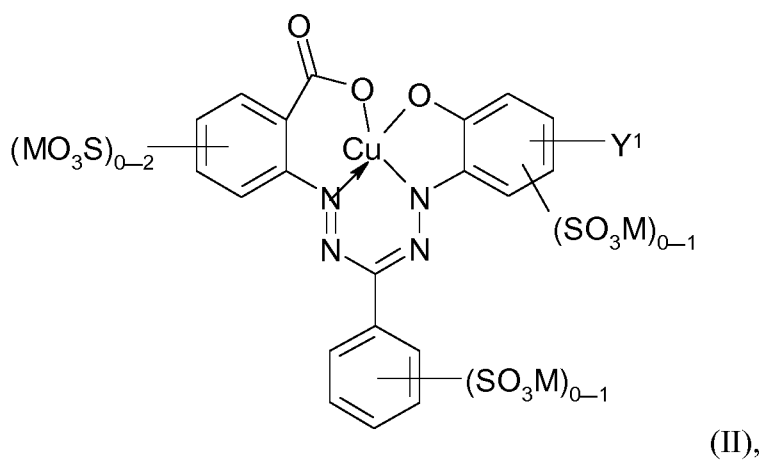
37	I-3	56	-		II-4	44	-	
38	I-4	68	-		II-4	32	-	
39	I-4	45	-		II-4	55	-	
40	I-4	30	-		II-4	70	-	
41	I-5	45	-		II-4	55	-	
42	I-6	36	-		II-4	64	-	
43	I-7	55	-		II-4	45	-	
44	I-8	60	-		II-4	40	-	
45	I-1	78	-		II-5	22	-	
46	I-1	33	-		II-5	77	-	
47	I-1	50	-		II-5	30	II-4	20
48	I-2	70	-		II-5	30	-	
49	I-2	38	-		II-5	62	-	
50	I-3	33	-		II-5	67	-	
51	I-4	67	-		II-5	33	-	
52	I-4	30	-		II-5	70	-	
53	I-5	20	I-6	25	II-5	55	-	
54	I-6	36	-		II-5	64	-	
55	I-7	55	-		II-5	45	-	
56	I-8	60	-		II-5	40	-	
57	I-1	45	-		II-3	55	-	
58	I-1	40	-		II-6	60	-	
59	I-1	48	-		II-7	52	-	
60	I-1	65	-		II-8	35	-	
61	I-1	33	-		II-9	67	-	
62	I-1	75	-		II-11	25	-	
63	I-1	30	-		II-12	70	-	
64	I-1	50	-		II-10	50	-	
65	I-1	52	-		II-13	48	-	
66	I-1	47	-		II-14	53	-	

Claims:

1. Dye mixture comprising at least one dye of formula (I)



- 5 and at least one dye of formula (II)

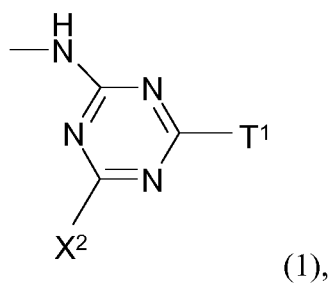


wherein independent from each other

Q^1 is OH and Q^2 is NH_2 or Q^1 is NH_2 and Q^2 is OH,

X^1 is Cl or F,

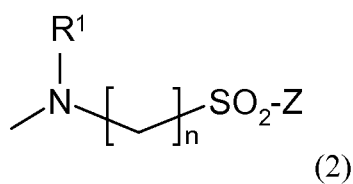
- 10 Y^1 is $-SO_2-Z$ or a group of formula (1)



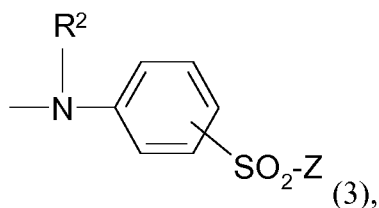
wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or



wherein independent from each other

 R^1 is methyl, ethyl or phenyl, R^2 is H, methyl or ethyl,

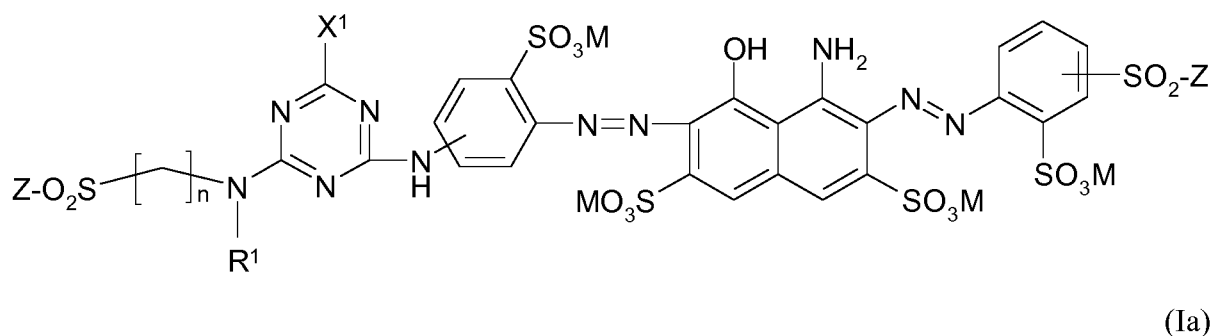
n is 2 or 3,

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

wherein G is a group that is removable under alkaline conditions and

M is H, an alkali metal or one equivalent of an alkaline earth metal.

2. Dye mixture according to claim 1, comprising at least one dye of formula (Ia)



wherein independent from each other

 X^1 is Cl or F, R^1 is methyl, ethyl or phenyl,

n is 2 or 3,

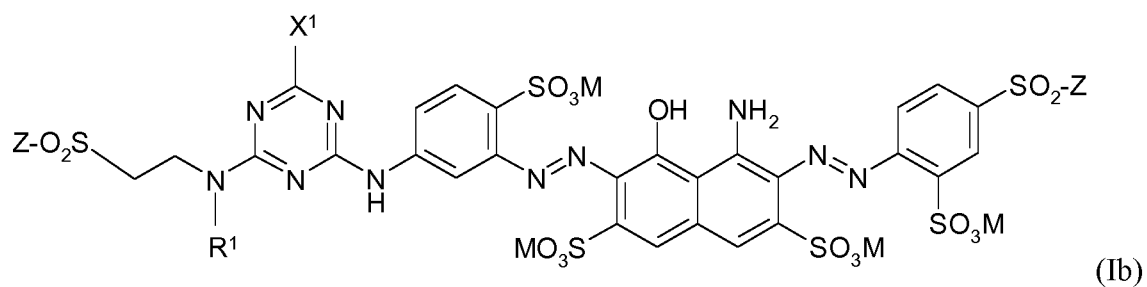
Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

wherein

G is $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{M}$ or $-\text{OPO}_3\text{M}_2$ and

M is H, Na, K or Li.

3. Dye mixture according to claim 1 or 2, comprising at least one dye of formula (Ib)



wherein independent from each other

X^1 is Cl or F,

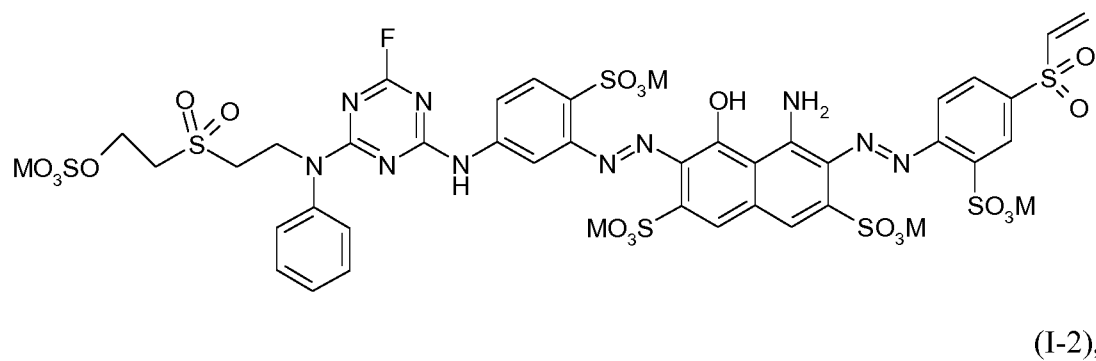
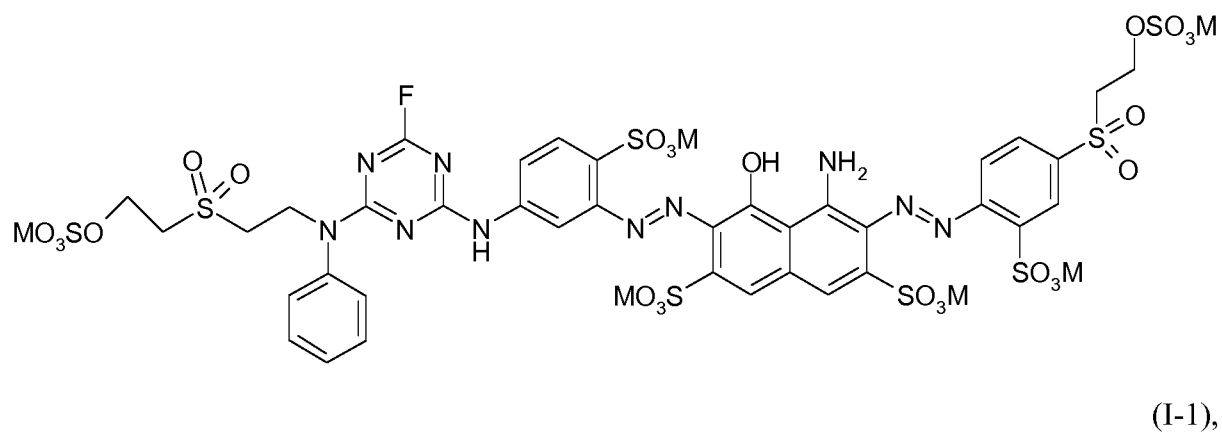
R^1 is methyl, ethyl or phenyl,

5 Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

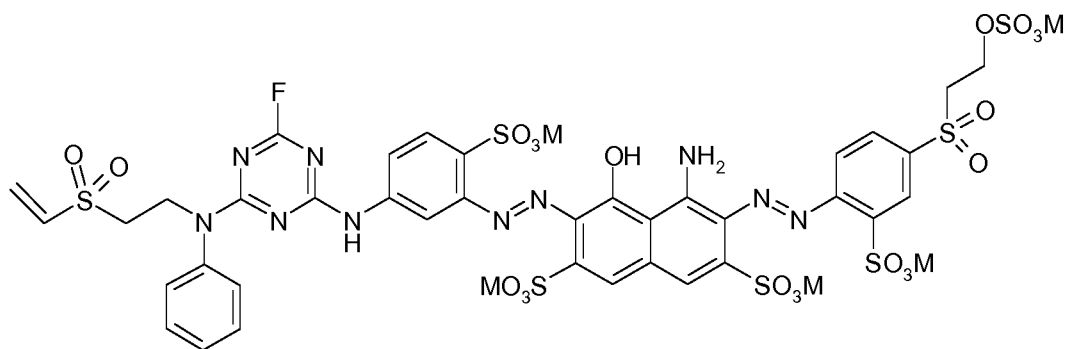
M is H or Na.

4. Dye mixture according to any one of claims 1 to 3, comprising at least one dye selected from the list consisting of:

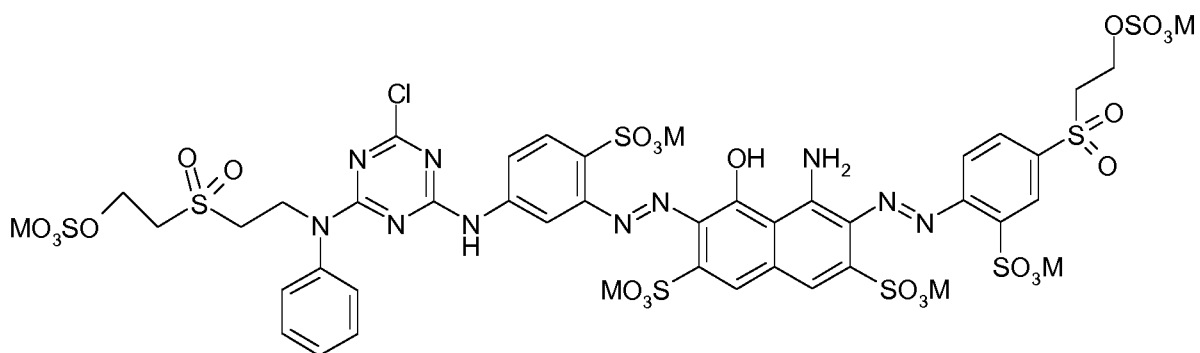
10



15

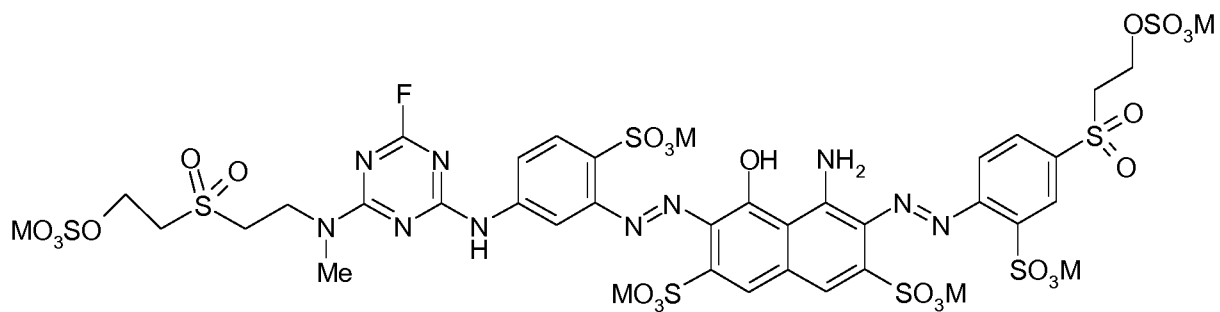


(I-3),

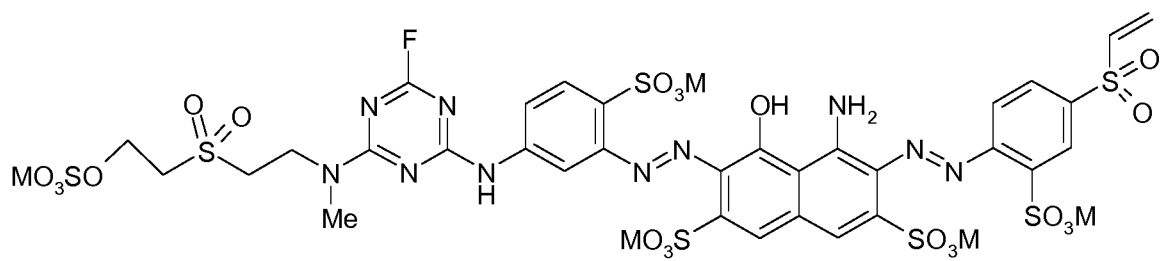


5

(I-4),

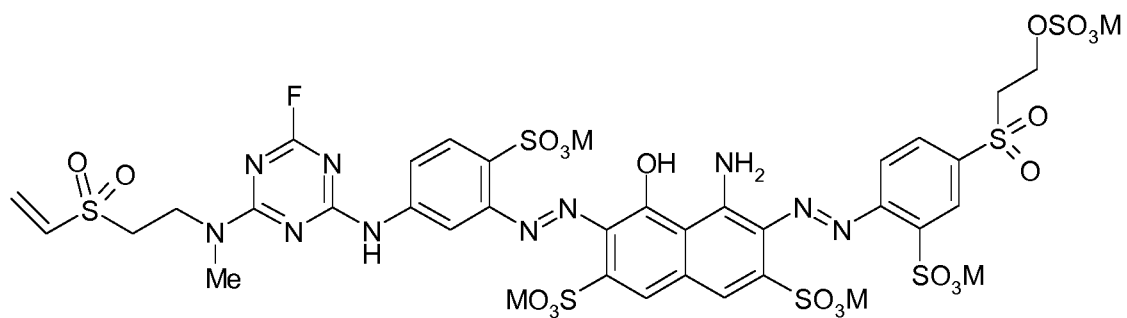


(I-5),



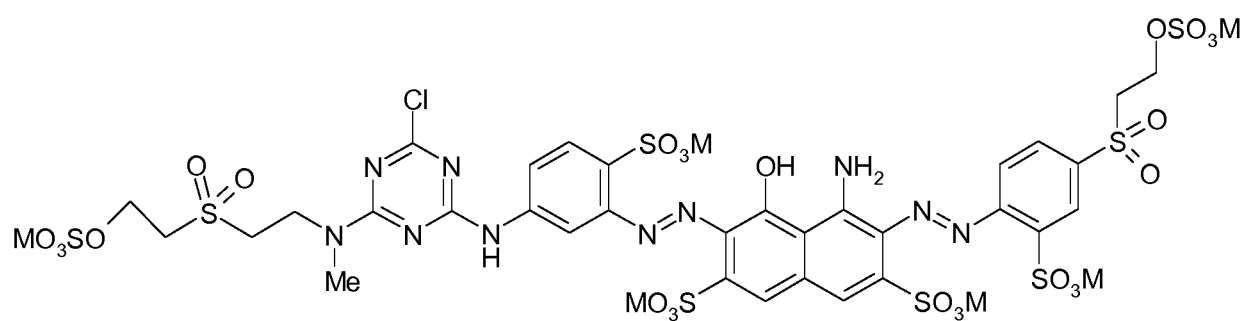
10

(I-6),



(I-7)

and



(I-8)

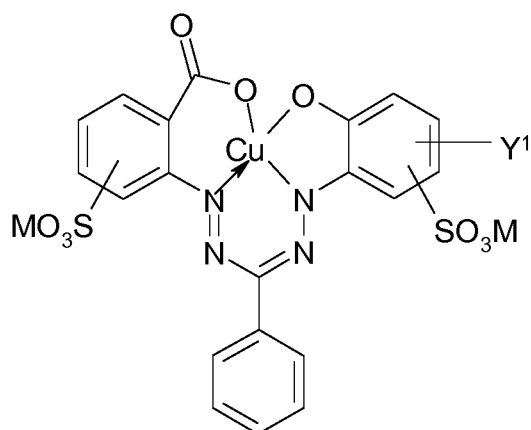
5

wherein

M is H or Na.

