

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
30 March 2017 (30.03.2017)

(10) International Publication Number
WO 2017/050597 A1

(51) International Patent Classification:

C09B 67/22 (2006.01) **D06P 1/384** (2006.01)
D06P 1/10 (2006.01) **D06P 3/02** (2006.01)
C09D 11/328 (2014.01) **D06P 3/10** (2006.01)
D06P 5/30 (2006.01) **D06P 3/66** (2006.01)

(21) International Application Number:

PCT/EP2016/071390

(22) International Filing Date:

12 September 2016 (12.09.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15186219.0 22 September 2015 (22.09.2015) EP

(71) Applicant: **DYSTAR COLOURS DISTRIBUTION GMBH** [DE/DE]; Am Prime Parc 10-12, 65479 Raunheim (DE).

(72) Inventors: **MURGATROYD, Adrian**; Wed 9, 65929 Frankfurt am Main (DE). **HANXLEDEN, Ulrich**; Hornauer Straße 141, 65779 Kelkheim (DE). **HOPPE, Manfred**; Ammerweg 23, 51515 Kürten (DE). **GRUND, Clemens**; Rossertstraße 66, 65795 Hattersheim (DE). **STING-ROSEN, Michael**; Zülpicher Weg 22, 50354 Hürth (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MIXTURES OF FIBRE-REACTIVE DYES

(57) Abstract: Mixtures of fibre reactive dyes and their use of for the dyeing of hydroxyl- and carboxamide-containing material in blue and navy shades.



WO 2017/050597 A1

Mixtures of fibre-reactive dyes.

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

Fiber-reactive copper-complex azo dyes are of interest due to their potential to produce blue to violet dyeings of high fastness to light. However, they often possess certain performance limitations, such as deficient build-up of colour to deeper shades, unlevel dyeing, a colour yield, which is too heavily dependent on variations in dyeing parameters, and low resistance to oxidative agents.

These performance defects can partly be overcome in some cases by the use of mixtures of fiber reactive copper complex azo dyes with selected other fiber reactive azo dyes. Such mixtures make it possible, for example, to achieve neutral to greenish Navy shades with high light and perspiration-light fastness, very good resistance to washing in the presence of modern oxidative detergents, and good colour constancy in different light sources. The use of such mixtures can give dyeings with superior fastness properties to existing mono-molecular fiber-reactive Navy dyes.

Additionally many existing commercial Navy and Black products include dyes, which, due to their chemistry, are causing problems of contamination with regulatory-controlled amines. C.I. Reactive Black 5 in particular is used quite often for commercial reasons - although it is known to involve a risk of p-chloroaniline contamination in the parabase ester intermediate used in its production. Alternative procedures for the production of parabase ester with low p-chloroaniline content are known (as described for example in German Patent DE 19 540 544) but have not been adopted as they are also not completely free of p-chloroaniline and involve higher cost.

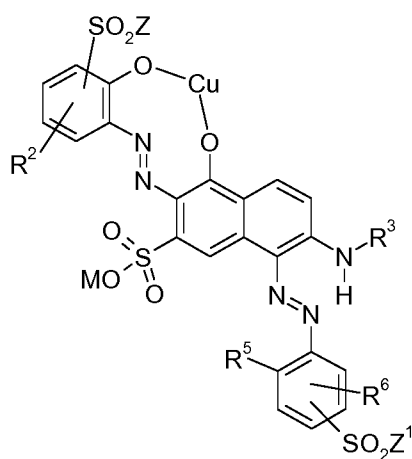
Because the compliance with ecological and toxicological standards is of increasing importance to retailers and consumers, there is a growing need for dyes, which due to their chemistry avoid common sources of contamination with regulatory-controlled amines – and the present invention bases on such dyes.

Due to developing consumer requirements there is still a need for new dyestuffs with good build-up and levelness, high light- and oxidative fastness and good colour constancy, which additionally comply with toxicological and ecological standards. Surprisingly it now was found, that there exist combinations of dyes, which can be produced without the risk of contamination with restricted substances, which combinations have the required properties. Thus, the present

invention provides dye mixtures, which possess these properties to a high degree and at the same time avoid contamination with restricted substances.

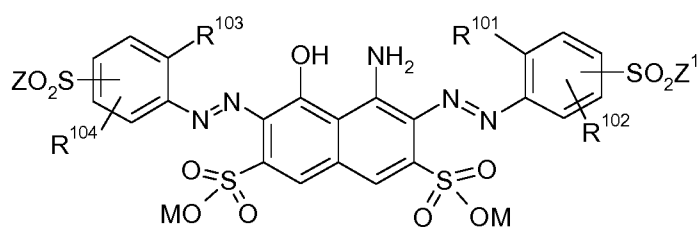
The present invention is directed to mixtures of fibre-reactive dyes comprising:

- 5 a dye of formula (I)



(I),

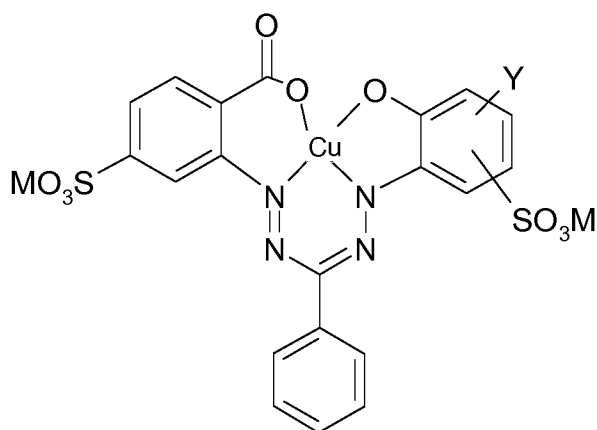
- a dye of formula (II)



(II)

10

- and optionally a dye of formula (III)



(III)

wherein independently of each other

- 15 R^2 is hydrogen, $(\text{C}_1\text{-C}_4)$ -alkyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R^3 is (C₁-C₄)-alkyl; (C₁-C₄)-alkyl substituted by sulfo, carboxyl, halogen, hydroxyl, amino or acetamido; phenyl; or phenyl substituted by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, sulfo, halogen, carboxyl, acetamido or ureido;

R^5 is (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

5 R^6 is hydrogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

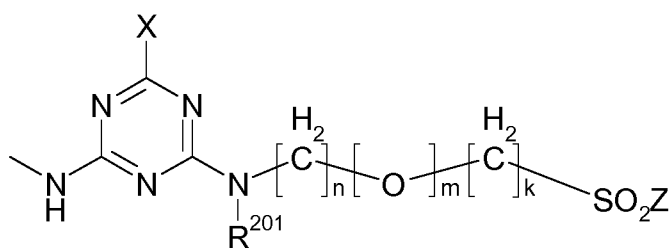
R^{101} and R^{103} are C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo or carboxyl,

R^{102} and R^{104} are hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo, carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

10 G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of the formula (100)



(100)

wherein

15 X is halogen,

R^{201} is hydrogen (C₁-C₄)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

20 and

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

(C₁-C₄)-alkyl groups may be straight-chain or branched and may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl. Preferred are (C₁-C₃)-alkyl groups. More preferred are (C₁-C₂)-alkyl groups - methyl and ethyl and ethyl being the most preferred alkyl groups.

The same selection as for the alkyl groups applies to alkoxy, sulfoalkyl and alkylene groups.

30 M is preferably hydrogen, lithium, sodium or potassium, more preferably hydrogen or sodium.

Non-limiting examples of alkali-detachable groups as represented by G are halogen, preferably chlorine and bromine, ester groups of organic carboxylic and sulfonic acids, such as alkylcarboxylic acids, unsubstituted or substituted benzenecarboxylic acids, and unsubstituted or substituted benzenesulfonic acids, such as the groups (C₂-C₅)-alkanoyloxy, including more particularly acetyloxy, benzoyloxy, sulfobenzoyloxy, phenylsulfonyloxy, and tolylsulfonyloxy; acidic ester groups of inorganic acids, such as of phosphoric acid, sulfuric acid, and thiosulfuric acid (phosphato, sulfato, and thiosulfato groups), or di-(C₁-C₄)-alkylamino groups, such as dimethylamino and diethylamino.

- 10 Z, Z¹ are preferably vinyl, β-sulfatoethyl or β-chloroethyl and more preferably β-sulfatoethyl or vinyl.

- 15 The groups "sulfo", "carboxyl", "thiosulfato", "phosphato", and "sulfato" include not only their acid form but also their salt form. Accordingly, sulfo groups have the formula -SO₃M, thiosulfato groups have the formula -S-SO₃M, carboxyl groups have the formula -COOM, phosphato groups have the formula -OPO₃M₂, and sulfato groups have the formula -OSO₃M, in each of which M is defined as indicated above.

- 20 Preferred are dye mixtures with a weight ratio of (I) 20 to 80 %, (II) 80 to 20 % adding up to 100 %. More preferred are mixtures, which comprise a dye of formula (III). They preferably have a weight ratio of (I) 20 to 60 %, (II) 50 to 20 % and (III) 30 to 20 % adding up to 100 %. All percentages are based on the dye.

- 25 More preferred are mixtures of fibre-reactive dyes comprising: dyes of the formula (I), (II) and optionally dyes of the formula (III) as described above, wherein independent of each other

R² is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R³ is (C₁-C₂)-alkyl or (C₁-C₂)-alkyl substituted by sulfo,

R⁵ is (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

- 30 R⁶ is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

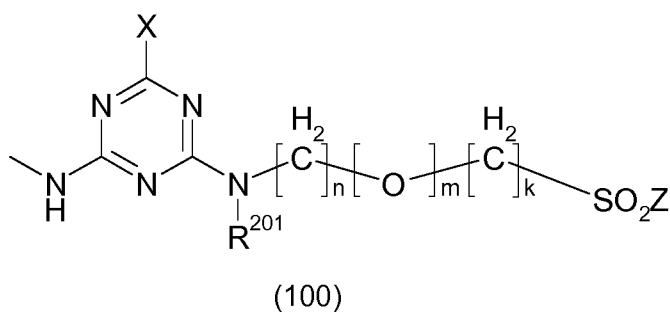
R¹⁰¹ and R¹⁰³ are C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

- 35 Y is -SO₂-Z or a group of formula (100)



wherein

X is Cl or F,

5 R^{201} is hydrogen, (C₁-C₂)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

10 M is hydrogen, Na, K or Li.

Even more preferred are mixtures of fibre-reactive dyes comprising:

dyes of formula (I), (II) and optionally dyes of formula (III) as described above,

wherein independent of each other

15 R^2 is hydrogen, methy, methoxy or sulfo,

R^3 is methyl or (C₁-C₂)-alkyl substituted by sulfo,

R^5 is methy, methoxy or sulfo,

R^6 is hydrogen, methy, methoxy or sulfo,

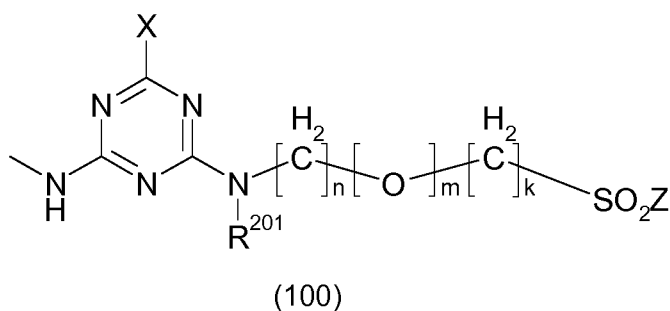
R^{101} and R^{103} are, methy, methoxy or sulfo,

20 R^{102} and R^{104} are hydrogen, methy, methoxy or sulfo,

Z and Z' are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



25

wherein

X is Cl or F,

R^{201} is hydrogen, methyl or phenyl,

n is 2 or 3,

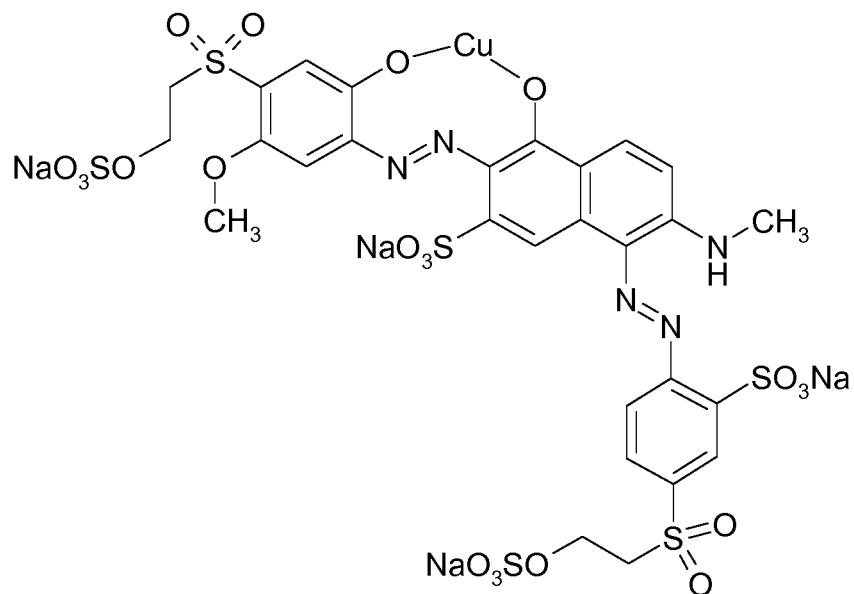
m is 0 or 1,

k is 0 to 3,

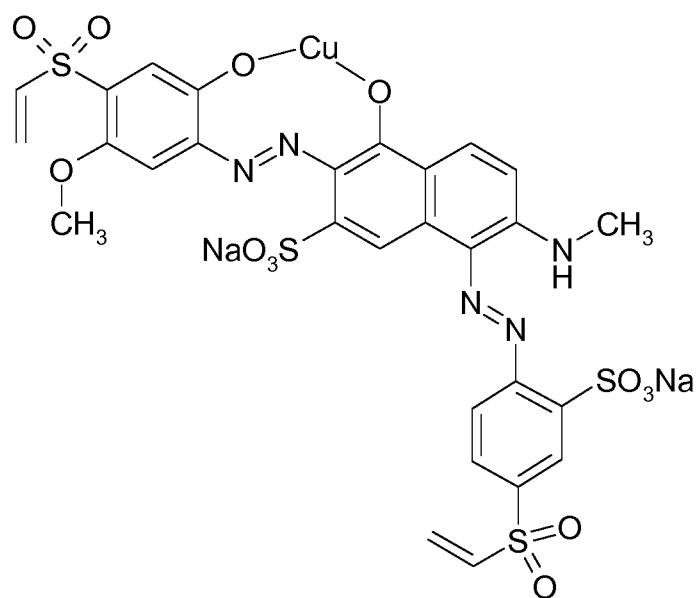
and

5 M is hydrogen, Na, K or Li.

Particularly preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of:

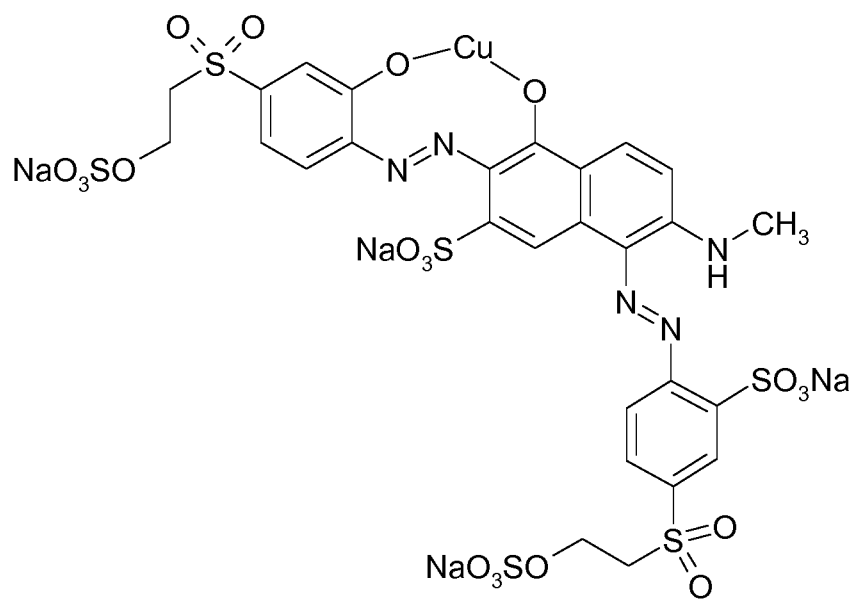


I-1,

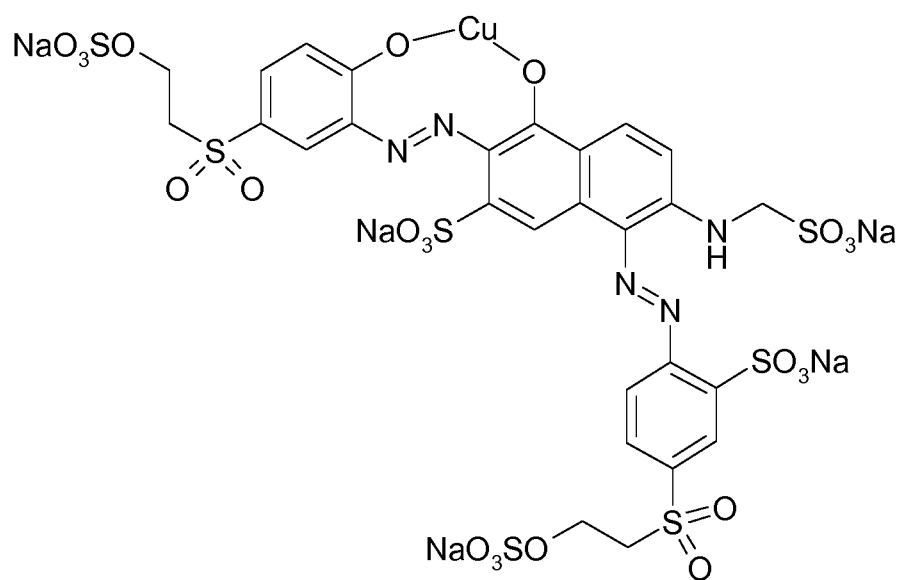


I-2,

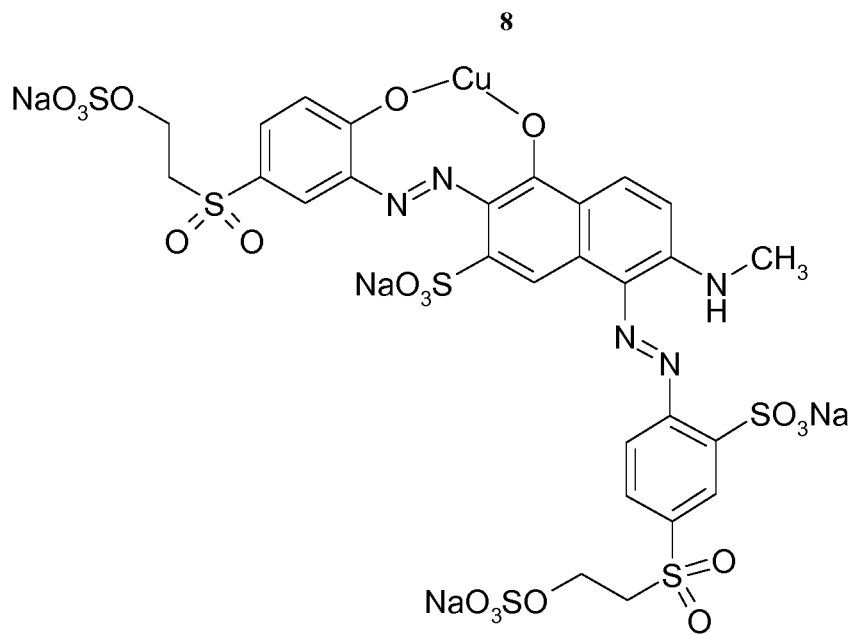
7



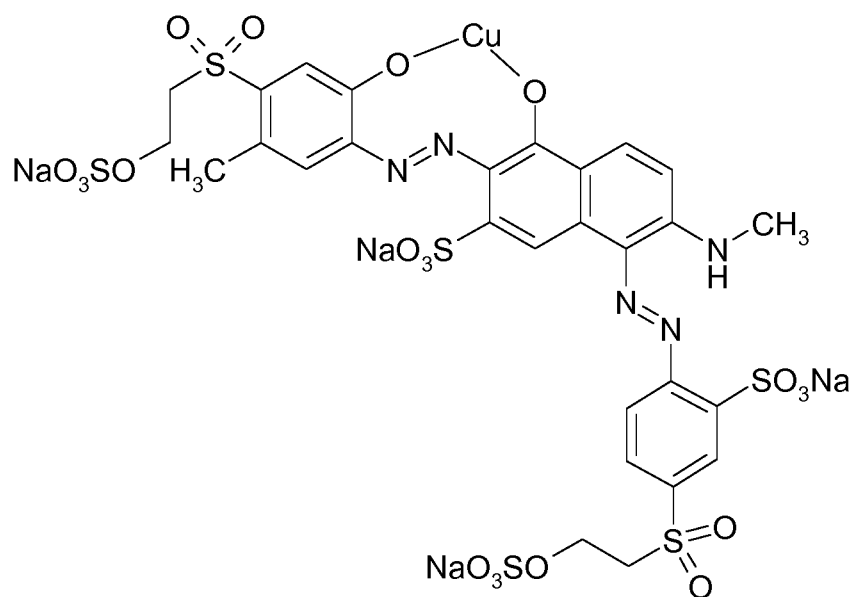
I-3,



I-4,

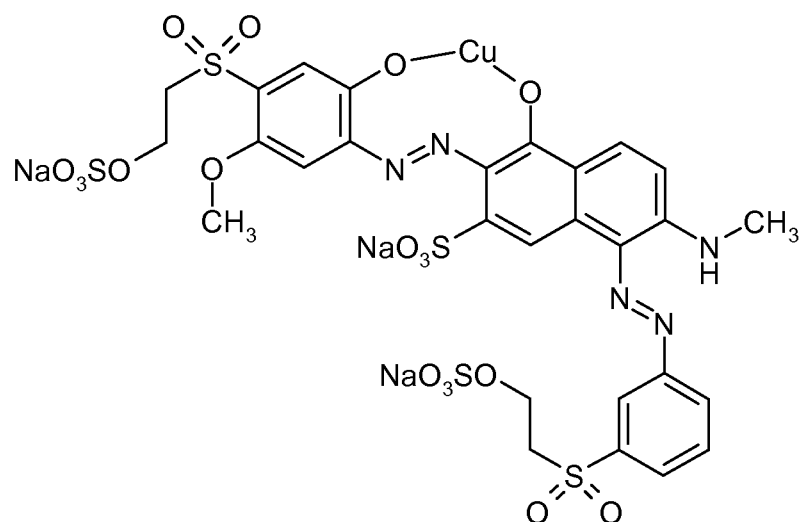


I-5,

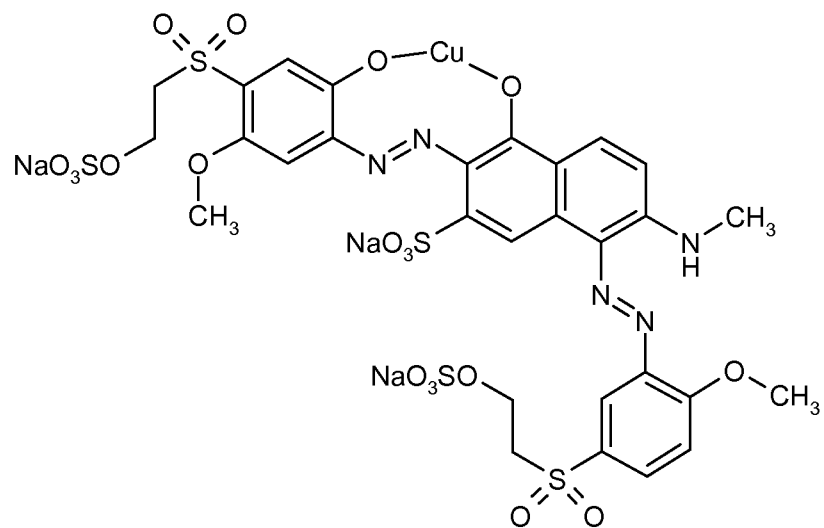


I-6,

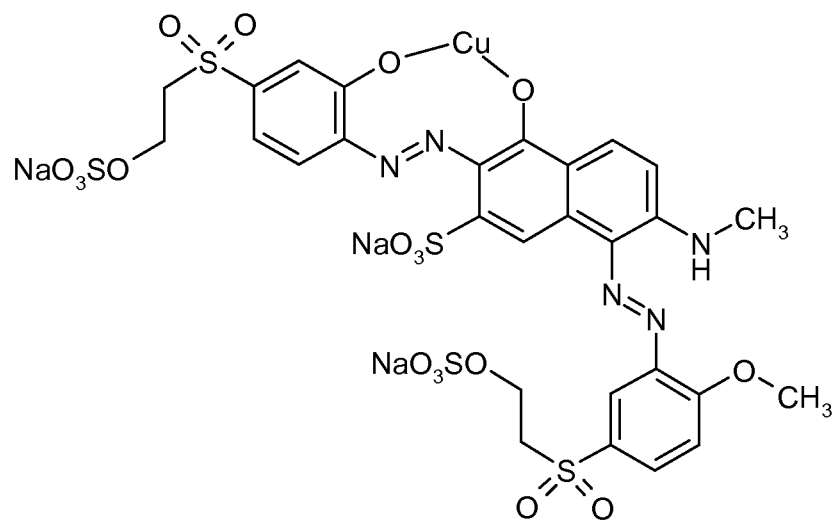
9



I-7,

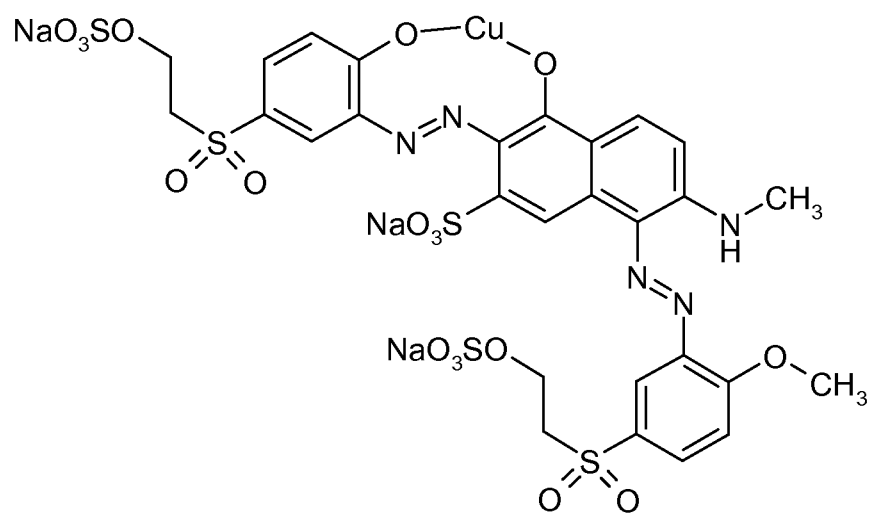


I-8,

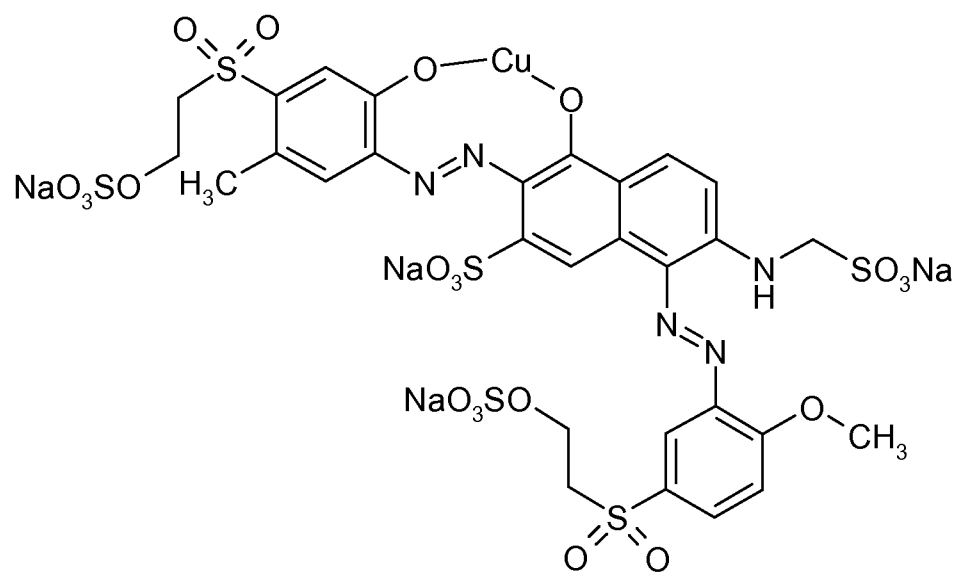


I-9,

10

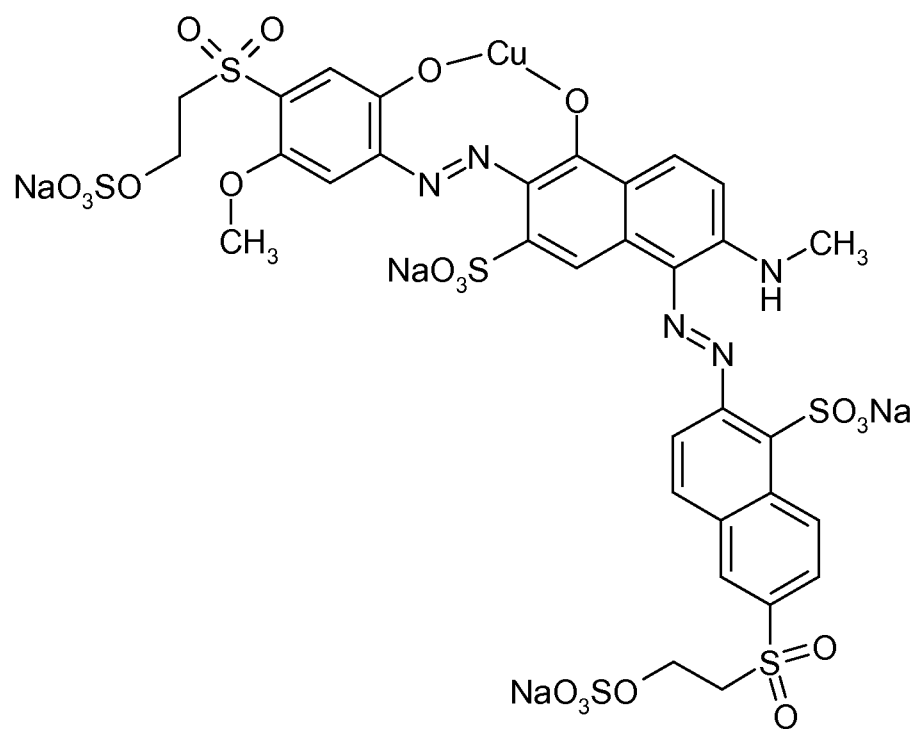


I-10,

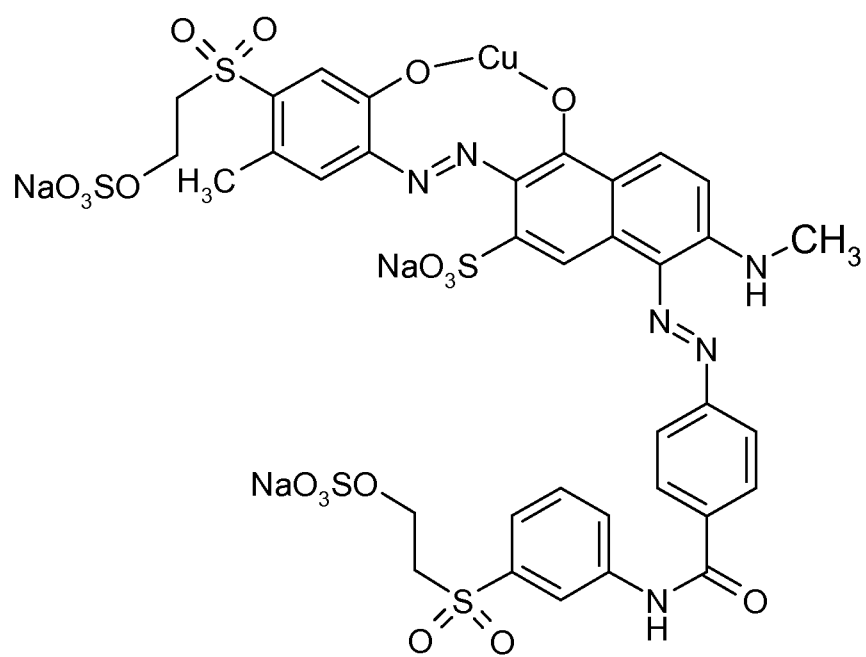


I-11,

11

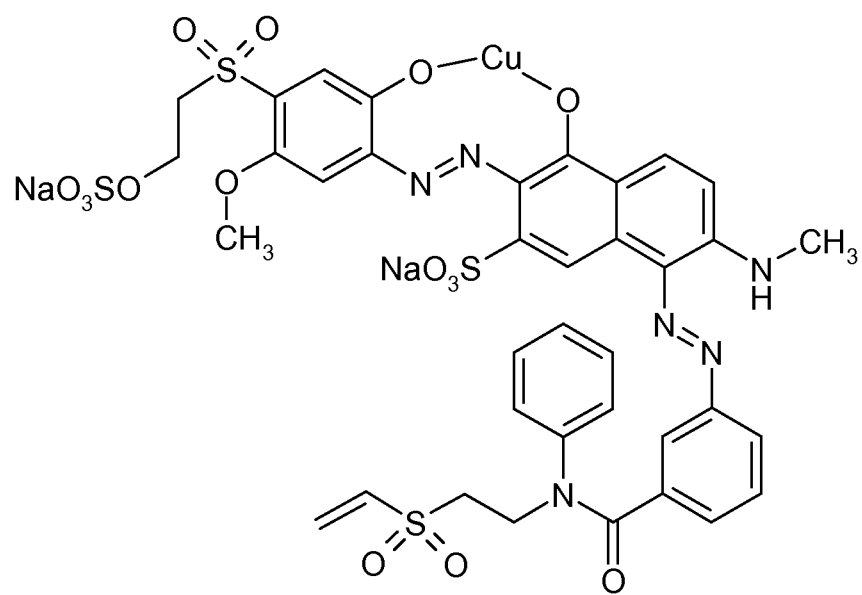


l-12,

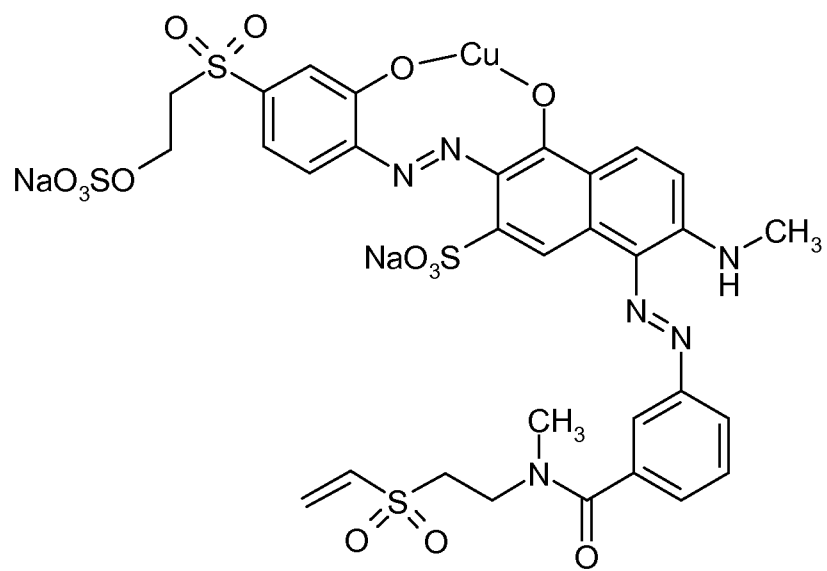


I-13,

12

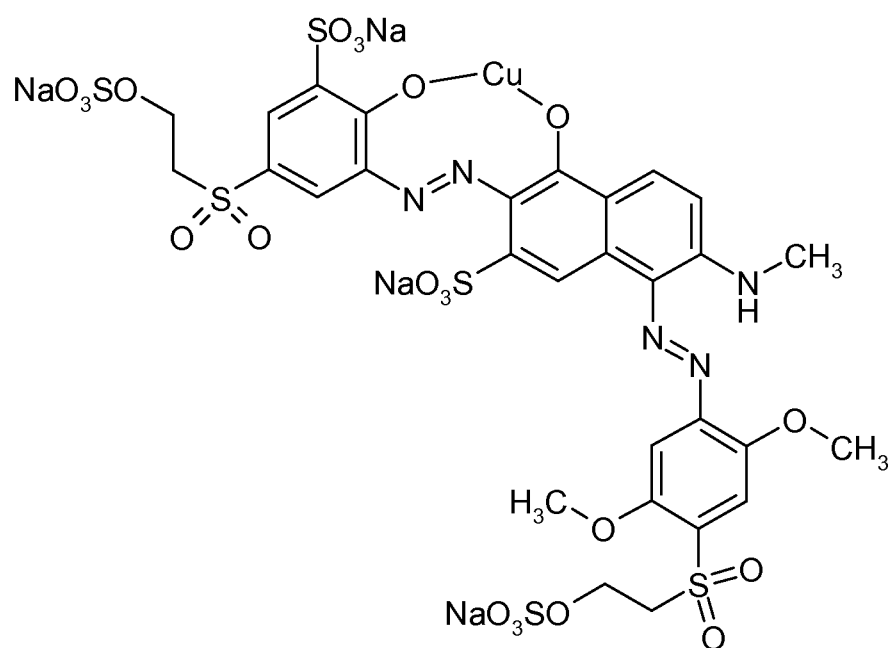


1-14,

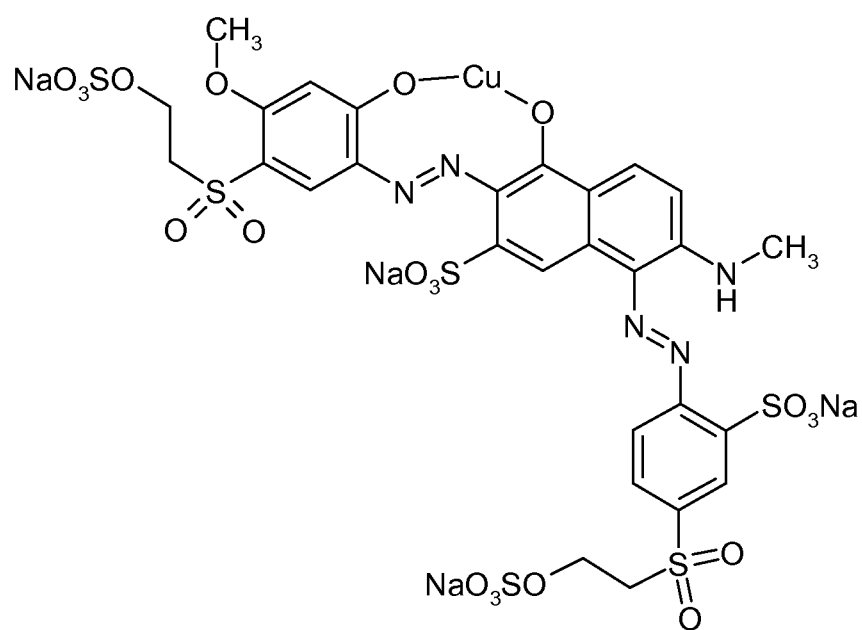


1-15,

13

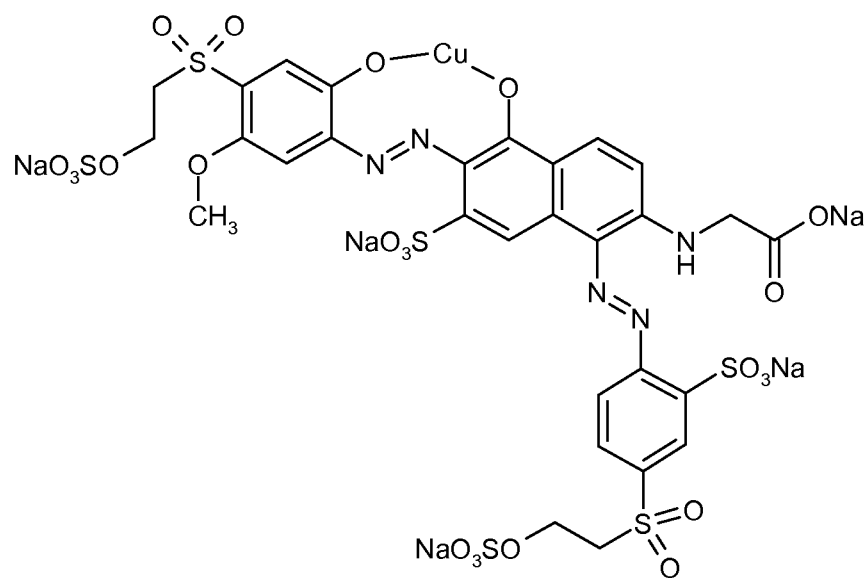


I-16,

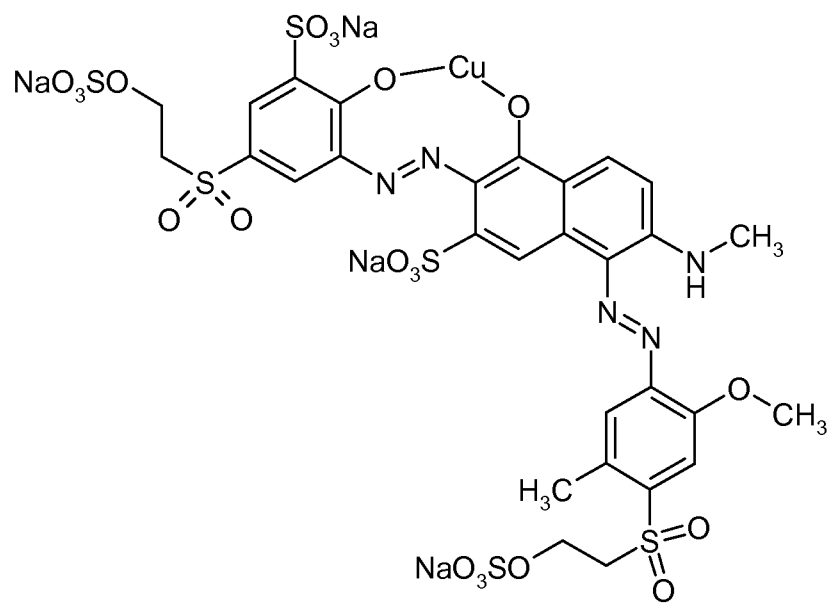


I-17,

14

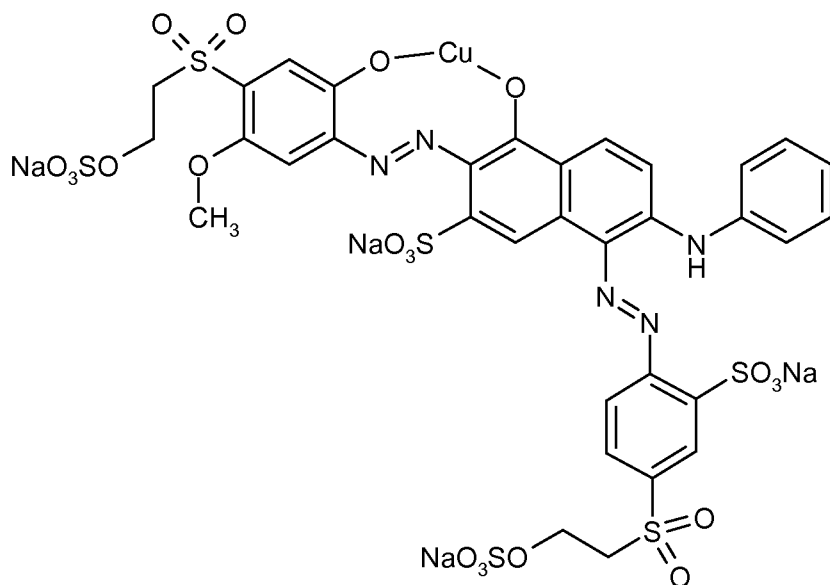


I-18,

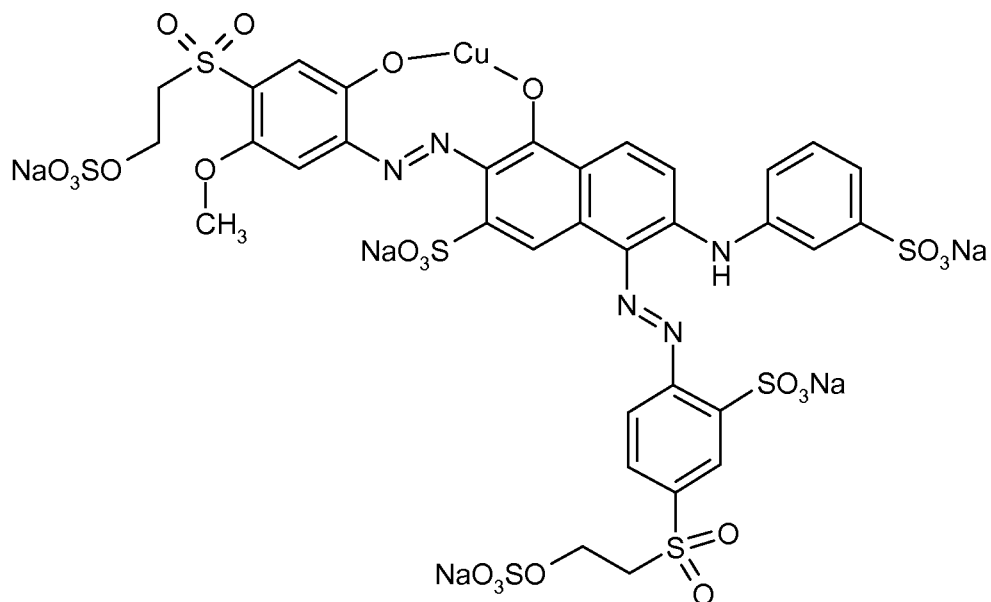


I-19,

15



I-20 and



I-21.

5

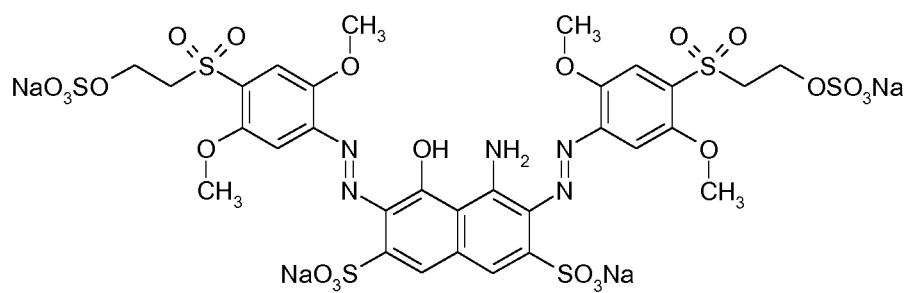
Even more preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21.

Most preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2 and I-4,

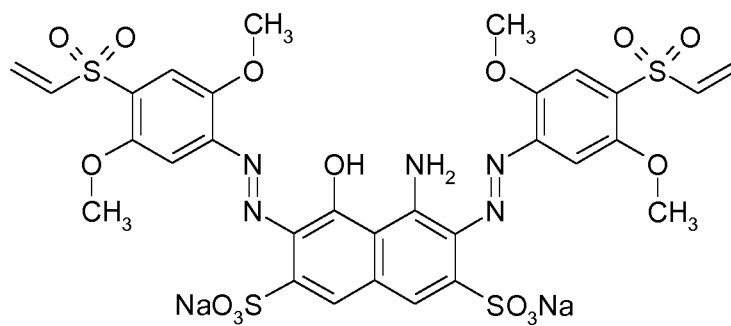
10

Particularly preferred are mixtures, wherein the dye of general structure (II) is selected from the group consisting of:

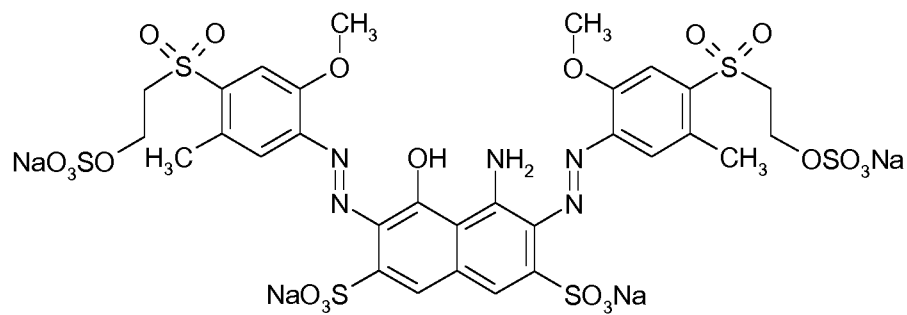
16



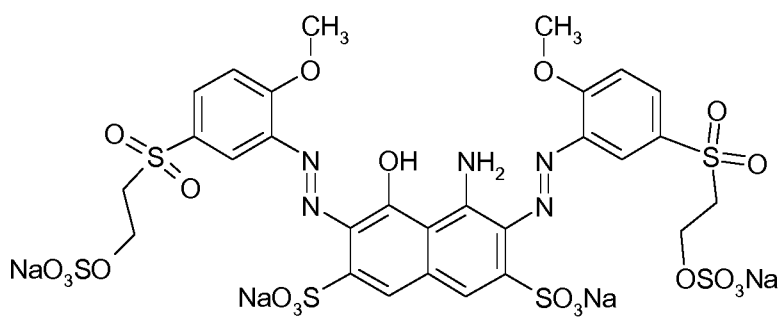
II-1,



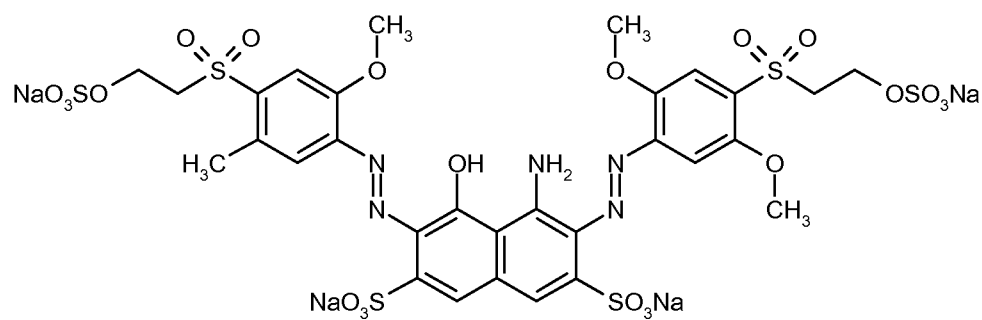
II-2,



II-3,

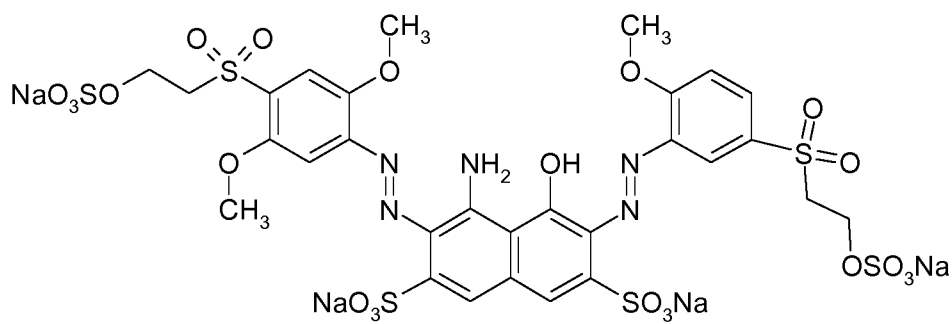


II-4,

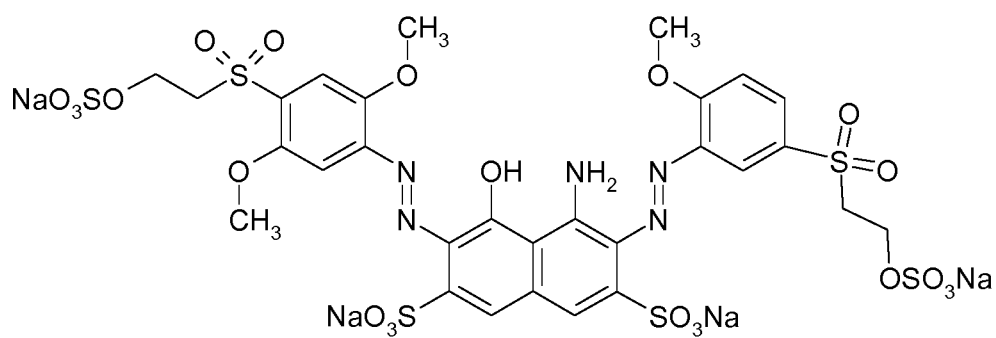


17

II-5,

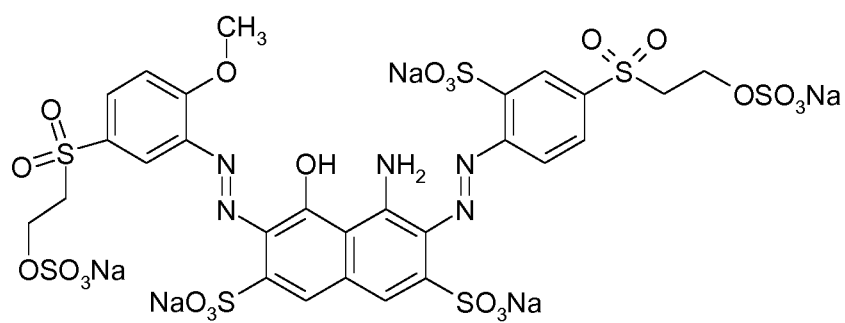


II-6,

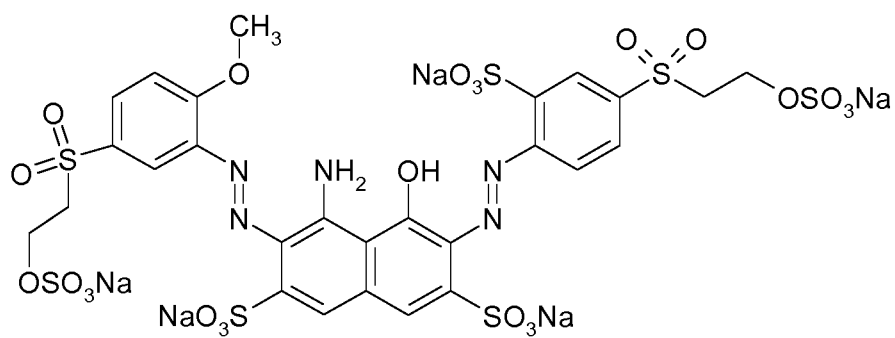


5

II-7,

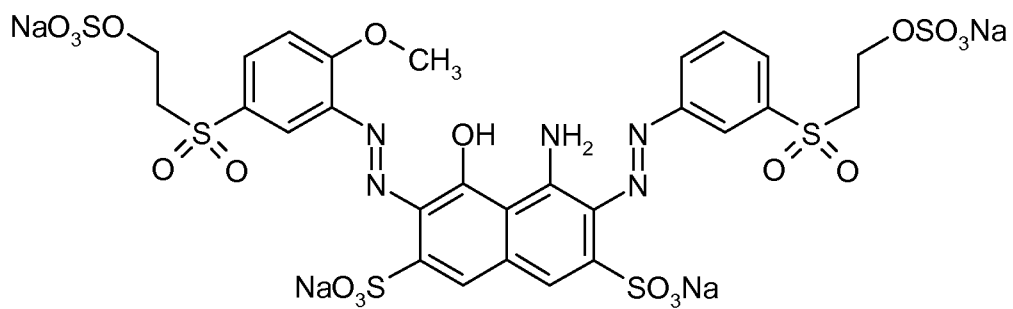


II-8,

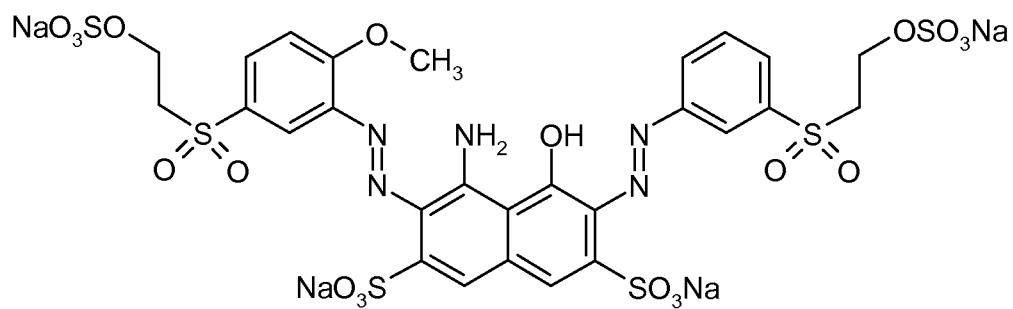


II-9,

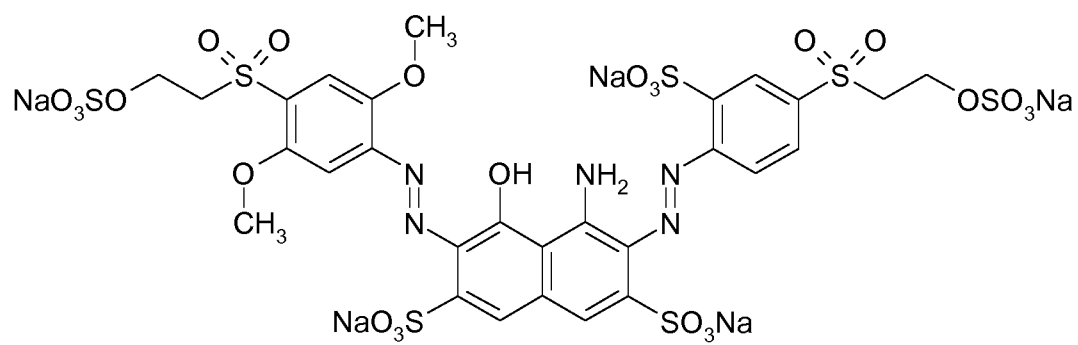
18



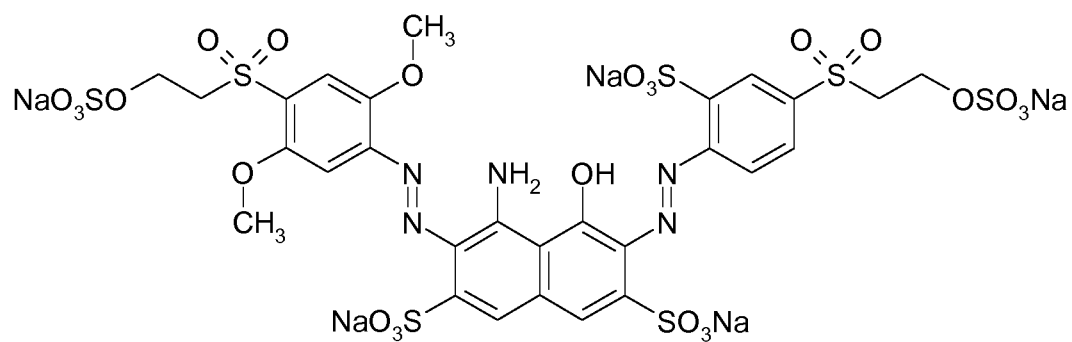
II-10,



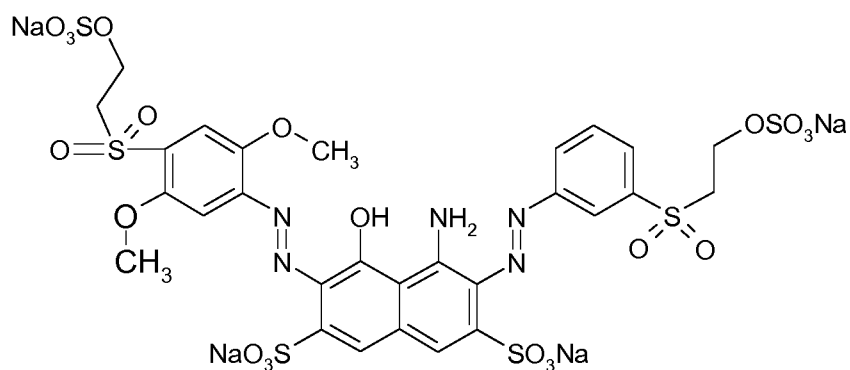
II-11,



II-12,



II-13 and

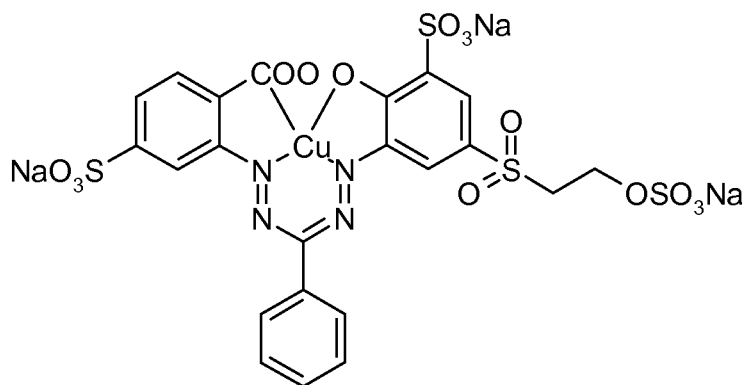


II-14.

Even more preferred are mixtures, wherein the dye of general structure (II) is selected from
 5 the group consisting of: II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

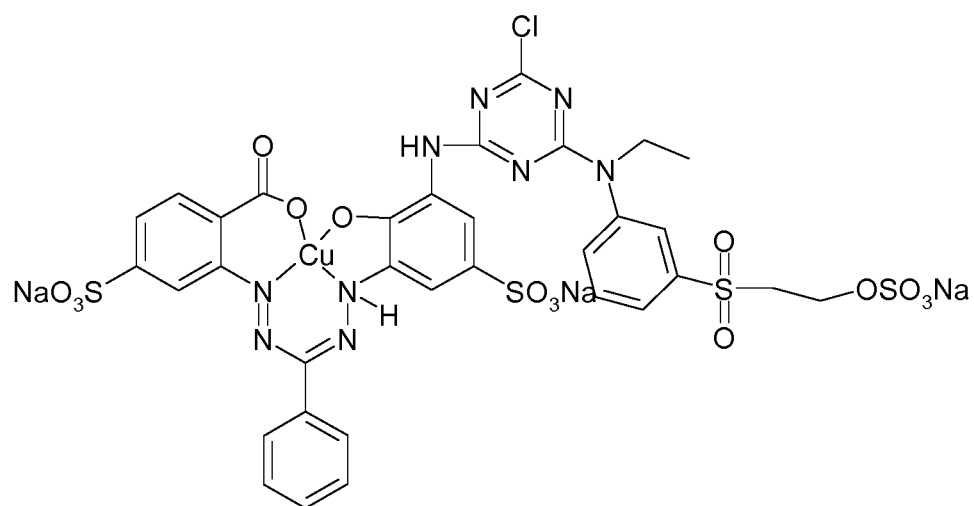
Most preferred are mixtures, wherein the dye of general structure (II) is selected from the group
 consisting of: II-1, II-2, II-6, II-7, II-12 and II-13.