5. Dye mixture according to any one of claims 1 to 4, comprising at least one dye of formula (IIa)

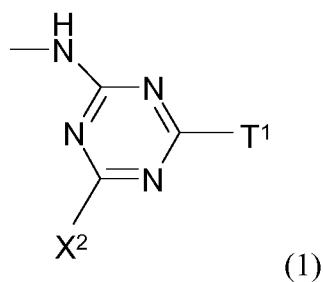
10



(IIa)

wherein

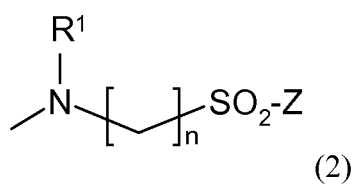
Y¹ is -SO₂-Z or a group of the formula (1)



wherein

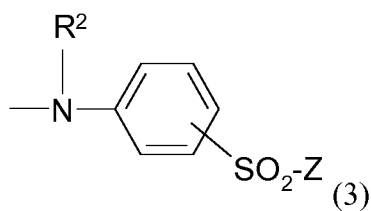
X^2 is Cl or F,

T^1 is a group of formula



wherein R^1 is methyl, ethyl or phenyl,

or



wherein R^2 is H, methyl or ethyl,

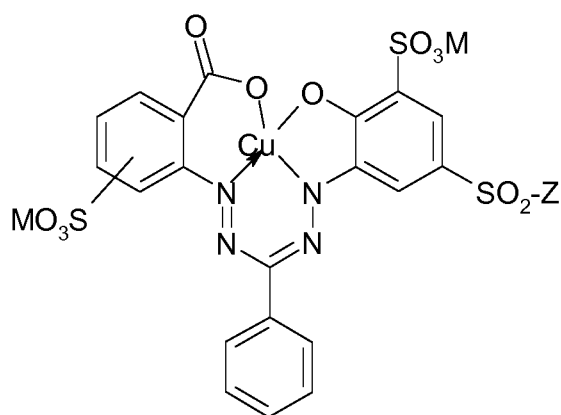
Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical,

wherein G is $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{M}$ or $-\text{OPO}_3\text{M}_2$

n is 2 or 3 and

M is H, Na, K or Li.

6. Dye mixture according to any one of claims 1 to 5, comprising at least one dye of formula (IIb)



(IIb)

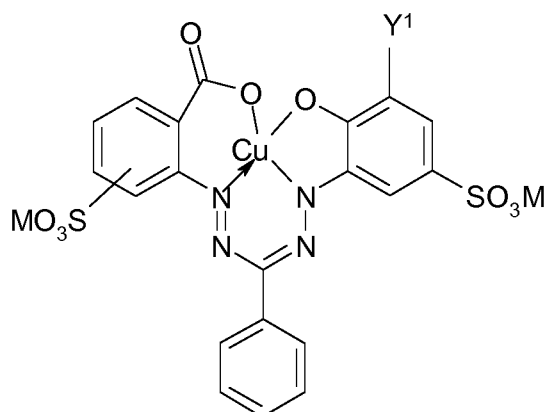
wherein independent from each other

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

M is H or Na.

5

7. Dye mixture according to any one of claims 1 to 6, comprising at least one dye of formula (IIc)

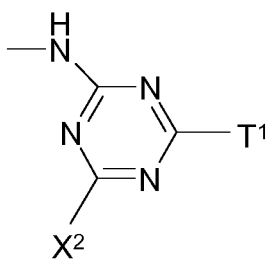


(IIc)

wherein independent from each other

Y^1 is a group of the formula (1)

10

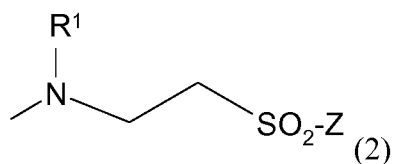


(1)

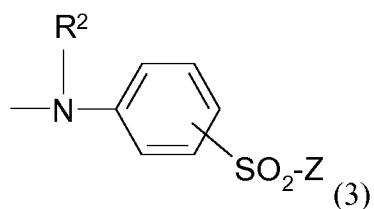
wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or

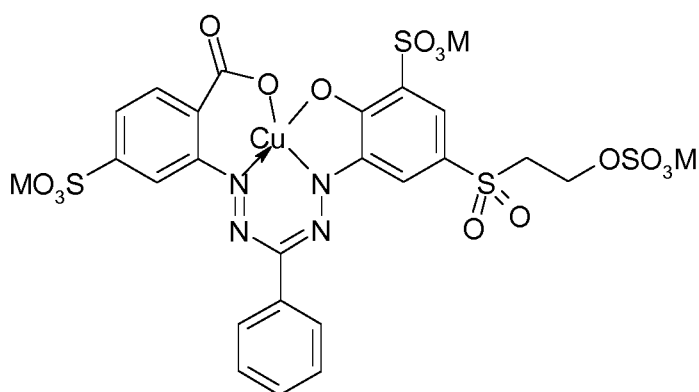


wherein independent from each other

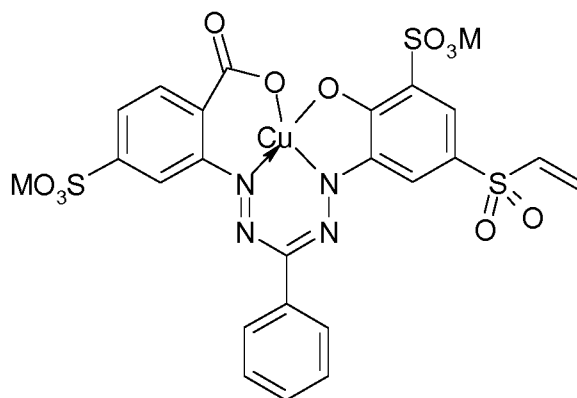
5

 R^1 is methyl, ethyl or phenyl, R^2 is H, methyl or ethyl, Z is ---CH=CH_2 or $\text{---CH}_2\text{---CH}_2\text{---OSO}_3\text{M}$ and M is H or Na.

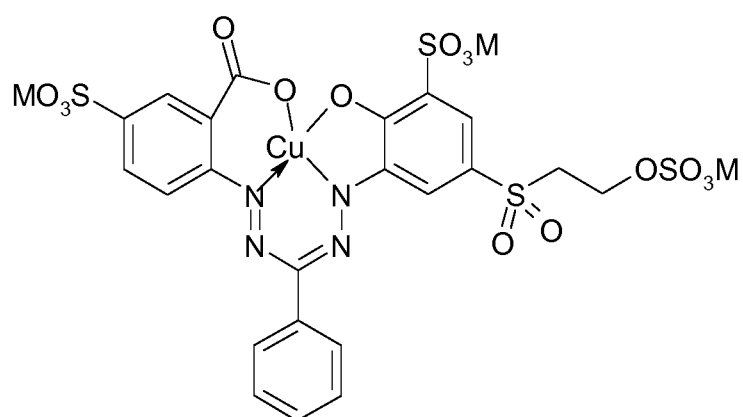
- 10 8. Dye mixture according to any one of claims 1 to 7, comprising at least one dye selected from the list consisting of:



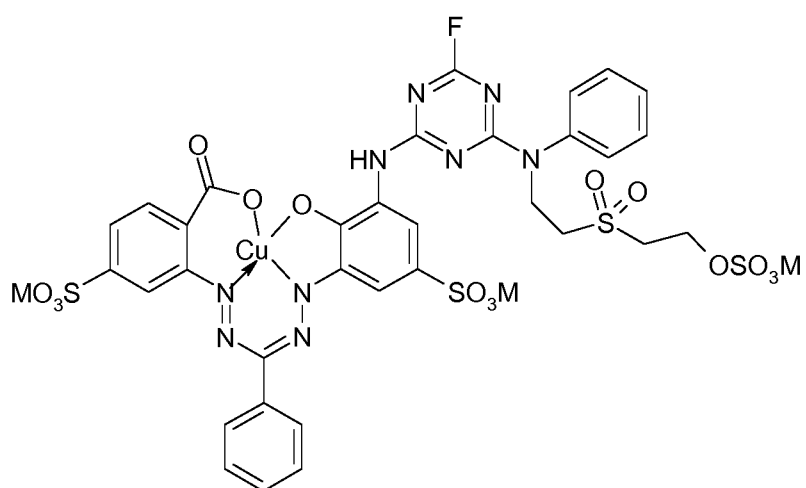
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(II-2),

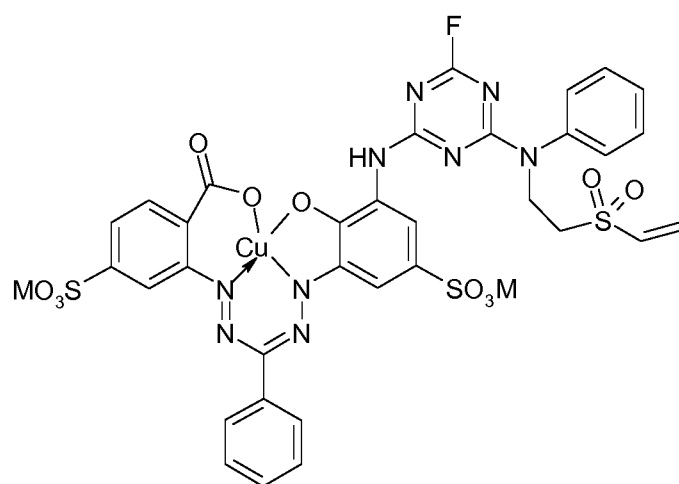


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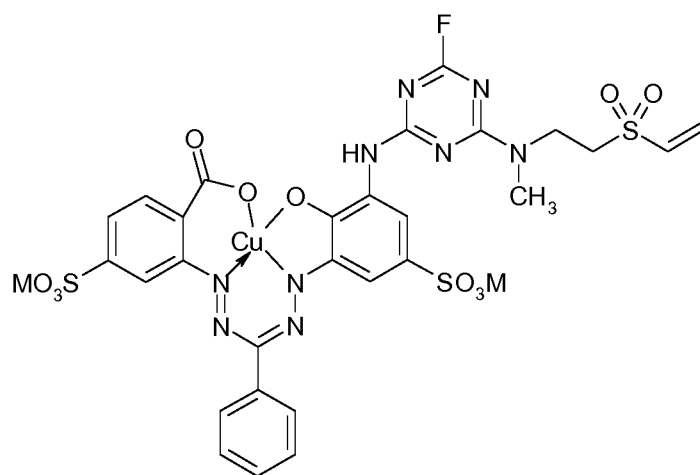
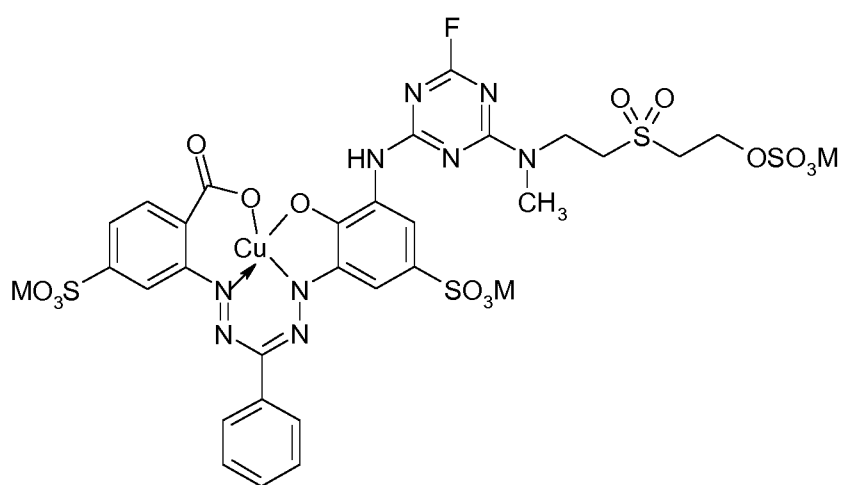
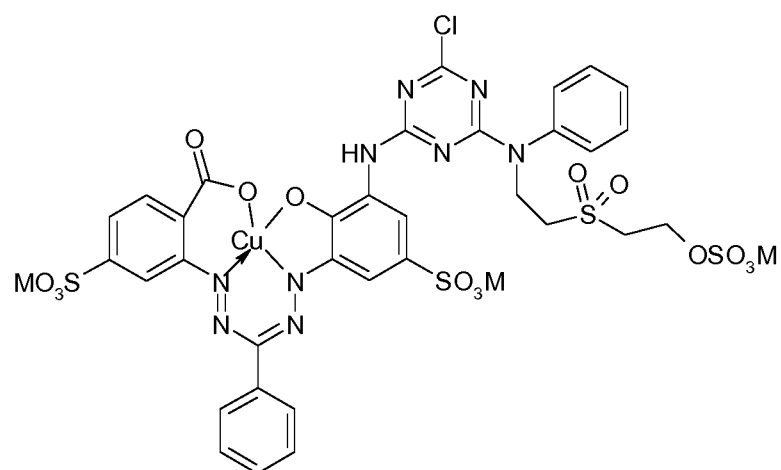


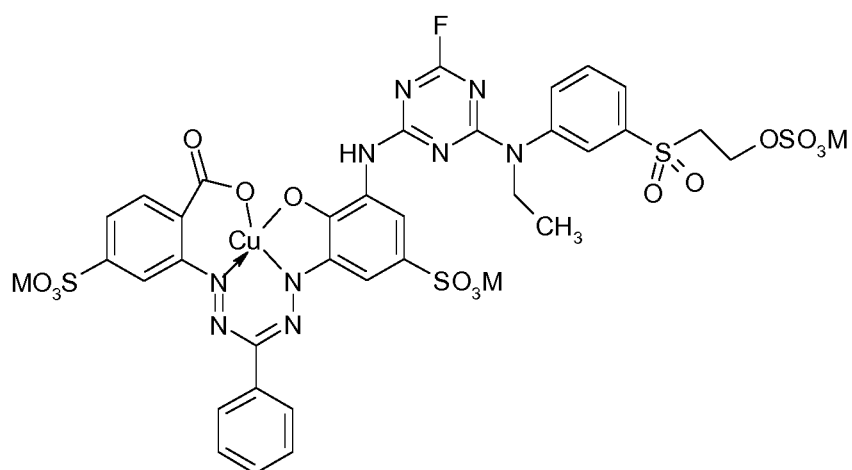
(II-4),

5

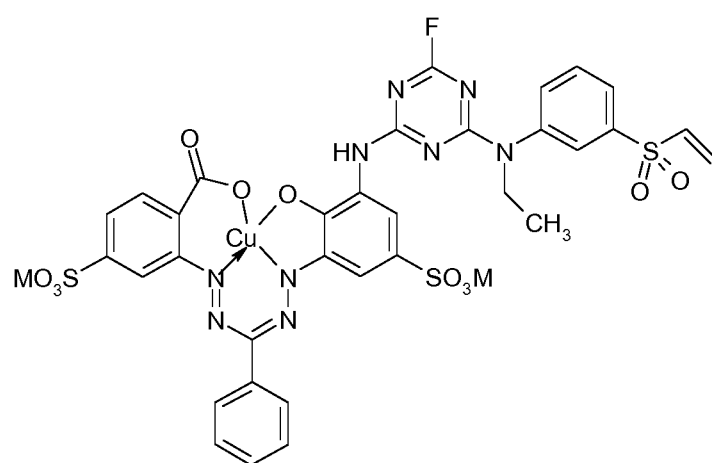


(II-5),

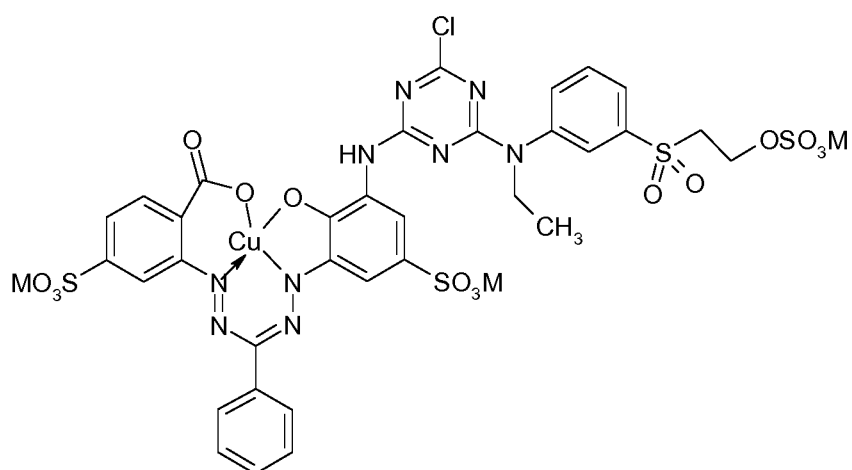




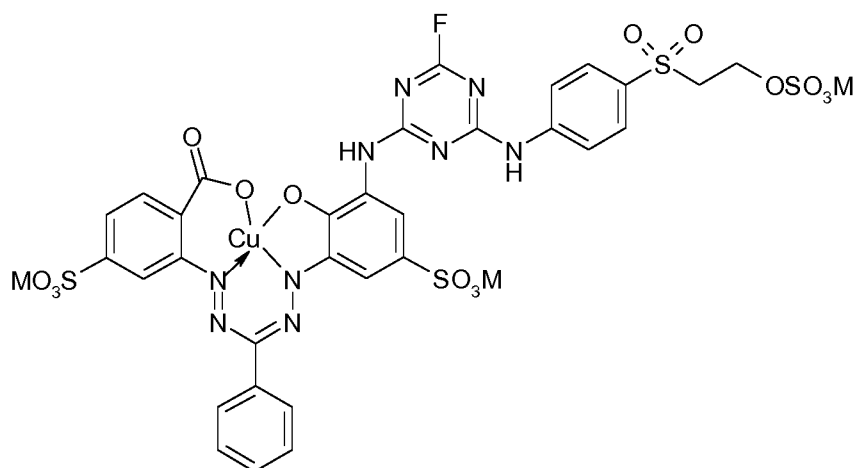
(II-9),



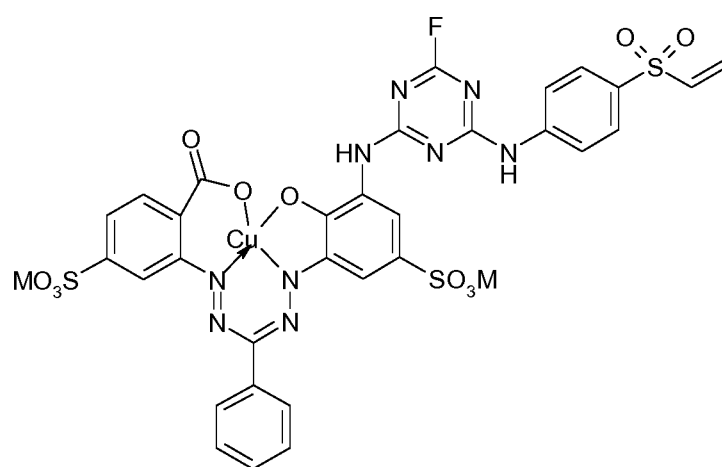
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(II-11),

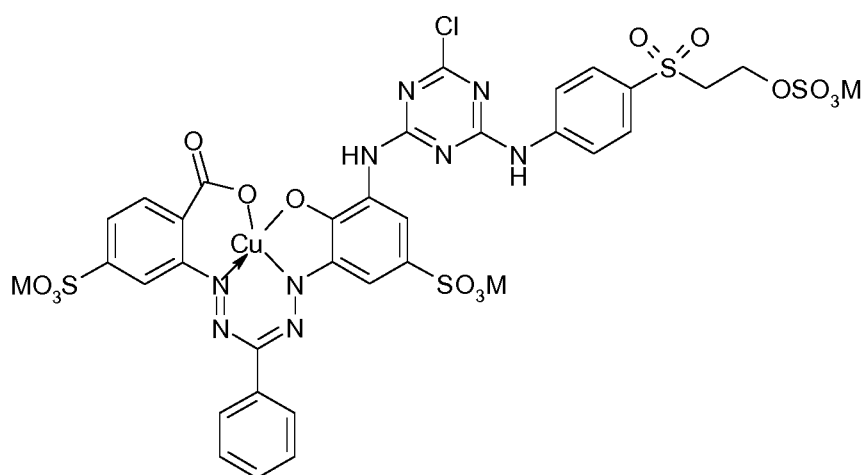


(II-12),



(II-13)

and



(II-14)

5

wherein

M is H or Na.

9. Dye mixtures according to any one of claims 1 to 8, wherein at least one dye of formula (I) is selected from the list consisting of (I-1), (I-2) and (I-4) and the at least one dye of formula (II) is selected from the list consisting of (II-1), (II-4) and (II-11).
- 5 10. Dye mixture according to any one of claims 1 to 9, wherein the amount of dye(s) of formula (I) is 80 to 20 wt% and the amount of dye(s) of formula (II) is 20 to 80 wt% of the total weight of dyes in the mixture.
- 10 11. Dye mixture according to claim 10, wherein the amount of dye(s) of formula (I) is 65 to 35 wt% and the amount of dye(s) of formula (II) is 35 to 65 wt% of the total weight of dyes in the mixture.
12. Solution for dyeing comprising a dye mixture according to any one of claims 1 to 11.
- 15 13. Process for the production of a dye mixture according to any one of claims 1 to 11, comprising
a) mixing the components of the dye mixture,
b) homogenizing the mixture obtained in step a).
- 20 14. Process for dyeing or printing material, comprising contacting the material with a dye mixture according to any one of claims 1 to 11 and/or a solution according to claim 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/081815

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09B67/22 D06P3/66 D06P1/38
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09B D06P

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 199921 Thomson Scientific, London, GB; AN 1999-248591 XP002769941, -& JP H11 71534 A (SUMITOMO CHEM CO LTD) 16 March 1999 (1999-03-16) abstract -& JP 3 405135 B2 (SUMITOMO CHEMICAL CO) 12 May 2003 (2003-05-12) page 18; compound 12 page 20; compound 20 page 22, paragraph 142; example 14; table 1 ----- -/--	1,5,7,8, 10-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 February 2018

Date of mailing of the international search report

02/03/2018

Name and mailing address of the ISA/

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Authorized officer

Ketterer, Michael

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/081815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/090485 A1 (CIBA SC HOLDING AG [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN GEORG [DE]) 29 September 2005 (2005-09-29) cited in the application examples 12,14,15 page 21, line 33 -----	1-14
A	WO 2007/003541 A2 (HUNTSMAN ADV MAT SWITZERLAND [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN G) 11 January 2007 (2007-01-11) page 12 - page 14 page 17 - page 19 -----	1-14
A	WO 2012/025279 A1 (HUNTSMAN ADV MAT SWITZERLAND [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN G) 1 March 2012 (2012-03-01) page 10 - page 13 -----	1-14
A	US 4 754 023 A (TZIKAS ATHANASSIOS [CH] ET AL) 28 June 1988 (1988-06-28) cited in the application examples 48,49 column 59 claim 15 -----	1-14
A	EP 0 644 240 A1 (HOECHST AG [DE]) 22 March 1995 (1995-03-22) claims 7,9; examples 1,3,5,7,9,11,13-22 -----	1-14
A	WO 2011/101185 A1 (HUNTSMAN ADV MAT SWITZERLAND [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN G) 25 August 2011 (2011-08-25) page 9 page 12 page 14 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/081815

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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JP 3405135 B2	12-05-2003	JP 3405135 B2 JP H1171534 A	12-05-2003 16-03-1999
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WO 2012025279 A1	01-03-2012	BR 112013004125 A2 CN 103080414 A EP 2609247 A1 KR 20130100133 A TW 201213449 A US 2013283546 A1 WO 2012025279 A1	28-06-2016 01-05-2013 03-07-2013 09-09-2013 01-04-2012 31-10-2013 01-03-2012
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EP 0644240 A1	22-03-1995	BR 9403787 A CA 2132480 A1 CN 1102842 A DE 4332047 A1 EP 0644240 A1 JP H07150065 A PL 305102 A1	23-05-1995 22-03-1995 24-05-1995 23-03-1995 22-03-1995 13-06-1995 03-04-1995
WO 2011101185 A1	25-08-2011	BR 112012020225 A2 CN 102753627 A	24-01-2017 24-10-2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/081815

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		CO 6561798 A2	15-11-2012
		DO P2012000198 A	31-12-2012
		EP 2536791 A1	26-12-2012
		ES 2634543 T3	28-09-2017
		GT 201200240 A	15-01-2014
		KR 20130026426 A	13-03-2013
		MA 34065 B1	05-03-2013
		PE 04942013 A1	24-04-2013
		PT 2536791 T	04-08-2017
		RU 2012139840 A	27-03-2014
		TW 201141961 A	01-12-2011
		US 2012302486 A1	29-11-2012
		WO 2011101185 A1	25-08-2011

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Date of mailing (day/month/year) 09 January 2018 (09.01.2018)	
Applicant's or agent's file reference DYS 2016/002	IMPORTANT NOTIFICATION
International application No. PCT/EP2017/081815	International filing date (day/month/year) 07 December 2017 (07.12.2017)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 15 December 2016 (15.12.2016)
Applicant DYSTAR COLOURS DISTRIBUTION GMBH	

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Priority datePriority application No.Country or regional Office
or PCT receiving OfficeDate of receipt
of priority document

15 December 2016 (15.12.2016)

16204294.9

EP

23 December 2017 (23.12.2017)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

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Facsimile No. +41 22 338 89 75	

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:	PCT/EP2017/081815
International filing date:	07 December 2017 (07.12.2017)
Document type:	Certified copy of priority document
Document details:	Country/Office: EP
	Number: 16204294.9
	Filing date: 15 December 2016 (15.12.2016)
Date of receipt at the International Bureau:	23 December 2017 (23.12.2017)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)

Bescheinigung

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Patent application No.

Demande de brevet n°

16204294.9 / EP16204294

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP16204294.

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.



V. Joseph

Anmeldung Nr:
Application no.: 16204294.9
Demande no :

Anmeldetag:
Date of filing: 15.12.16
Date de dépôt :

Anmelder / Applicant(s) / Demandeur(s):

DyStar Colours Distribution GmbH
Am Prime Parc 10-12
65479 Raunheim/DE

Bezeichnung der Erfindung / Title of the invention / Titre de l'invention:

(Falls die Bezeichnung der Erfindung nicht angegeben ist, oder falls die Anmeldung in einer Nicht-Amtssprache des EPA eingereicht wurde, siehe Beschreibung bezüglich ursprünglicher Bezeichnung.

If no title is shown, or if the application has been filed in a non-EPO language, please refer to the description for the original title.

Si aucun titre n'est indiqué, ou si la demande a été déposée dans une langue autre qu'une langue officielle de l'OEB, se référer à la description pour le titre original.)

BLUE AND NAVY FIBRE REACTIVE DYES MIXTURES

In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)

Staat/Tag/Aktenzeichen / State/Date/File no. / Pays/Date/Numéro de dépôt:

Am Anmeldetag benannte Vertragsstaaten / Contracting States designated at date of filing / Etats contractants désignés lors du dépôt:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO RS SE SI SK SM TR

Blue and navy fibre reactive dye mixtures

The present invention relates to the use of mixtures of fibre reactive formazan dyes with fibre reactive azo dyes and their use for the dyeing of hydroxyl- and carboxamide-containing material in blue and navy shades.

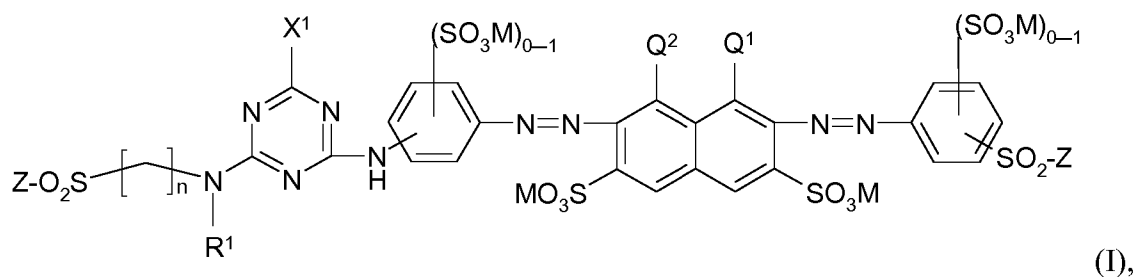
Fibre reactive formazan dyes are of interest due to their potential to produce neutral to greenish blue dyeings with high fastness to light. However, they often possess certain performance limitations, such as deficient build-up of colour to deeper shades and low resistance to oxidative agents.

These performance limitations can partly be overcome in some cases by the use of mixtures of fibre reactive formazan dyes with selected other fibre reactive azo dyes. Such mixtures make it possible, for example, to achieve neutral to greenish Navy shades with high light and perspiration-light fastness, good resistance to washing in the presence of modern oxidative detergents, and good colour constancy in different light sources. The use of such mixtures (as described for example in WO 2005/090485, JP 2001098183 A, JP 3405135 B2) can give dyeings with superior fastness properties to existing mono-molecular fibre reactive Navy dyes (described for example in CN 102504582 A or EP 0568876).

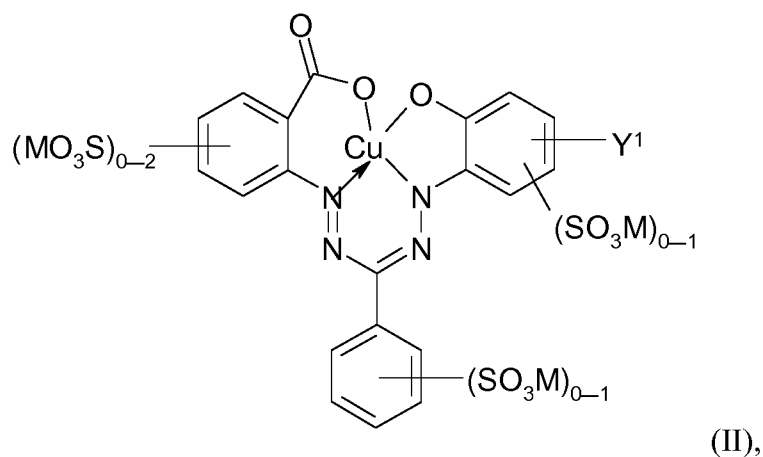
Due to developing consumer requirements there is still a need for new dyestuffs with even better build-up and levelness, high light- and oxidative fastness, especially peroxide and NO_x (moist) fastness.

Surprisingly it was now found, that combinations of specific Formazane dyes with special types of azo Navy dyes have these required properties in a very high degree.

The present invention is thus directed to a dye mixture comprising at least one dye of formula (I)



and at least one dye of formula (II)

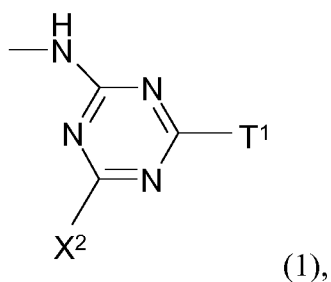


5 wherein independent from each other

Q^1 is OH and Q^2 is NH_2 or Q^1 is NH_2 and Q^2 is OH,

X^1 is Cl or F,

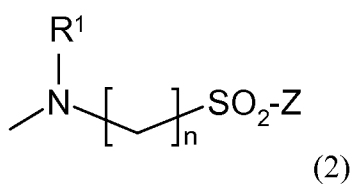
Y^1 is $-SO_2-Z$ or a group of formula (1)



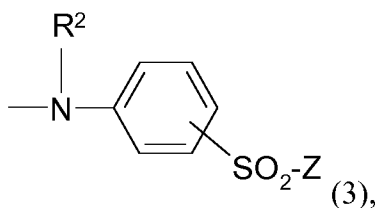
10 wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or



wherein independent from each other

R^1 is methyl, ethyl or phenyl,

R^2 is H, methyl or ethyl,

5 n is 2 or 3,

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

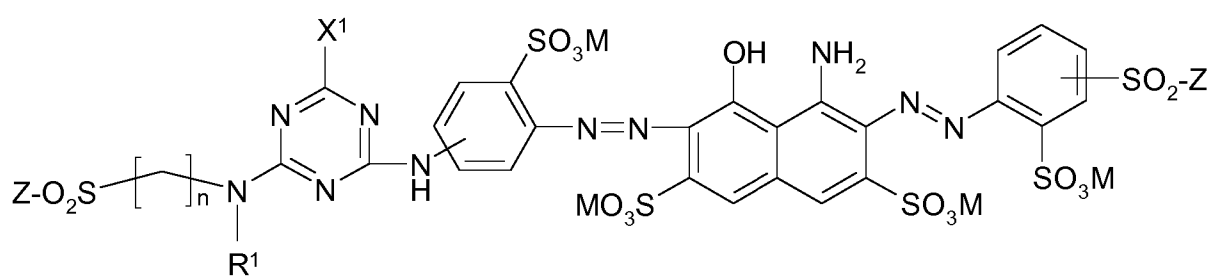
wherein G is a group that is removable under alkaline conditions and

M is H, an alkali metal or one equivalent of an alkaline earth metal.

10 The dyes of formulae (I) and (II) are known or can be prepared according to methods known per se. Dyes of formula (I) are described, for example, in CN 102504582 A and EP 0 568 876. Dyes of formula (II) are described, for example, in US 4,336,190 and US 4,754,023.

A group that is removable under alkaline conditions is e.g. $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{M}$, $-\text{OPO}_3\text{M}_2$,
 15 $-\text{O}-\text{CO}-\text{CH}_3$, $-\text{O}-\text{CO}-\text{C}_6\text{H}_5$.

Of course there exist preferred versions and a dye mixture as described above, comprising at least one dye of formula (Ia)



20 (Ia)

wherein independent from each other

X^1 is Cl or F,

R^1 is methyl, ethyl or phenyl,

n is 2 or 3,

25 Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{G}$ radical

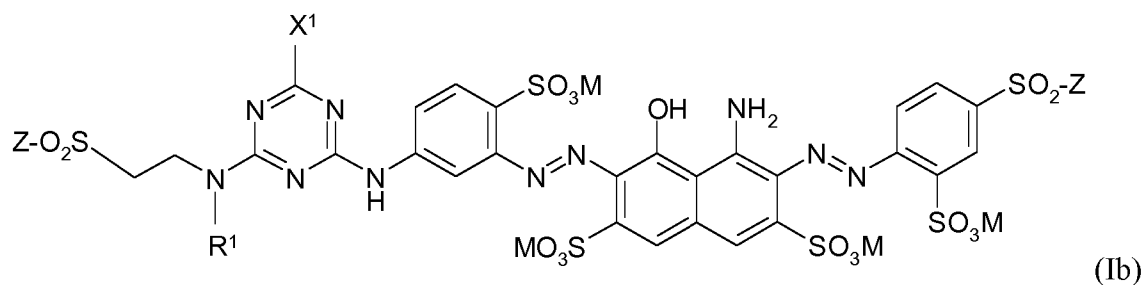
wherein

G is -Cl, -Br, -F, -OSO₃M or -OPO₃M₂ and

M is H, Na, K or Li

is preferred.