10 Another particularly preferred group of mixtures according to the present invention are those,
 wherein a dye of general structure (III) is present and said dye is selected from the group
 consisting of:

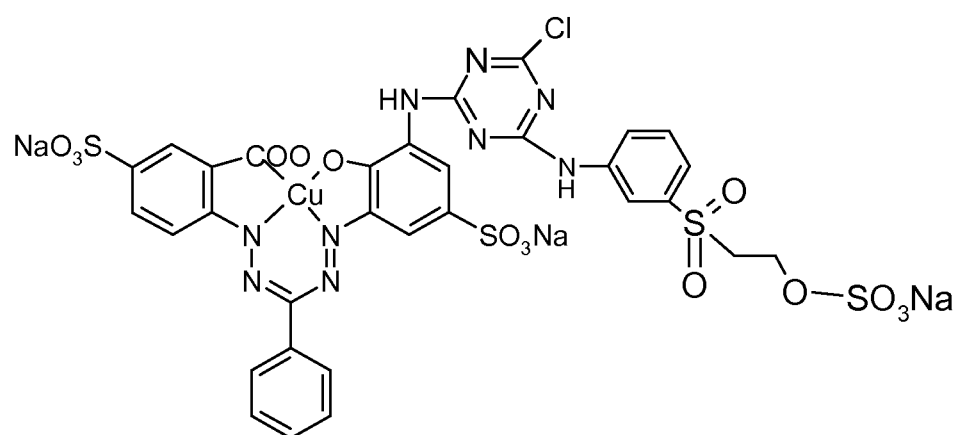


III-1,

20

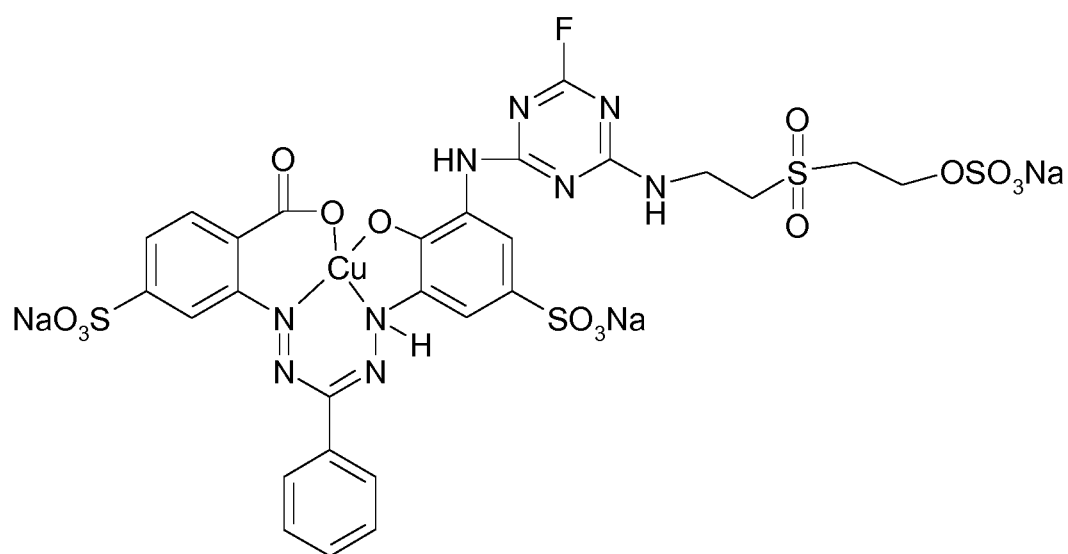


III-2,



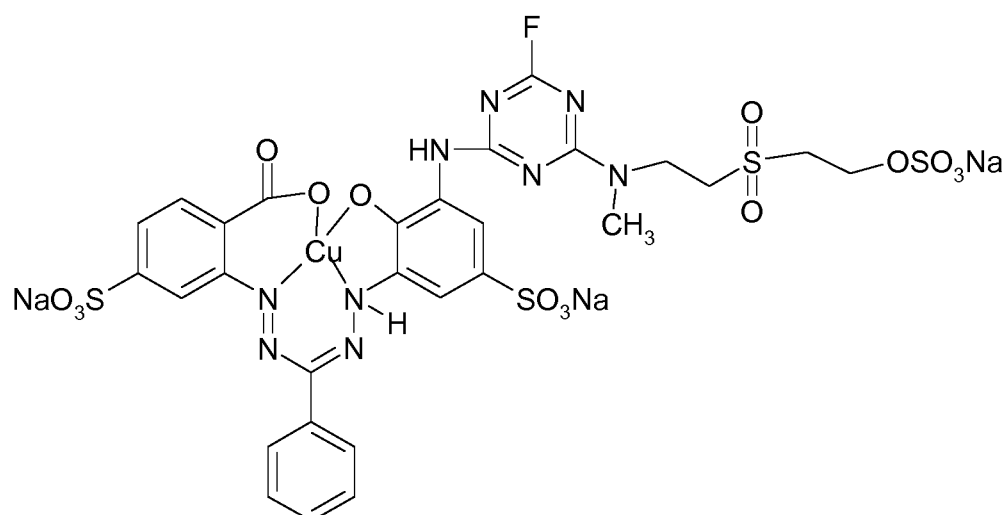
III-3,

5

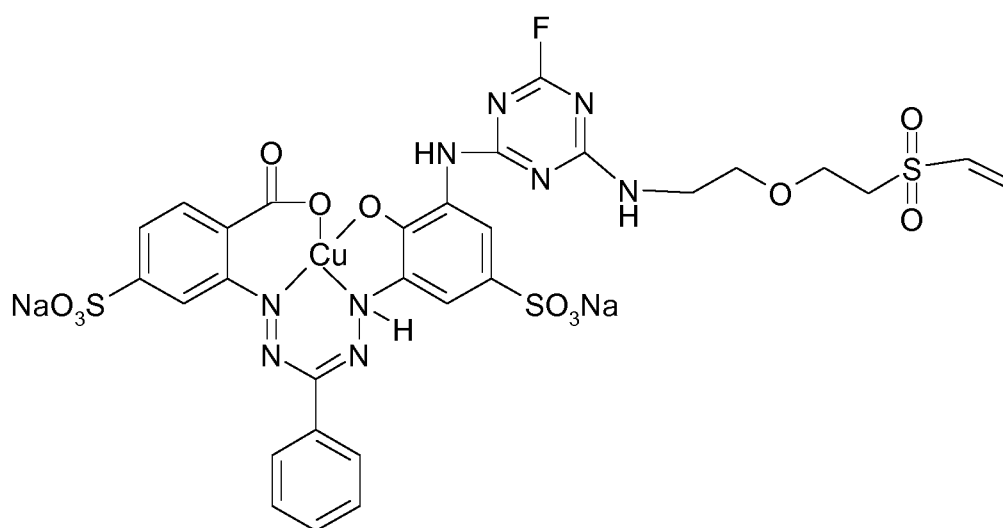


III-4,

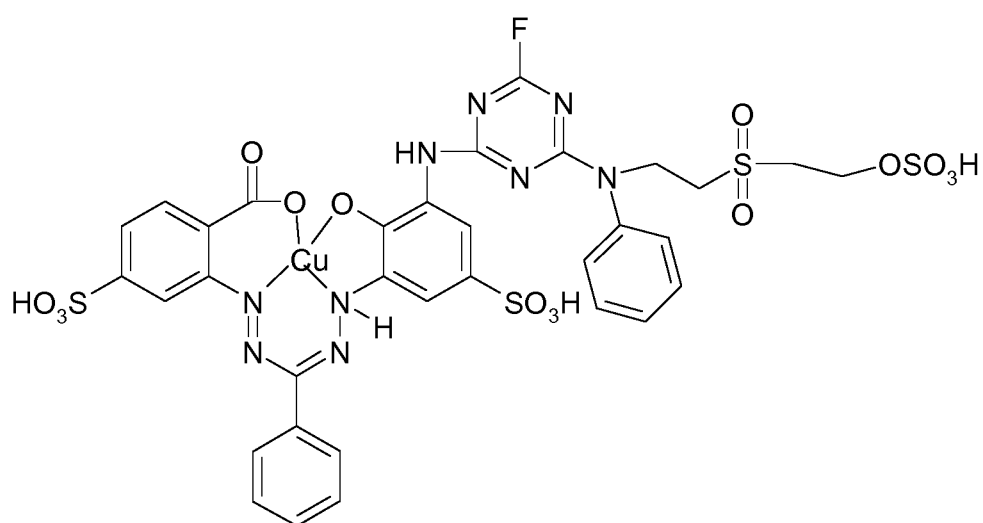
21



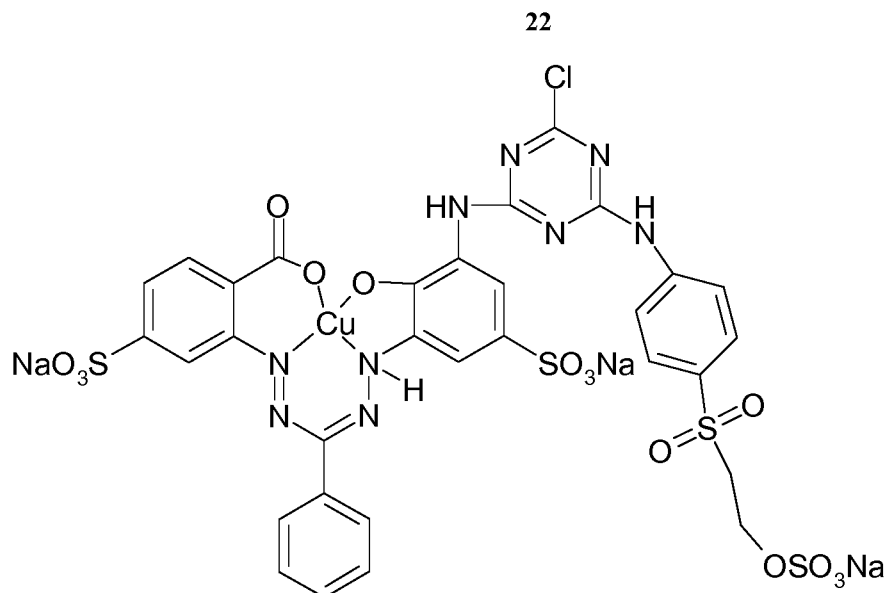
III-5,



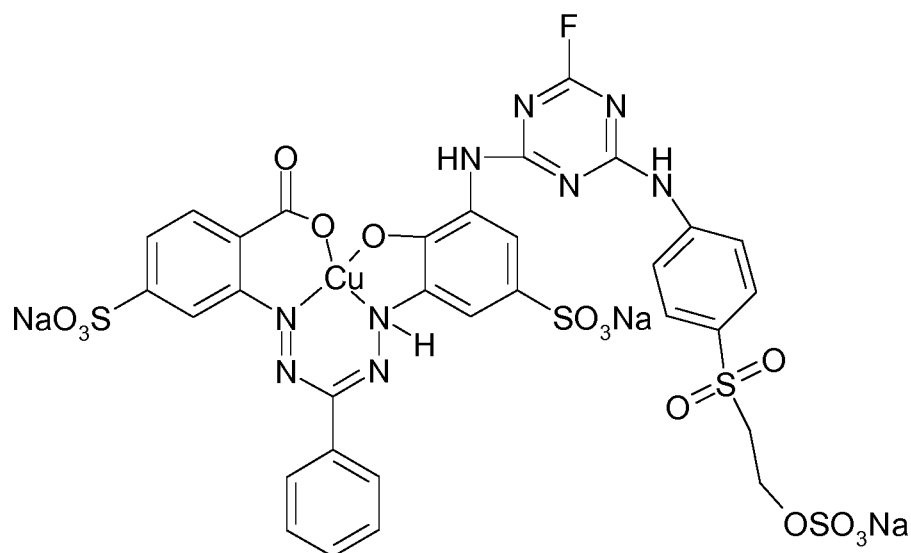
III-6,



III-7 and



III-8.



III-9.

5

Even more preferred are mixtures, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-4, III-6, III-7 and III-8.

- 10 Most preferred are mixtures, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-6, III-7 and III-8.

A preferred group of mixtures according to the present invention are those mixtures, wherein both dyes (I) and (II) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (II) being selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-

15

8, II-10, II-11, II-12 and II-13. Even more preferred is the group of mixtures wherein both dyes (I) and (II) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (II) being selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13.

5

From those mixtures wherein also a dye of structure (III) is present those are preferred, wherein both dyes (I) and (III) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8. More preferred are those, wherein both dyes (I) and (III) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

10

Another preferred subgroup wherein also a dye of structure (III) is present are those mixtures, wherein both dyes (II) and (III) are specifically selected - with the dye of the formula (II) being selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8. A more preferred subgroup wherein also a dye of structure (III) is present are those mixtures, wherein both dyes (II) and (III) are specifically selected - with the dye of the formula (II) being selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

15

20

The most preferred subgroup of such mixtures are those wherein all three dyes of structures (I), (II) and (III) are selected from the lists consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 for the dye of structure (I), of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 for the dye of structure (II) and of III-1, III-2, III-4, III-6, III-7 and III-8 for the dye of formula (III). Within this group mixtures wherein all three dyes of structures (I), (II) and (III) are selected from the lists consisting of I-1, I-2 and I-4 for the dye of structure (I), of II-1, II-2, II-6, II-7, II-12 and II-13 for the dye of structure (II) and of III-1, III-2, III-6, III-7 and III-8 for the dye of formula (III) are the most preferred.

25

30

The dyes of formula (I), (II) and/or (III) 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 as buffer substances capable of setting a pH of between 3 and 7 in aqueous

35

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 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), (II) and/or (III) and also the dye mixture according to the invention are typically in the form of powders or granules which contain electrolyte salts (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), (II) and/or (III) 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.

The dyes of formula (I), (II) and (III) 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.

The mixtures of dyes of formula (I), (II) and (III) according to the present invention possess valuable performance properties and can be used for dyeing and printing carboxamido- and/or hydroxyl-containing materials. 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 take the form of fibers of the stated materials.

The mixtures of the dyes of formula (I), (II) and optionally (III) according to the 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 fibers.

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

The use of the mixtures of formula (I), (II) and optionally (III) 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.

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.

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.

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.

5

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.

10

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).

15

Besides mixtures of the general formula (I), (II), optionally (III) 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, the a dye mixture of the formula (I), (II) and optionally (III) 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.

25

30

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.

35

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.

5

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.

10

The padding process on cellulose fibers likewise produces excellent colour yields and a very good colour buildup, 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.

15

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.

25

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.

30

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 potassium compounds. Examples of such acid-binding agents include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium

35

formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate, or mixtures thereof.

5 The mixtures of the general formula (I), (II) and optionally (III) 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 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.

15 The present invention also provides inks for digital textile printing by the inkjet process, which comprise a dye mixture of the formula (I), (II) and optionally (III) according to the invention.

20 The inks of the invention comprise a dye mixture of the formula (I), (II) and optionally (III) 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.

25 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.

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

30 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-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.: 35 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.

5

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.

- 10 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,
15 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.

- 20 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
25 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
30 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,
35 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.

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 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 a dye mixture of the formula (I), (II) and optionally (III) according to the invention 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 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 potassium salts.

The dyes were synthesized as outlined in European patents EP 1 490 441 and WO 2010/050495. The dye mixtures were then prepared as in the following examples.

Example 1

- 5 70 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-1), and 30 parts of an electrolyte-containing dye powder containing the greenish navy azo dye of the formula (II-1), were mixed mechanically with one another.

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

Example 2

- 15 50 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-1), 30 parts of an electrolyte-containing dye powder containing the greenish navy azo dye of the formula (II-1), and 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (III-7) were mixed mechanically with one another.

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

Example 3

- 25 50 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-4), 30 parts of an electrolyte-containing dye powder containing the navy azo dye of the formula (II-6), and 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (III-1) were mixed mechanically with one another.

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

Example No	Component I	%	Component II	%	Component II	%
4	I.1	60	II.1	40	-	-
5	I.1	50	II.1	50	-	-
6	I.1	50	II.1	30	III.1	20
7	I.1	20	II.1	30	III.1	50
8	I.1	50	II.1	30	III.2	20
9	I.1	50	II.1	30	III.3	20
10	I.1	50	II.1	30	III.4	20
11	I.1	50	II.1	30	III.5	20

12	I.1	50	II.1	30	III.6	20
13	I.2	70	II.2	30	-	-
14	I.2	60	II.2	40	-	-
15	I.2	50	II.2	50	-	-
16	I.2	50	II.2	30	III.1	20
17	I.2	50	II.2	30	III.7	20
18	I.3	70	II.1	30	-	-
19	I.3	60	II.1	40	-	-
20	I.3	50	II.1	50	-	-
21	I.4	70	II.1	30	-	-
22	I.4	60	II.1	40	-	-
23	I.4	50	II.1	50	-	-
24	I.4	50	II.1	30	III.1	20
25	I.4	50	II.1	30	III.7	20
26	I.5	70	II.1	30	-	-
27	I.5	60	II.1	40	-	-
28	I.5	50	II.1	50	-	-
29	I.6	70	II.1	30	-	-
30	I.6	60	II.1	40	-	-
31	I.6	50	II.1	50	-	-
32	I.12	70	II.1	30	-	-
33	I.12	60	II.1	40	-	-
34	I.12	50	II.1	50	-	-
35	I.13	70	II.1	30	-	-
36	I.13	60	II.1	40	-	-
37	I.13	50	II.1	50	-	-
38	I.17	70	II.1	30	-	-
39	I.17	60	II.1	40	-	-
40	I.17	50	II.1	50	-	-
41	I.18	70	II.1	30	-	-
42	I.18	60	II.1	40	-	-
43	I.18	50	II.1	50	-	-
44	I.20	70	II.1	30	-	-
45	I.20	60	II.1	40	-	-
46	I.20	50	II.1	50	-	-
47	I.21	70	II.1	30	-	-
48	I.21	60	II.1	40	-	-
49	I.21	50	II.1	50	-	-
50	I.1	70	II.4	30	-	-
51	I.1	60	II.4	40	-	-
52	I.1	50	II.4	50	-	-
53	I.1	70	II.5	30	-	-
54	I.1	60	II.5	40	-	-
55	I.1	50	II.5	50	-	-
56	I.1	70	II.6	30	-	-

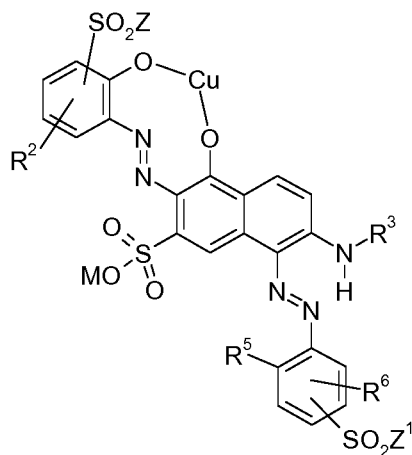
57	I.1	60	II.6	40	-	-
58	I.1	50	II.6	50	-	-
59	I.1	50	II.6	30	III.1	20
60	I.1	50	II.6	30	III.7	20
61	I.1	70	II.8	30	-	-
62	I.1	60	II.8	40	-	-
63	I.1	50	II.8	50	-	-
64	I.1	70	II.10	30	-	-
65	I.1	60	II.10	40	-	-
66	I.1	50	II.10	50	-	-
67	I.1	70	II.11	30	-	-
68	I.1	60	II.11	40	-	-
69	I.1	50	II.11	50	-	-
70	I.1	70	II.12	30	-	-
71	I.1	60	II.12	40	-	-
72	I.1	50	II.12	50	-	-
73	I.1	50	II.12	30	III.1	20
74	I.1	50	II.12	30	III.7	20
75	I.1	70	II.13	30	-	-
76	I.1	60	II.13	40	-	-
77	I.1	50	II.13	50	-	-
78	I.1	50	II.13	30	III.1	20
79	I.1	50	II.13	30	III.7	20
80	I.1	70	II.14	30	-	-
81	I.1	60	II.14	40	-	-
82	I.1	50	II.14	50	-	-
83	I.1	50	II.14	30	III.1	20
84	I.1	50	II.14	30	III.7	20

Application example 1

5 parts of the dye obtained in example 1 and 50 parts of sodium chloride were dissolved in 999 parts of water, and 5 parts of sodium carbonate, 0.7 parts of sodium hydroxide (in the form of a 32.5 % strength aqueous solution) and, if necessary, 1 part of a wetting agent are added. This dyebath was entered with 100 g of a woven cotton fabric. The temperature of the dyebath was maintained at 25 °C for 10 minutes to start with, then raised over 30 minutes to the final temperature 60 °C and held at that temperature for a further 60 to 90 minutes. Thereafter the dyed goods were rinsed first for 2 minutes with water and subsequently for 5 minutes with water. The dyed goods were neutralized at 40 °C in 1000 parts of an aqueous solution containing 1 part of 50 % strength acetic acid for 10 minutes. This was followed by rinsing with deionized water at 70 °C and then by soaping off at the boil for 15 minutes with a laundry detergent, rinsing again, and drying. This gives a strongly colored navy dyeing having very good fastness properties.

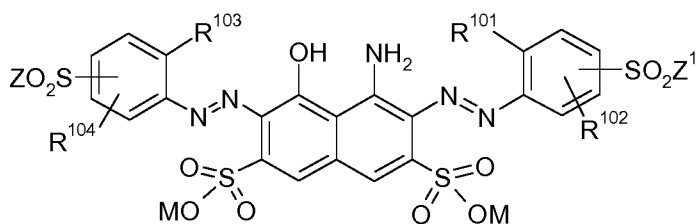
Claims:

1. Mixtures of fibre-reactive dyes comprising:
a dye of formula (I)



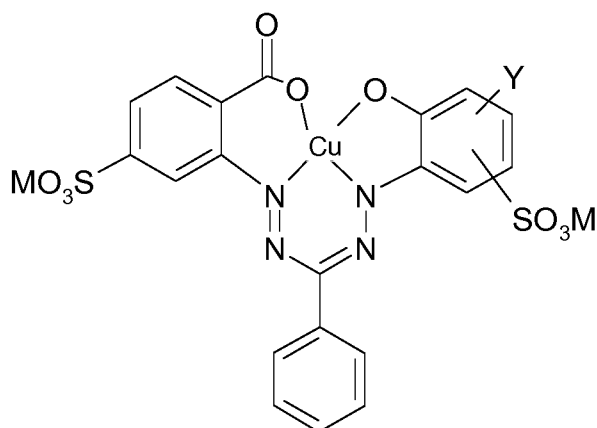
(I),

a dye of formula (II)



(II)

and optionally a dye of formula (III)



(III)

wherein independently of each other

R^2 is hydrogen, $(\text{C}_1\text{-C}_4)$ -alkyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R^3 is $(\text{C}_1\text{-C}_4)$ -alkyl; $(\text{C}_1\text{-C}_4)$ -alkyl substituted by sulfo, carboxyl, halogen, hydroxyl, amino

or acetamido; phenyl; or phenyl substituted by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, sulfo, halogen, carboxyl, acetamido or ureido;

R⁵ is (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R⁶ is hydrogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

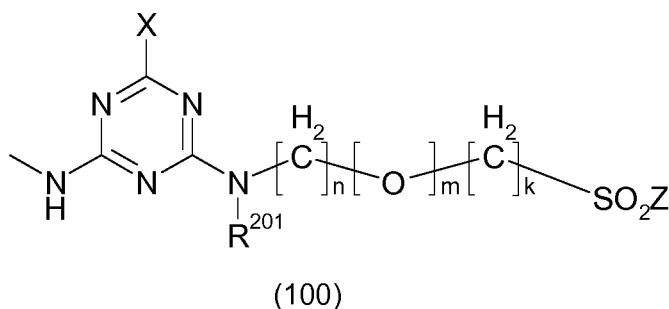
R¹⁰¹ and R¹⁰³ are C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo, carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of the formula (100)



wherein

X is halogen,

R²⁰¹ is hydrogen (C₁-C₄)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

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

2. Mixtures of fibre-reactive dyes according to claim 1, wherein independent of each other

R² is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R³ is (C₁-C₂)-alkyl or (C₁-C₂)-alkyl substituted by sulfo,

R⁵ is (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R⁶ is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

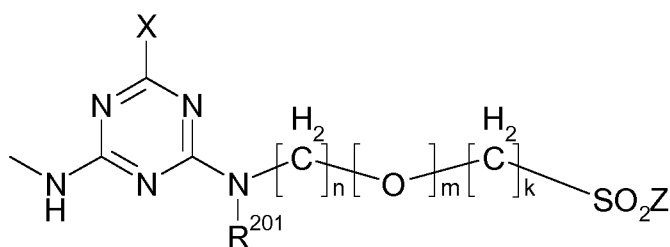
R¹⁰¹ and R¹⁰³ are C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



(100)

wherein

X is Cl or F,

5 R^{201} is hydrogen, (C₁-C₂)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

10 M is hydrogen, Na, K or Li.

3. Mixtures of fibre-reactive dyes according to claim 1 or 2, wherein independent of each other

R^2 is hydrogen, methy, methoxy or sulfo,

15 R^3 is methyl or (C₁-C₂)-alkyl substituted by sulfo,

R^5 is methy, methoxy or sulfo,

R^6 is hydrogen, methy, methoxy or sulfo,

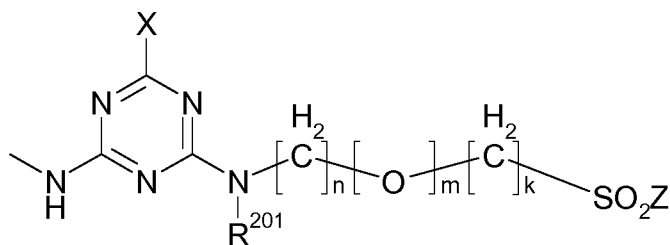
R^{101} and R^{103} are, methy, methox or sulfo,

R^{102} and R^{104} are hydrogen, methy, methoxy or sulfo,

20 Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



(100)

wherein

X is Cl or F,

R^{201} is hydrogen, methyl or phenyl,

n is 2 or 3,

25

m is 0 or 1,

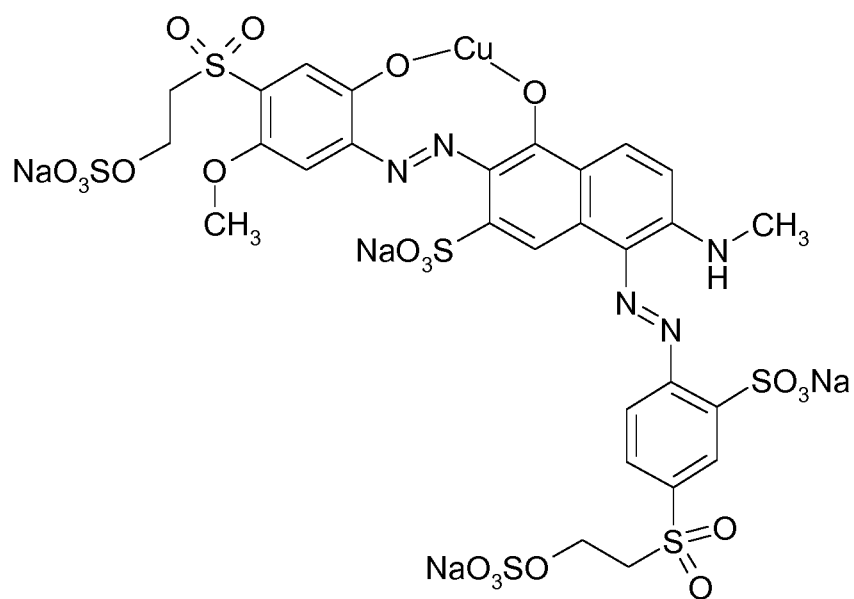
k is 0 to 3,

and

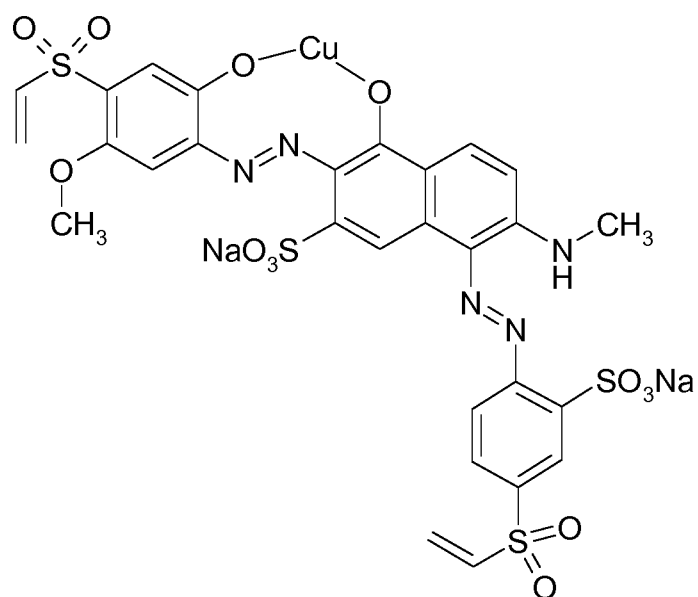
M is hydrogen, Na, K or Li.

5

4. Mixtures according to any one of claims 1 to 3, wherein the dye of general structure (I) is selected from the group consisting of:

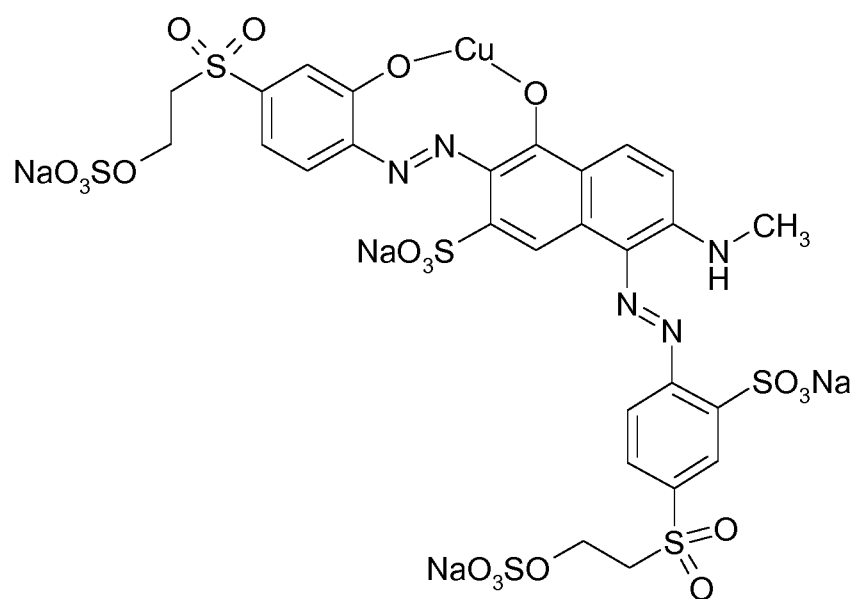


I-1,

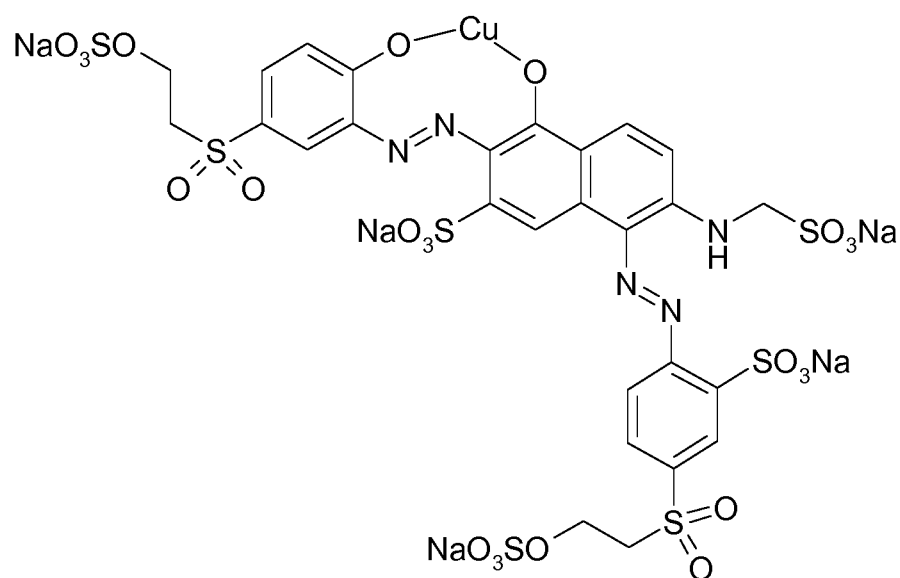


I-2,

39

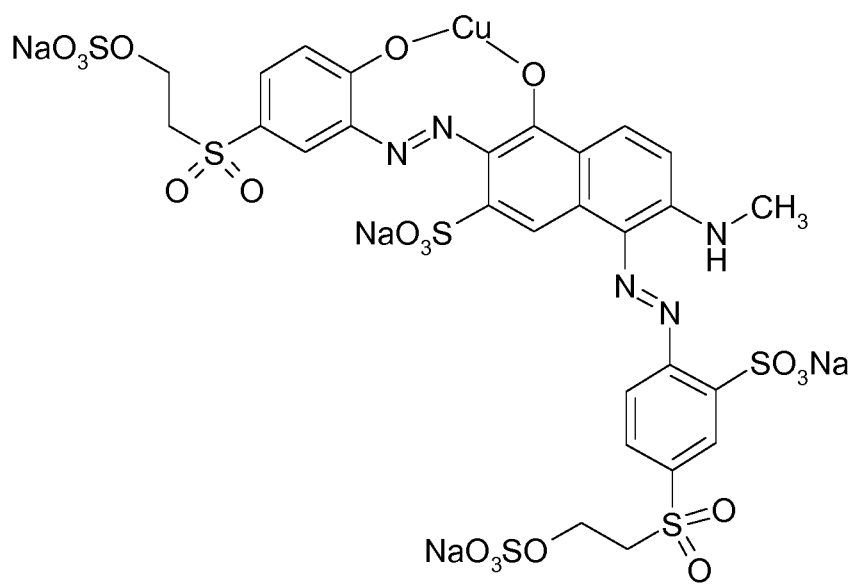


I-3,

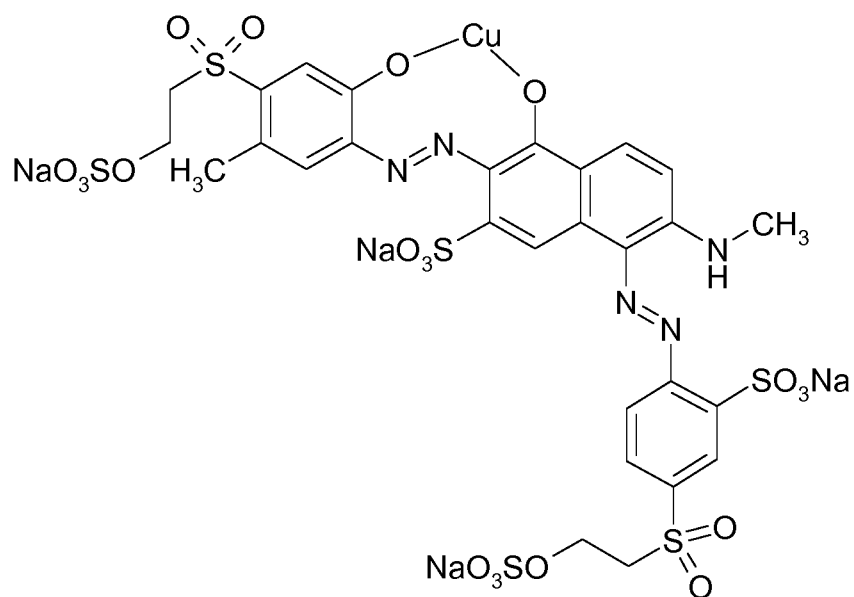


I-4,

40

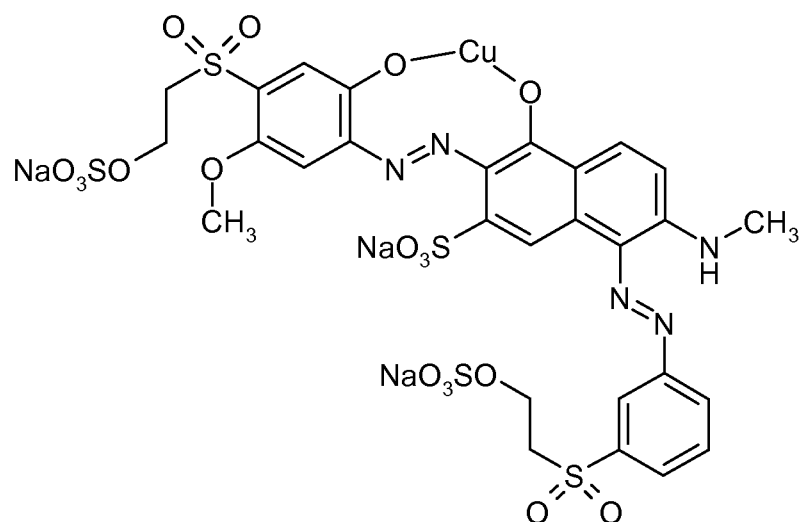


I-5,

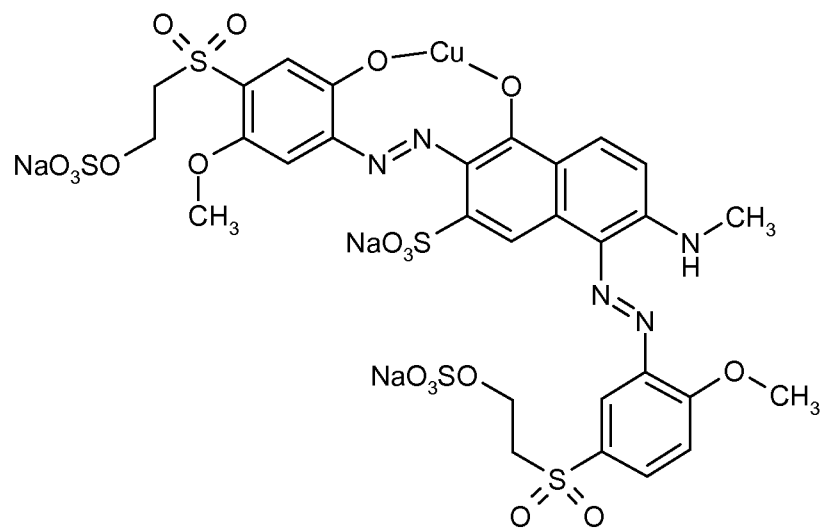


I-6,

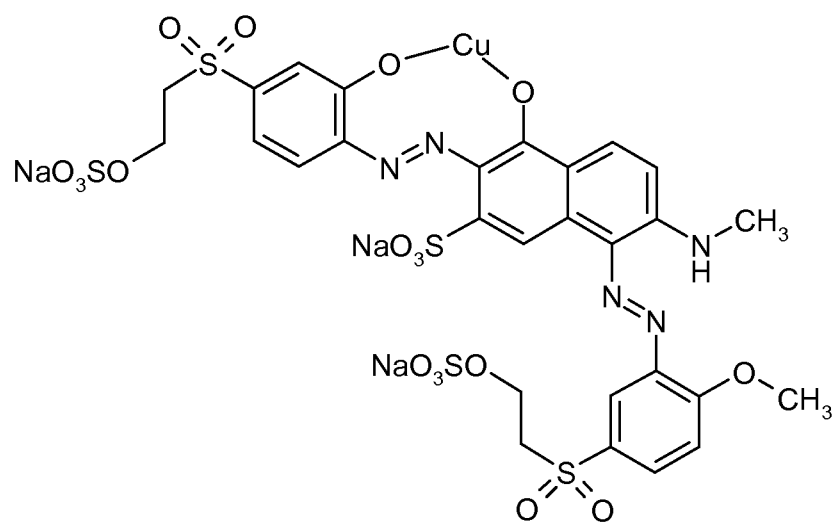
41



I-7,

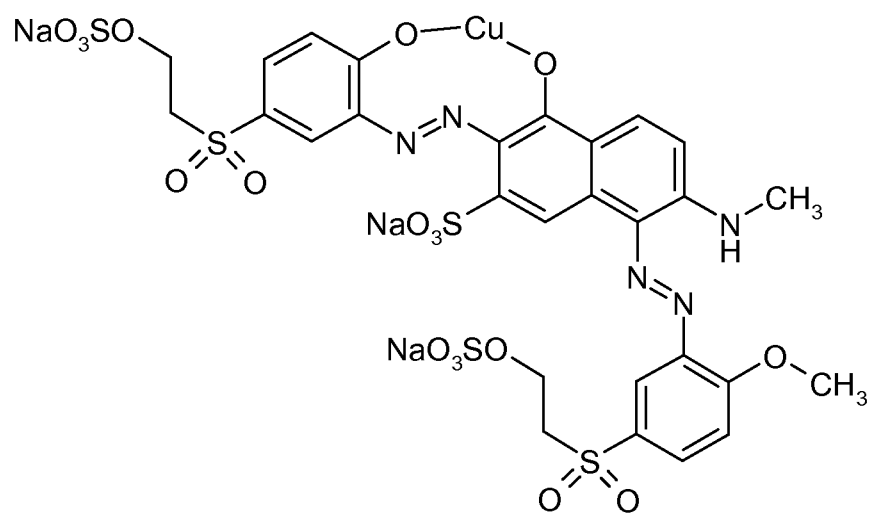


I-8,

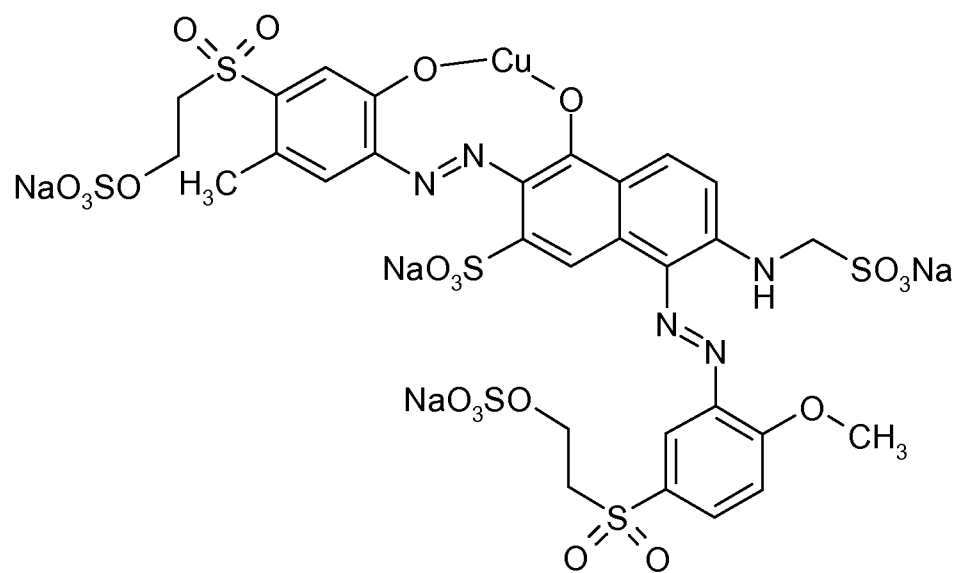


I-9,

42

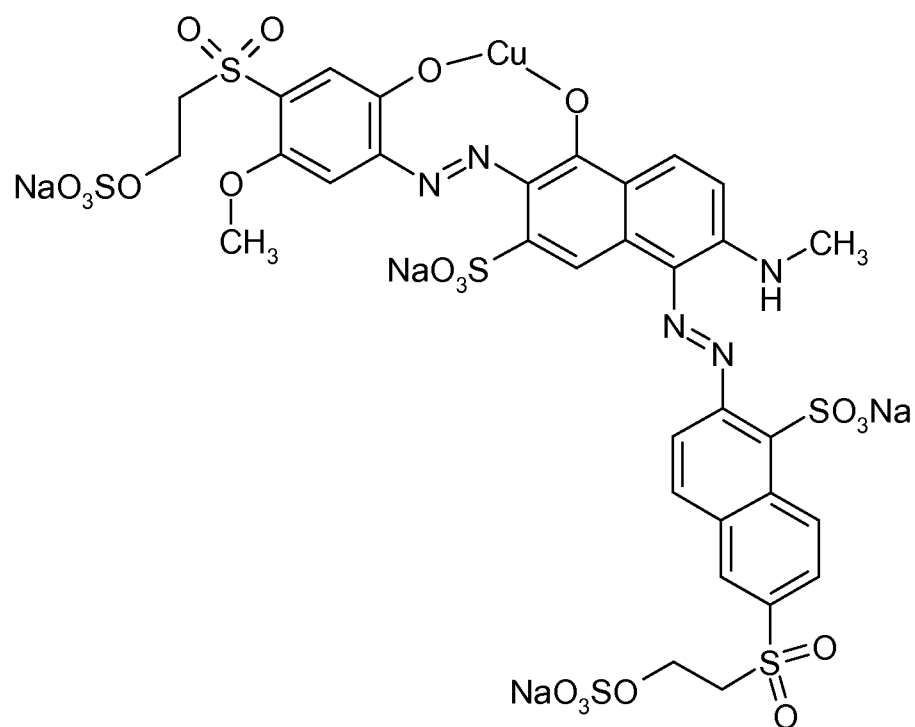


I-10,

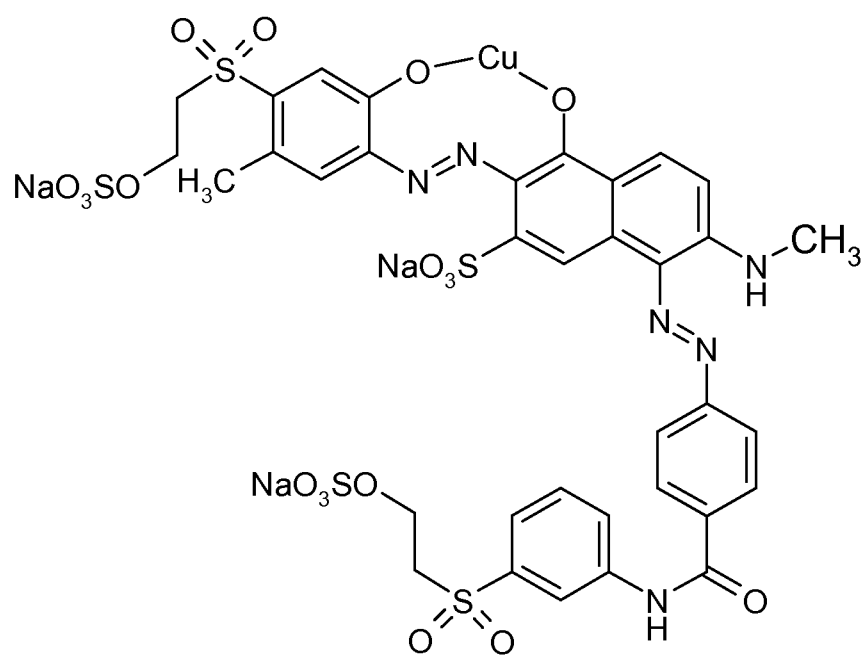


I-11,

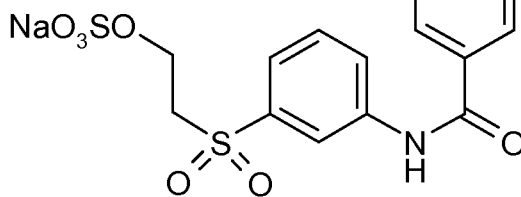
43



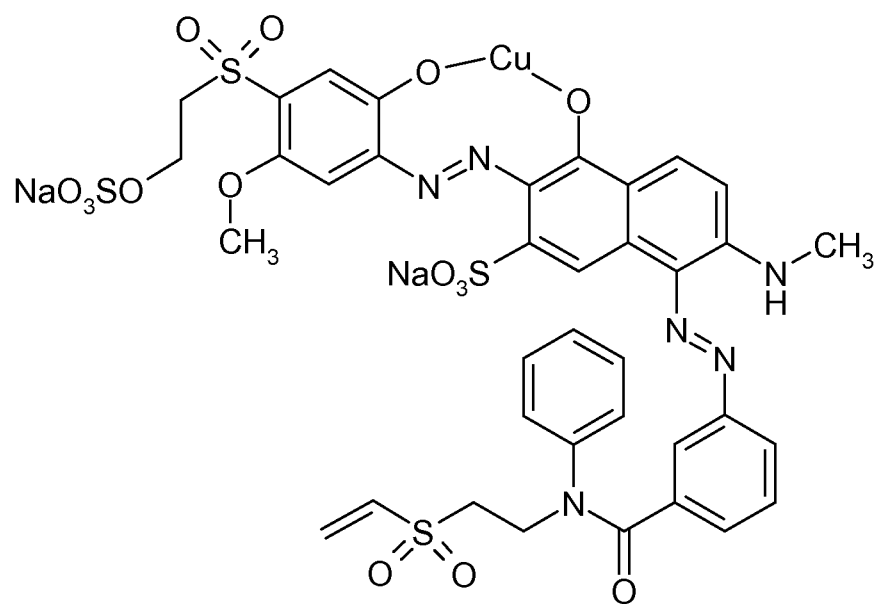
I-12,



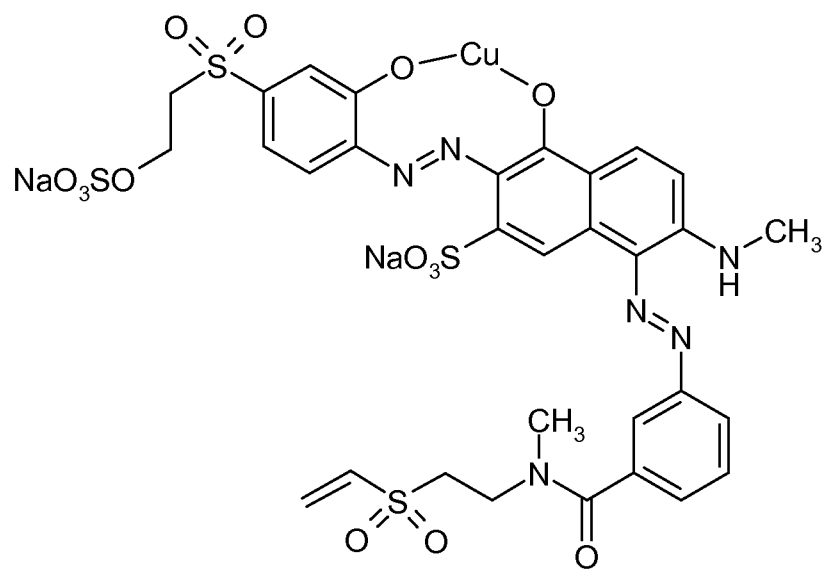
I-13,



44

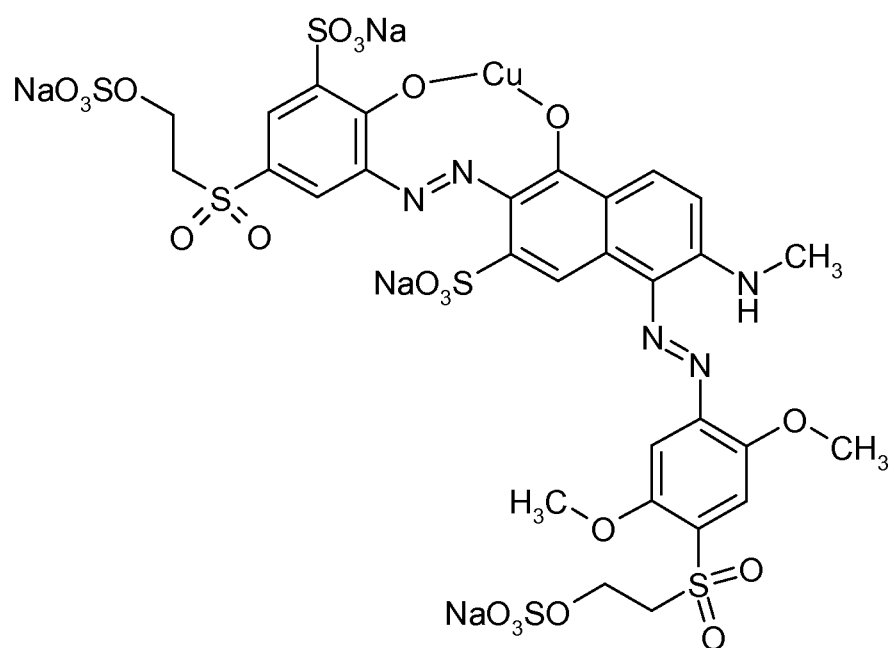


I-14,

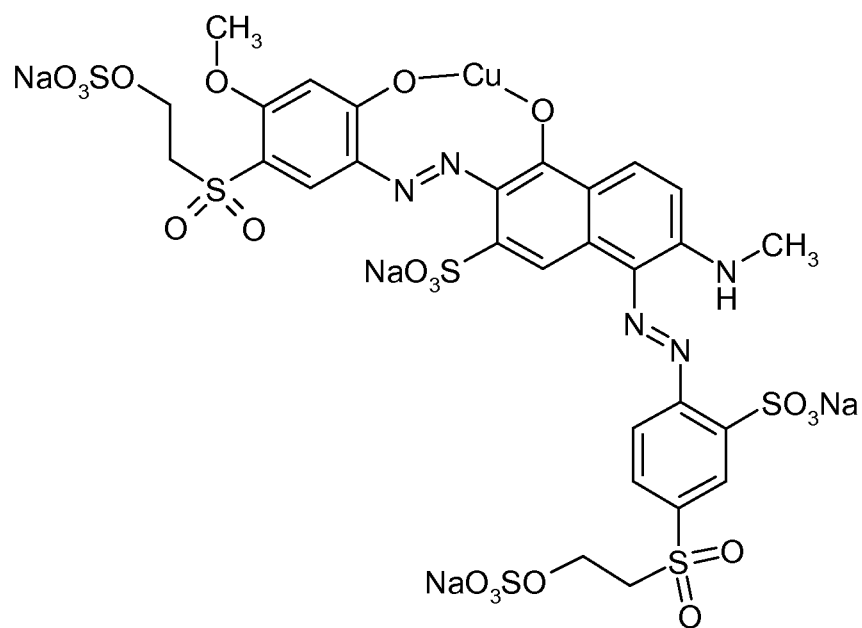


I-15,

45

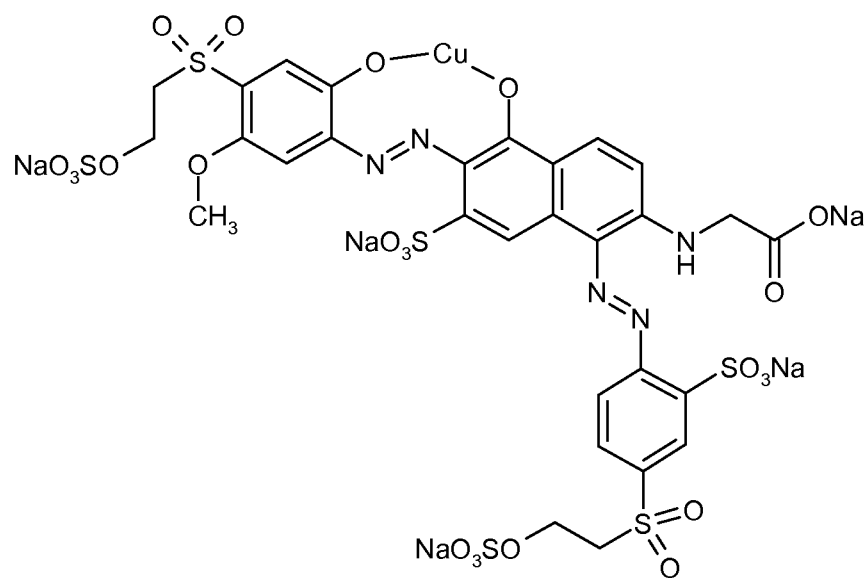


I-16,

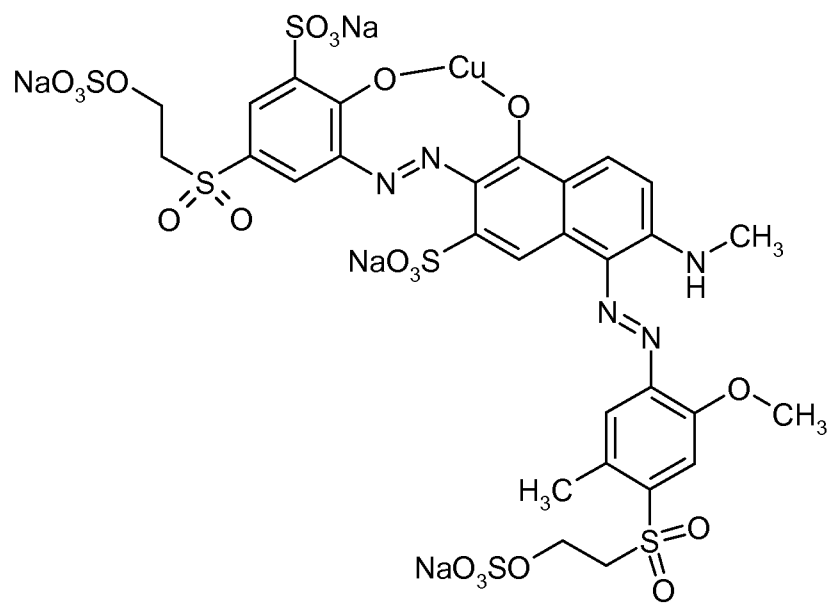


1-17,

46

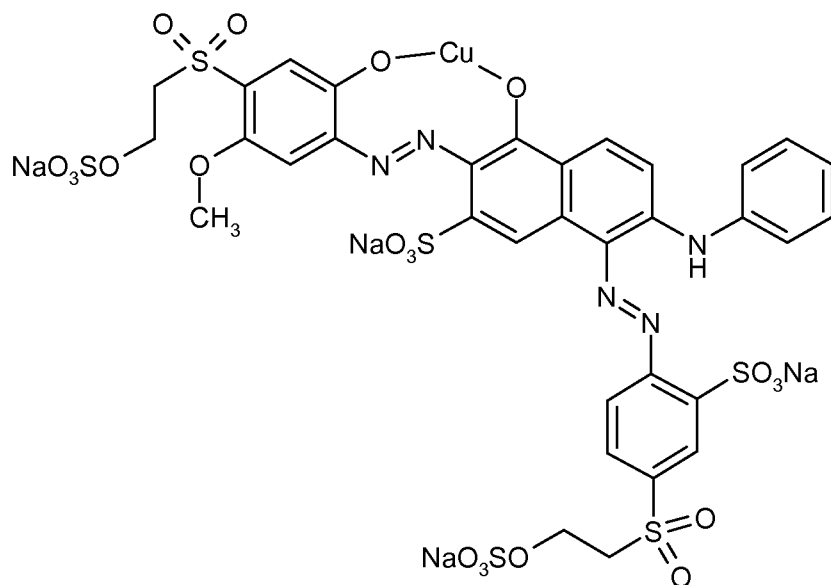


1-18,

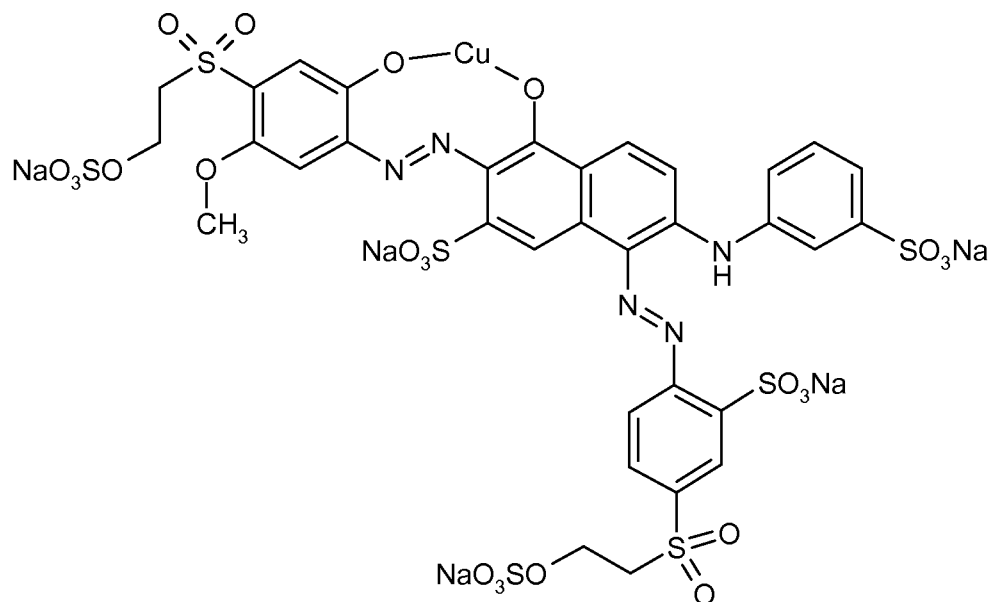


I-19,

47



I-20 and



I-21.

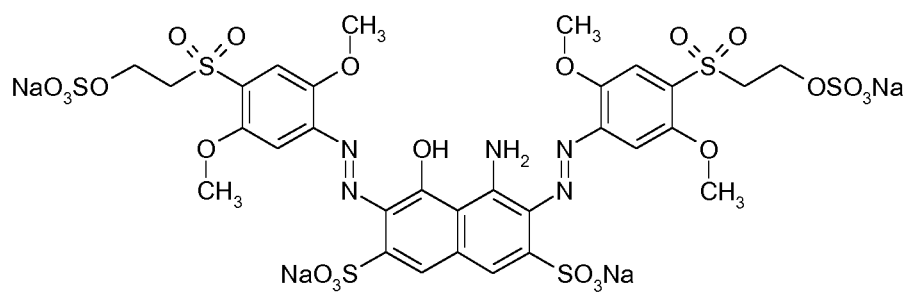
5

5. Mixtures according to any one of claims 1 to 4 wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21.

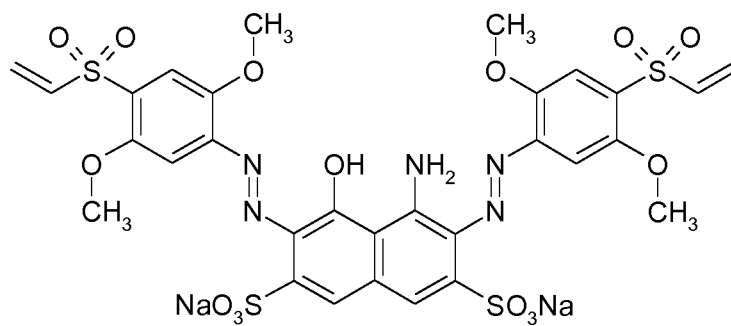
- 10 6. Mixtures according to any one of claims 1 to 5, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2 and I-4.

7. Mixtures according to any one of calims 1 to 6, wherein the dye of general structure (II) is selected from the group consisting of:

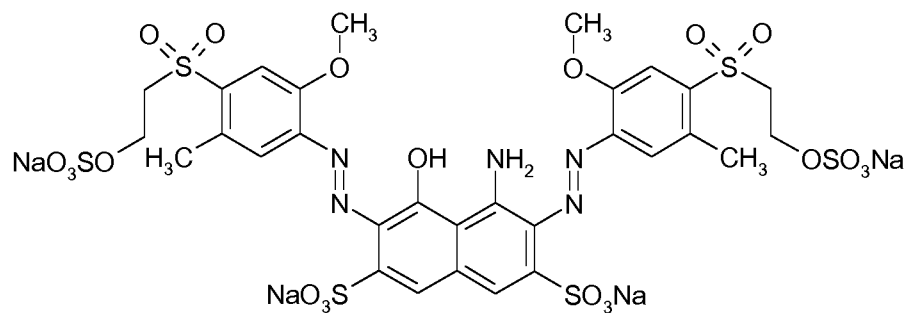
48



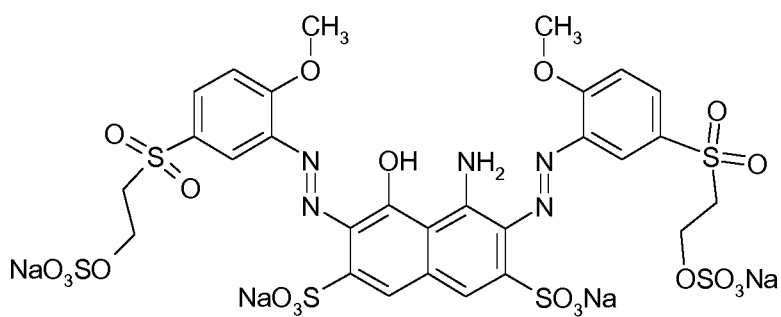
II-1,



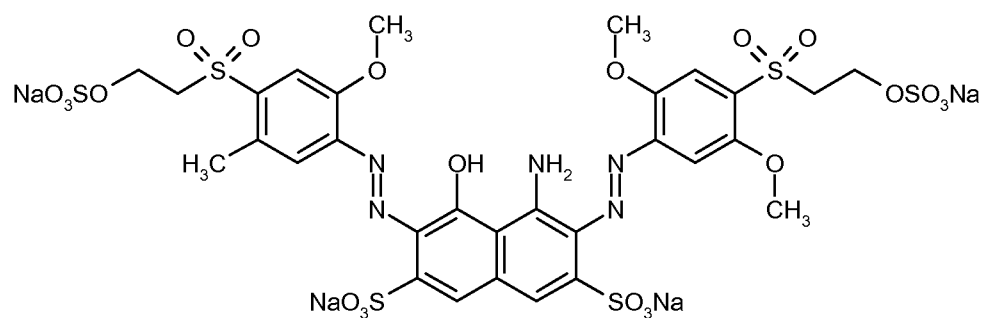
II-2,



II-3,

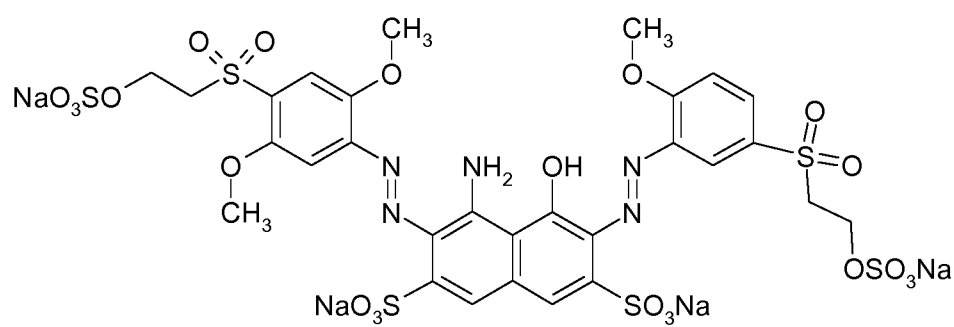


II-4,

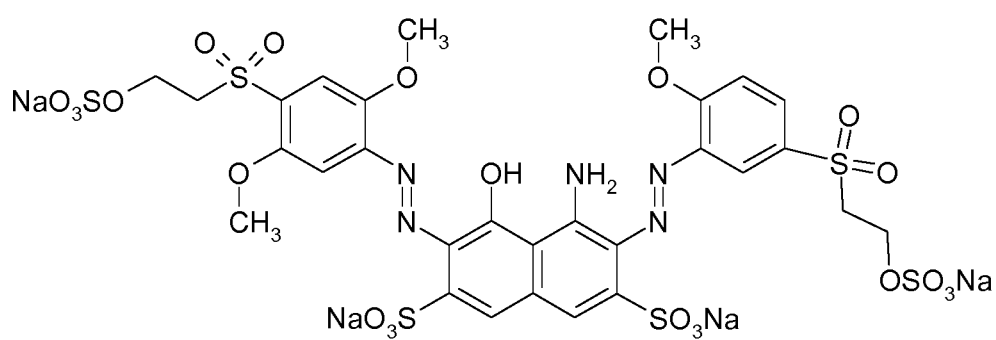


49

II-5,

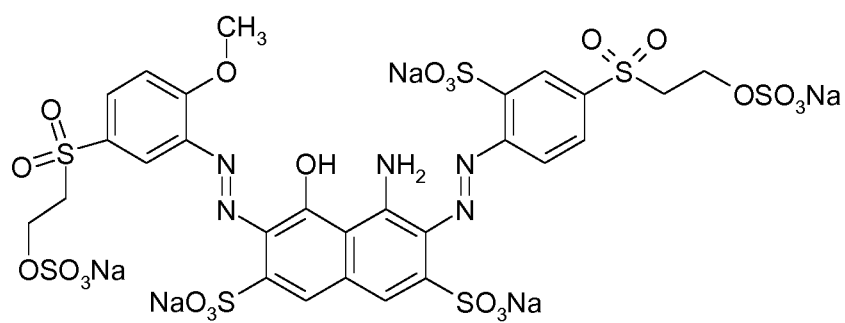


II-6,

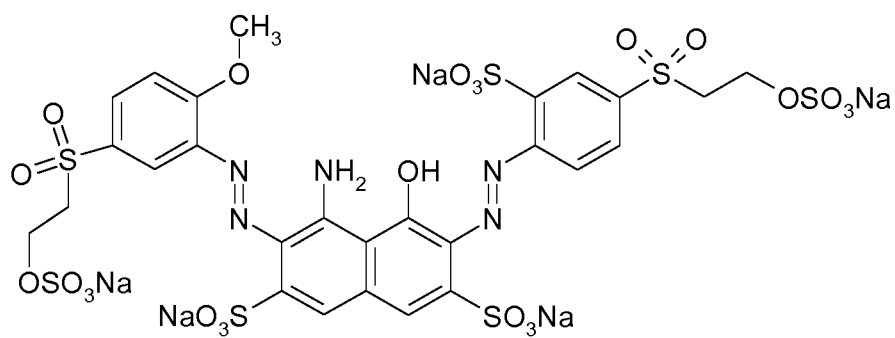


5

II-7,

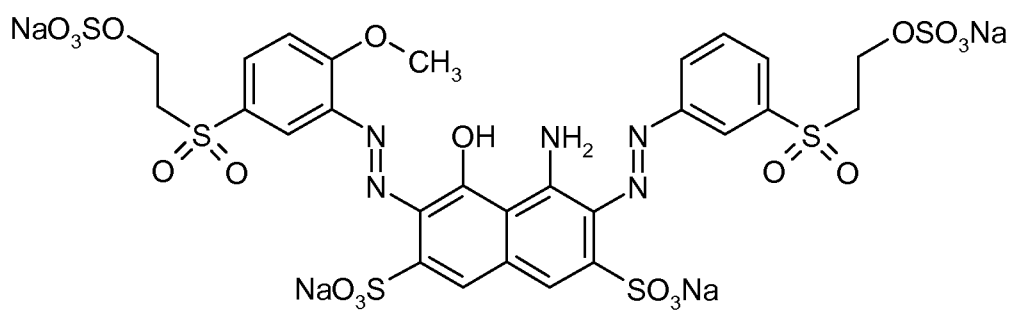


II-8,

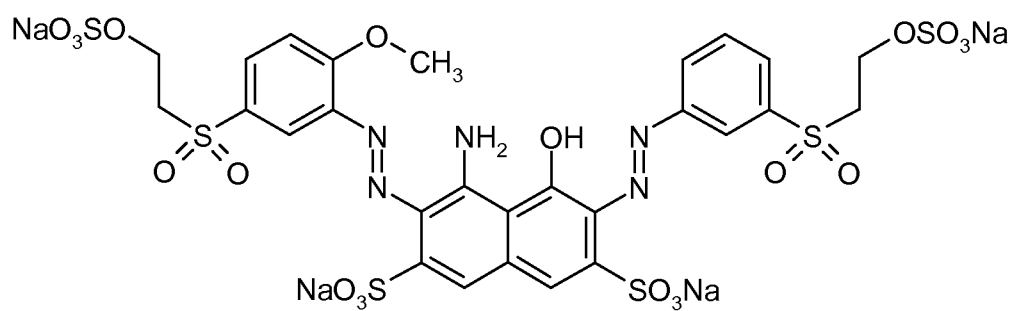


II-9,

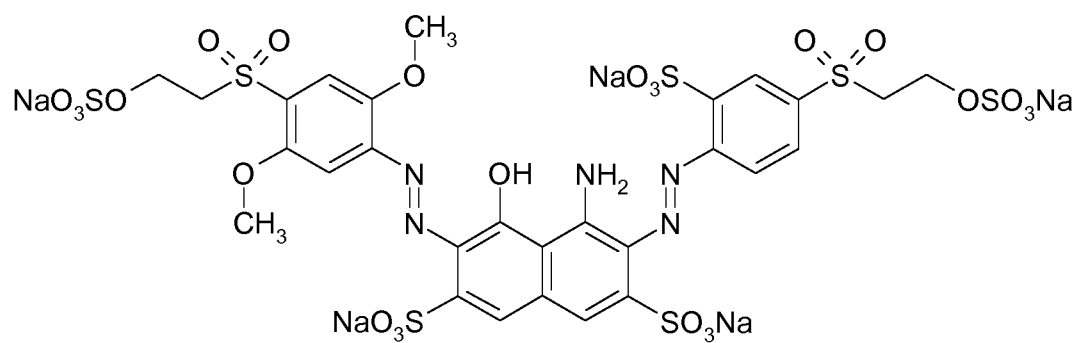
50



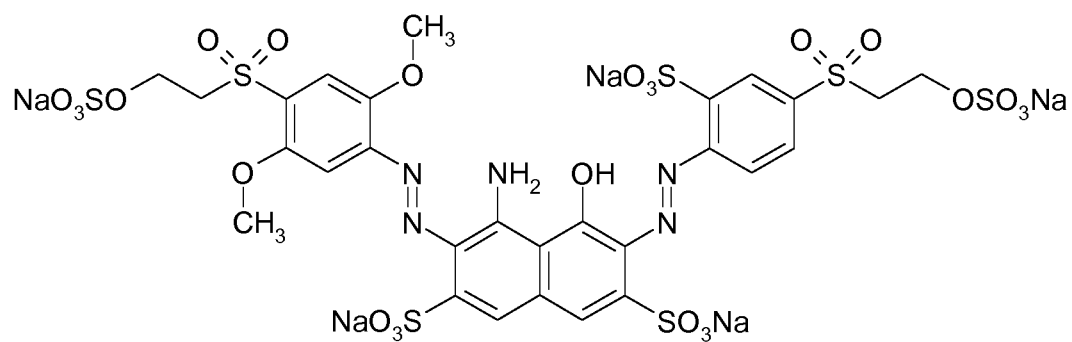
II-10,



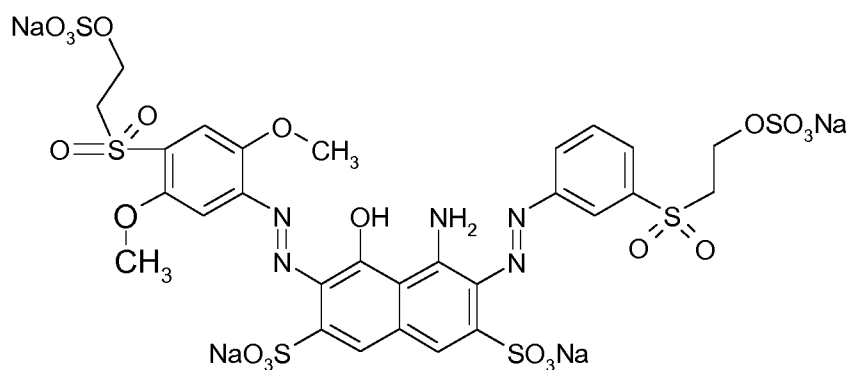
II-11,



II-12,



II-13 and

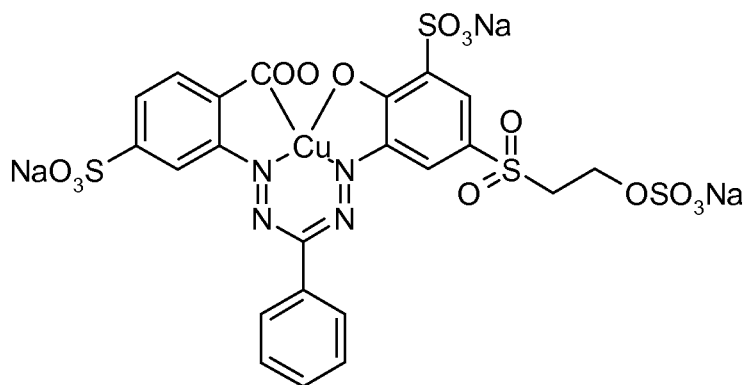


II-14.