- 5 More preferred is a dye mixture as described above, comprising at least one dye of formula (Ib)



wherein independent from each other

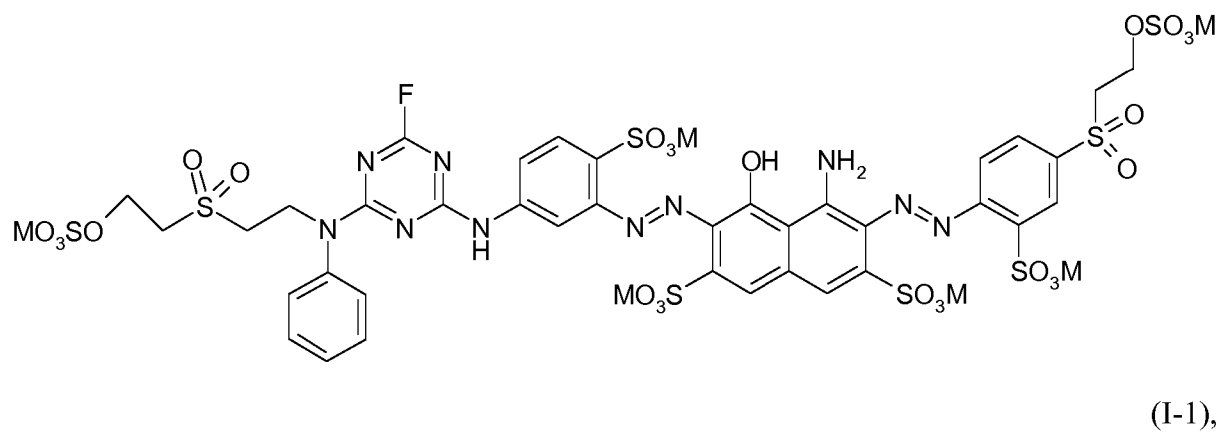
X¹ is Cl or F,

R¹ is methyl, ethyl or phenyl,

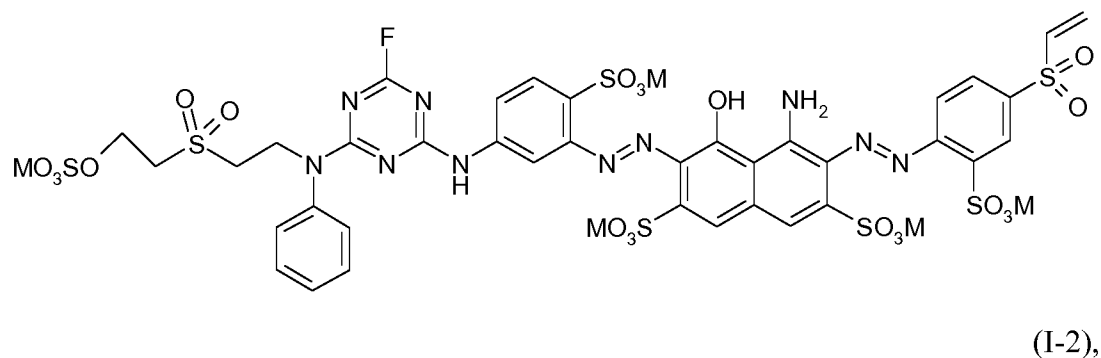
- 10 Z is -CH=CH₂ or a -CH₂-CH₂-OSO₃M and

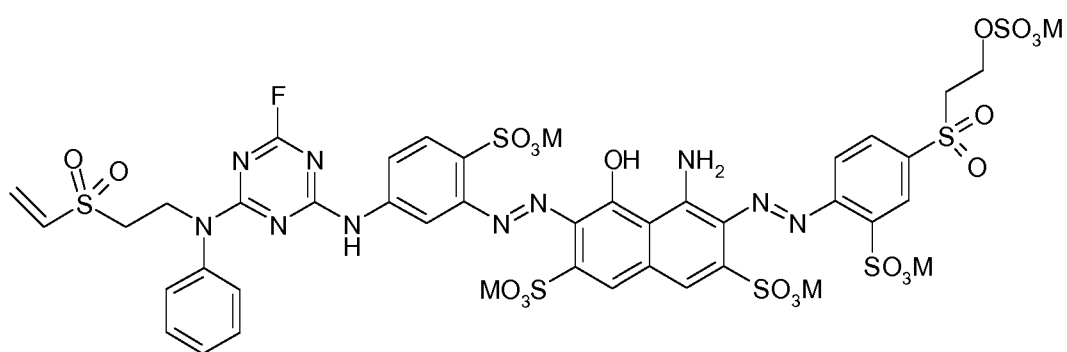
M is H or Na.

Even more preferred is a dye mixture as described above, comprising at least one dye selected from the list consisting of:

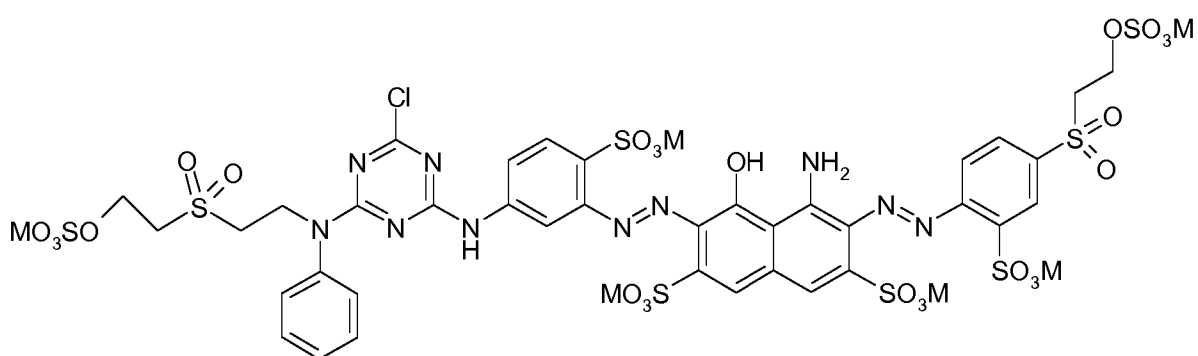


15

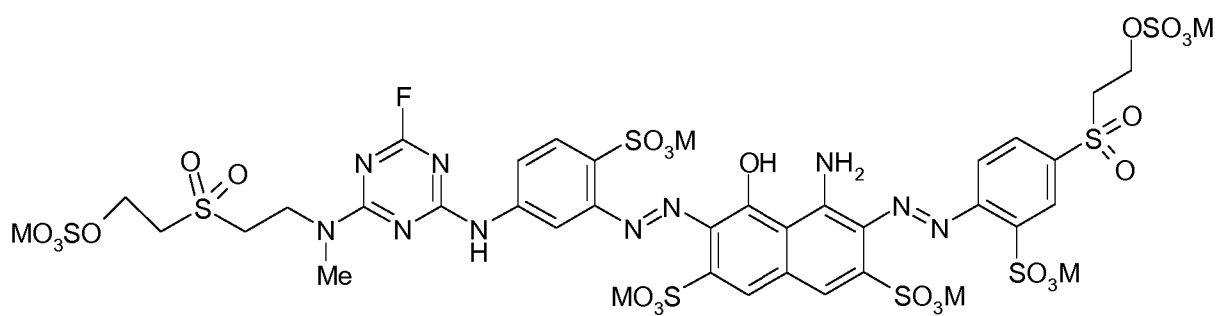




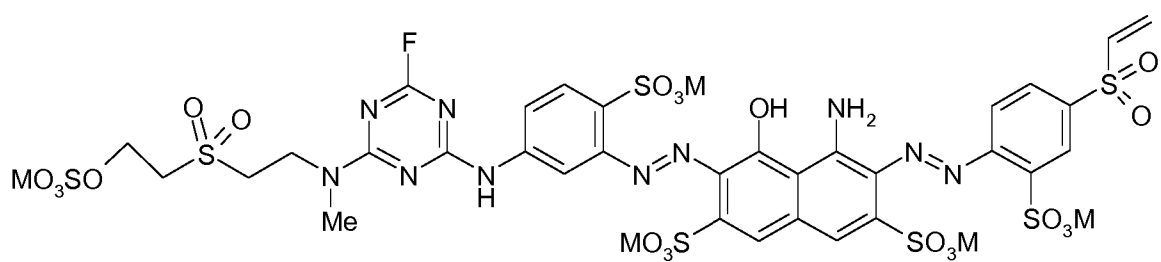
(I-3),



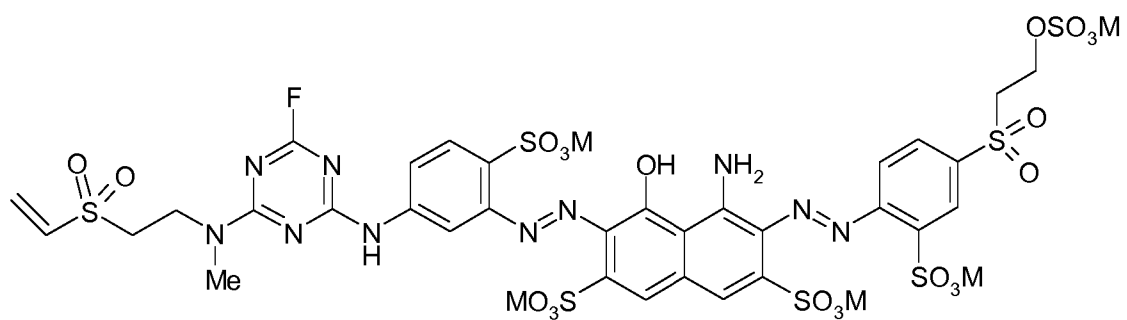
(I-4),



(I-5),

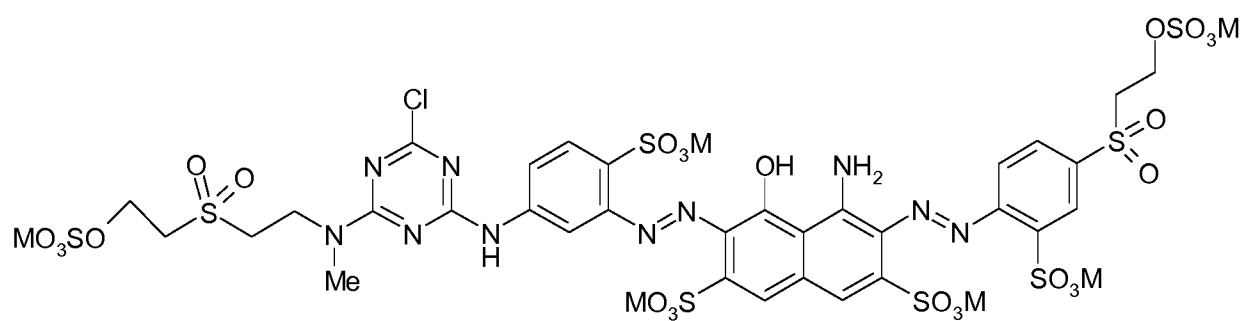


(I-6),



(I-7)

and



(I-8),

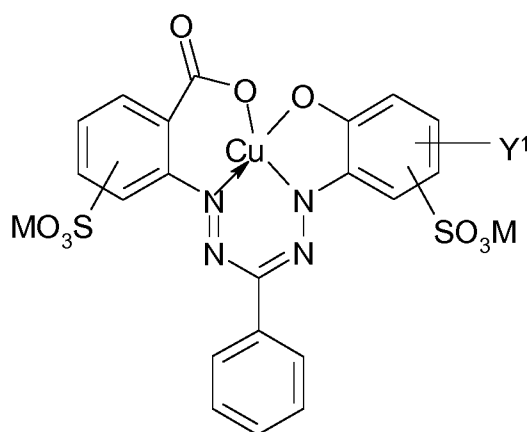
5

wherein

M is H or Na.

Also regarding the selection of the dyes of formula (II) there exist preferred versions and a dye mixture as described above, comprising at least one dye of formula (IIa)

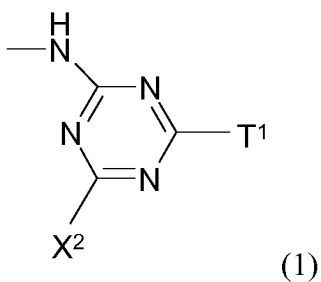
10



(IIa)

wherein

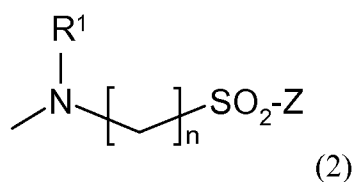
Y¹ is -SO₂-Z or a group of the formula (1)



wherein

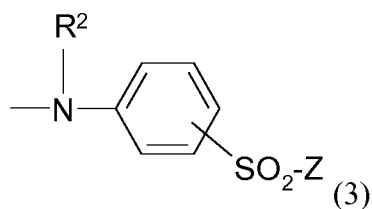
X^2 is Cl or F,

T^1 is a group of formula



wherein R^1 is methyl, ethyl or phenyl,

or



wherein R^2 is H, methyl or ethyl,

Z is ---CH=CH_2 or a $\text{---CH}_2\text{---CH}_2\text{---G}$ radical,

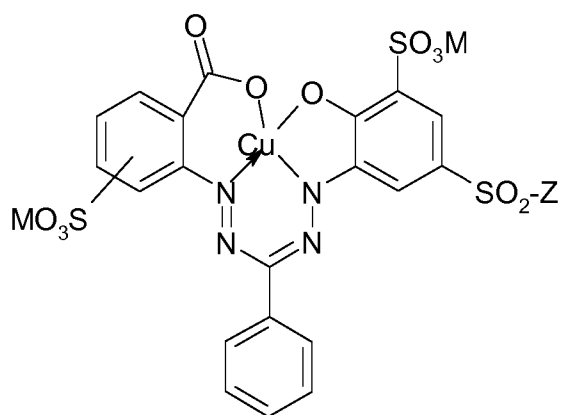
wherein G is ---Cl , ---Br , ---F , $\text{---OSO}_3\text{M}$ or $\text{---OPO}_3\text{M}_2$

n is 2 or 3 and

M is H, Na, K or Li

is preferred.

More preferred is a dye mixture as described above, comprising at least one dye of formula (IIb)



(IIb)

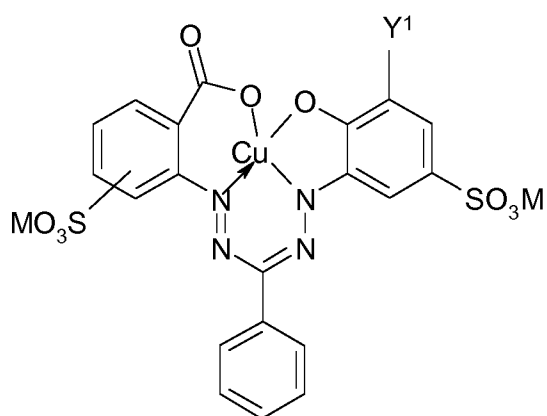
wherein independent from each other

Z is $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

M is H or Na.

5

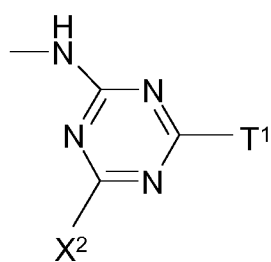
Also preferred is a dye mixture as described above, comprising at least one dye of formula (IIc)



(IIc)

wherein independent from each other

Y^1 is a group of the formula (1)



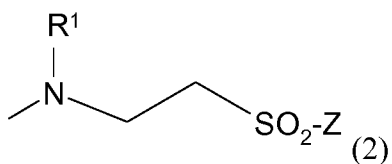
(1)

wherein independent from each other

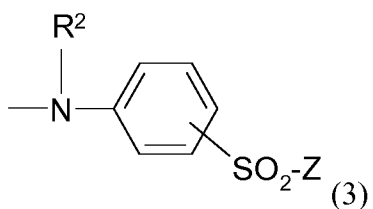
X^2 is Cl or F,

T^1 is a group of formula

10



or



wherein independent from each other

5

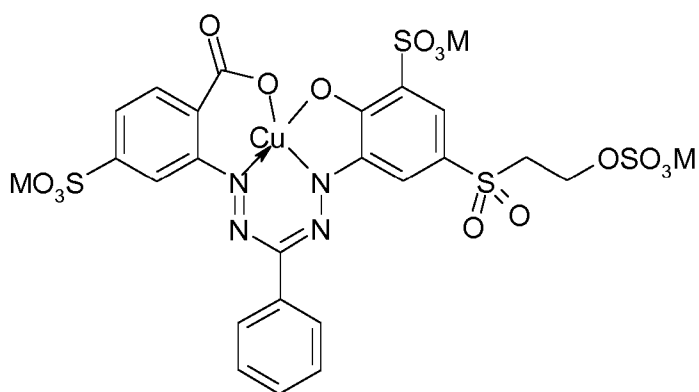
R^1 is methyl, ethyl or phenyl,

R^2 is H, methyl or ethyl,

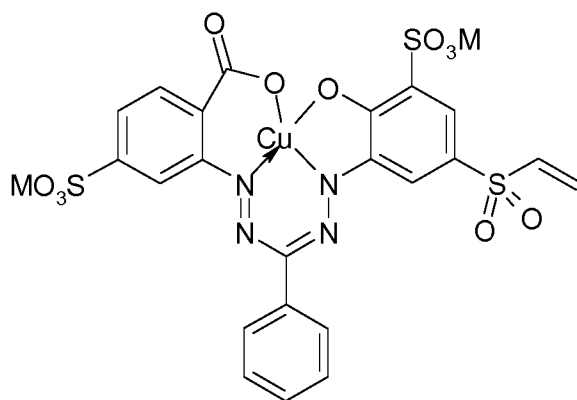
Z is $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{---CH}_2\text{---OSO}_3\text{M}$ and

M is H or Na.

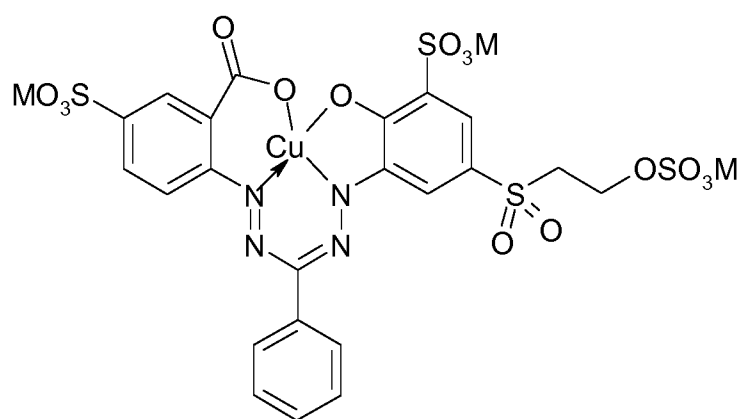
- 10 Even more preferred is a dye mixture as described above, comprising at least one dye selected from the list consisting of:



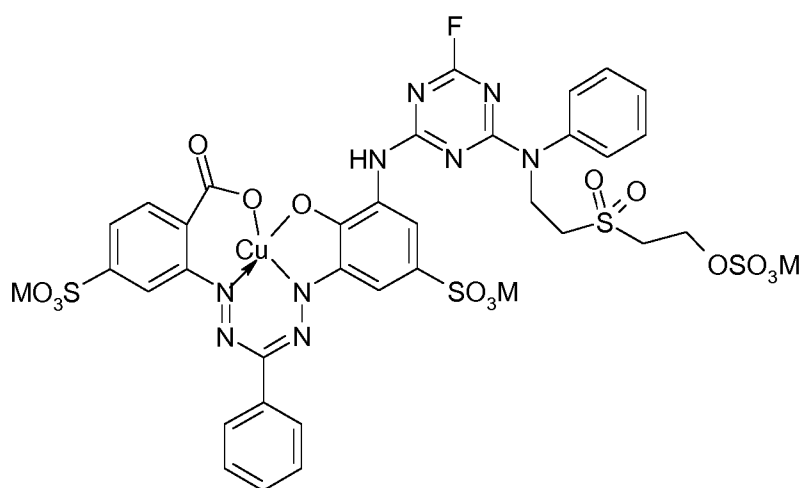
(II-1),



(II-2),

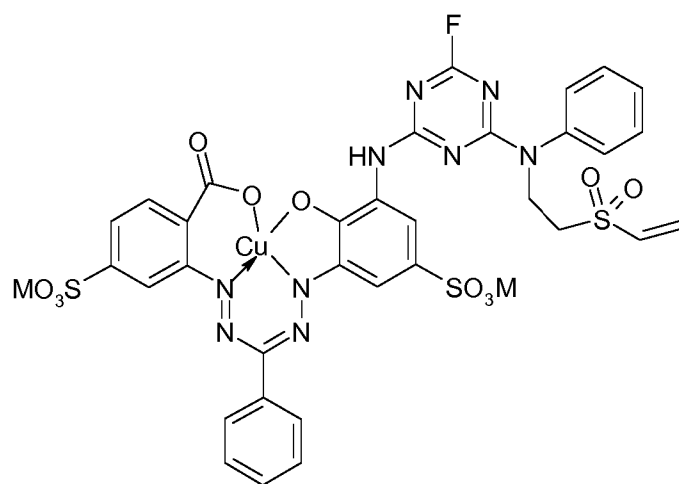


(II-3),



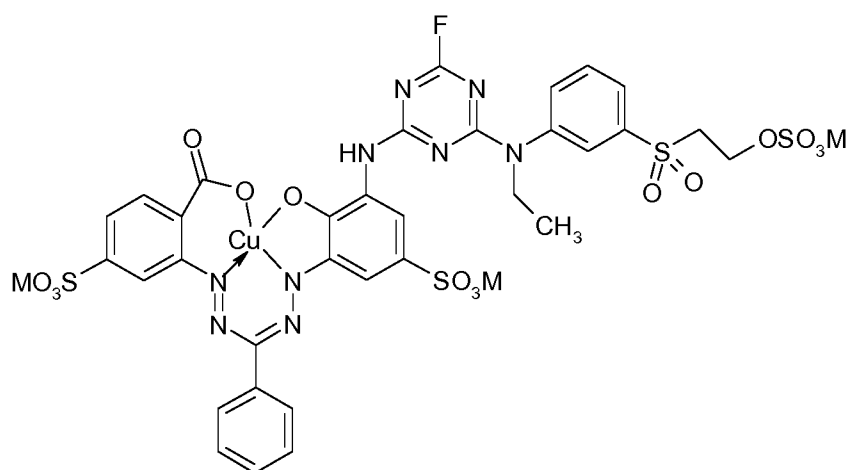
(II-4),

5

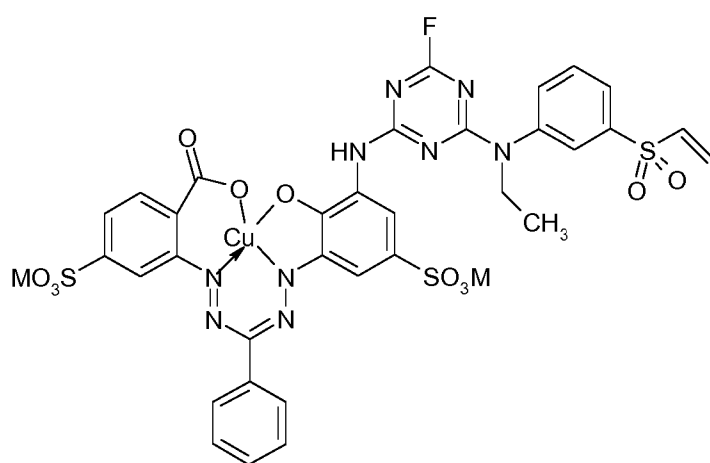


(II-5),

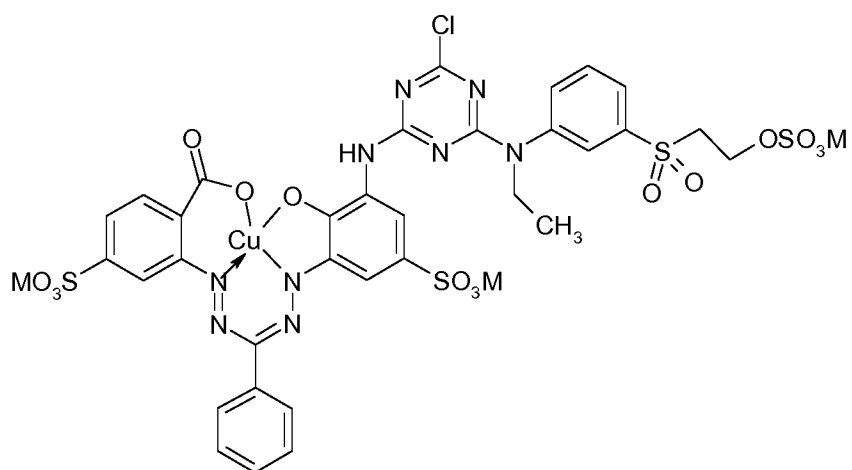




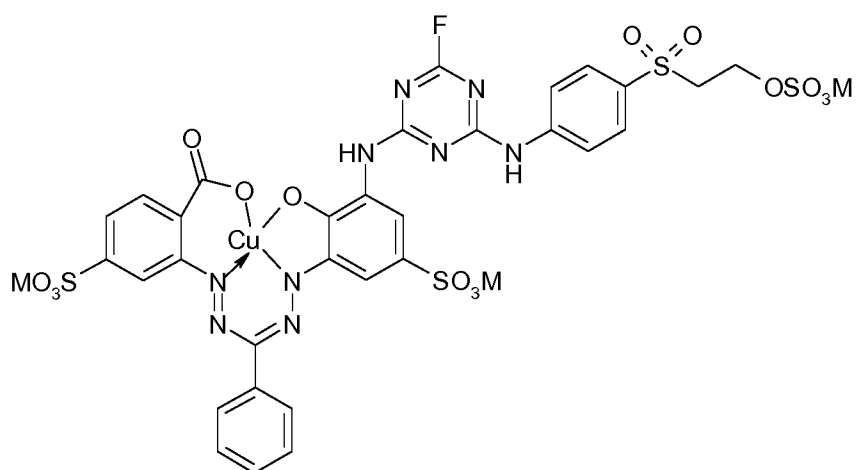
(II-9),



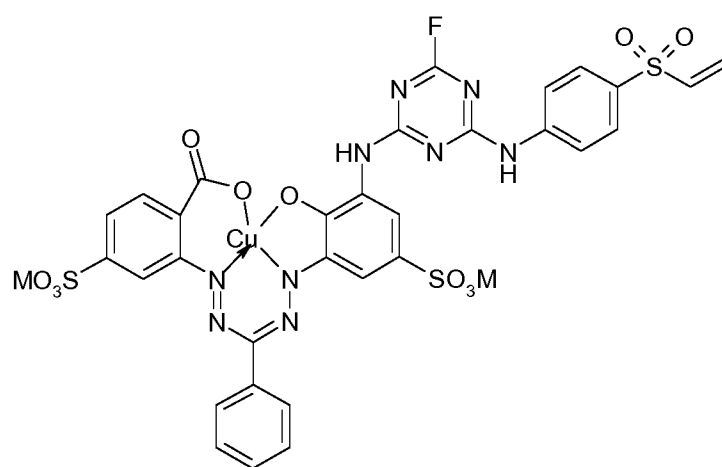
(II-10),



(II-11),

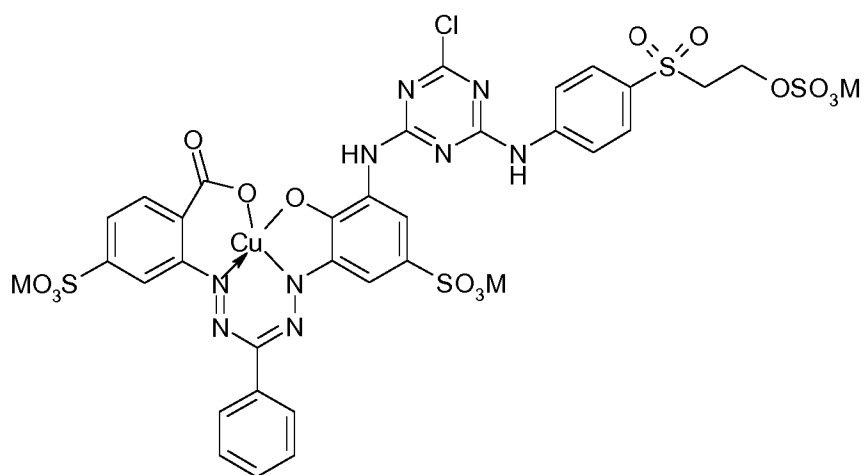


(II-12),



(II-13)

and



(II-14)

5

wherein

M is H or Na.

Combinations of preferred selections of dye(s) (I) and of dye(s) (II) are particularly preferred. Accordingly dye mixtures comprising at least one dye of formula (Ia) and at least one dye of formula (IIa) are preferred. Even more preferred are dye mixtures comprising at least one dye of formula (Ib) and at least one dye of formula (IIb) and/or (IIc). Those dye mixtures, in which
5 dyes selected from the list of dyes of formula (I-1) to (I-8) are combined with dyes selected from the list of dyes of formula (II-1) to (II-14) are particularly preferred. Within this group the most preferred dye mixtures are those, wherein at least one dye of formula (I) is selected from the list consisting of (I-1), (I-2) and (I-4) and the at least one dye of formula (II) is selected from the list consisting of (II-1), (II-4) and (II-11).

10

The most preferred dye mixtures are comprising dyes of formula:

(I-1) and (II-1), (I-1) and (II-4), (I-1) and (II-11), (I-2) and (II-1), (I-2) and (II-4), (I-2) and (II-11), (I-4) and (II-1), (I-4) and (II-4) or (I-4) and (II-11).

15 The dyes of formula (I) and (II) and also the dye mixture according to the present invention may be present as a preparation in solid or in liquid (dissolved) form. In solid form they comprise, to the extent necessary, the electrolyte salts, which are customary for water-soluble and, in particular, fiber-reactive dyes, such as sodium chloride, potassium chloride, and sodium sulfate, and may further comprise the auxiliaries that are customary in commercial dyes, such
20 as buffer substances capable of setting a pH of between 3 and 7 in aqueous solution, such as sodium acetate, sodium citrate, sodium borate, sodium hydrogencarbonate, sodium dihydrogenphosphate and disodium hydrogenphosphate, and additionally dyeing auxiliaries, antidust agents, and small amounts of siccatives. If they are present in liquid, aqueous solution (including the content of thickeners of the kind customary for print pastes), they may also
25 comprise substances which ensure a long life for these preparations, such as mold preventatives, for example.

In solid form, the dyes of the formula (I) and (II) and also the dye mixture according to the invention are typically in the form of powders or granules which contain electrolyte salts
30 (referred to generally, below, as preparations) with, where appropriate, one or more of the abovementioned auxiliaries. In the preparations the dyes are present at 20 % to 90 % by weight, based on the preparation. The buffer substances are generally present in a total amount of up to 5 % by weight, based on the preparation.

Where the dyes of the formula (I) and (II) as well as the dye mixture according to the invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, such as, for example, between 5 % and 50 % by weight, the electrolyte salt content of these aqueous solutions being preferably below 10 % by weight, based on the aqueous solution; the aqueous solutions (liquid preparations) may contain the aforementioned buffer substances in general in an amount of up to 5 % by weight, preferably up to 2 % by weight.

For the dyes as such there exist preferred ranges as well. And a dye mixture as described above, wherein the amount of dye(s) of formula (I) is 80 to 20 wt% and the amount of dye(s) of formula (II) is 20 to 80 wt% of the total weight of dyes in the mixture is preferred. More preferred is a dye mixture as described above, wherein the amount of dye(s) of formula (I) is 65 to 35 wt% and the amount of dye(s) of formula (II) is 35 to 65 wt% of the total weight of dyes in the mixture. The total weight of dyes in the mixture is 100 wt%.

The dyes of formula (I) and (II) can be isolated in conventional manner by being salted out, using common salt or potassium chloride, for example, or by spray drying or evaporation. An alternative option is to put the as-synthesized solutions, where necessary following addition of a buffer substance and if desired after concentration, to dyeing use directly, in the form of liquid preparations.

A solution for dyeing comprising a dye mixture as described above thus is another aspect of the present invention.

A process for the production of a dye mixture as described above, comprising
a) mixing the components of the dye mixture,
b) homogenizing the mixture obtained in step a)
forms yet another aspect of the present invention.

The mixtures of dyes of formula (I) and (II) according to the present invention possess valuable performance properties and can be used for dyeing and printing carboxamido- and/or hydroxyl-containing materials. Accordingly the process for dyeing or printing material, comprising contacting the material with a dye mixture as described above and/or a solution as described above forms another aspect of the present invention.

The stated materials may take the form, for example, of sheet-like structures such as paper and leather, the form of films, such as polyamide films, for example, or the form of a bulk composition, as of polyamide or polyurethane, for example. More particularly, however, they
5 take the form of fibers of the stated materials.

The mixtures of the dyes of formula (I) and (II) according to the present invention are used for dyeing and printing cellulosic fiber materials of all kinds. They are preferably also suitable for dyeing or printing polyamide fibers or blend fabrics of polyamide with cotton or with polyester
10 fibers.

It is also possible to use the dye mixture of dyes having formula (I) and (II) according to the invention to print textiles or paper by the inkjet process.

15 The use of the mixtures of formula (I) and (II) as described above for dyeing or printing carboxamido- and/or hydroxyl-containing materials forms another aspect of the present invention, and processes for dyeing or printing carboxamido- and/or hydroxyl-containing materials in conventional procedures, by using one or more dyes of the general formula (I) according to the invention as colourants forms yet another aspect of the present invention.

20 Fibers or fiber materials for the purposes of the present invention are more particularly textile fibers, which may be present as woven fabrics or as yarns or in the form of hanks or wound packages.

25 Carboxamido-containing materials are, for example, synthetic and natural polyamides and polyurethanes, more particularly in the form of fibers, examples being wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11 and nylon-4.

30 Hydroxyl-containing materials are those of natural or synthetic origin, such as, for example, cellulose fiber materials or their regenerated products and polyvinyl alcohols. Cellulose fiber materials are preferably cotton, but also other plant fibers, such as linen, hemp, jute, and ramie fibers. Regenerated cellulose fibers are, for example, staple viscose and filament viscose.

The mixtures according to the present invention can be applied to and fixed on the stated

materials, more particularly the stated fiber materials, by the application techniques that are known for water-soluble dyes, and particularly for fiber-reactive dyes.

Wool, which has been given a non-felting or low-felting finish (cf., for example, H. Rath, Lehrbuch der Textilchemie, Springer-Verlag, 3rd edition (1972), pp. 295-299, especially wool finished by the Hercosett process (p. 298); J. Soc. Dyers and Colourists 1972, 93-99, and 1975, 33-44) can be dyed with very good fastness properties. The process of dyeing on wool takes place in a conventional dyeing procedure from an acidic medium. For example, acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate can be added to the dyebath in order to obtain the desired pH. To achieve a useful levelness in the dyeing, it is advisable to add customary levelling assistants, such as, for example, a levelling assistant based on a reaction product of cyanuric chloride with three times the molar amount of aminobenzenesulfonic acid and/or of an aminonaphthalenesulfonic acid, or one based on a reaction product of, for example, stearylamine with ethylene oxide.

Thus, for example, the dye mixture of the invention is preferably first subjected to the exhaust process from an acidic dyebath having a pH of about 3.5 to 5.5, with monitoring of the pH, and then, toward the end of the dyeing time, the pH is shifted into the neutral and optionally weakly alkaline range, to a pH of up to 8.5, in order, in particular, to induce the full reactive binding between the dyes of the dye mixtures of the invention and the fiber, in order to obtain high depths of colour. At the same time the fraction of dye which has not been reactively bound is removed.

The procedure described here also applies to the production of dyeings on fiber materials composed of other natural polyamides or of synthetic polyamides and polyurethanes. These materials can be dyed using the customary dyeing and printing processes that are described in the literature and known to the person skilled in the art (see, for example, H.-K. Rouette, Handbuch der Textilveredlung, Deutscher Fachverlag GmbH, Frankfurt am Main).

Besides mixtures of the general formula (I) and (II) and water, the dyeing liquors and print pastes may comprise further additives. Additives are, for example, wetting agents, antifoams, levelling agents, and agents that influence the properties of the textile material, such as softeners, flame retardant finish additives, and agents, which impart dirt, water, and oil repellency or that soften water. Print pastes in particular may also comprise natural or synthetic

thickeners, such as alginates and cellulose ethers, for example. In the dyebaths and print pastes, the amounts of dye may vary within wide limits, in accordance with the desired depth of colour. Generally speaking, a dye mixture of the formula (I) and (II) according to the present invention is present in amounts of 0.01 % to 15 % by weight, more particularly in amounts of 0.1 % to 10 % by weight, based on the dyeing goods or the print paste, respectively.

On cellulose fibers, dyeings having very good colour yields are obtained by the exhaust processes from a long liquor, using a wide variety of acid-binding agents and, where appropriate, neutral salts, such as sodium chloride or sodium sulfate. In the case of the exhaust process, it is preferred to carry out dyeing at a pH of 3 to 7, more particularly at a pH of 4 to 6. The liquor ratio may be selected within a wide range and is for example between 3 : 1 and 50 : 1, preferably between 5 : 1 and 30 : 1. Dyeing is done preferably in an aqueous bath at temperatures between 40 and 105 °C, optionally at a temperature up to 130 °C under superatmospheric pressure, and where appropriate in the presence of customary dyeing auxiliaries. The wet fastness properties of the dyed material can be enhanced by an aftertreatment to remove unfixed dye. This aftertreatment takes place more particularly at a pH of 8 to 9 and at temperatures of 75 to 80 °C.

One possible exhaust process procedure is to introduce the material into the warm bath and to gradually heat the bath to the desired temperature and complete the dyeing operation. The neutral salts, which accelerate the exhaustion of the dyes can also, if desired, not be added to the bath until the actual dyeing temperature has been reached.

The padding process on cellulose fibers likewise produces excellent colour yields and a very good colour build-up, with fixing able to take place in conventional manner by batching at room temperature or elevated temperature, at up to about 60 °C, for example, by steaming or by means of dry heat.

The customary printing processes for cellulose fibers as well, which can be carried out in one step - as for example by printing with a print paste comprising sodium bicarbonate or another acid-binding agent and by subsequent steaming at 100 to 103 °C - or in two steps - as for example by printing with a neutral or weakly acidic printing ink, followed by fixing either by passage of the printed materials through a hot, electrolyte-containing alkaline bath or by overpadding with an alkaline, electrolyte-containing padding liquor, and subsequent batching

or steaming or dry heat treatment of the alkali-overpadded material - produces strongly coloured prints with well-defined contours and a clear white ground. The outcome of the prints is affected little, if at all, by variations in the fixing conditions.