8. Mixtures according to any one of claims 1 to 7, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

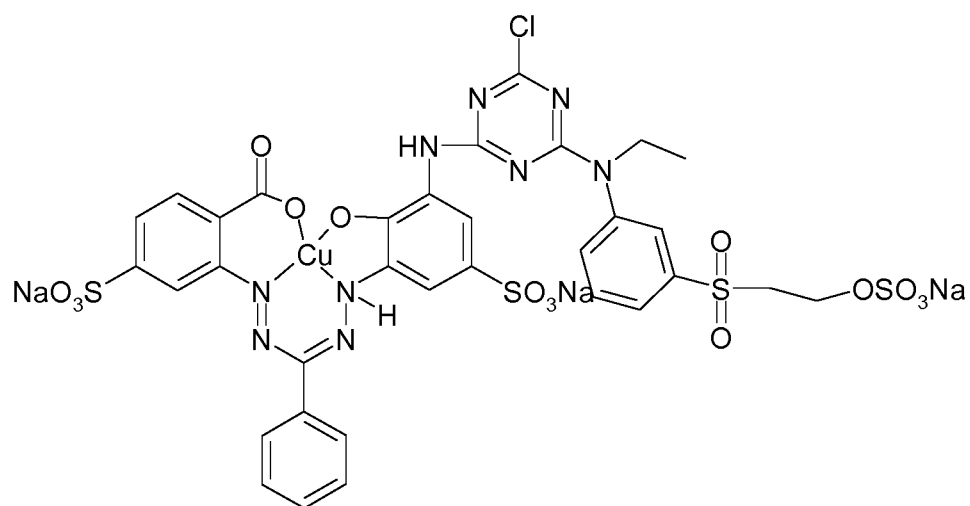
9. Mixtures according to any one of claims 1 to 8, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-6, II-7, II-12 and II-13.

10. Mixtures according to any one of claims 1 to 9, wherein a dye of general structure (III) is present and said dye is selected from the group consisting of:

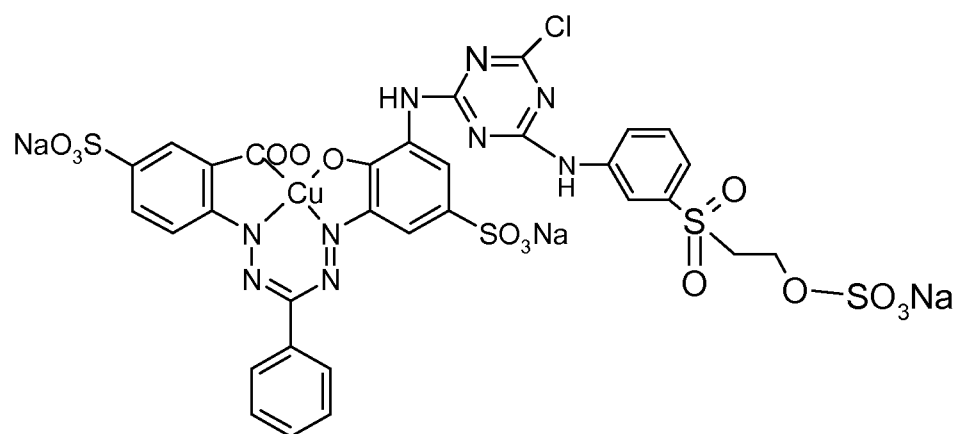


III-1,

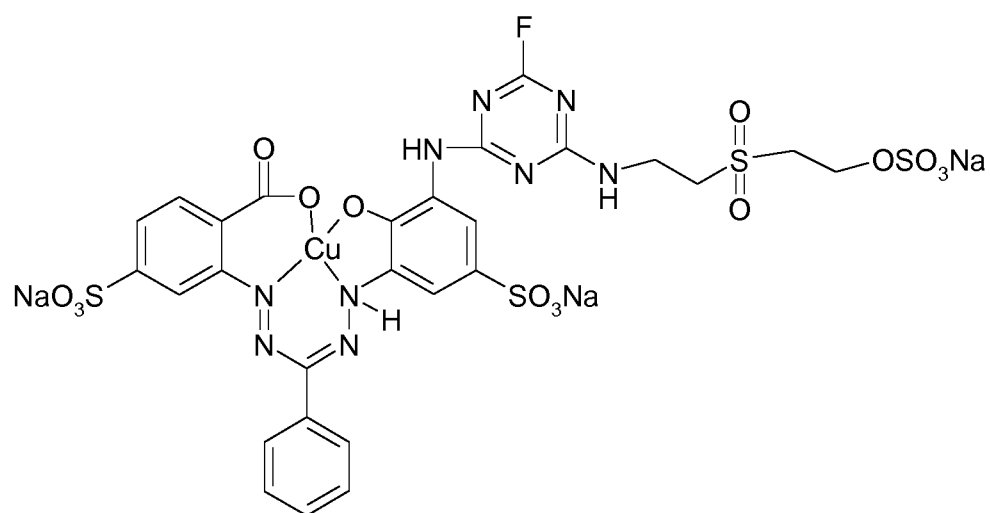
52



III-2,

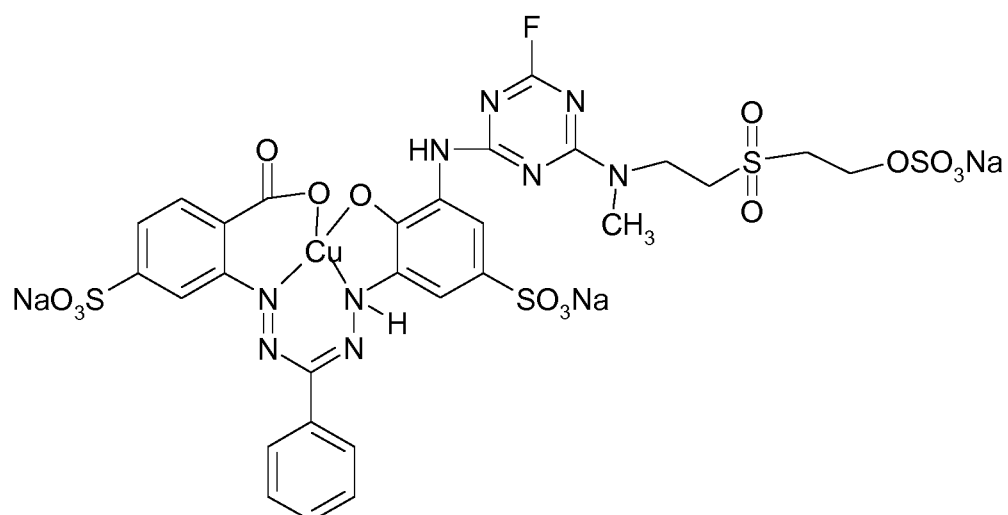


III-3,

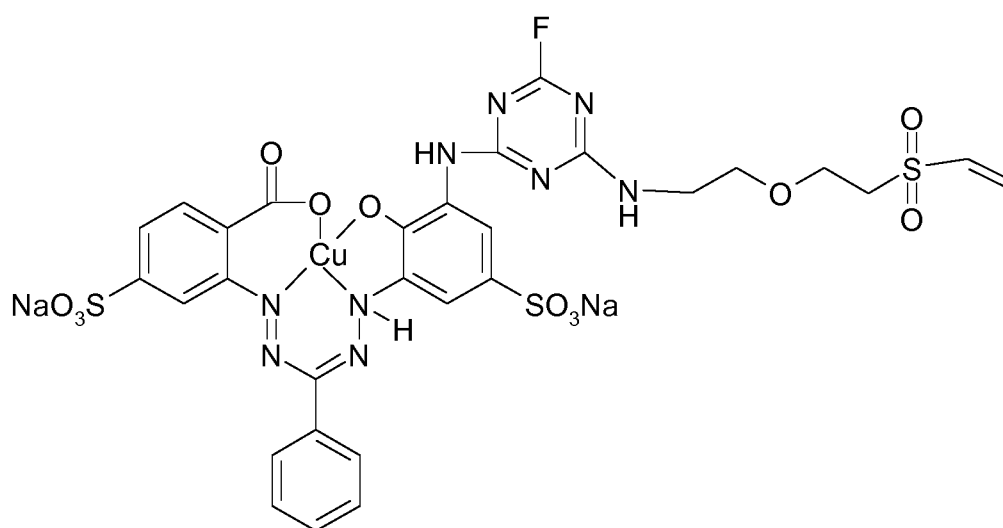


III-4,

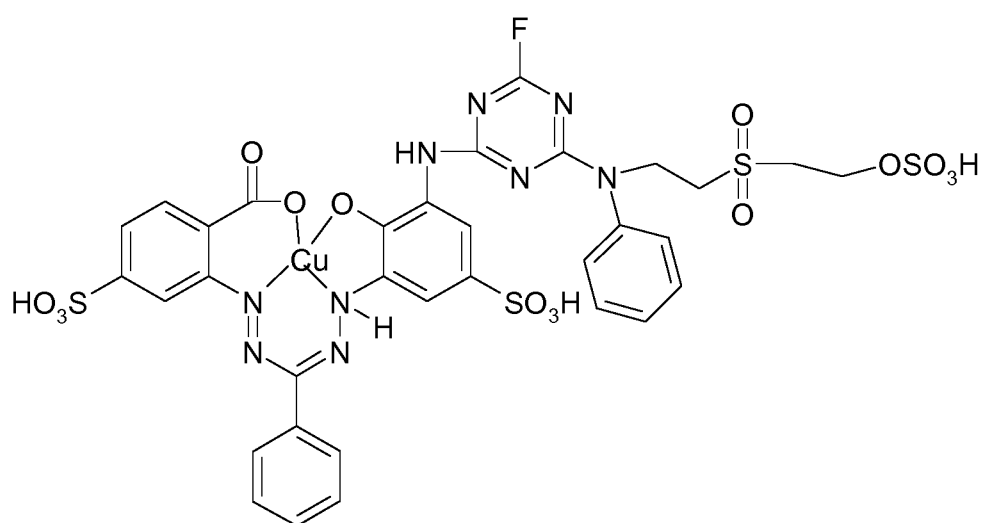
53



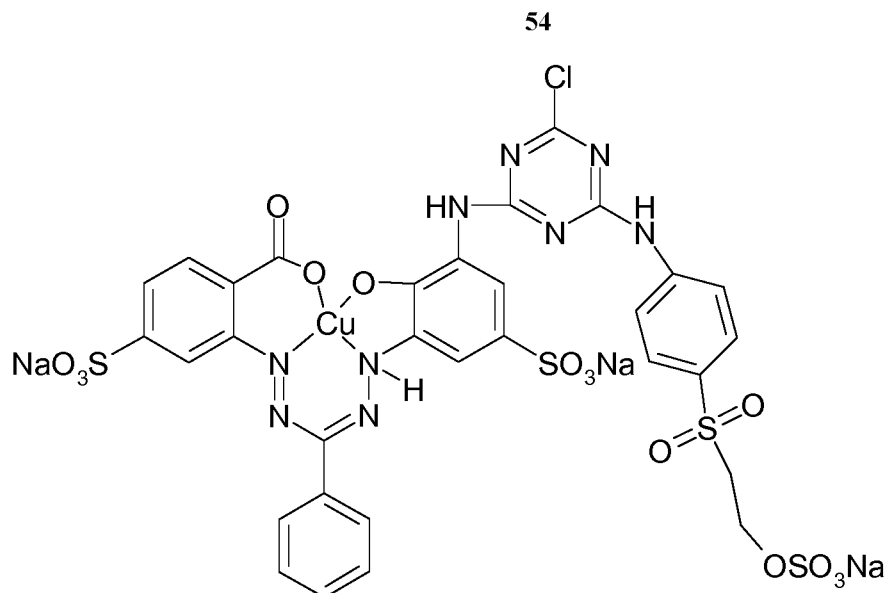
III-5,



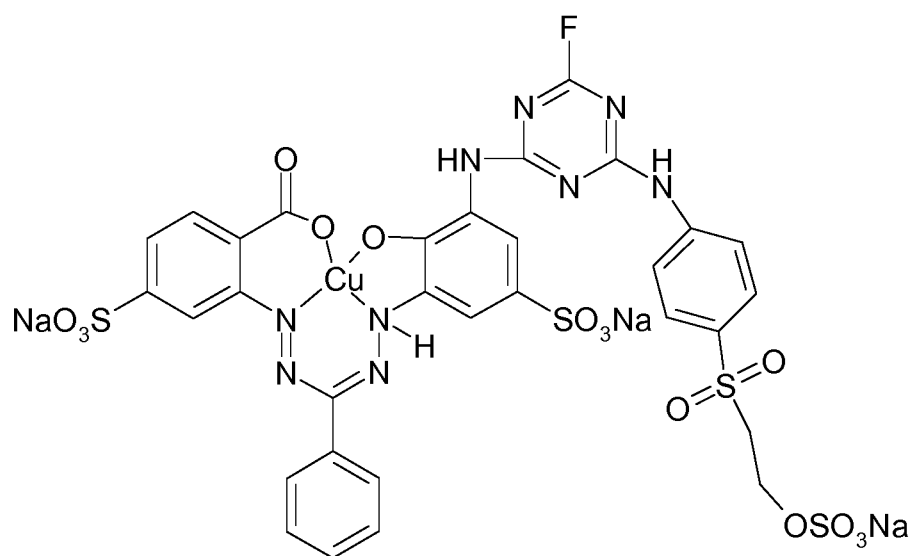
III-6,



III-7



III-8 and



III-9.

5

11. Mixtures according to any one of claims 1 to 10, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-4, III-6, III-7 and III-8.

10 12. Mixtures according to any one of claims 1 to 11, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-6, III-7 and III-8.

13. Mixtures according to any one of claims 1 to 12, wherein the dye of the formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

15

14. Mixtures according to any one of claims 1 to 13, wherein the dye of the formula (I) is selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13.
- 5
15. Mixtures according to any one of claims 1 to 14, a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8.
- 10
16. Mixtures according to any one of claims 1 to 15, a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.
- 15
17. Mixtures according to any one of claims 1 to 16, wherein a dye of structure (III) is present and wherein the dye of formula (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8.
- 20
18. Mixtures according to any one of claims 1 to 17, wherein a dye of structure (III) is present and wherein the dye of formula (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.
- 25
19. Mixtures according to any one of claims 1 to 18, wherein a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21, the dye of structure (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of structure (III) is selected from the group consisting of III-1, III-2, III-4, III-6, III-7 and III-8.
- 30
20. Mixtures according to any one of claims 1 to 18, wherein a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2 and I-4, the dye of structure (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of structure (III) is selected from the group consisting of III-1, III-2, III-6, III-7 and III-8.
- 35

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/071390

A. CLASSIFICATION OF SUBJECT MATTER INV. C09B67/22 D06P1/10 C09D11/328 D06P5/30 D06P1/384 D06P3/02 D06P3/10 D06P3/66 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 C09D 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, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/088031 A2 (CIBA SC HOLDING AG [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN GEORG [DE]) 14 October 2004 (2004-10-14) compounds (1), (2) claims 1-11 -----	1-20
A	WO 2007/003541 A2 (HUNTSMAN ADV MAT SWITZERLAND [CH]; TZIKAS ATHANASSIOS [CH]; ROENTGEN G) 11 January 2007 (2007-01-11) compounds (1), (2), (4), (5) claims 1-10 -----	1-20
A	EP 0 668 328 A2 (HOECHST AG [DE]) 23 August 1995 (1995-08-23) compounds (10), (20), (21), (24), (25) claims 2, 3 ----- -/-	1-20
☒ 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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 24 October 2016		Date of mailing of the international search report 18/11/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Constantinescu, R

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/071390

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 2010/086243 A2 (DYSTAR COLOURS DEUTSCHLAND GMB [DE]; EICHHORN JOACHIM [DE]; SCHRELL AN) 5 August 2010 (2010-08-05) claims 1-10 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/071390

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004088031	A2	14-10-2004	AT 541012 T 15-01-2012
		EP 1608708 A2 28-12-2005	
		ES 2380195 T3 09-05-2012	
		HK 1083875 A1 29-06-2012	
		KR 20050123136 A 29-12-2005	
		PT 1608708 E 27-03-2012	
		US 2006207038 A1 21-09-2006	
		US 2010024138 A1 04-02-2010	
		WO 2004088031 A2 14-10-2004	
WO 2007003541	A2	11-01-2007	AT 428753 T 15-05-2009
		BR PI0612758 A2 30-11-2010	
		CN 101331194 A 24-12-2008	
		EP 1899419 A2 19-03-2008	
		ES 2321979 T3 15-06-2009	
		HN 2008000006 A 09-02-2009	
		KR 20080031392 A 08-04-2008	
		MY 139986 A 30-11-2009	
		PT 1899419 E 12-06-2009	
		TW I405820 B 21-08-2013	
		US 2009178213 A1 16-07-2009	
		WO 2007003541 A2 11-01-2007	
EP 0668328	A2	23-08-1995	BR 9500672 A 24-10-1995
		CA 2142742 A1 20-08-1995	
		CN 1114664 A 10-01-1996	
		CZ 9500440 A3 15-11-1995	
		DE 4405358 A1 24-08-1995	
		EP 0668328 A2 23-08-1995	
		EP 0964034 A1 15-12-1999	
		EP 0969050 A1 05-01-2000	
		EP 0971002 A1 12-01-2000	
		EP 0976794 A1 02-02-2000	
		EP 0978543 A1 09-02-2000	
		EP 0978544 A1 09-02-2000	
		EP 0982375 A1 01-03-2000	
		JP H07304986 A 21-11-1995	
		PL 307324 A1 21-08-1995	
		TW 305865 B 21-05-1997	
WO 2010086243	A2	05-08-2010	BR PI1007270 A2 16-02-2016
		CA 2750792 A1 05-08-2010	
		CN 102292400 A 21-12-2011	
		DE 102009000423 A1 29-07-2010	
		EP 2391683 A2 07-12-2011	
		HN 2011002062 A 25-08-2014	
		JP 5781945 B2 24-09-2015	
		JP 2012515823 A 12-07-2012	
		KR 20110108375 A 05-10-2011	
		MA 32993 B1 02-01-2012	
		TW 201035249 A 01-10-2010	
		US 2011283465 A1 24-11-2011	
		WO 2010086243 A2 05-08-2010	

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING SUBMISSION,
OBTENTION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

DYSTAR COLOURS DISTRIBUTION GMBH
Global Intellectual Property
Am Prime Parc 10-12
65479 Raunheim
ALLEMAGNE

Date of mailing (day/month/year) 12 October 2016 (12.10.2016)	
Applicant's or agent's file reference 2015/001	IMPORTANT NOTIFICATION
International application No. PCT/EP2016/071390	International filing date (day/month/year) 12 September 2016 (12.09.2016)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 22 September 2015 (22.09.2015)
Applicant DYSTAR COLOURS DISTRIBUTION GMBH	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
22 September 2015 (22.09.2015)	15186219.0	EP	05 October 2016 (05.10.2016)

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.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-bis) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-bis)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-bis), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) 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.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 89 75	Authorized officer Nora Lindner e-mail pt05.pct@wipo.int Telephone No. +41 22 338 74 05
---	---

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:	PCT/EP2016/071390
International filing date:	12 September 2016 (12.09.2016)
Document type:	Certified copy of priority document
Document details:	Country/Office: EP
	Number: 15186219.0
	Filing date: 22 September 2015 (22.09.2015)
Date of receipt at the International Bureau:	05 October 2016 (05.10.2016)

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

Bescheinigung

Die angehefteten
Unterlagen stimmen mit der
als ursprünglich eingereicht
geltenden Fassung der auf
dem nächsten Blatt
bezeichneten europäischen
Patentanmeldung überein.

Certificate

The attached documents are
exact copies of the text in
which the European patent
application described on the
following page is deemed to
have been filed.

Attestation

Les documents joints à la
présente attestation sont
conformes au texte,
considéré comme
initialement déposé, de la
demande de brevet
européen qui est spécifiée à
la page suivante.

Patentanmeldung Nr.

Patent application No.

Demande de brevet n°

15186219.0 / EP15186219

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP15186219.

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.: 15186219.0
Demande no :

Anmeldetag:
Date of filing: 22.09.15
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.)

MIXTURES OF FIBRE-REACTIVE DYES

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 désignées 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

Mixtures of fibre-reactive dyes.

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

Fiber-reactive copper-complex azo dyes are of interest due to their potential to produce blue to violet dyeings of high fastness to light. However, they often possess certain performance limitations, such as deficient build-up of colour to deeper shades, unlevel dyeing, a colour yield, which is too heavily dependent on variations in dyeing parameters, and low resistance to oxidative agents.

These performance defects can partly be overcome in some cases by the use of mixtures of fiber reactive copper complex azo dyes with selected other fiber reactive azo dyes. Such mixtures make it possible, for example, to achieve neutral to greenish Navy shades with high light and perspiration-light fastness, very good resistance to washing in the presence of modern oxidative detergents, and good colour constancy in different light sources. The use of such mixtures can give dyeings with superior fastness properties to existing mono-molecular fiber-reactive Navy dyes.

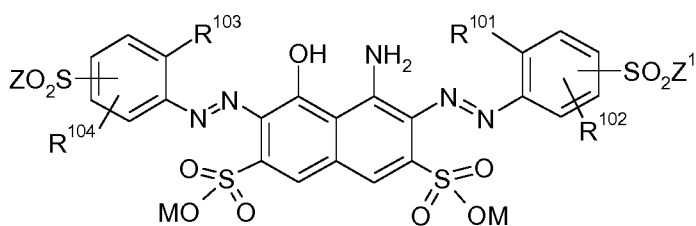
Additionally many existing commercial Navy and Black products include dyes, which, due to their chemistry, are causing problems of contamination with regulatory-controlled amines. C.I. Reactive Black 5 in particular is used quite often for commercial reasons - although it is known to involve a risk of p-chloroaniline contamination in the parabase ester intermediate used in its production. Alternative procedures for the production of parabase ester with low p-chloroaniline content are known (as described for example in German Patent DE 19 540 544) but have not been adopted as they are also not completely free of p-chloroaniline and involve higher cost.

Because the compliance with ecological and toxicological standards is of increasing importance to retailers and consumers, there is a growing need for dyes, which due to their chemistry avoid common sources of contamination with regulatory-controlled amines – and the present invention bases on such dyes.

Due to developing consumer requirements there is still a need for new dyestuffs with good build-up and levelness, high light- and oxidative fastness and good colour constancy, which additionally comply with toxicological and ecological standards. Surprisingly it now was found, that there exist combinations of dyes, which can be produced without the risk of contamination with restricted substances, which combinations have the required properties. Thus, the present

The present invention is directed to mixtures of fibre-reactive dyes comprising:

a dye of formula (II)



10

wherein independently of each other

15 R² is hydrogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R^3 is (C₁-C₄)-alkyl; (C₁-C₄)-alkyl substituted by sulfo, carboxyl, halogen, hydroxyl, amino or acetamido; phenyl; or phenyl substituted by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, sulfo, halogen, carboxyl, acetamido or ureido;

R^5 is (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

5 R^6 is hydrogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

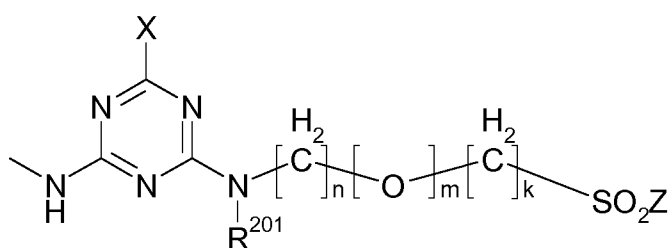
R^{101} and R^{103} are C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo or carboxyl,

R^{102} and R^{104} are hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo, carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

10 G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of the formula (100)



(100)

wherein

15 X is halogen,

R^{201} is hydrogen (C₁-C₄)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

20 and

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

(C₁-C₄)-alkyl groups may be straight-chain or branched and may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl. Preferred are (C₁-C₃)-alkyl groups. More preferred are (C₁-C₂)-alkyl groups - methyl and ethyl and ethyl being the most preferred alkyl groups.

The same selection as for the alkyl groups applies to alkoxy, sulfoalkyl and alkylene groups.

30 M is preferably hydrogen, lithium, sodium or potassium, more preferably hydrogen or sodium.

Non-limiting examples of alkali-detachable groups as represented by G are halogen, preferably chlorine and bromine, ester groups of organic carboxylic and sulfonic acids, such as alkylcarboxylic acids, unsubstituted or substituted benzenecarboxylic acids, and unsubstituted or substituted benzenesulfonic acids, such as the groups (C₂-C₅)-alkanoyloxy, including more particularly acetyloxy, benzoyloxy, sulfobenzoyloxy, phenylsulfonyloxy, and tolylsulfonyloxy; acidic ester groups of inorganic acids, such as of phosphoric acid, sulfuric acid, and thiosulfuric acid (phosphato, sulfato, and thiosulfato groups), or di-(C₁-C₄)-alkylamino groups, such as dimethylamino and diethylamino.

- 10 Z, Z¹ are preferably vinyl, β-sulfatoethyl or β-chloroethyl and more preferably β-sulfatoethyl or vinyl.

- 15 The groups "sulfo", "carboxyl", "thiosulfato", "phosphato", and "sulfato" include not only their acid form but also their salt form. Accordingly, sulfo groups have the formula -SO₃M, thiosulfato groups have the formula -S-SO₃M, carboxyl groups have the formula -COOM, phosphato groups have the formula -OPO₃M₂, and sulfato groups have the formula -OSO₃M, in each of which M is defined as indicated above.

- 20 Preferred are dye mixtures with a weight ratio of (I) 20 to 80 %, (II) 80 to 20 % adding up to 100 %. More preferred are mixtures, which comprise a dye of formula (III). They preferably have a weight ratio of (I) 20 to 60 %, (II) 50 to 20 % and (III) 30 to 20 % adding up to 100 %. All percentages are based on the dye.

- 25 More preferred are mixtures of fibre-reactive dyes comprising:
dyes of the formula (I), (II) and optionally dyes of the formula (III) as described above,
wherein independent of each other

R² is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R³ is (C₁-C₂)-alkyl or (C₁-C₂)-alkyl substituted by sulfo,

R⁵ is (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

- 30 R⁶ is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

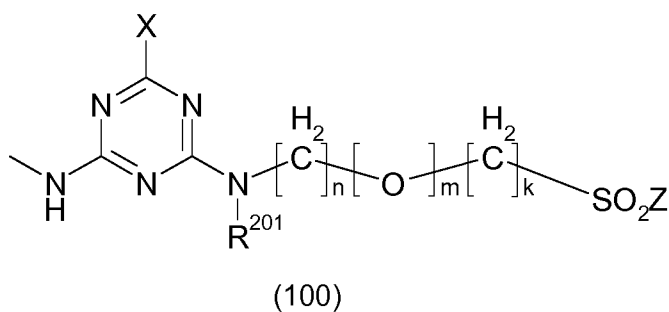
R¹⁰¹ and R¹⁰³ are C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

- 35 Y is -SO₂-Z or a group of formula (100)



wherein

X is Cl or F,

5 R^{201} is hydrogen, (C₁-C₂)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

10 M is hydrogen, Na, K or Li.

Even more preferred are mixtures of fibre-reactive dyes comprising:

dyes of formula (I), (II) and optionally dyes of formula (III) as described above,

wherein independent of each other

15 R^2 is hydrogen, methy, methoxy or sulfo,

R^3 is methyl or (C₁-C₂)-alkyl substituted by sulfo,

R^5 is methy, methoxy or sulfo,

R^6 is hydrogen, methy, methoxy or sulfo,

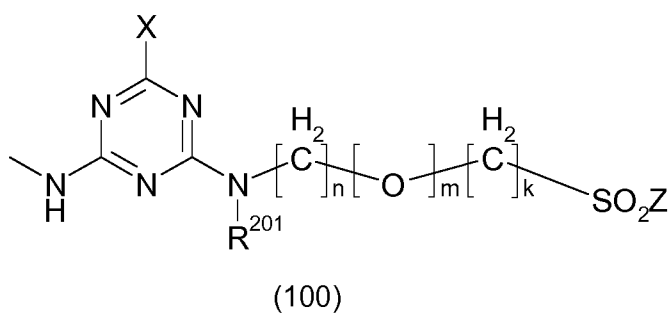
R^{101} and R^{103} are, methy, methoxy or sulfo,

20 R^{102} and R^{104} are hydrogen, methy, methoxy or sulfo,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



25

wherein

X is Cl or F,

R^{201} is hydrogen, methyl or phenyl,

n is 2 or 3,

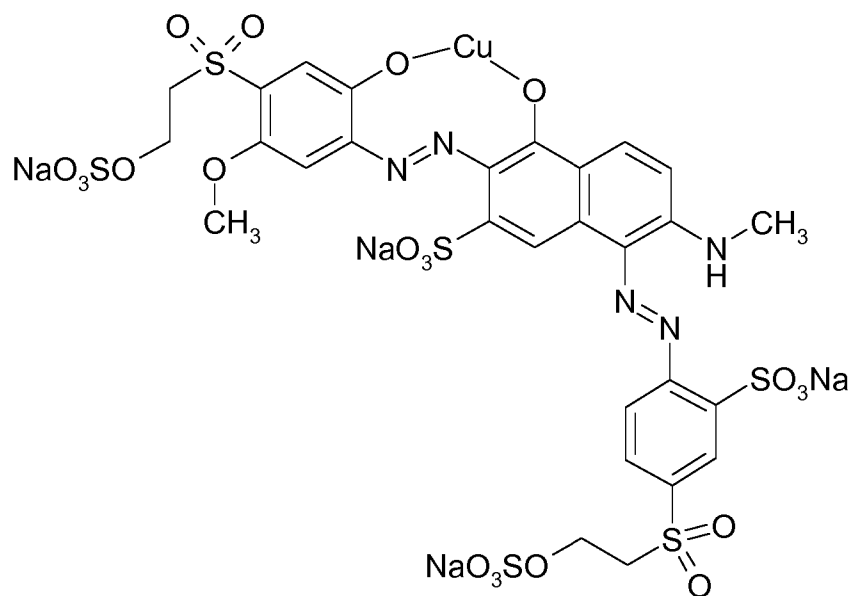
m is 0 or 1,

k is 0 to 3,

and

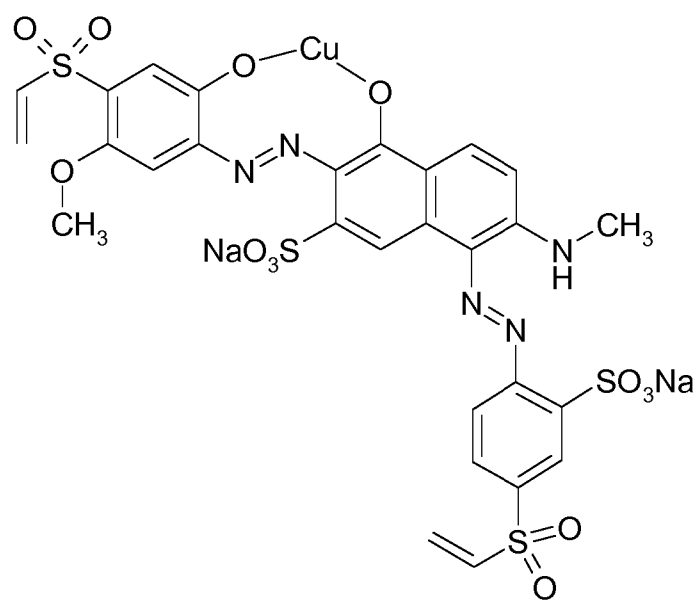
5 M is hydrogen, Na, K or Li.