- 5 In the case of fixing by means of dry heat, in accordance with the customary thermofix processes, hot air at 120 to 200 °C is used. Besides 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.
- 10 The acid-binding agents which effect the fixation of the dyes on the cellulose fibers are, for example, water-soluble basic salts of the alkali metals and likewise alkaline earth metals of organic or inorganic acids or compounds which liberate alkali in the heat. Particularly included are the alkali metal hydroxides and alkali metal salts of weak to moderately strong organic or inorganic acids, the preferred alkali metal compounds being the sodium compounds and
- 15 potassium compounds. Examples of such acid-binding agents include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate, or mixtures thereof.
- 20 The dye mixtures comprising dyes of formula (I) and (II) according to the invention are notable in particular for high colour strengths and fixing yields and ease of wash-off of the portions not fixed on the fiber. Moreover, the dyeings and prints have good all-round fastness properties, such as high light fastness and very good wet fastnesses, such as fastness to washing, to water, to salt water, to cross-dyeing, and to perspiration, for example, and also good fastness to
- 25 pleating, hot pressing, and rubbing. They exhibit, furthermore, little tendency to stain polyamide in cotton/polyamide blend fabrics. All in all, therefore, they have an improved profile of properties relative to the dyes known from JP 47 036 838.

The present invention also provides inks for digital textile printing by the inkjet process, which

30 comprise a dye mixture of the formula (I) and (II) according to the invention.

The inks of the invention comprise a dye mixture comprising dyes of formula (I) and (II) according to the invention, in amounts, for example, of 0.1 % to 50 % by weight, preferably in amounts of 1 % to 30 % by weight, and more preferably in amounts of 1 % to 15 % by weight,

based on the total weight of the ink. It will be appreciated that the inks may also comprise mixtures of dyes of the general formula (I) according to the invention and other dyes used in textile printing.

- 5 For the use of the inks in the continuous flow process, a conductivity of 0.5 to 25 mS/m can be set by addition of electrolyte. Examples of suitable electrolyte include lithium nitrate and potassium nitrate.

- 10 The inks of the invention may contain organic solvents with a total content of 1 to 50 %, preferably of 5 to 30 % by weight.

- Examples of suitable organic solvents include alcohols, such as methanol, ethanol, 1-propanol, isopropanol, 1-butanol, tert-butanol, pentyl alcohol, polyhydric alcohols, such as 1,2-ethanediol, 1,2,3-propanetriol, butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-propanediol, 1,3-
15 propanediol, pentanediol, 1,4-pentanediol, 1,5-pentanediol, hexanediol, D,L-1,2-hexanediol, 1,6-hexanediol, 1,2,6-hexanetriol, 1,2-octanediol, polyalkylene glycols, such as polyethylene glycol, polypropylene glycol, alkylene glycols having 2 to 8 alkylene groups, e.g.: monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, thioglycol, thiodiglycol, butyltriglycol, hexylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol monohexyl ether, triethylene glycol monomethyl ether, triethylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monobutyl ether, tetraethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, tripropylene glycol isopropyl ether, polyalkylene glycol ethers, such as polyethylene glycol monomethyl ether, polypropylene glycol glycerol ether, polyethylene glycol tridecyl ether, and polyethylene glycol nonylphenyl ether, amines, such as methylamine, ethylamine, diethylamine, triethylamine, diethylamine, dimethylamine, trimethylamine, dibutylamine, diethanolamine, triethanolamine, ethylenediamine, urea derivatives, such as urea, thiourea, N-methylurea, N,N'-dimethylurea, ethyleneurea, and 1,1,3,3-tetramethylurea, amides, such as dimethylformamide, dimethylacetamide, acetamide, N-formylethanolamine, N-acetyethanolamine, ketones or keto alcohols, such as acetone, diacetone alcohol, cyclic
- 20
25
30

ethers, such as tetrahydrofuran, dioxane, and also trimethylolethane, trimethylolpropane, 2-butoxyethanol, benzyl alcohol, gamma-butyrolactone, epsilon-caprolactam, and additionally sulfolane, methylsulfolane, 2,4-dimethylsulfolane, dimethyl sulfone, butadiene sulfone, dimethyl sulfoxide, dibutyl sulfoxide, N-cyclohexylpyrrolidone, N-methyl-2-pyrrolidone, N-ethylpyrrolidone, 2-pyrrolidone, 1-(2-hydroxyethyl)-2-pyrrolidone, 1-(3-hydroxypropyl)-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-2-imidazolinone, 1,3-bismethoxymethylimidazolidine, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-(2-butoxyethoxy) ethanol, 2-(2-propoxyethoxy)ethanol, 1,2-dimethoxypropane, trimethoxypropane, pyridine, piperidine, ethyl acetate, ethylenediaminetetraacetate, and ethyl pentyl ether.

The inks of the invention may further comprise the customary additives, such as, for example, viscosity moderators to set viscosities in the range from 1.5 to 40 mPas in a temperature range from 20 to 50 °C. Preferred inks have a viscosity of 1.5 to 20 mPas, and particularly preferred inks have a viscosity of 1.5 to 15 mPas.

Suitable viscosity moderators are rheological additives, examples being the following: polyvinylcaprolactam, polyvinylpyrrolidone, and also their copolymers, polyetherpolyol, associative thickeners, polyurea, polyurethane, sodium alginates, modified galactomannans, polyetherurea, polyurethane, and nonionic cellulose ethers.

As further additives the inks of the invention may include surface-active substances for setting surface tensions of 20 to 65 mN/m, which are adapted if necessary as a function of the process used (thermo or piezoelectric technology).

Examples of suitable surface-active substances include the following: surfactants of all kinds, preferably nonionic surfactants, butyldiglycol, and 1,2-hexanediol.

The inks may further comprise customary additives, such as substances for inhibiting fungal and bacterial growth, for example, in amounts of 0.01 % to 1 % by weight, based on the total weight of the ink.

The inks of the invention may be prepared in conventional manner by mixing of the components in water.

The inks of the invention are suitable for use in inkjet printing processes for printing a very wide variety of pretreated materials, such as silk, leather, wool, polyamide fibers and polyurethanes, and more particularly cellulosic fiber materials of all kinds. The printing inks of the invention are also suitable for printing pretreated hydroxyl- and/or amino-containing fibers that are present in blend fabrics; for example, mixtures of cotton, silk, wool with polyester fibers or polyamide fibers.

In contrast to conventional textile printing, where the printing ink already contains all of the fixing chemicals and thickeners for a reactive dye, it is necessary in the case of inkjet printing to apply the auxiliaries to the textile substrate in a separate pretreatment step.

The pretreatment of the textile substrate, such as, for example, cellulose fibers and regenerated cellulose fibers, and also silk and wool, takes place with an aqueous alkaline liquor prior to printing. Fixing reactive dyes requires alkali, for example sodium carbonate, sodium bicarbonate, sodium acetate, trisodium phosphate, sodium silicate, sodium hydroxide, alkali donors such as, for example, sodium chloroacetate, sodium formate, hydrotropic substances such as, for example, urea, reduction inhibitors, such as, for example, sodium nitrobenzenesulfonates, and also thickeners to prevent flowing of the motifs when the printing ink is applied, examples thereof being sodium alginates, modified polyacrylates or highly etherified galactomannans.

These pretreatment reagents are applied uniformly to the textile substrate in a defined amount, using suitable applicators, as for example with a 2- or 3-roll pad mangle, by contactless spraying technologies, by means of foam application, or with appropriately adapted inkjet technologies, and are subsequently dried.

After printing has taken place, the textile fiber material is dried at 120 to 150 °C and then fixed.

Fixing the inkjet prints produced with reactive dyes can be accomplished at room temperature, or with saturated steam, with superheated steam, with hot air, with microwaves, with infrared radiation, with laser beams or electron beams, or with other suitable energy transfer techniques.

A distinction is made between one- and two-phase fixing operations. In one-phase fixing, the chemicals needed for fixing are already on the textile substrate. In two-phase fixing, this

pretreatment is unnecessary. Fixing requires only alkali, which, following inkjet printing, is applied prior to the fixing operation, without drying in between. Further additives such as urea or thickeners are redundant.

- 5 Following the fixing operation, the print is aftertreated, which is a prerequisite for good fastness properties, high brilliance, and an impeccable white ground.

The prints produced with the inks of the invention possess high colour strength and a high fiber-dye bond stability, not only in the acidic range but also in the alkaline range, and also have good
10 light fastness and very good wet fastness properties, such as fastness to washing, water, salt water, cross-dyeing, and perspiration, and also good fastness to pleating, hot pressing, and rubbing.

The dye mixtures comprising dyes of formula (I) and (II) according to the present invention
15 furnish blue / navy blue dyeings and prints, and inkjet prints, on the materials specified.

The examples herein below serve to illustrate the invention. The parts are parts by weight and the percentages are percent by weight, unless noted otherwise. The relationship between parts by weight and parts by volume is that of the kilogram to the liter. The compounds described by
20 formula in the examples are written in the form of the sodium salts, since in general they are prepared and isolated in the form of their salts, preferably sodium salts or potassium salts, and used for dyeing in the form of their salts. The starting compounds specified in the examples below, especially the tabular examples, can be used in the synthesis in the form of the free acid or likewise in the form of their salts, preferably alkali metal salts, such as sodium salts or
25 potassium salts.

The dyes of formulae (I) and (II) are known or can be prepared according to methods known per se. Dyes of formula (I) are described, for example, in CN 102504582 A and EP0568876. Dyes of formula (II) are described, for example, in US 4336190 and US 4754023. The dye
30 mixtures were then prepared as in the following examples.

Examples:

Example 1:

53 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-3) [component (I)], and 47 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-6) [component (II)], were mixed mechanically with one another.

5

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

Example 2:

10 45 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-1) [component (I)], 35 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-1) [component (II)], and 20 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-2) [component (II)'] were mixed mechanically with one another.

15

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

Example 3:

20 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-4) [component (I)], 24 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (I-3) [component (I)'], 30 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-1) [component (II)] and 26 parts of an electrolyte-containing dye powder containing the blue formazan dye of the formula (II-5) [component (II)'] were mixed mechanically with one another.

25

The resultant dye mixture of the invention provides blue dyeings and prints, on cotton for example, under the dyeing conditions customary for reactive dyes.

30 Further mixtures are described in the following table:

Table 1:

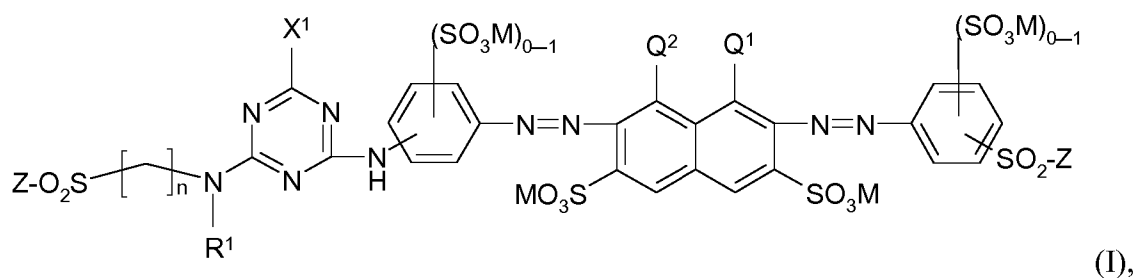
Example	(I)	wt. %	(I)'	wt. %	(II)	wt. %	(II)'	wt. %
4	I-1	39	I-2	39	II-1	22	-	

5	I-1	35	-		II-1	65	-	
6	I-1	45	-		II-1	55	-	
7	I-1	50	-		II-1	30	II-4	20
8	I-2	53	-		II-1	47	-	
9	I-2	19	I-2	19	II-1	62	-	
10	I-3	75	-		II-1	25	-	
11	I-3	56	-		II-1	44	-	
12	I-3	33	-		II-1	67	-	
13	I-4	68	-		II-1	32	-	
14	I-4	45	-		II-1	55	-	
15	I-4	30	-		II-1	70	-	
16	I-5	25	I-6	20	II-1	55	-	
17	I-6	36	-		II-1	64	-	
18	I-7	55	-		II-1	45	-	
19	I-8	60	-		II-1	40	-	
20	I-1	78	-		II-2	22	-	
21	I-1	35	-		II-2	65	-	
22	I-1	45	-		II-2	55	-	
23	I-1	80	-		II-2	10	II-4	10
24	I-1	20	-		II-2	30	II-4	50
25	I-2	72	-		II-2	28	-	
26	I-2	53	-		II-2	47	-	
27	I-3	75	-		II-2	25	-	
28	I-4	45	-		II-2	55	-	
29	I-5	45	-		II-2	55	-	
30	I-6	36	-		II-2	64	-	
31	I-7	55	-		II-2	45	-	
32	I-8	60	-		II-2	40	-	
33	I-1	25	-		II-4	75	-	
34	I-1	50	-		II-4	30	II-6	20
35	I-2	72	-		II-4	28	-	
36	I-2	38	-		II-4	62	-	

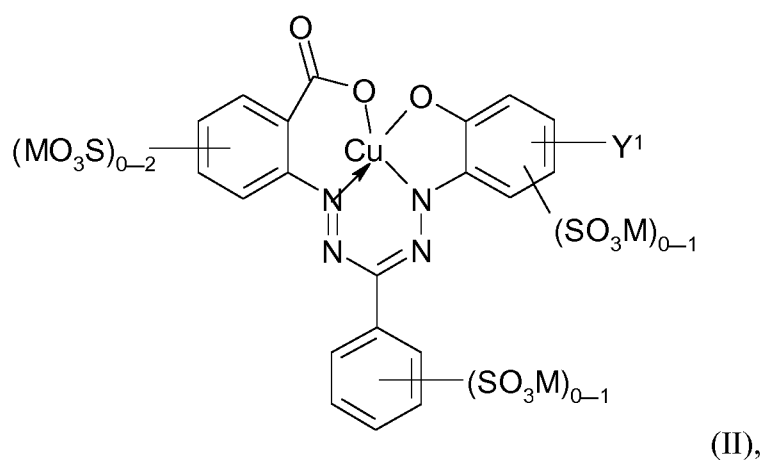
37	I-3	56	-		II-4	44	-	
38	I-4	68	-		II-4	32	-	
39	I-4	45	-		II-4	55	-	
40	I-4	30	-		II-4	70	-	
41	I-5	45	-		II-4	55	-	
42	I-6	36	-		II-4	64	-	
43	I-7	55	-		II-4	45	-	
44	I-8	60	-		II-4	40	-	
45	I-1	78	-		II-5	22	-	
46	I-1	33	-		II-5	77	-	
47	I-1	50	-		II-5	30	II-4	20
48	I-2	70	-		II-5	30	-	
49	I-2	38	-		II-5	62	-	
50	I-3	33	-		II-5	67	-	
51	I-4	67	-		II-5	33	-	
52	I-4	30	-		II-5	70	-	
53	I-5	20	I-6	25	II-5	55	-	
54	I-6	36	-		II-5	64	-	
55	I-7	55	-		II-5	45	-	
56	I-8	60	-		II-5	40	-	
57	I-1	45	-		II-3	55	-	
58	I-1	40	-		II-6	60	-	
59	I-1	48	-		II-7	52	-	
60	I-1	65	-		II-8	35	-	
61	I-1	33	-		II-9	67	-	
62	I-1	75	-		II-11	25	-	
63	I-1	30	-		II-12	70	-	
64	I-1	50	-		II-10	50	-	
65	I-1	52	-		II-13	48	-	
66	I-1	47	-		II-14	53	-	

1. Dye mixture comprising at least one dye of formula (I)

1. Dye mixture comprising at least one dye of formula (I)



5 and at least one dye of formula (II)

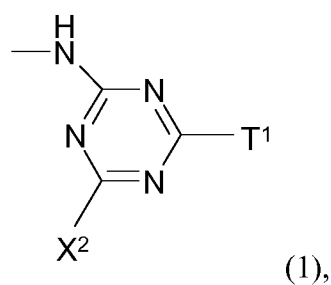


wherein independent from each other

Q^1 is OH and Q^2 is NH_2 or Q^1 is NH_2 and Q^2 is OH,

X^1 is Cl or F,

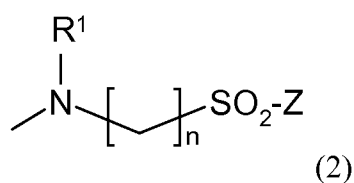
10 Y¹ is -SO₂-Z or a group of formula (1)



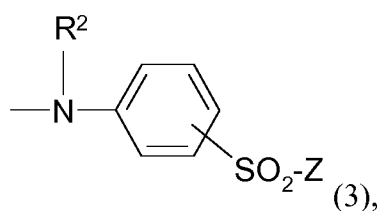
wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or



wherein independent from each other

R¹ is methyl, ethyl or phenyl,

R² is H, methyl or ethyl,

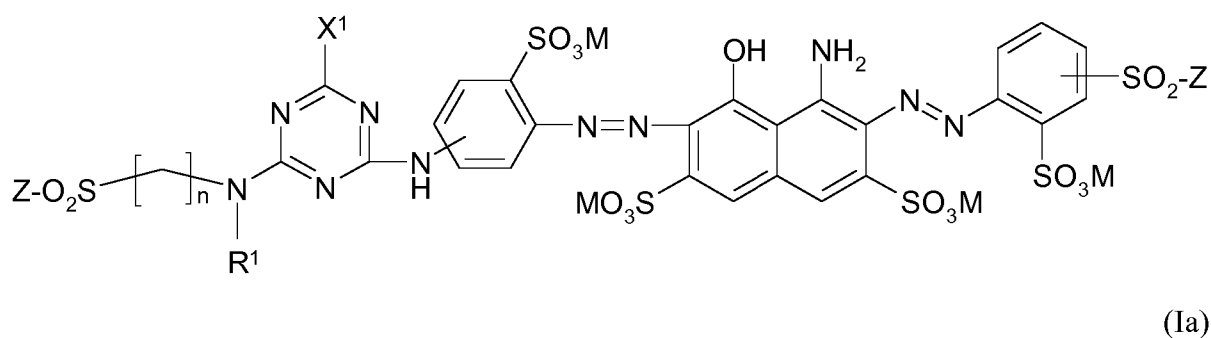
n is 2 or 3,

Z is -CH=CH₂ or a -CH₂-CH₂-G radical

wherein G is a group that is removable under alkaline conditions and

M is H, an alkali metal or one equivalent of an alkaline earth metal.