Particularly preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of:

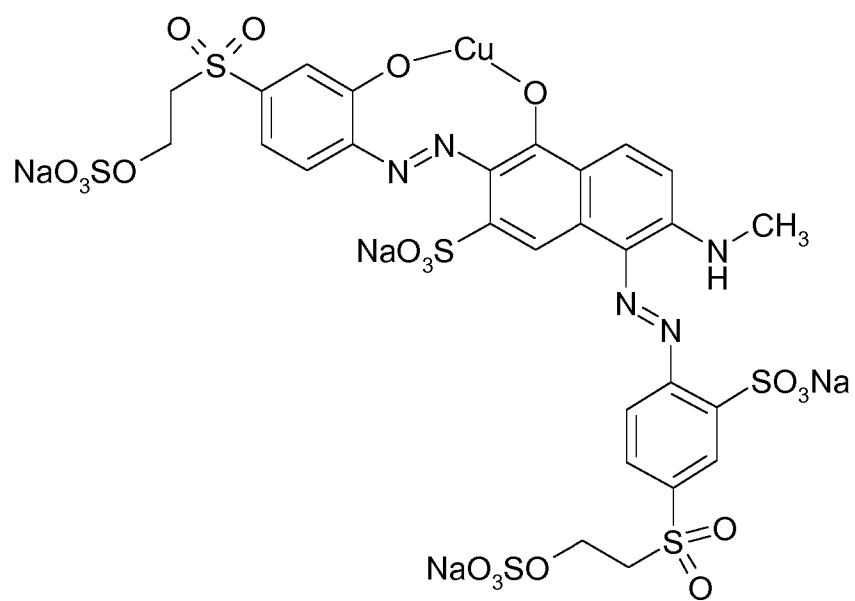


10

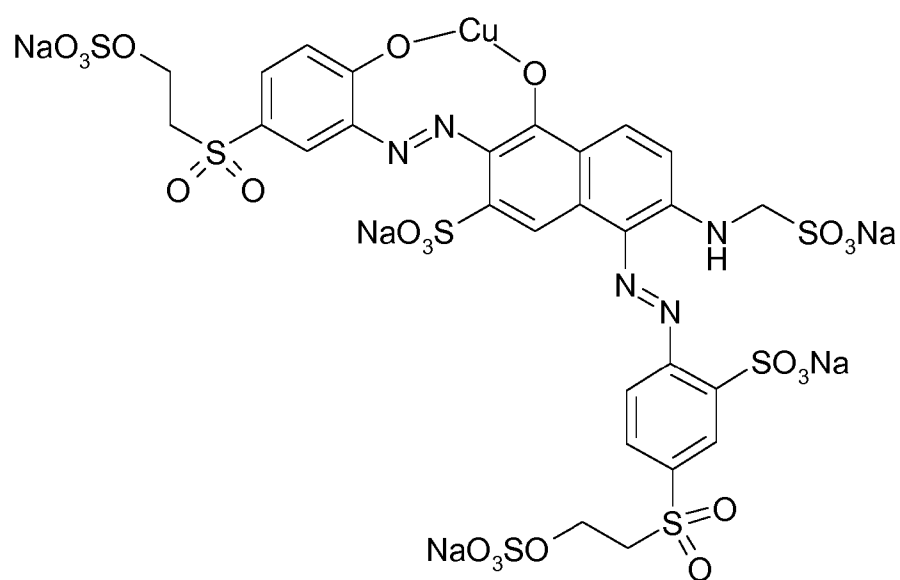
I-1,



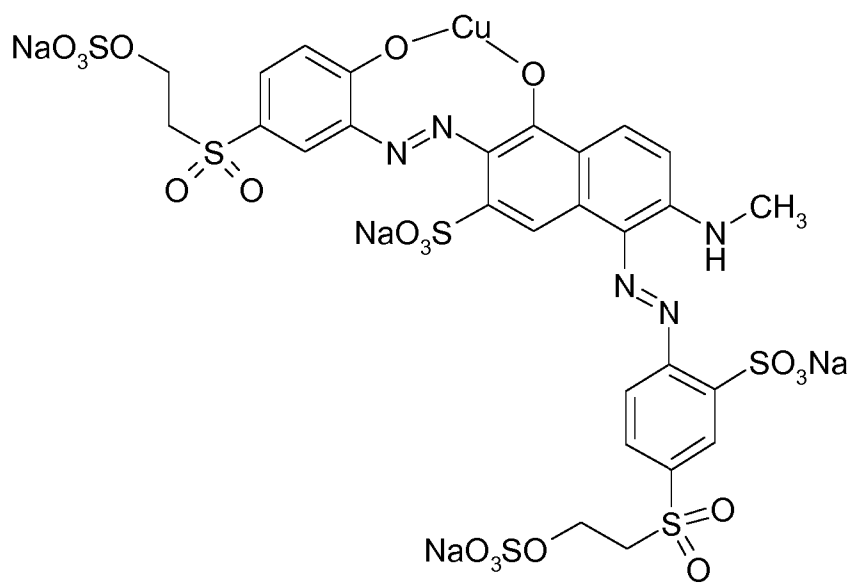
I-2,



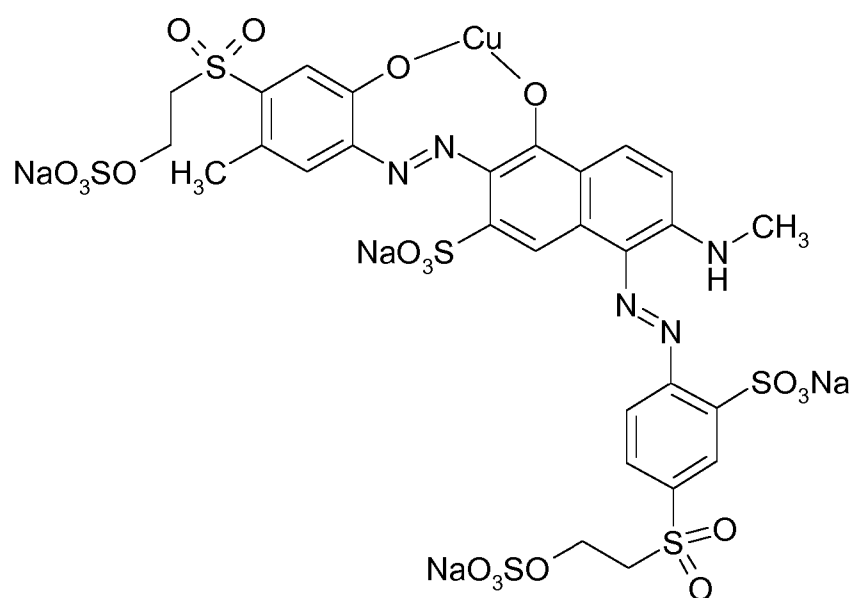
I-3,



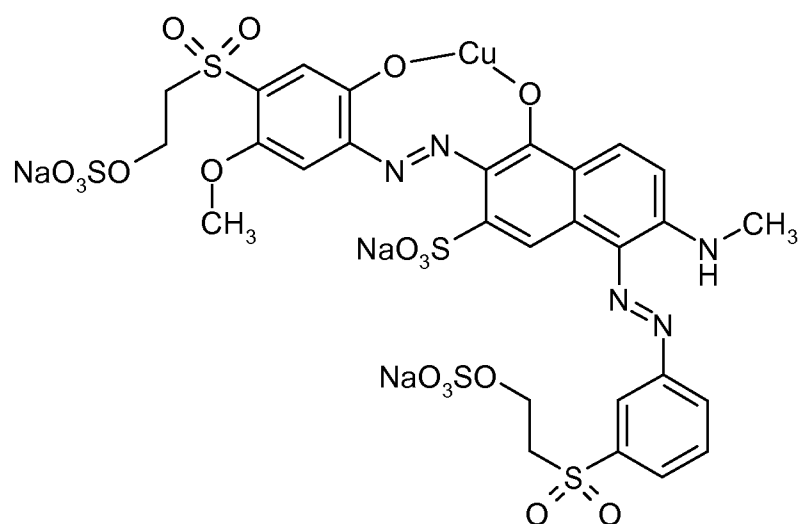
I-4,



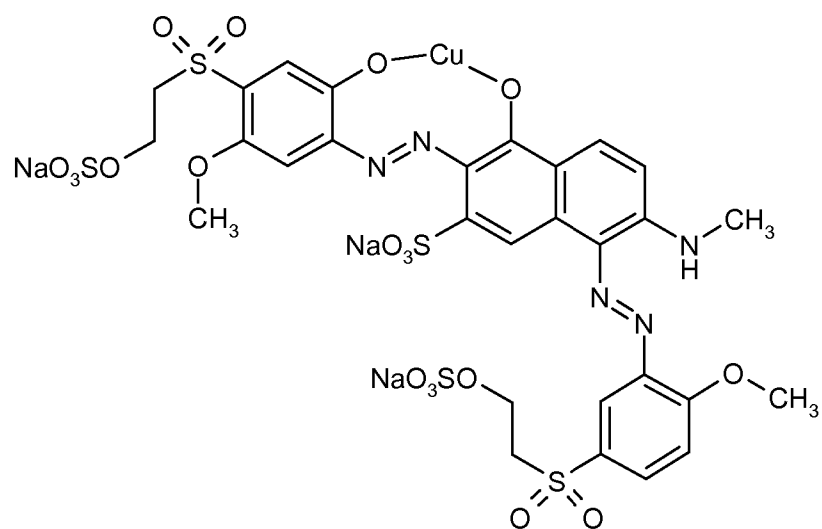
I-5,



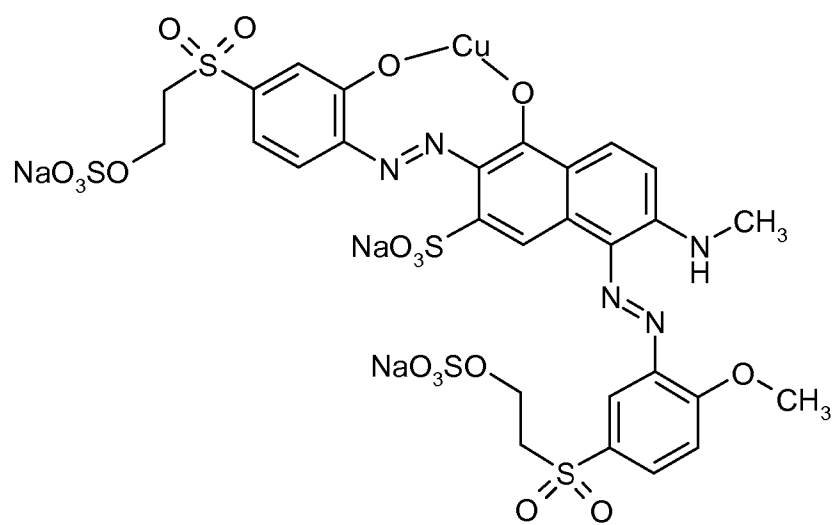
I-6,



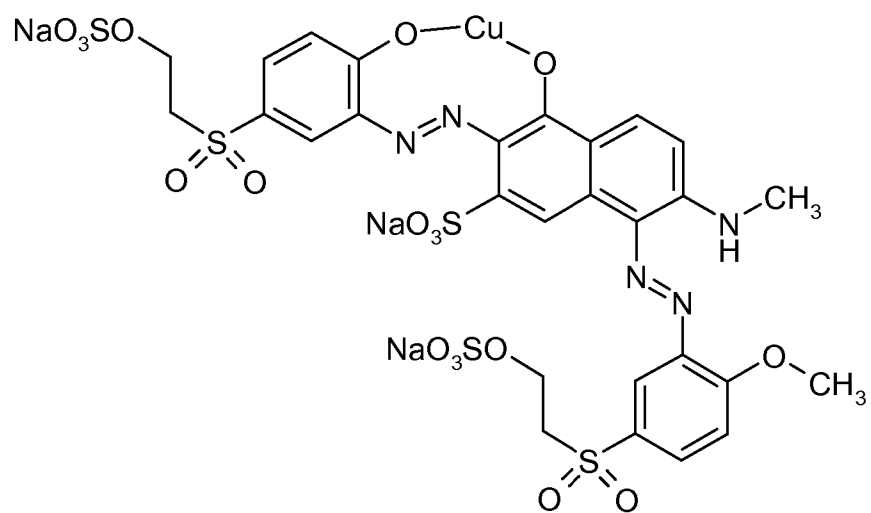
I-7,



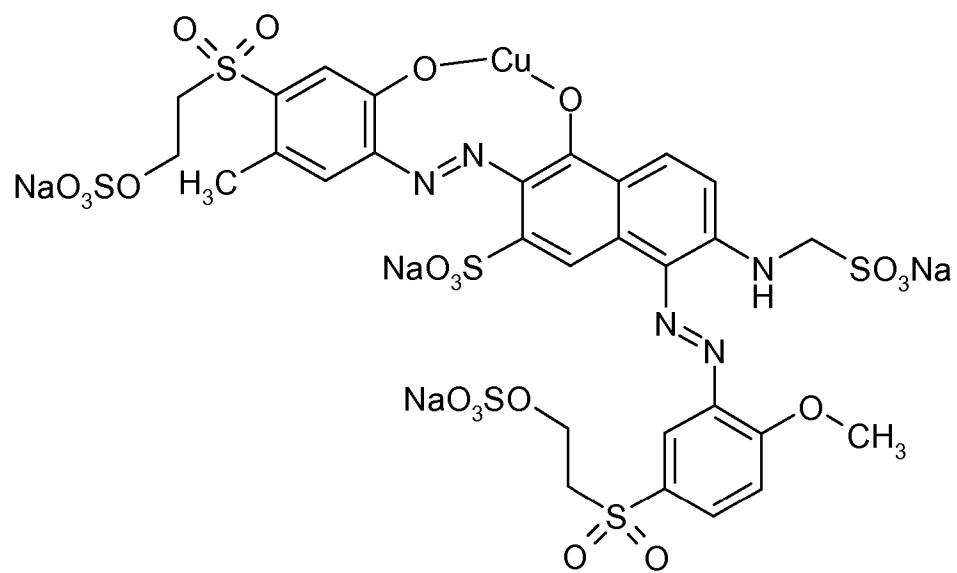
I-8,



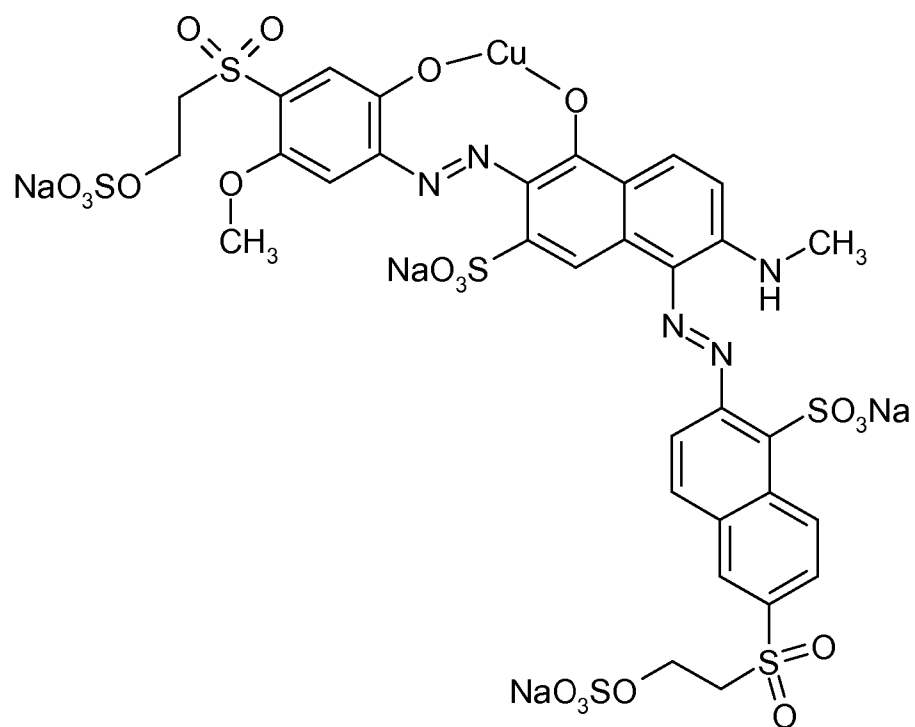
I-9,



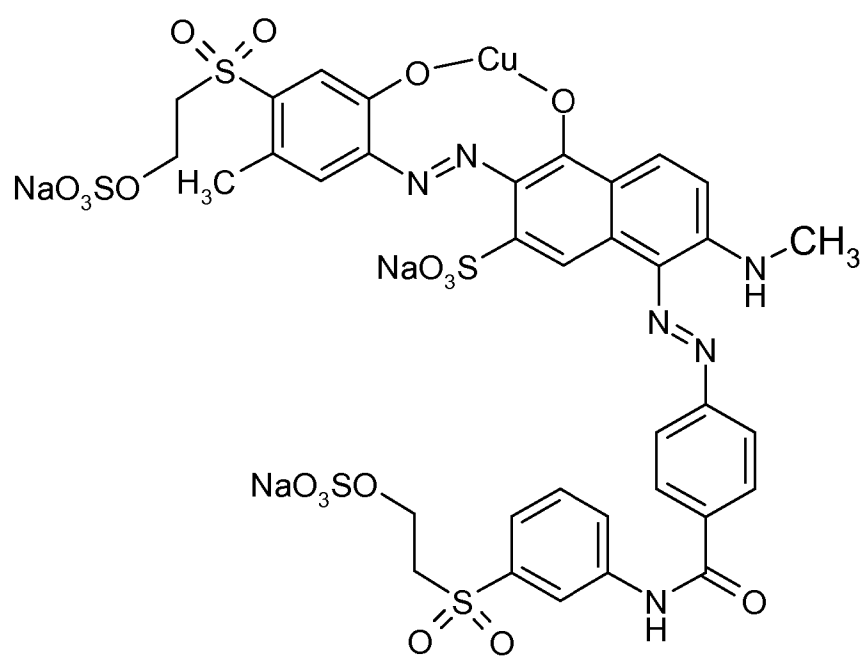
1-10,



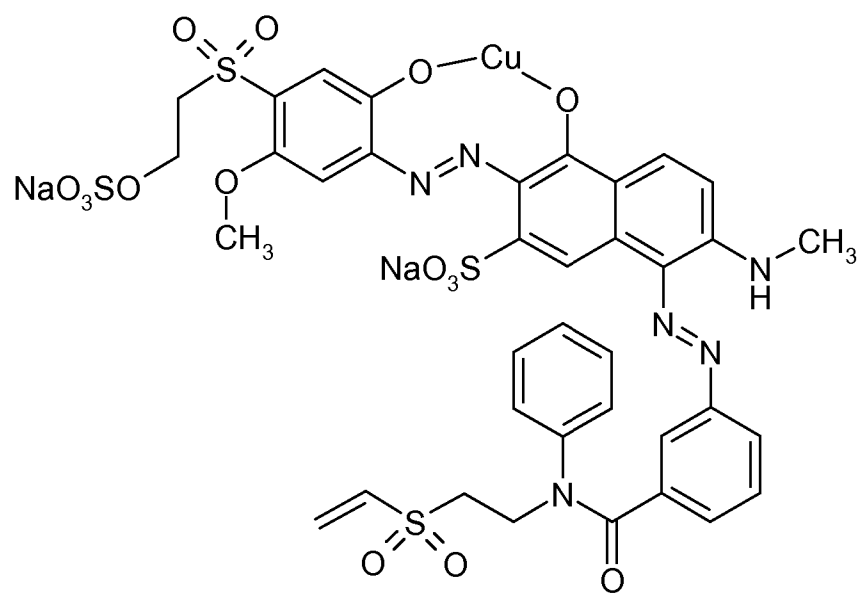
1-11,



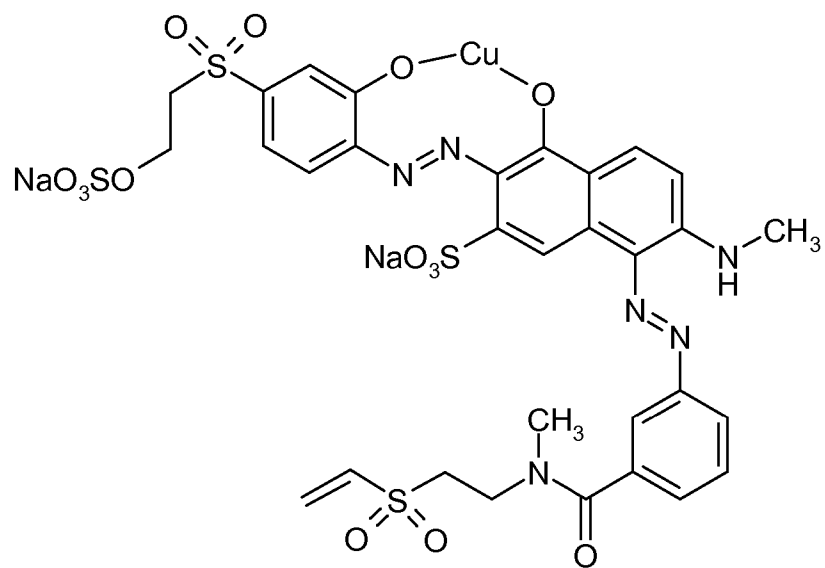
I-12,



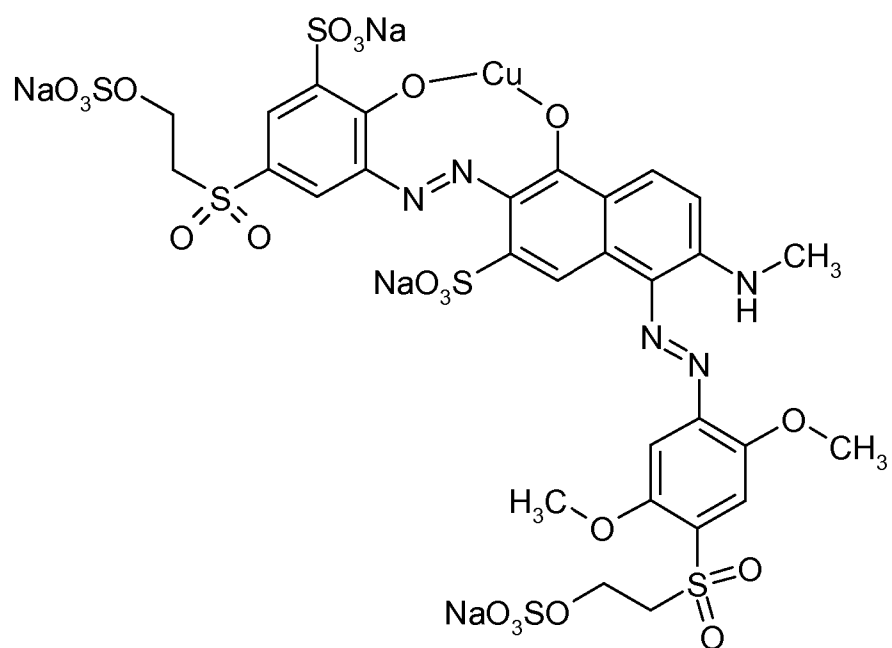
I-13,



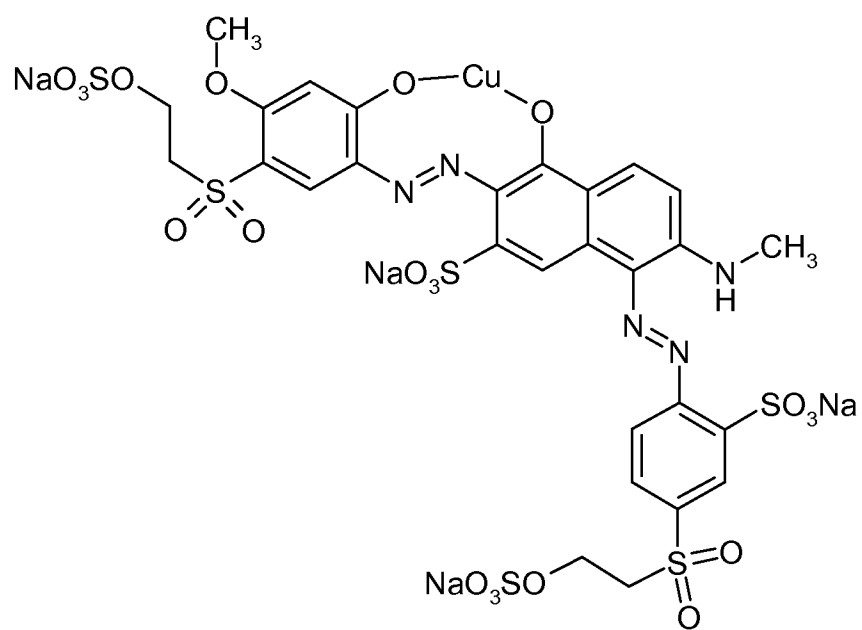
1-14,



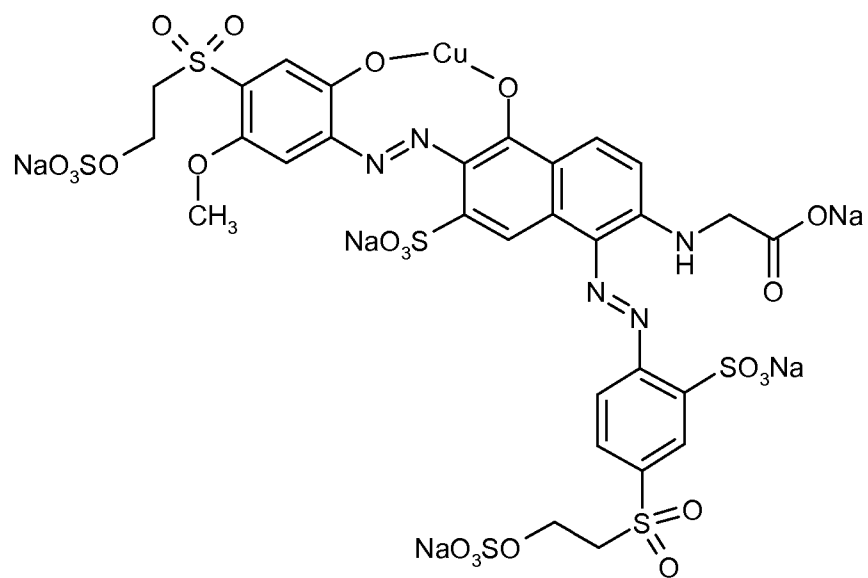
1-15,



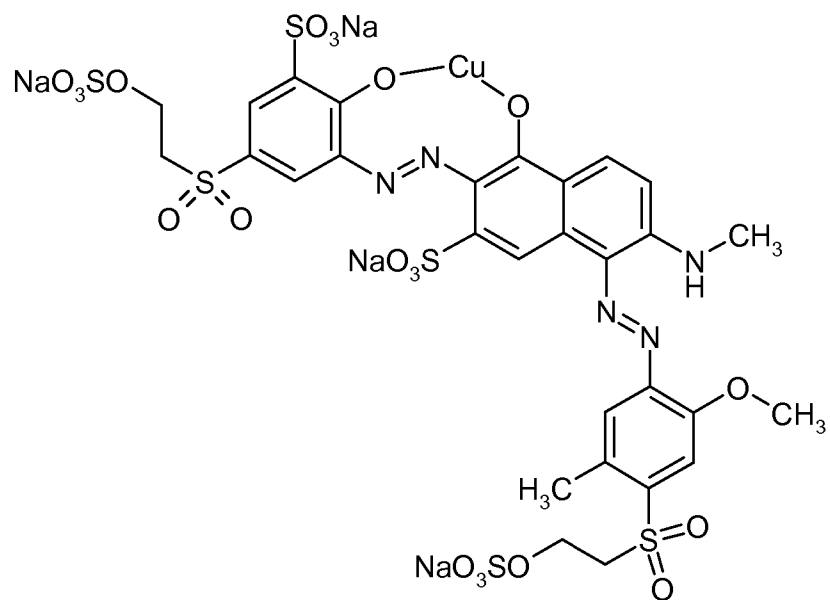
1-16,



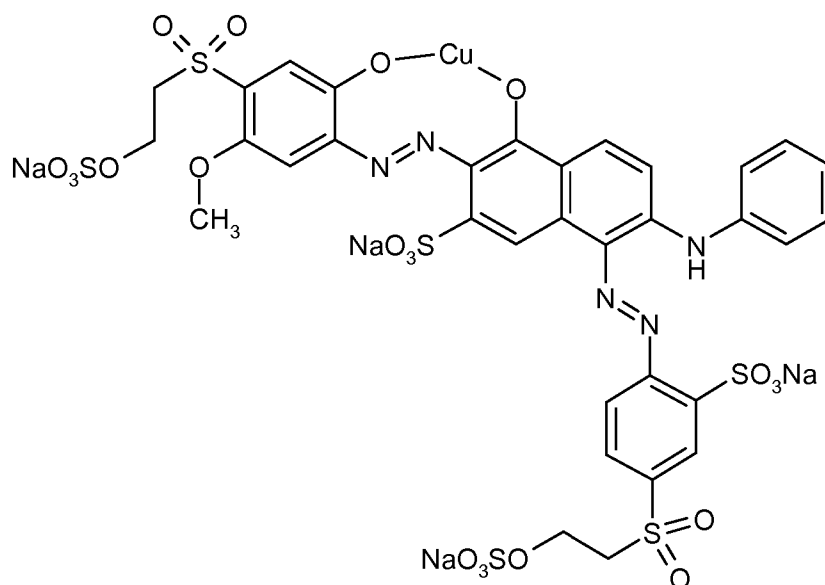
1-17,



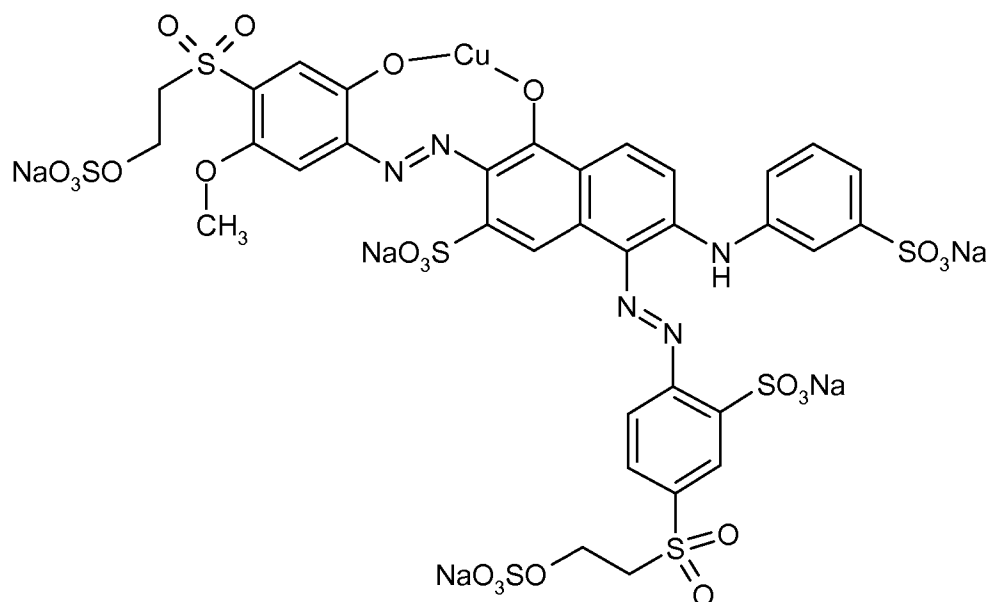
I-18,



1-19,



I-20 and



I-21.