2. Dye mixture according to claim 1, comprising at least one dye of formula (Ia)



wherein independent from each other

X¹ is Cl or F,

R¹ is methyl, ethyl or phenyl,

n is 2 or 3,

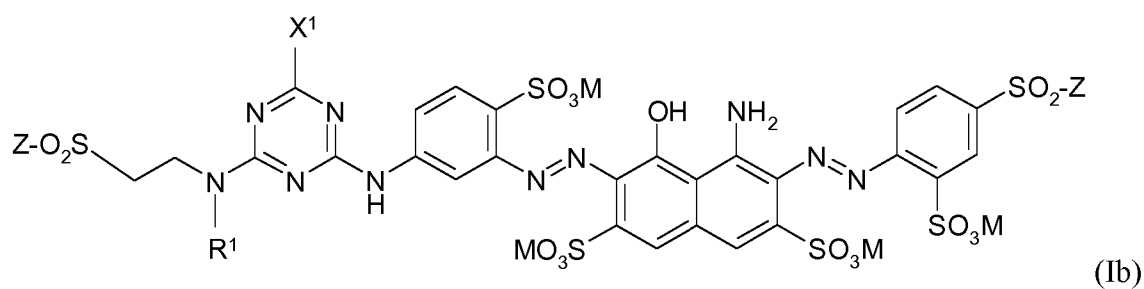
Z is -CH=CH₂ or a -CH₂-CH₂-G radical

wherein

G is -Cl, -Br, -F, -OSO₃M or -OPO₃M₂ and

M is H, Na, K or Li.

3. Dye mixture according to claim 1 or 2, comprising at least one dye of formula (Ib)



wherein independent from each other

X^1 is Cl or F,

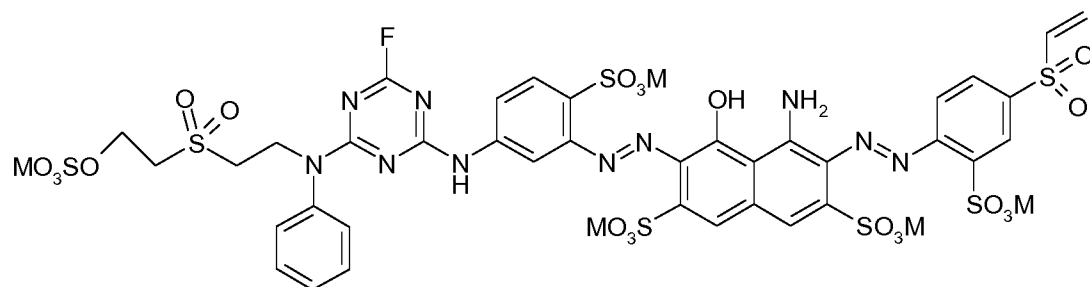
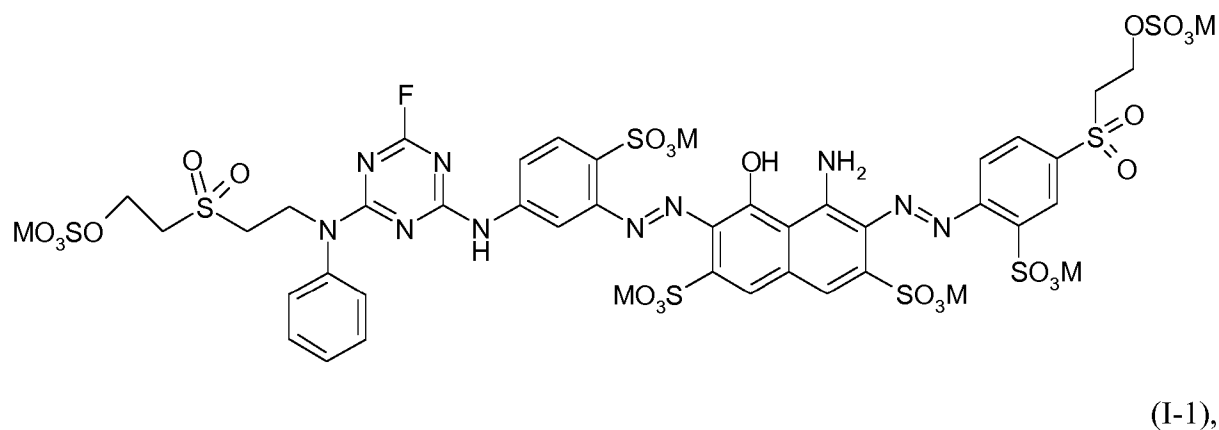
R^1 is methyl, ethyl or phenyl,

5 Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

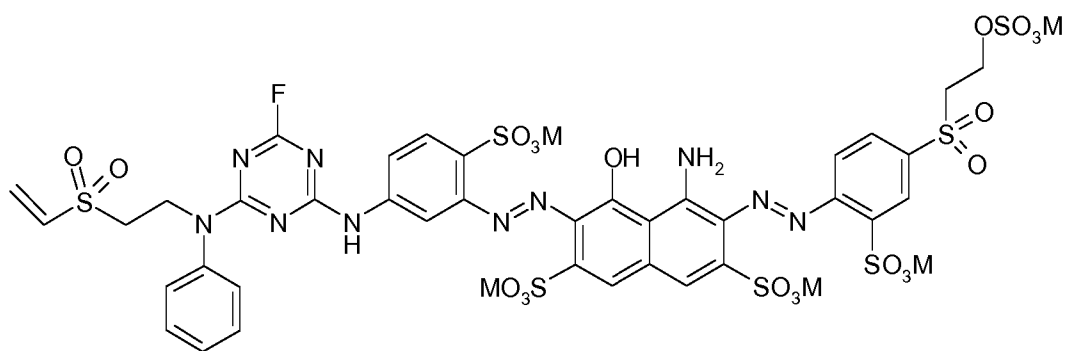
M is H or Na.

4. Dye mixture according to any one of claims 1 to 3, comprising at least one dye selected from the list consisting of:

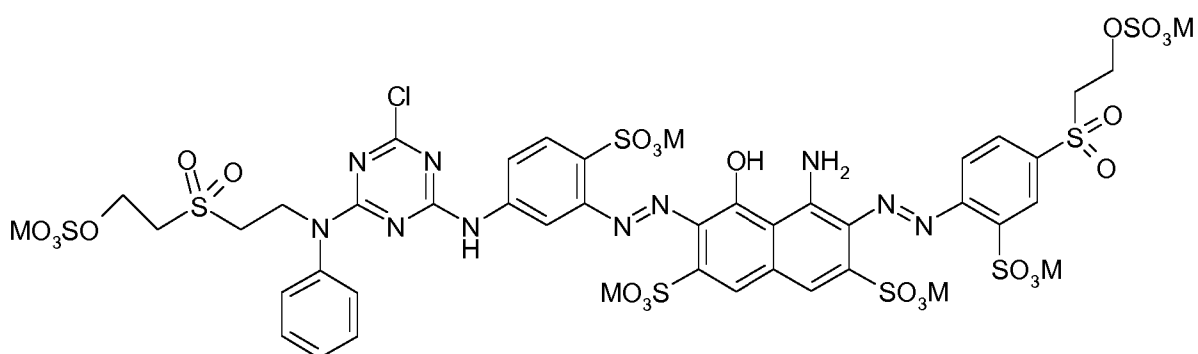
10



15

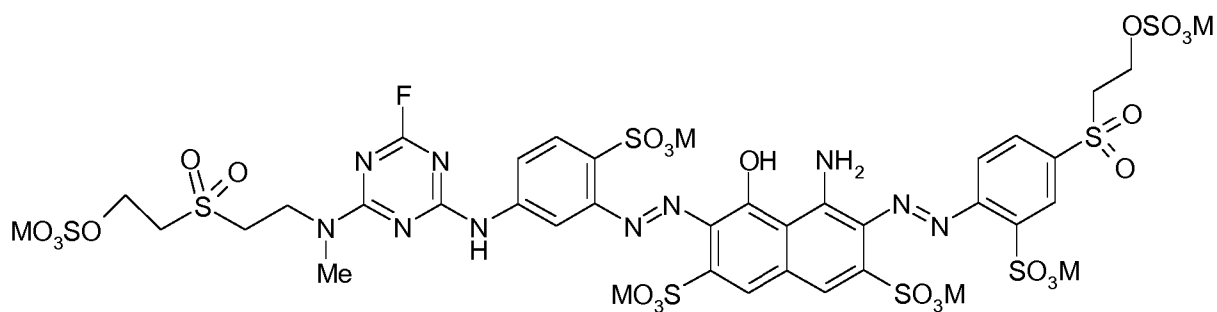


(I-3),

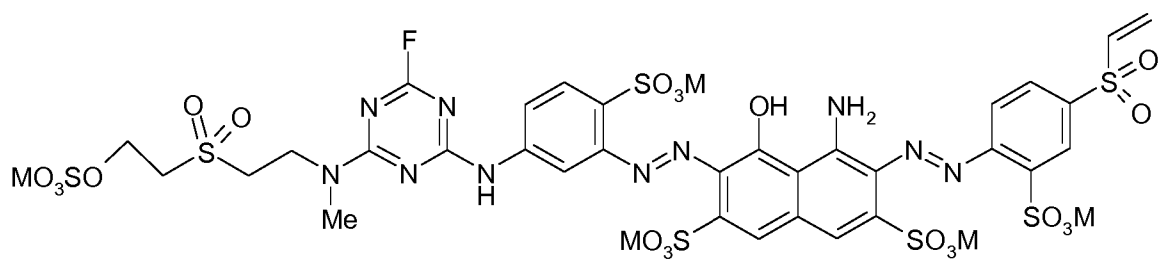


5

(I-4),

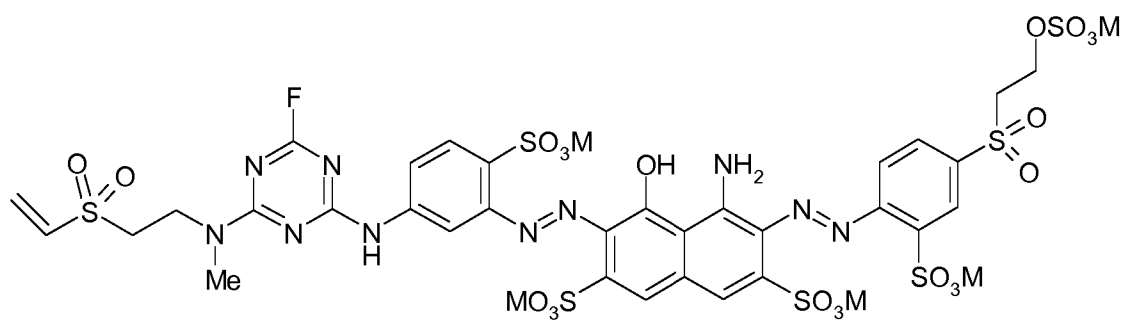


(I-5),



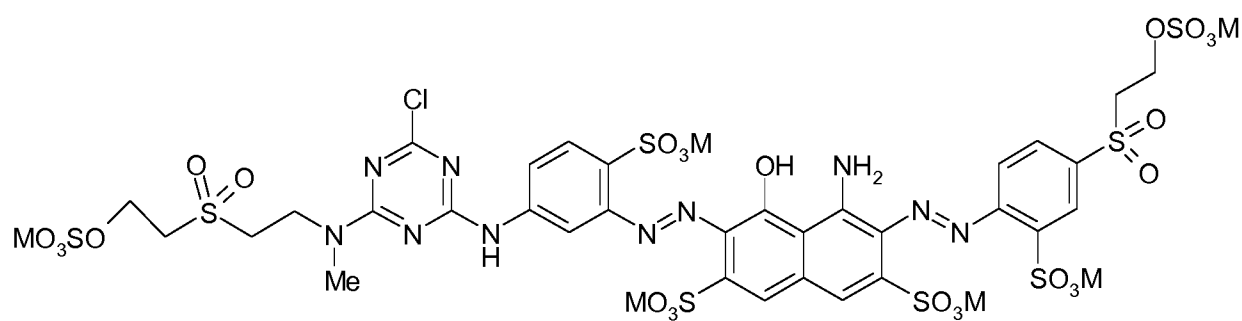
10

(I-6),



(I-7)

and



(I-8)

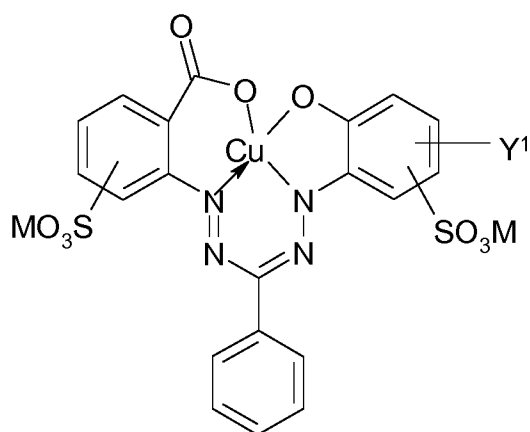
5

wherein

M is H or Na.

5. Dye mixture according to any one of claims 1 to 4, comprising at least one dye of formula (IIa)

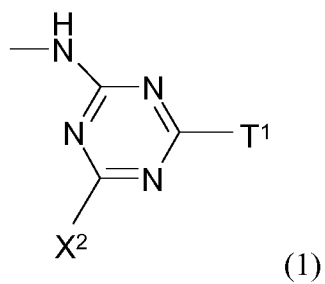
10



(IIa)

wherein

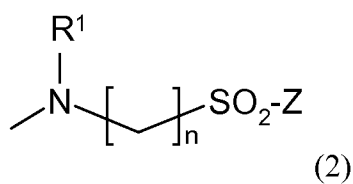
Y¹ is -SO₂-Z or a group of the formula (1)



wherein

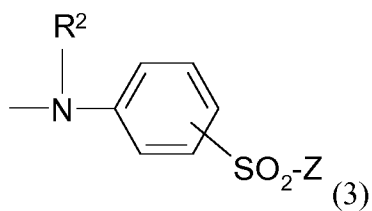
X^2 is Cl or F,

T^1 is a group of formula



wherein R^1 is methyl, ethyl or phenyl,

or



wherein R^2 is H, methyl or ethyl,

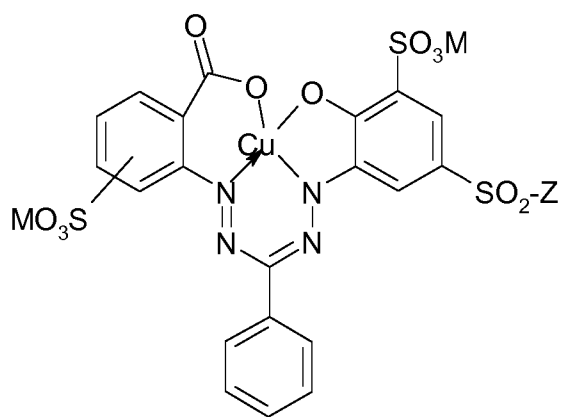
Z is $-CH=CH_2$ or a $-CH_2-CH_2-G$ radical,

wherein G is $-Cl$, $-Br$, $-F$, $-OSO_3M$ or $-OPO_3M_2$

n is 2 or 3 and

M is H, Na, K or Li.

6. Dye mixture according to any one of claims 1 to 5, comprising at least one dye of formula (IIb)



(IIb)

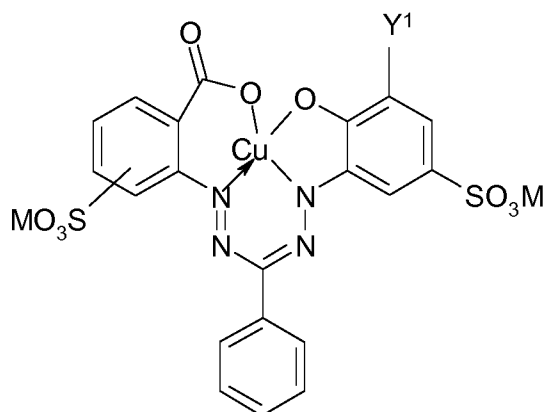
wherein independent from each other

Z is $-\text{CH}=\text{CH}_2$ or a $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{M}$ and

M is H or Na.

5

7. Dye mixture according to any one of claims 1 to 6, comprising at least one dye of formula (IIc)

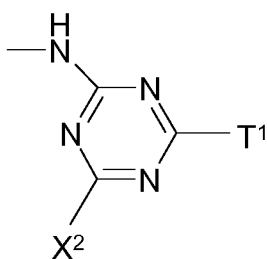


(IIc)

wherein independent from each other

Y^1 is a group of the formula (1)

10

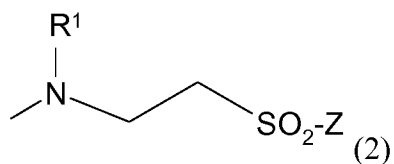


(1)

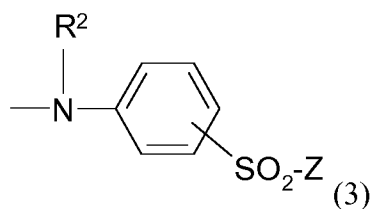
wherein independent from each other

X^2 is Cl or F,

T^1 is a group of formula



or



wherein independent from each other

R^1 is methyl, ethyl or phenyl,

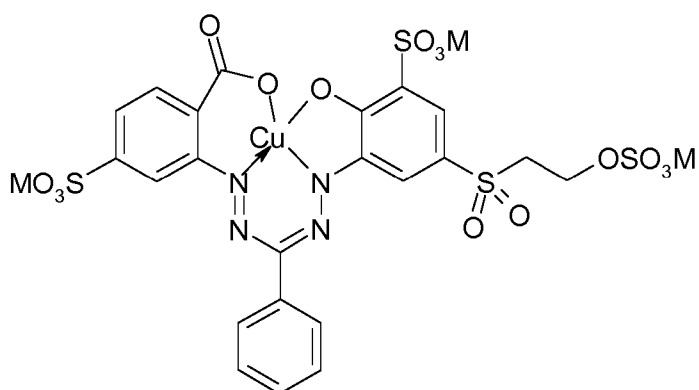
R^2 is H, methyl or ethyl,

Z is $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{---CH}_2\text{---OSO}_3\text{M}$ and

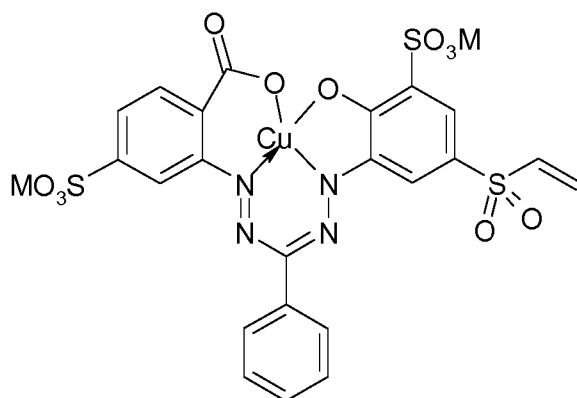
M is H or Na.

5

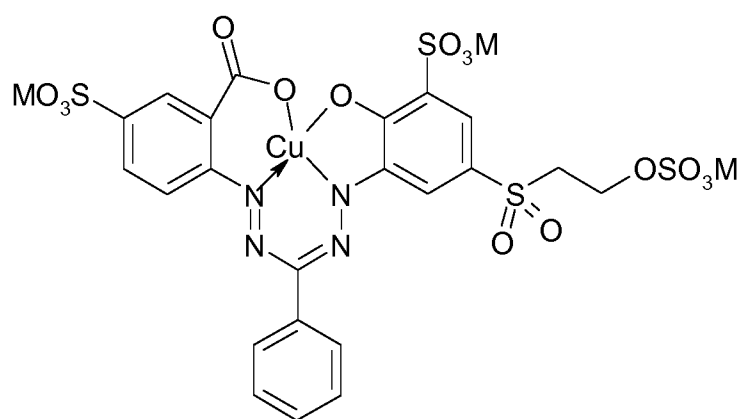
- 10 8. Dye mixture according to any one of claims 1 to 7, comprising at least one dye selected from the list consisting of:



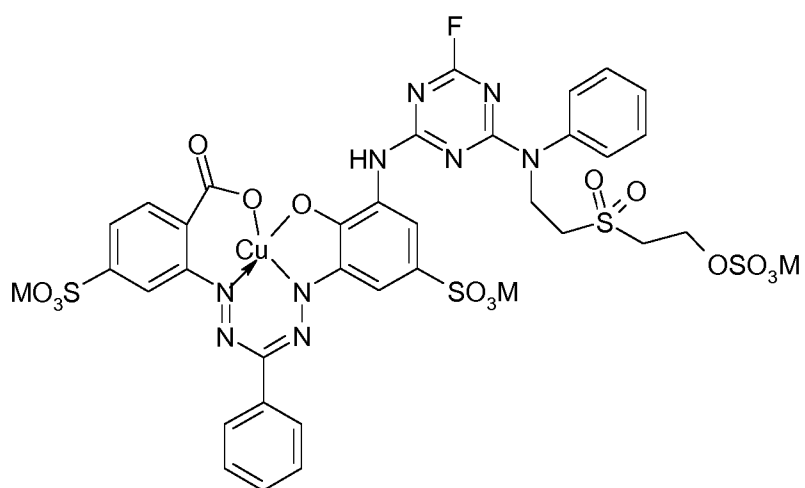
(II-1),



(II-2),

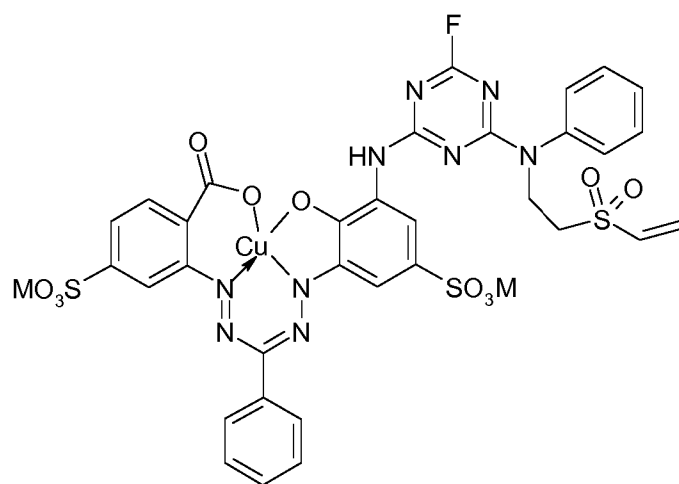


(II-3),

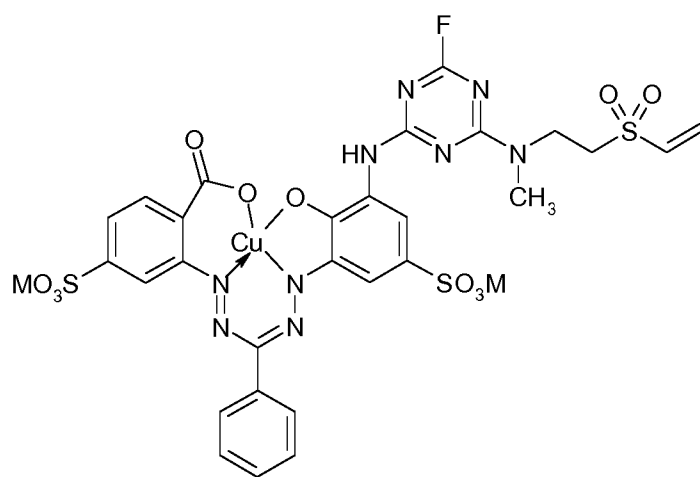
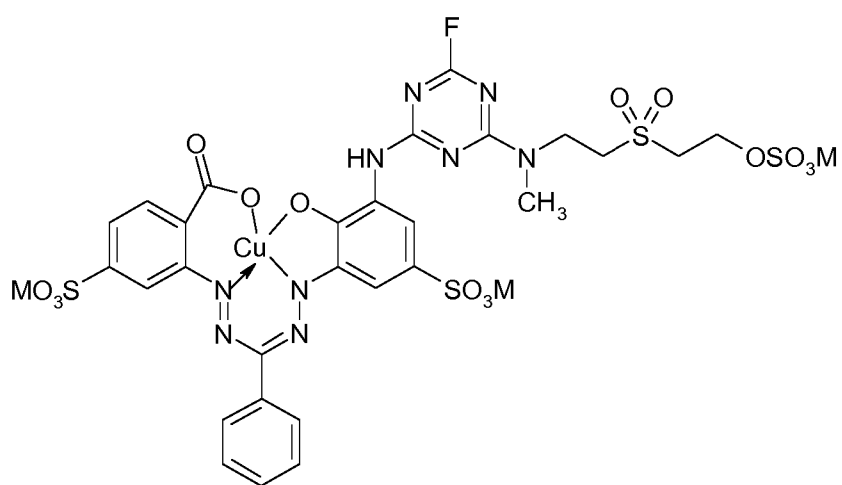
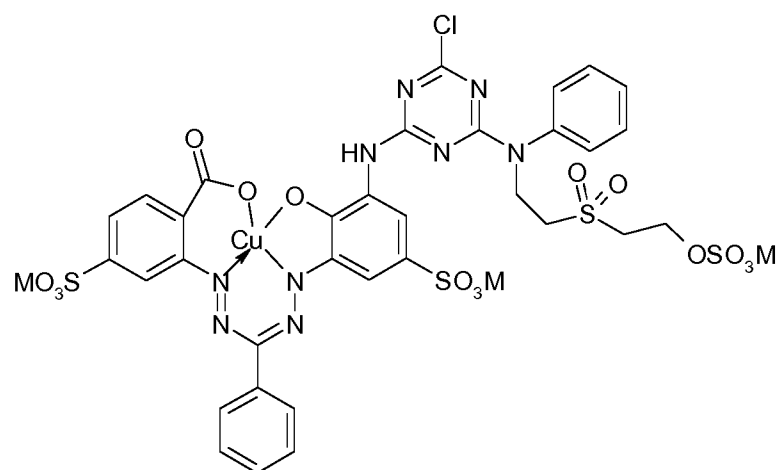


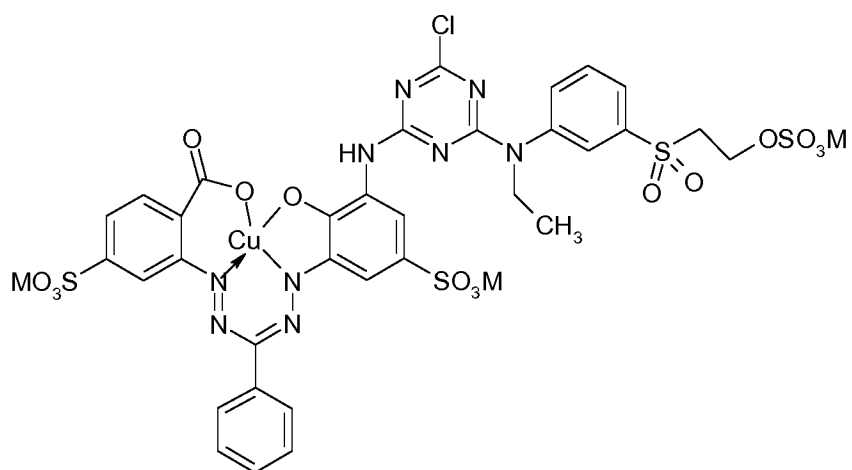
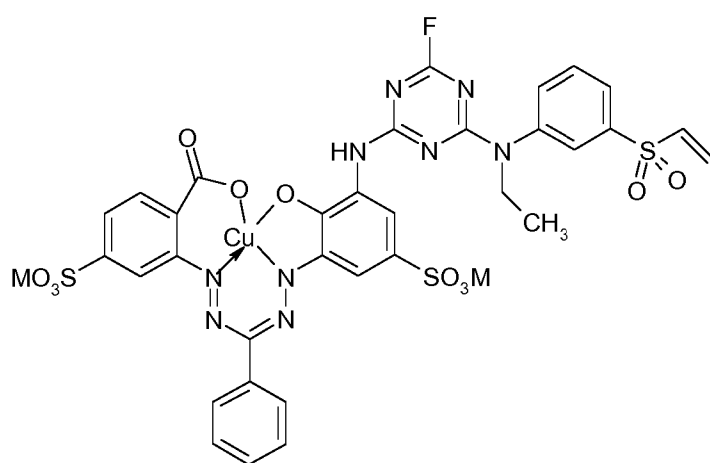
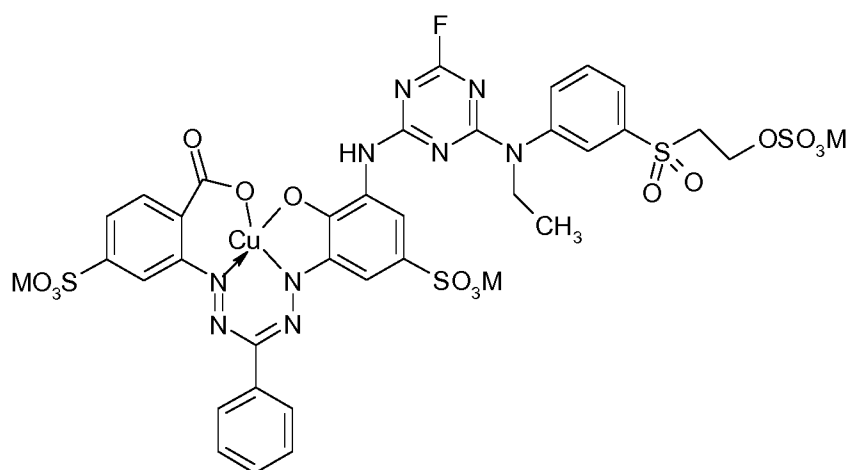
(II-4),

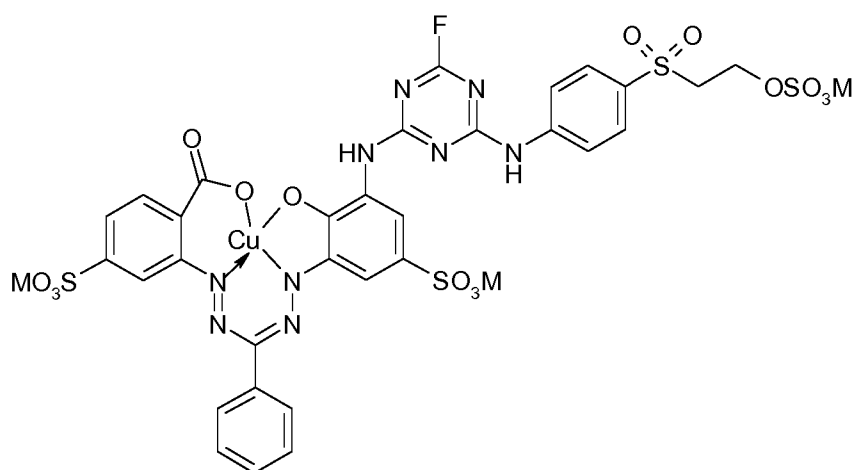
5



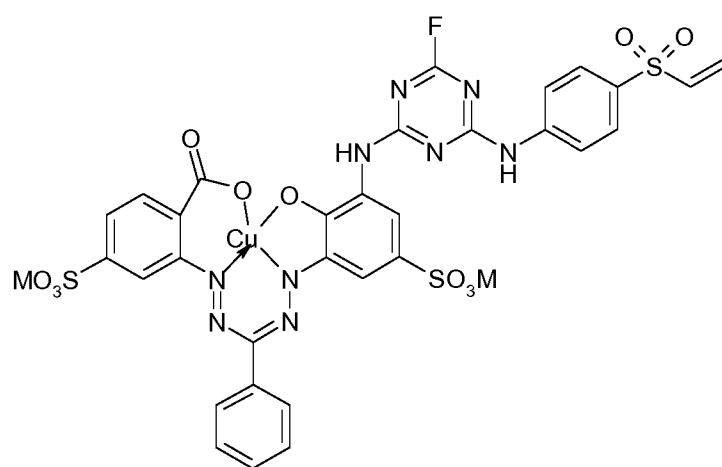
(II-5),





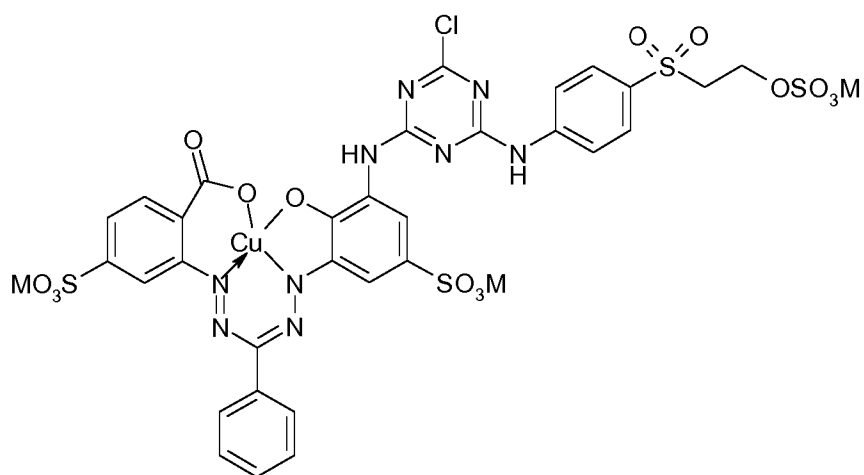


(II-12),



(II-13)

and



(II-14)

5

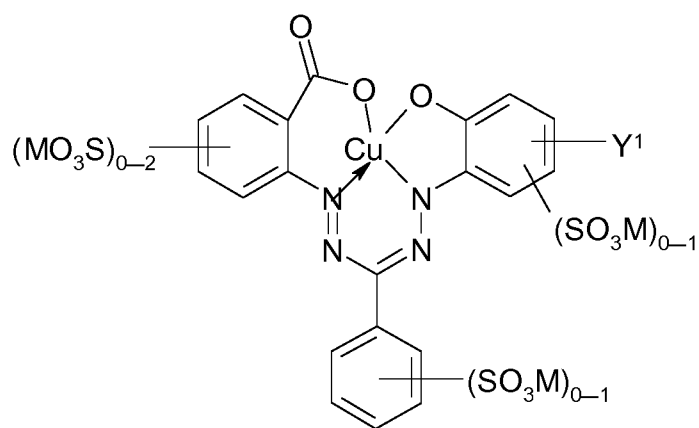
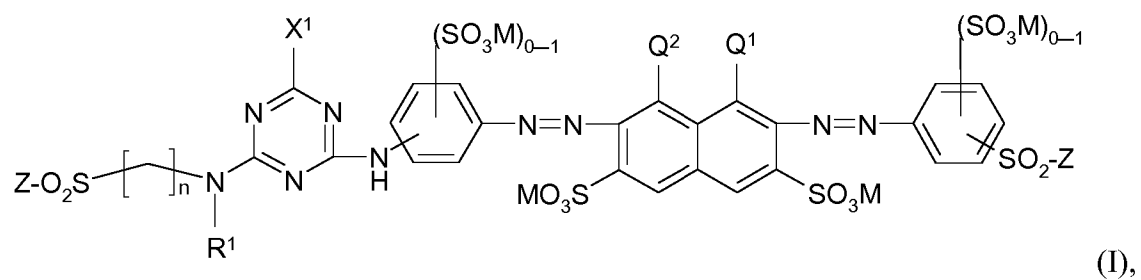
wherein

M is H or Na.

9. Dye mixtures according to any one of claims 1 to 8, wherein at least one dye of formula (I) is selected from the list consisting of (I-1), (I-2) and (I-4) and the at least one dye of formula (II) is selected from the list consisting of (II-1), (II-4) and (II-11).
- 5 10. Dye mixture according to any one of claims 1 to 9, wherein the amount of dye(s) of formula (I) is 80 to 20 wt% and the amount of dye(s) of formula (II) is 20 to 80 wt% of the total weight of dyes in the mixture.
- 10 11. Dye mixture according to claim 10, wherein the amount of dye(s) of formula (I) is 65 to 35 wt% and the amount of dye(s) of formula (II) is 35 to 65 wt% of the total weight of dyes in the mixture.
12. Solution for dyeing comprising a dye mixture according to any one of claims 1 to 11.
- 15 13. Process for the production of a dye mixture according to any one of claims 1 to 11, comprising
a) mixing the components of the dye mixture,
b) homogenizing the mixture obtained in step a).
- 20 14. Process for dyeing or printing material, comprising contacting the material with a dye mixture according to any one of claims 1 to 11 and/or a solution according to claim 12.

Abstract:

Dye mixtures comprising dyes of formula (I) and (II)



5

process for the production thereof and use of said mixtures.