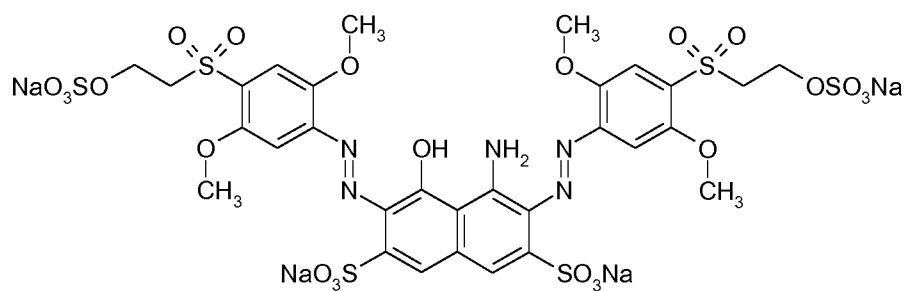
5

Even more preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21.

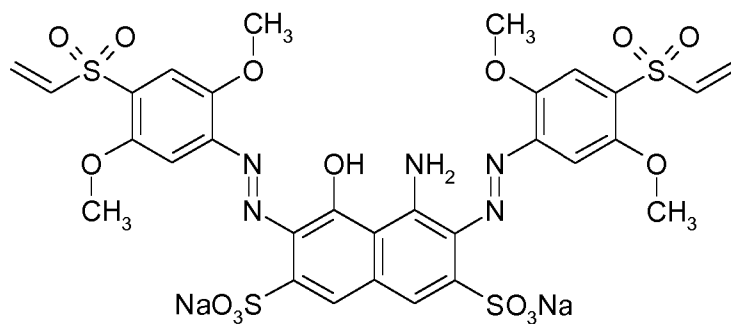
Most preferred are mixtures, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2 and I-4,

10

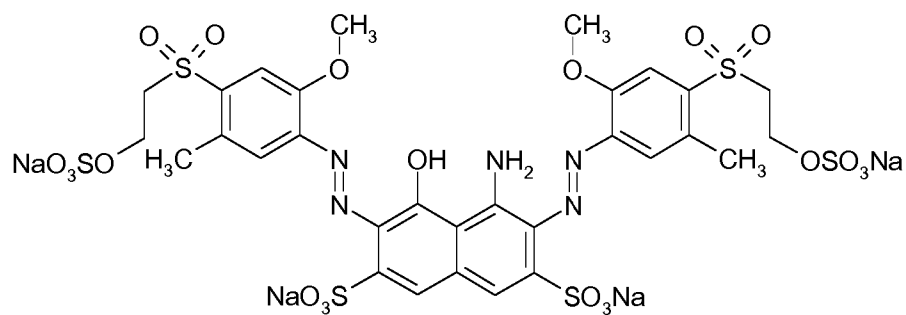
Particularly preferred are mixtures, wherein the dye of general structure (II) is selected from the group consisting of:



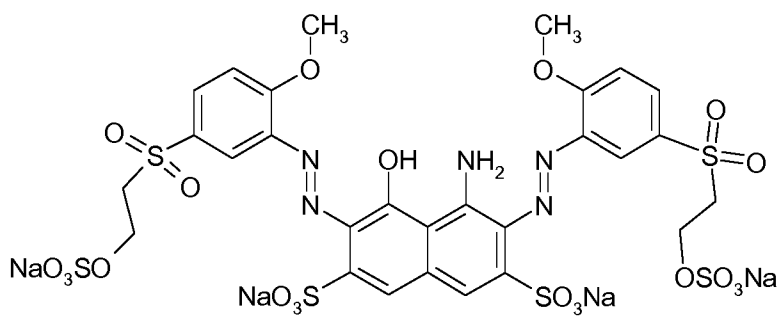
II-1,



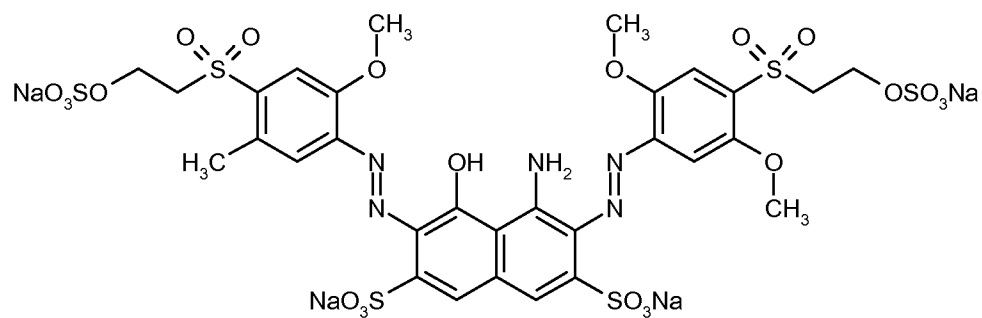
II-2,



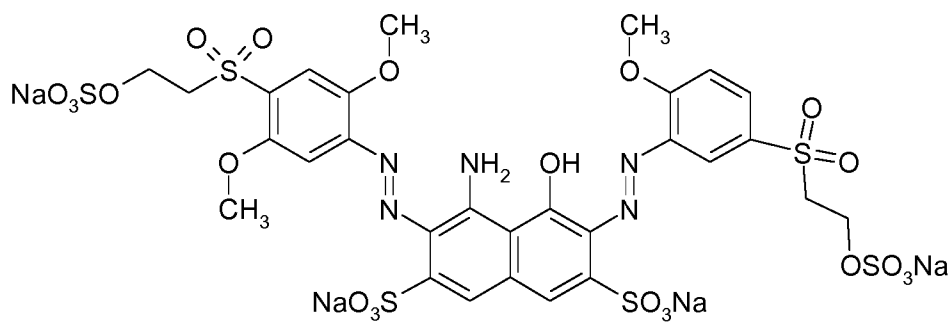
II-3,



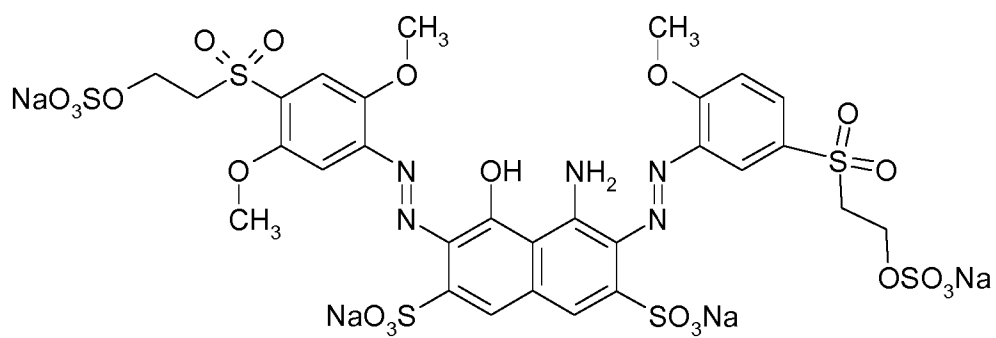
II-4,



II-5,

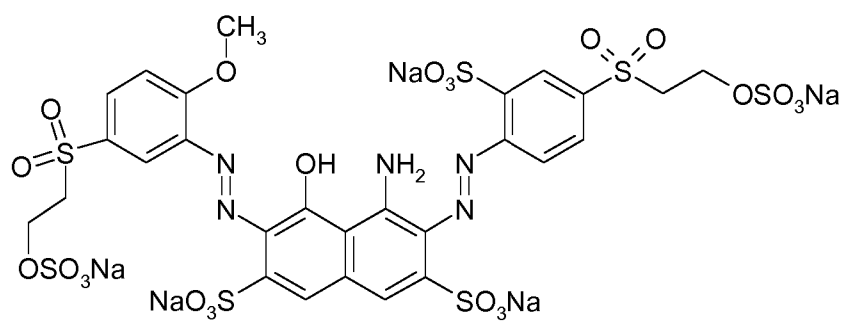


II-6,

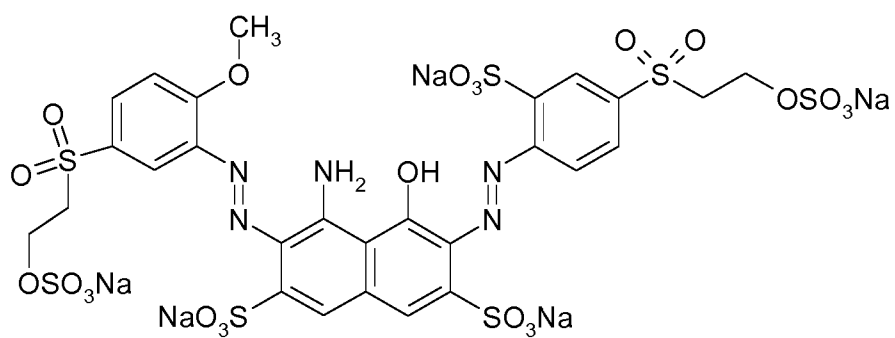


5

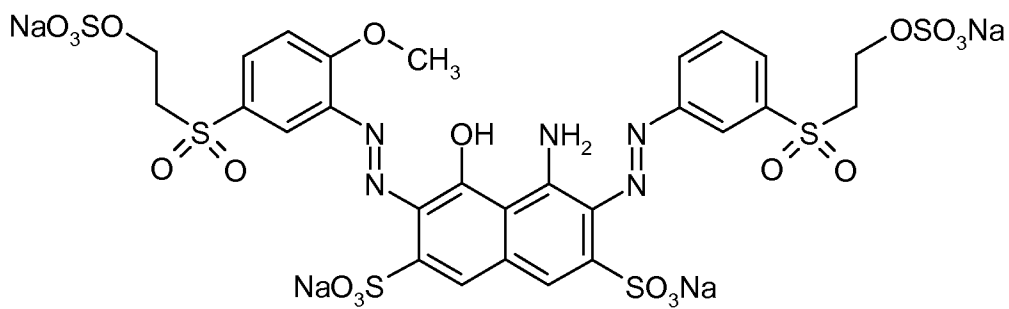
II-7,



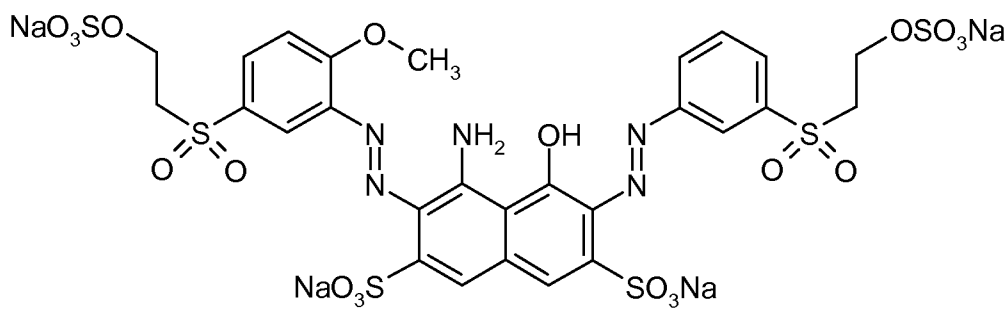
II-8,



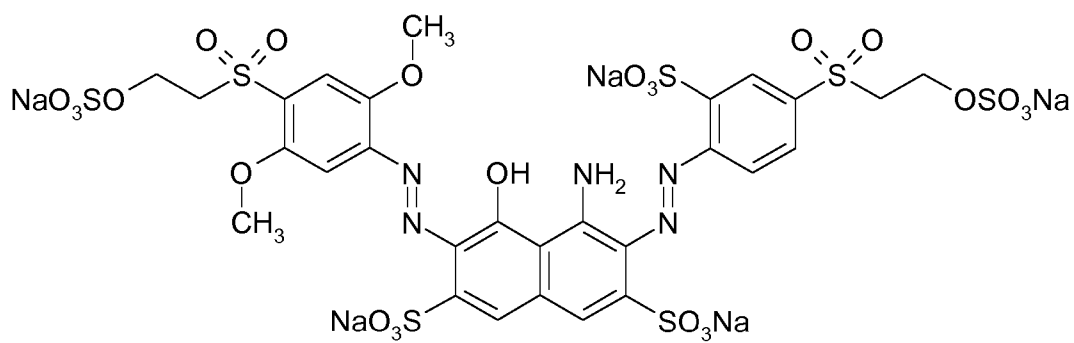
II-9,



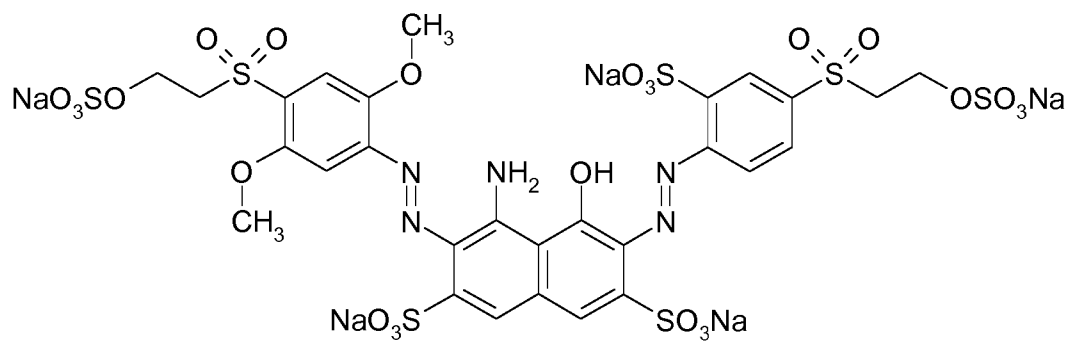
II-10,



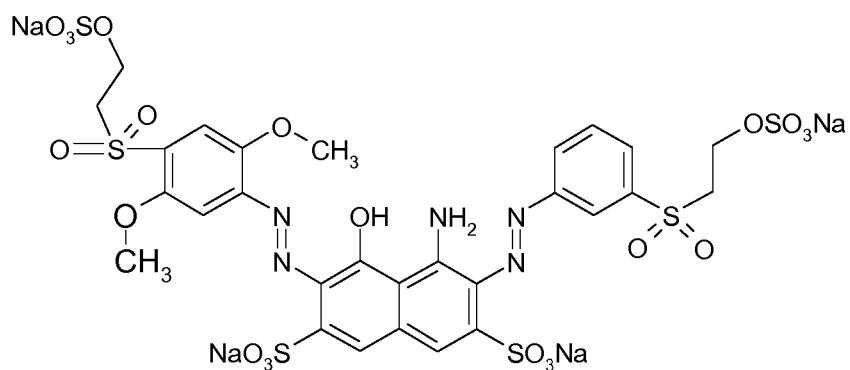
II-11,



II-12,



II-13 and

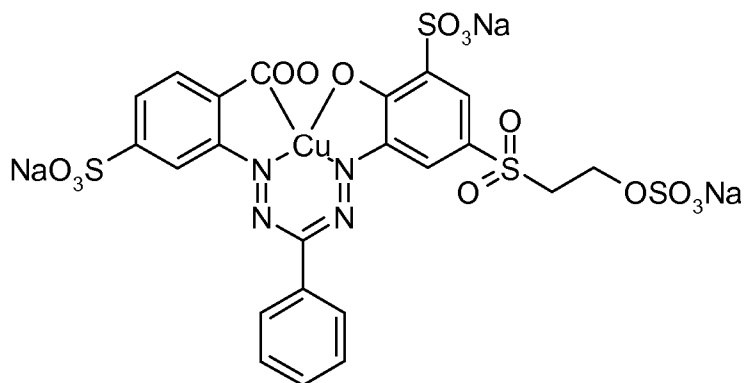


II-14.

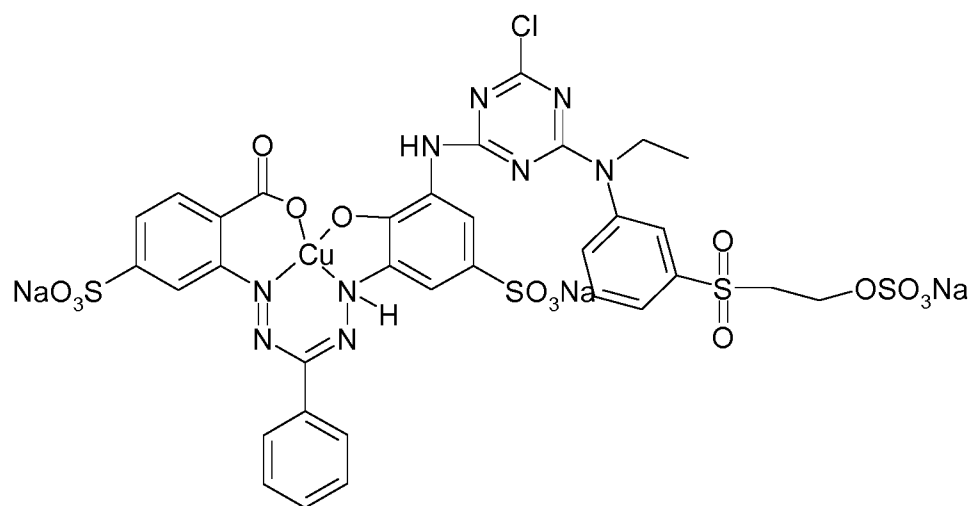
Even more preferred are mixtures, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

Most preferred are mixtures, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-6, II-7, II-12 and II-13.

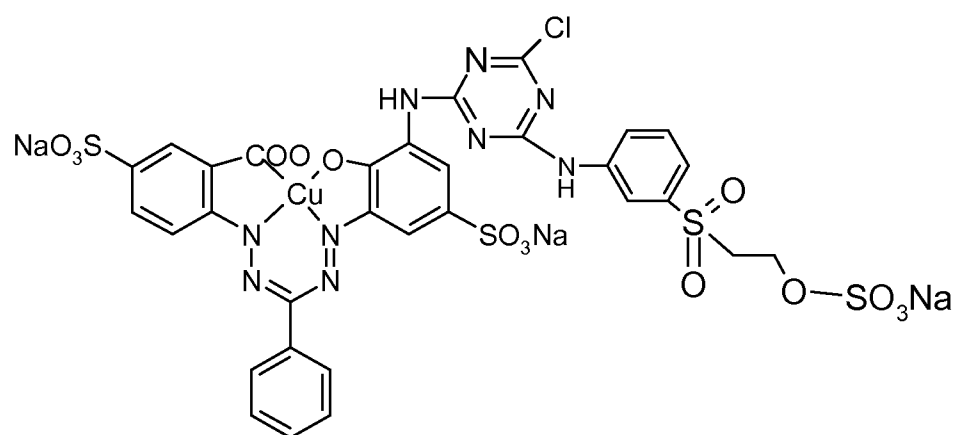
Another particularly preferred group of mixtures according to the present invention are those, wherein a dye of general structure (III) is present and said dye is selected from the group consisting of:



III-1,

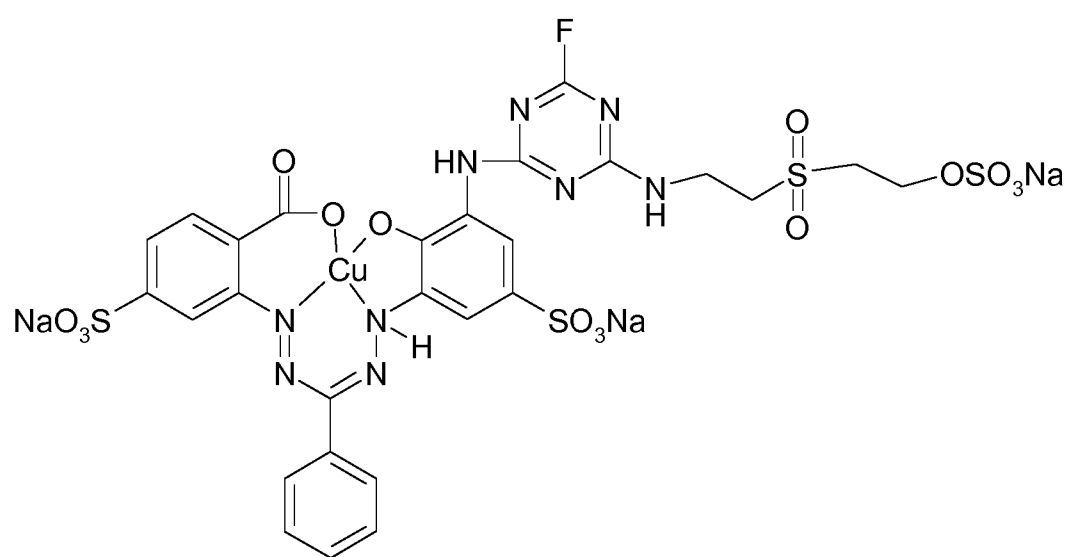


III-2,

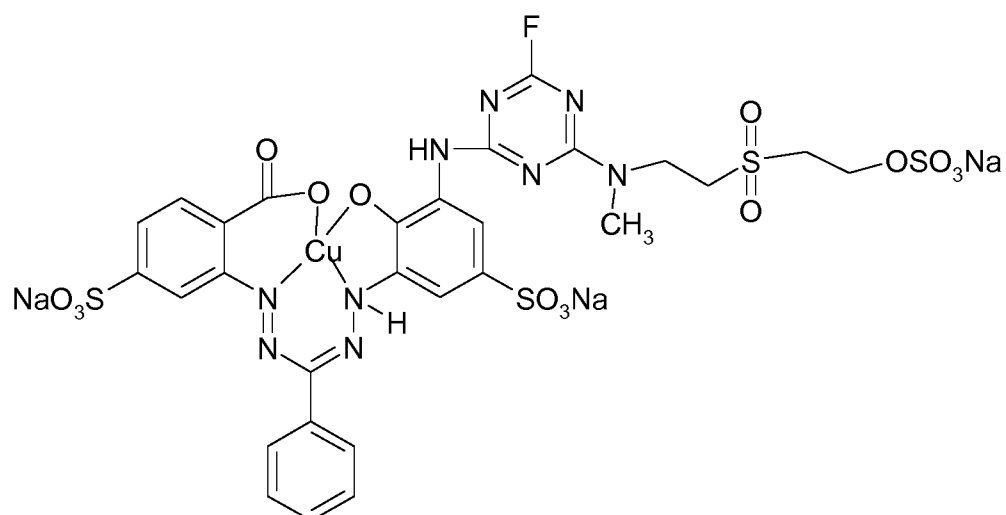


III-3,

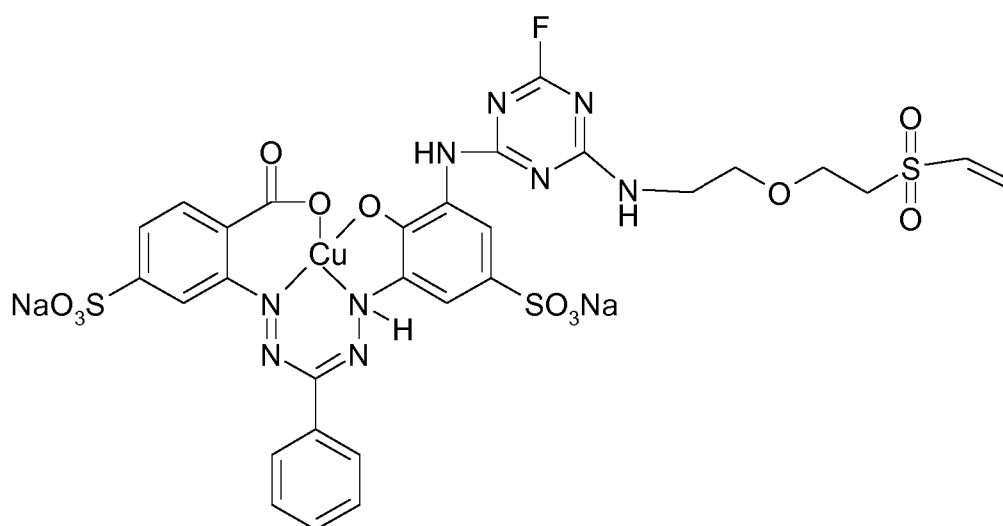
5



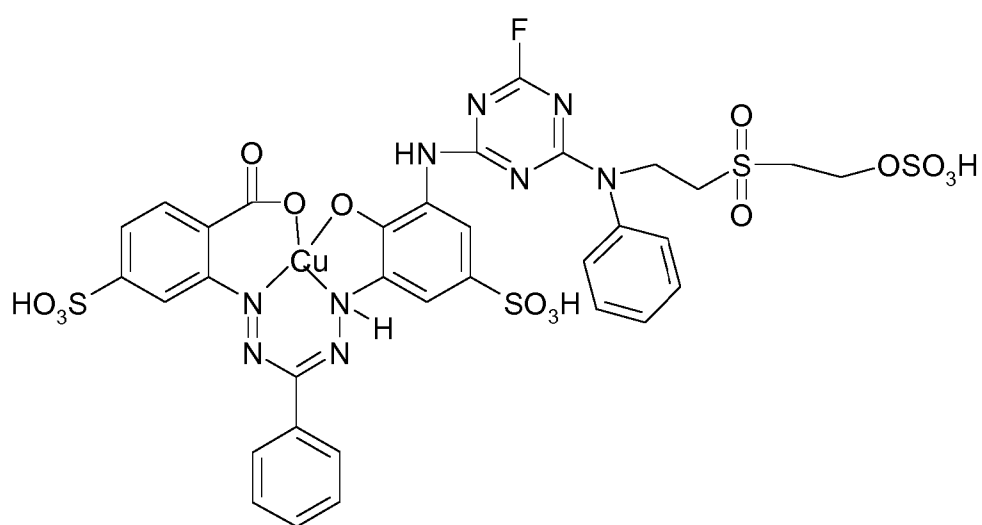
III-4,



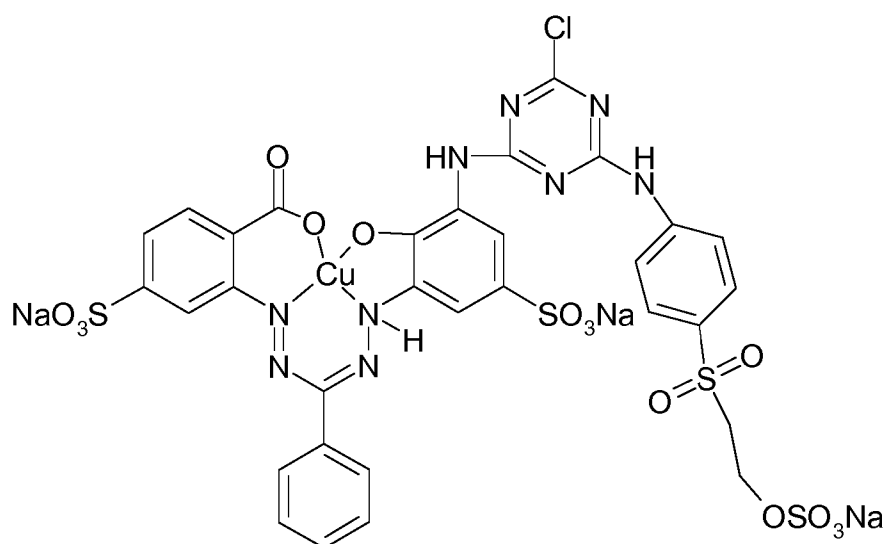
III-5,



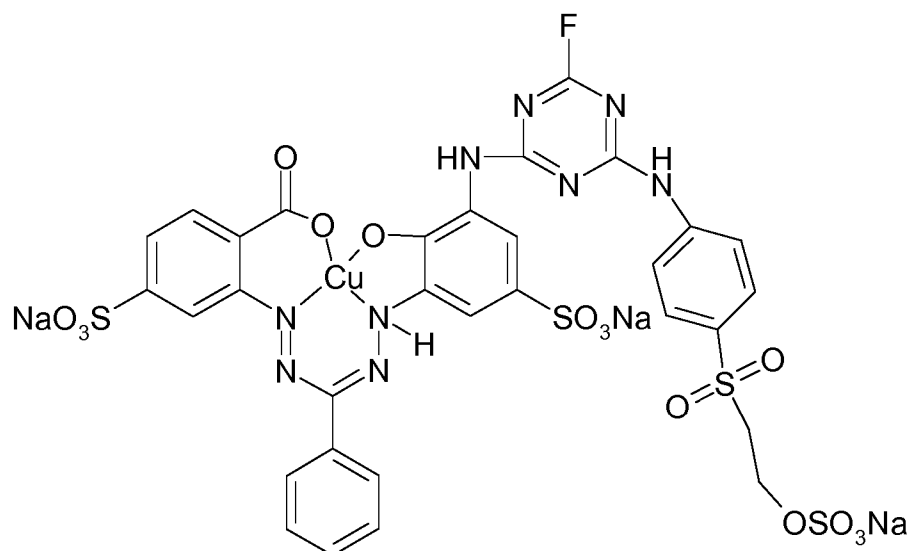
III-6,



III-7 and



III-8.



III-9.

5

Even more preferred are mixtures, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-4, III-6, III-7 and III-8.

- 10 Most preferred are mixtures, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-6, III-7 and III-8.

A preferred group of mixtures according to the present invention are those mixtures, wherein both dyes (I) and (II) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (II) being selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-

15

8, II-10, II-11, II-12 and II-13. Even more preferred is the group of mixtures wherein both dyes (I) and (II) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (II) being selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13.

5

From those mixtures wherein also a dye of structure (III) is present those are preferred, wherein both dyes (I) and (III) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8. More preferred are those, wherein both dyes (I) and (III) are specifically selected - with the dye of the formula (I) being selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

10

Another preferred subgroup wherein also a dye of structure (III) is present are those mixtures, wherein both dyes (II) and (III) are specifically selected - with the dye of the formula (II) being selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8. A more preferred subgroup wherein also a dye of structure (III) is present are those mixtures, wherein both dyes (II) and (III) are specifically selected - with the dye of the formula (II) being selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of formula (III) being selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

15

20

The most preferred subgroup of such mixtures are those wherein all three dyes of structures (I), (II) and (III) are selected from the lists consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 for the dye of structure (I), of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 for the dye of structure (II) and of III-1, III-2, III-4, III-6, III-7 and III-8 for the dye of formula (III). Within this group mixtures wherein all three dyes of structures (I), (II) and (III) are selected from the lists consisting of I-1, I-2 and I-4 for the dye of structure (I), of II-1, II-2, II-6, II-7, II-12 and II-13 for the dye of structure (II) and of III-1, III-2, III-6, III-7 and III-8 for the dye of formula (III) are the most preferred.

25

30

The dyes of formula (I), (II) and/or (III) 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 as buffer substances capable of setting a pH of between 3 and 7 in aqueous

35

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 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), (II) and/or (III) and also the dye mixture according to the invention are typically in the form of powders or granules which contain electrolyte salts (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), (II) and/or (III) 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.

The dyes of formula (I), (II) and (III) 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.

The mixtures of dyes of formula (I), (II) and (III) according to the present invention possess valuable performance properties and can be used for dyeing and printing carboxamido- and/or hydroxyl-containing materials. 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 take the form of fibers of the stated materials.

The mixtures of the dyes of formula (I), (II) and optionally (III) according to the 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 fibers.

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

The use of the mixtures of formula (I), (II) and optionally (III) 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.

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.

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.

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.

5

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
10 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
15 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).

20 Besides mixtures of the general formula (I), (II), optionally (III) 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
25 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, the a dye mixture of the formula (I), (II) and optionally (III) 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.

30

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.

35 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.

5

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.

10

The padding process on cellulose fibers likewise produces excellent colour yields and a very good colour buildup, 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.

15

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.

25

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.

30

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 potassium compounds. Examples of such acid-binding agents include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium

35

formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate, or mixtures thereof.

5 The mixtures of the general formula (I), (II) and optionally (III) 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 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.

15 The present invention also provides inks for digital textile printing by the inkjet process, which comprise a dye mixture of the formula (I), (II) and optionally (III) according to the invention.

The inks of the invention comprise a dye mixture of the formula (I), (II) and optionally (III) 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.

25 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.

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

30 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-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.: 35 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.

5

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.

10 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,
15 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.

20 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
25 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
30 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,
35 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.

5 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.

10 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.

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

20 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 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.

25 The a dye mixture of the formula (I), (II) and optionally (III) according to the invention furnish blue / navy blue dyeings and prints, and inkjet prints, on the materials specified.

30 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 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
35 potassium salts.

The dyes were synthesized as outlined in European patents EP 1 490 441 and WO 2010/050495. The dye mixtures were then prepared as in the following examples.

Example 1

- 5 70 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-1), and 30 parts of an electrolyte-containing dye powder containing the greenish navy azo dye of the formula (II-1), were mixed mechanically with one another.

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

Example 2

- 15 50 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-1), 30 parts of an electrolyte-containing dye powder containing the greenish navy azo dye of the formula (II-1), and 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (III-7) were mixed mechanically with one another.

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

Example 3

- 25 50 parts of an electrolyte-containing dye powder containing the reddish blue azo dye of the formula (I-4), 30 parts of an electrolyte-containing dye powder containing the navy azo dye of the formula (II-6), and 20 parts of an electrolyte-containing dye powder containing the blue azo dye of the formula (III-1) were mixed mechanically with one another.

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

Example No	Component I	%	Component II	%	Component II	%
4	I.1	60	II.1	40	-	-
5	I.1	50	II.1	50	-	-
6	I.1	50	II.1	30	III.1	20
7	I.1	20	II.1	30	III.1	50
8	I.1	50	II.1	30	III.2	20
9	I.1	50	II.1	30	III.3	20
10	I.1	50	II.1	30	III.4	20
11	I.1	50	II.1	30	III.5	20

12	I.1	50	II.1	30	III.6	20
13	I.2	70	II.2	30	-	-
14	I.2	60	II.2	40	-	-
15	I.2	50	II.2	50	-	-
16	I.2	50	II.2	30	III.1	20
17	I.2	50	II.2	30	III.7	20
18	I.3	70	II.1	30	-	-
19	I.3	60	II.1	40	-	-
20	I.3	50	II.1	50	-	-
21	I.4	70	II.1	30	-	-
22	I.4	60	II.1	40	-	-
23	I.4	50	II.1	50	-	-
24	I.4	50	II.1	30	III.1	20
25	I.4	50	II.1	30	III.7	20
26	I.5	70	II.1	30	-	-
27	I.5	60	II.1	40	-	-
28	I.5	50	II.1	50	-	-
29	I.6	70	II.1	30	-	-
30	I.6	60	II.1	40	-	-
31	I.6	50	II.1	50	-	-
32	I.12	70	II.1	30	-	-
33	I.12	60	II.1	40	-	-
34	I.12	50	II.1	50	-	-
35	I.13	70	II.1	30	-	-
36	I.13	60	II.1	40	-	-
37	I.13	50	II.1	50	-	-
38	I.17	70	II.1	30	-	-
39	I.17	60	II.1	40	-	-
40	I.17	50	II.1	50	-	-
41	I.18	70	II.1	30	-	-
42	I.18	60	II.1	40	-	-
43	I.18	50	II.1	50	-	-
44	I.20	70	II.1	30	-	-
45	I.20	60	II.1	40	-	-
46	I.20	50	II.1	50	-	-
47	I.21	70	II.1	30	-	-
48	I.21	60	II.1	40	-	-
49	I.21	50	II.1	50	-	-
50	I.1	70	II.4	30	-	-
51	I.1	60	II.4	40	-	-
52	I.1	50	II.4	50	-	-
53	I.1	70	II.5	30	-	-
54	I.1	60	II.5	40	-	-
55	I.1	50	II.5	50	-	-
56	I.1	70	II.6	30	-	-

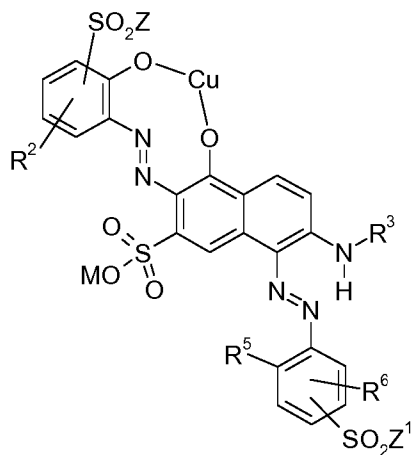
57	I.1	60	II.6	40	-	-
58	I.1	50	II.6	50	-	-
59	I.1	50	II.6	30	III.1	20
60	I.1	50	II.6	30	III.7	20
61	I.1	70	II.8	30	-	-
62	I.1	60	II.8	40	-	-
63	I.1	50	II.8	50	-	-
64	I.1	70	II.10	30	-	-
65	I.1	60	II.10	40	-	-
66	I.1	50	II.10	50	-	-
67	I.1	70	II.11	30	-	-
68	I.1	60	II.11	40	-	-
69	I.1	50	II.11	50	-	-
70	I.1	70	II.12	30	-	-
71	I.1	60	II.12	40	-	-
72	I.1	50	II.12	50	-	-
73	I.1	50	II.12	30	III.1	20
74	I.1	50	II.12	30	III.7	20
75	I.1	70	II.13	30	-	-
76	I.1	60	II.13	40	-	-
77	I.1	50	II.13	50	-	-
78	I.1	50	II.13	30	III.1	20
79	I.1	50	II.13	30	III.7	20
80	I.1	70	II.14	30	-	-
81	I.1	60	II.14	40	-	-
82	I.1	50	II.14	50	-	-
83	I.1	50	II.14	30	III.1	20
84	I.1	50	II.14	30	III.7	20

Application example 1

5 parts of the dye obtained in example 1 and 50 parts of sodium chloride were dissolved in 999 parts of water, and 5 parts of sodium carbonate, 0.7 parts of sodium hydroxide (in the form of a 32.5 % strength aqueous solution) and, if necessary, 1 part of a wetting agent are added. This dyebath was entered with 100 g of a woven cotton fabric. The temperature of the dyebath was maintained at 25 °C for 10 minutes to start with, then raised over 30 minutes to the final temperature 60 °C and held at that temperature for a further 60 to 90 minutes. Thereafter the dyed goods were rinsed first for 2 minutes with water and subsequently for 5 minutes with water. The dyed goods were neutralized at 40 °C in 1000 parts of an aqueous solution containing 1 part of 50 % strength acetic acid for 10 minutes. This was followed by rinsing with deionized water at 70 °C and then by soaping off at the boil for 15 minutes with a laundry detergent, rinsing again, and drying. This gives a strongly colored navy dyeing having very good fastness properties.

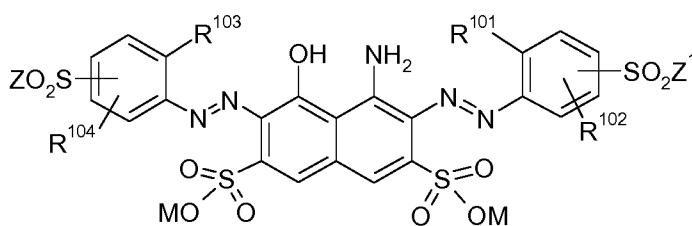
Claims:

1. Mixtures of fibre-reactive dyes comprising:
a dye of formula (I)



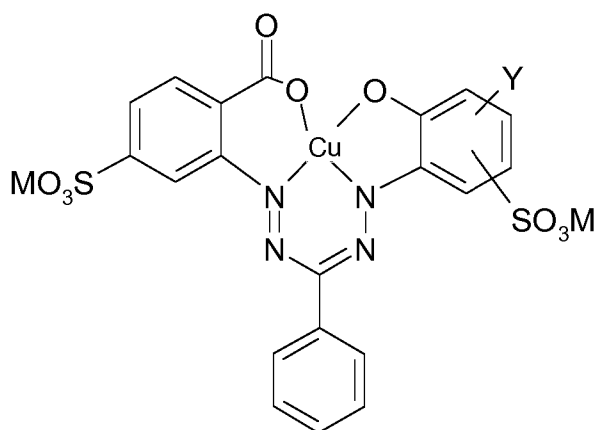
(I),

a dye of formula (II)



(II)

and optionally a dye of formula (III)



(III)

wherein independently of each other

R^2 is hydrogen, $(\text{C}_1\text{-C}_4)$ -alkyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R^3 is $(\text{C}_1\text{-C}_4)$ -alkyl; $(\text{C}_1\text{-C}_4)$ -alkyl substituted by sulfo, carboxyl, halogen, hydroxyl, amino

or acetamido; phenyl; or phenyl substituted by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, sulfo, halogen, carboxyl, acetamido or ureido;

R⁵ is (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

R⁶ is hydrogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido or halogen,

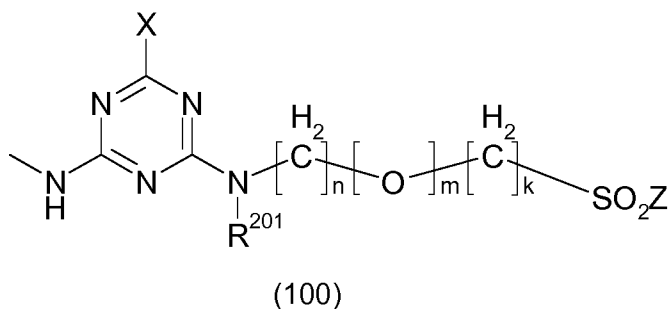
R¹⁰¹ and R¹⁰³ are C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, sulfo, carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of the formula (100)



wherein

X is halogen,

R²⁰¹ is hydrogen (C₁-C₄)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

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

2. Mixtures of fibre-reactive dyes according to claim 1, wherein independent of each other

R² is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R³ is (C₁-C₂)-alkyl or (C₁-C₂)-alkyl substituted by sulfo,

R⁵ is (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

R⁶ is hydrogen, (C₁-C₂)-alkyl, (C₁-C₂)-alkoxy or sulfo,

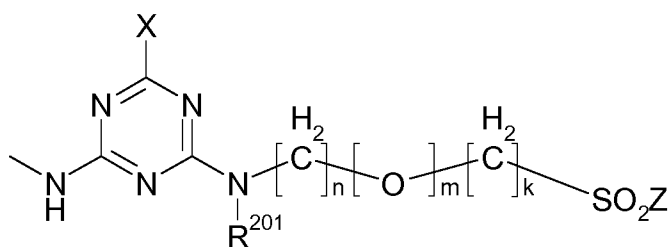
R¹⁰¹ and R¹⁰³ are C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

R¹⁰² and R¹⁰⁴ are hydrogen, C₁-C₂-alkyl, C₁-C₂-alkoxy, sulfo or carboxyl,

Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



(100)

wherein

X is Cl or F,

5 R^{201} is hydrogen, (C₁-C₂)-alkyl or phenyl,

n is 2 or 3,

m is 0 or 1,

k is 0 to 3

and

10 M is hydrogen, Na, K or Li.

3. Mixtures of fibre-reactive dyes according to claim 1 or 2, wherein independent of each other

R^2 is hydrogen, methy, methoxy or sulfo,

15 R^3 is methyl or (C₁-C₂)-alkyl substituted by sulfo,

R^5 is methy, methoxy or sulfo,

R^6 is hydrogen, methy, methoxy or sulfo,

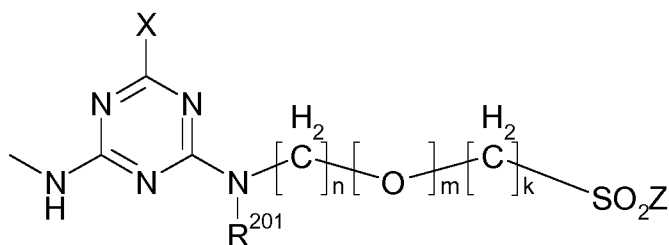
R^{101} and R^{103} are, methy, methox or sulfo,

R^{102} and R^{104} are hydrogen, methy, methoxy or sulfo,

20 Z and Z¹ are -CH=CH₂, -CH₂CH₂G or hydroxyl,

G is hydroxyl or an alkali-detachable group,

Y is -SO₂-Z or a group of formula (100)



(100)

25 wherein

X is Cl or F,

R^{201} is hydrogen, methyl or phenyl,

n is 2 or 3,

m is 0 or 1,

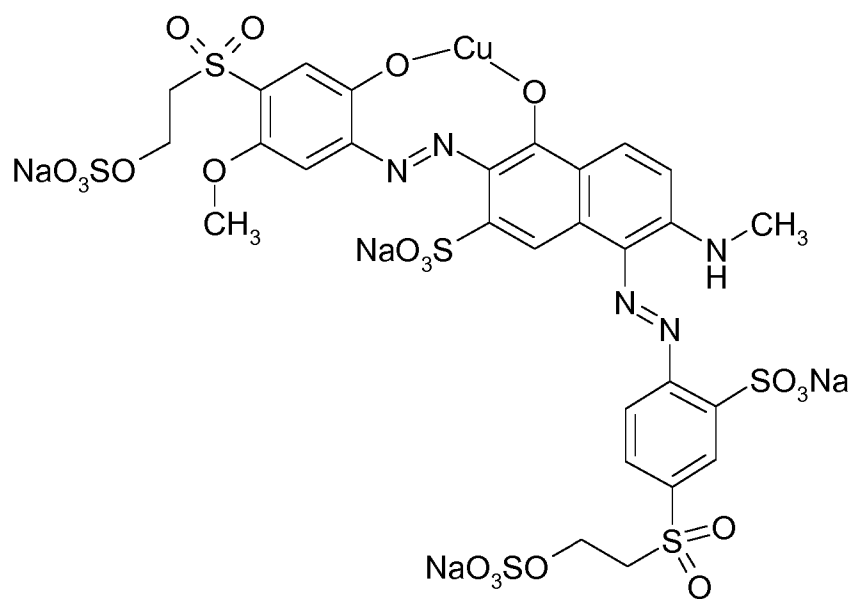
k is 0 to 3,

and

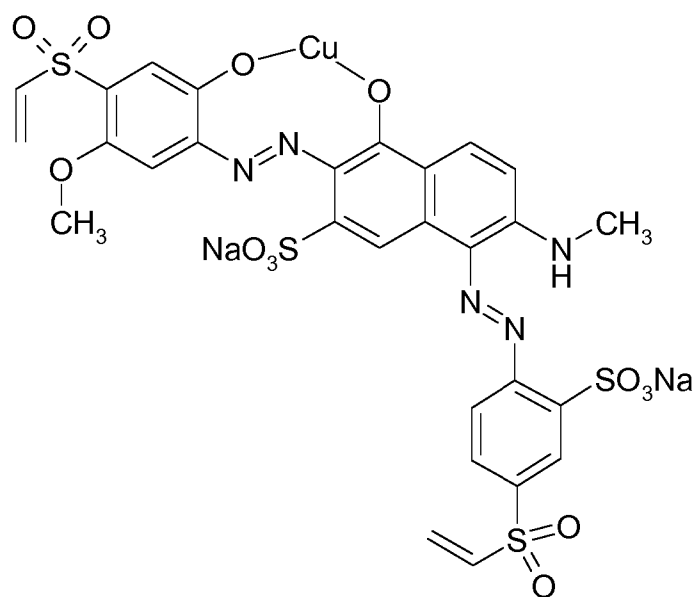
M is hydrogen, Na, K or Li.

5

4. Mixtures according to any one of claims 1 to 3, wherein the dye of general structure (I) is selected from the group consisting of:

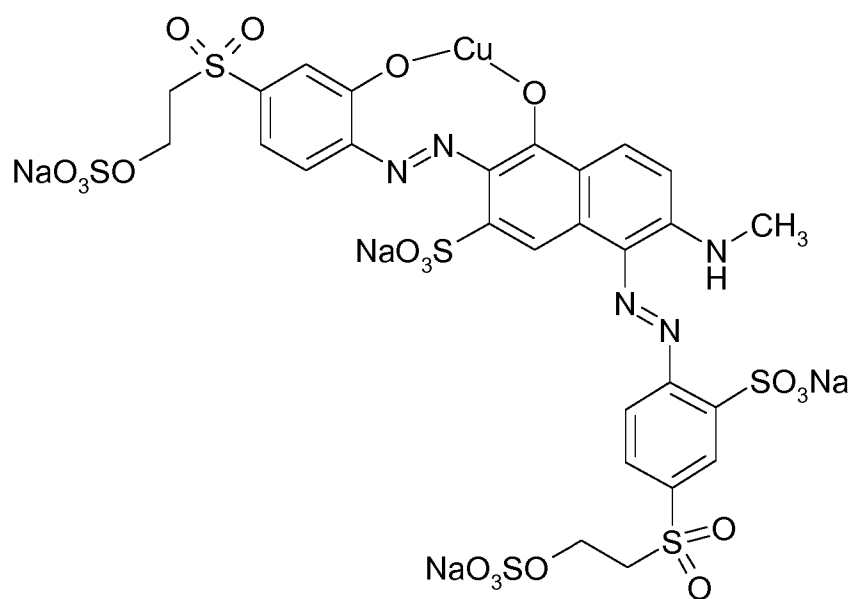


I-1,

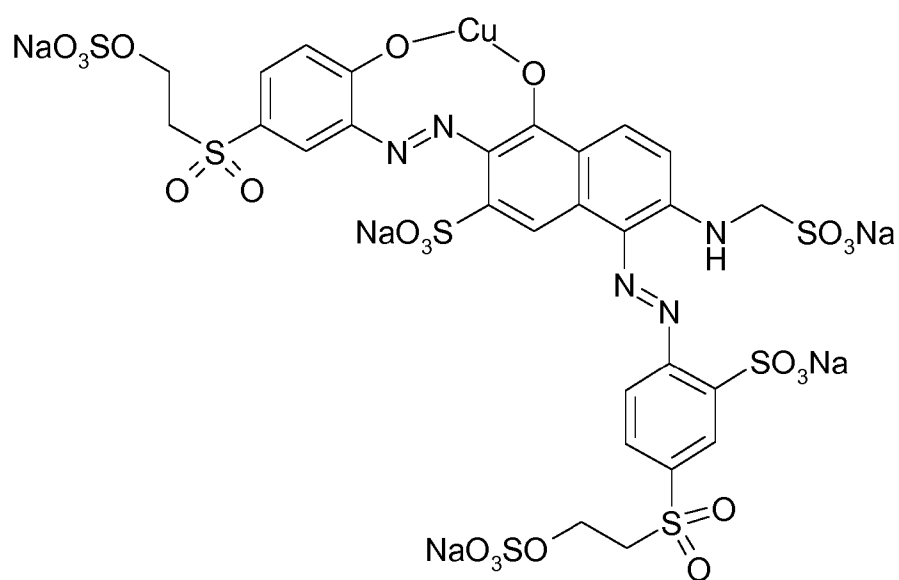


I-2,

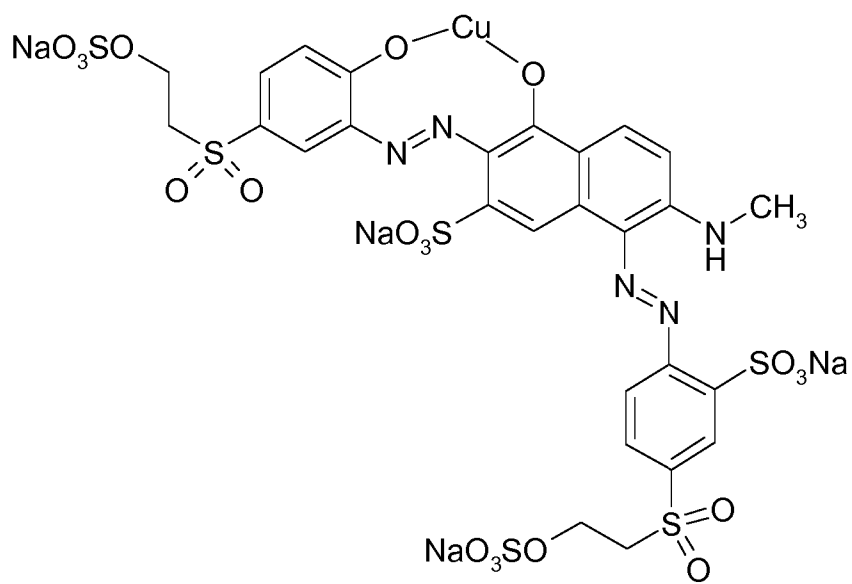
10



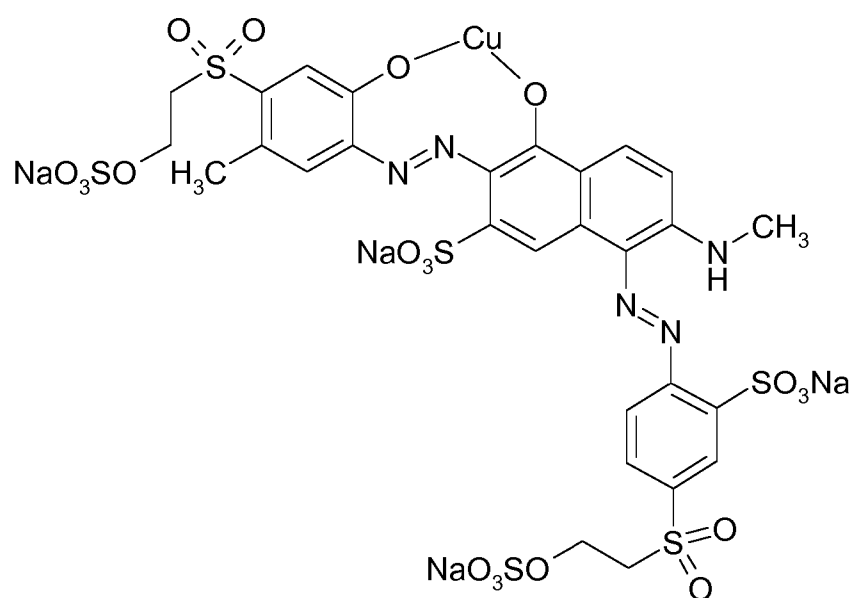
I-3,



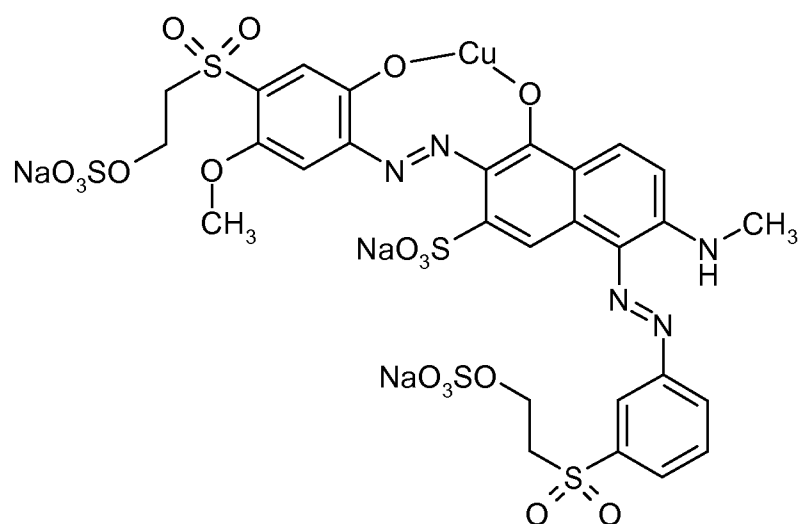
I-4,



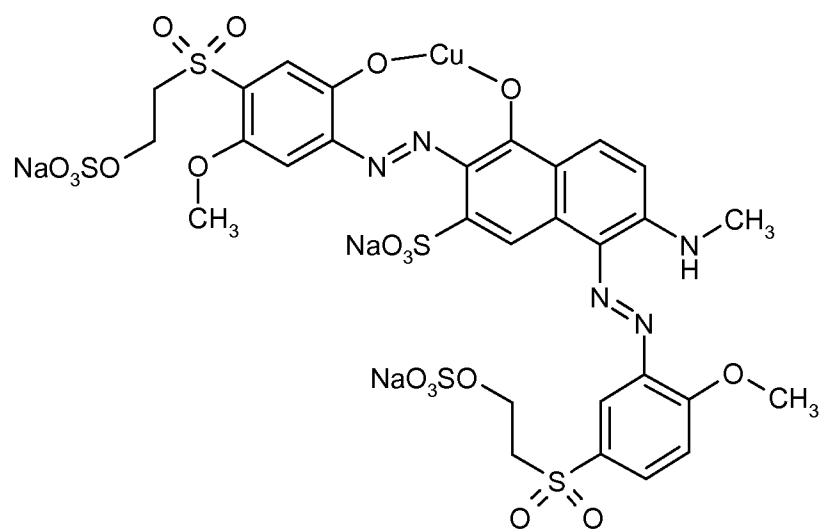
I-5,



I-6,

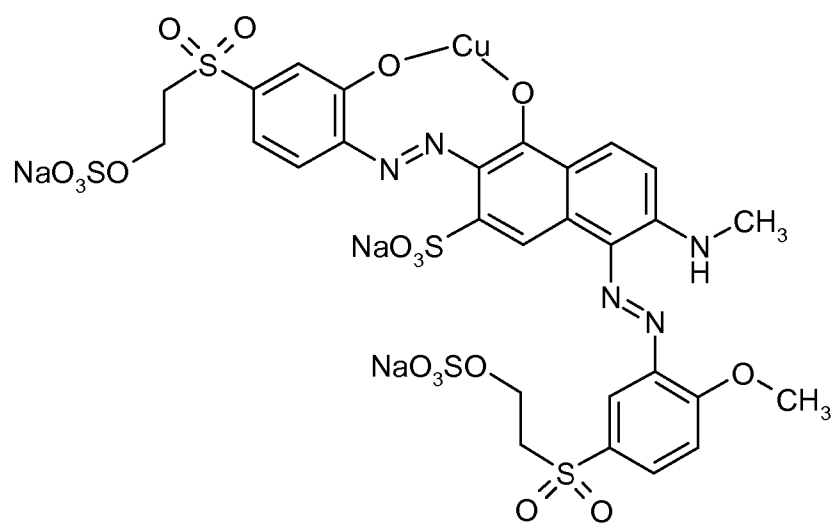


I-7,

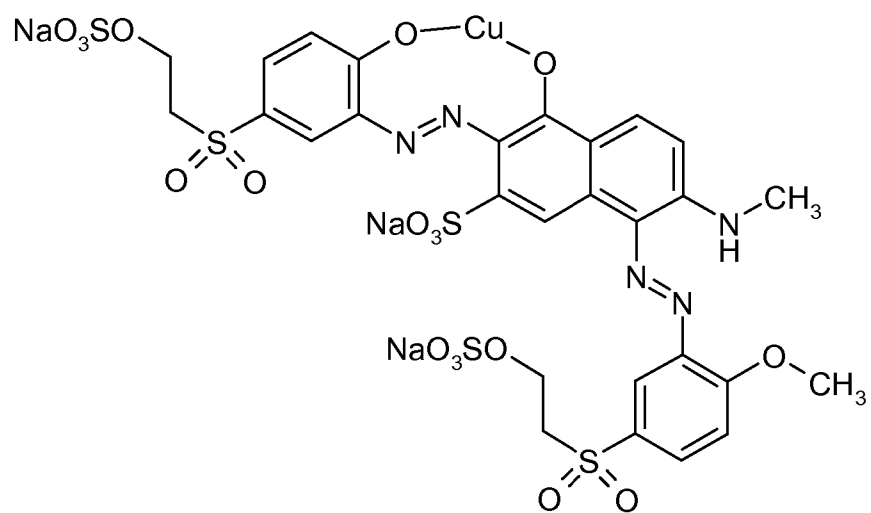


I-8,

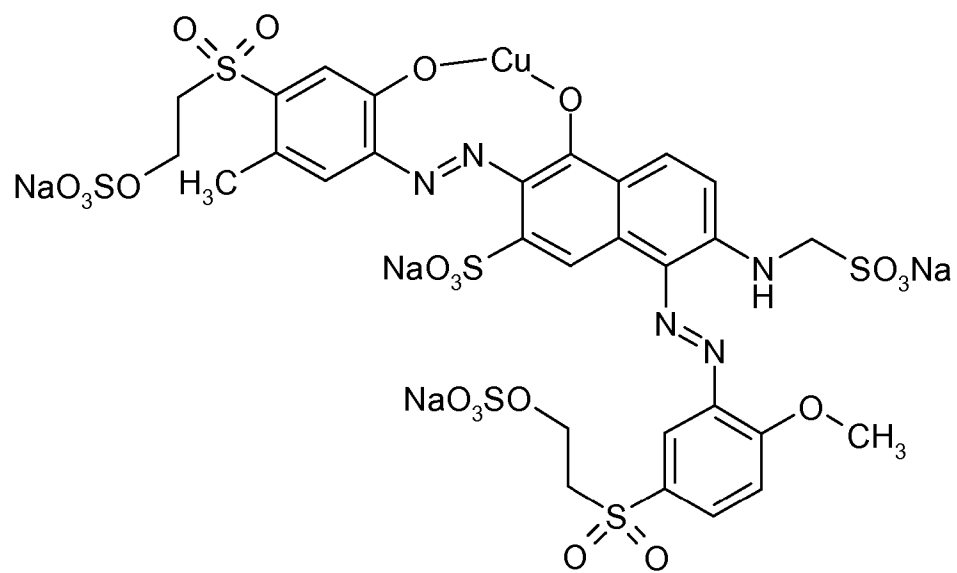
5



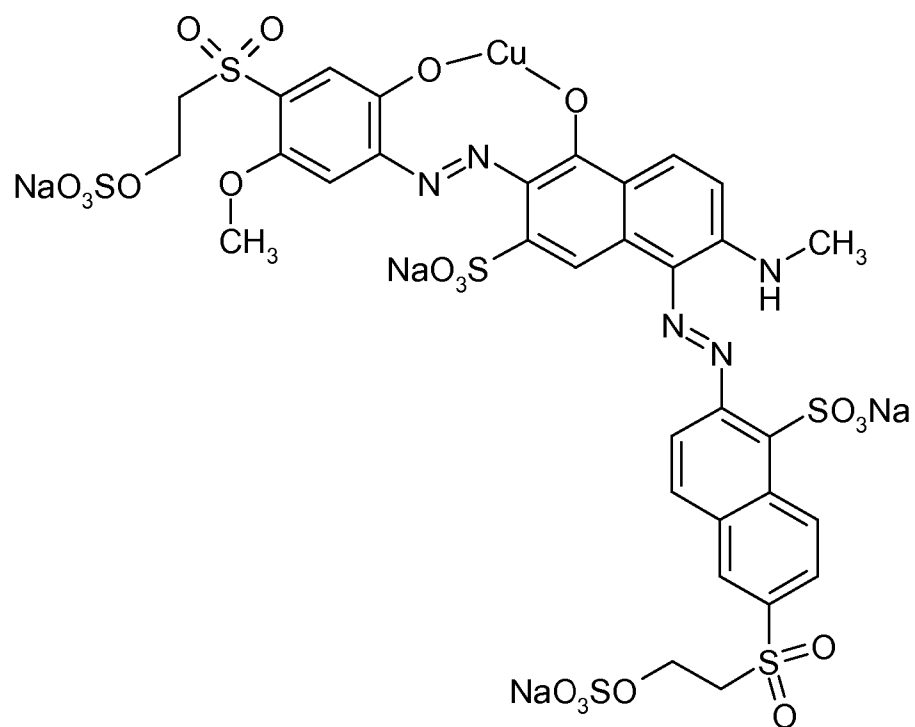
I-9,



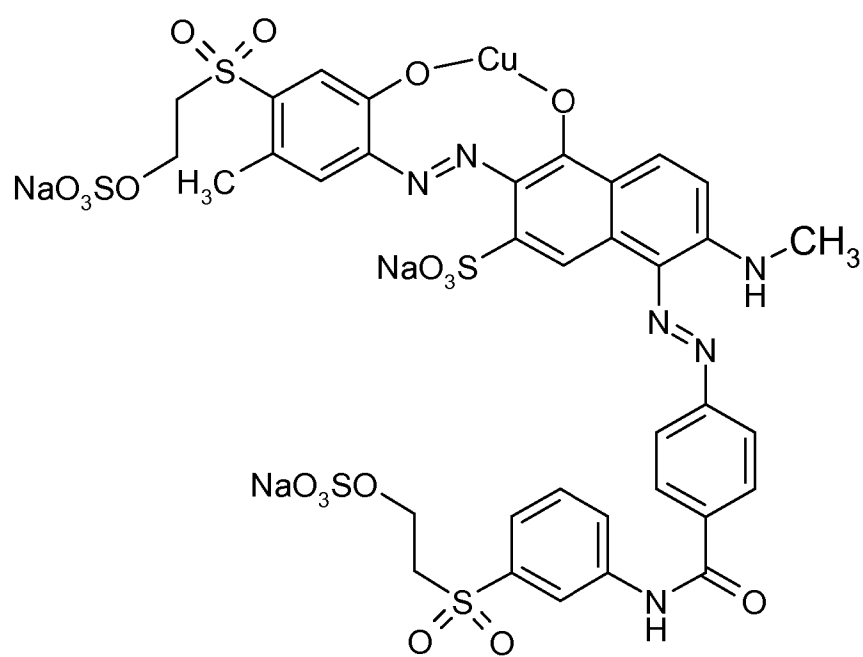
I-10,



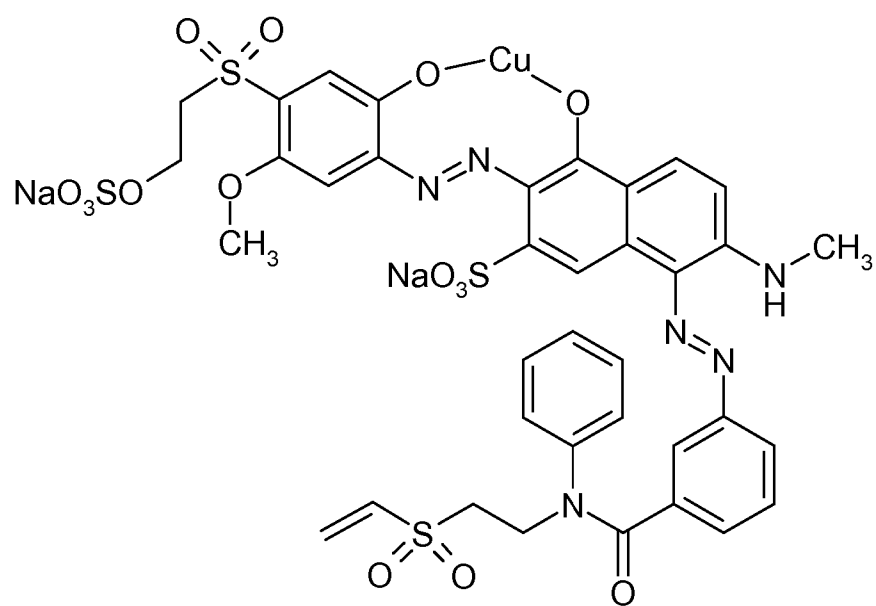
I-11,



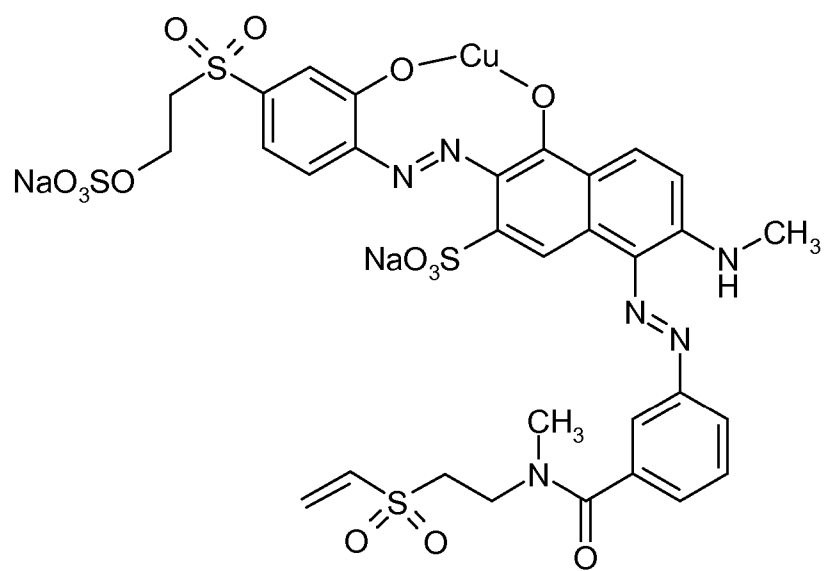
I-12,



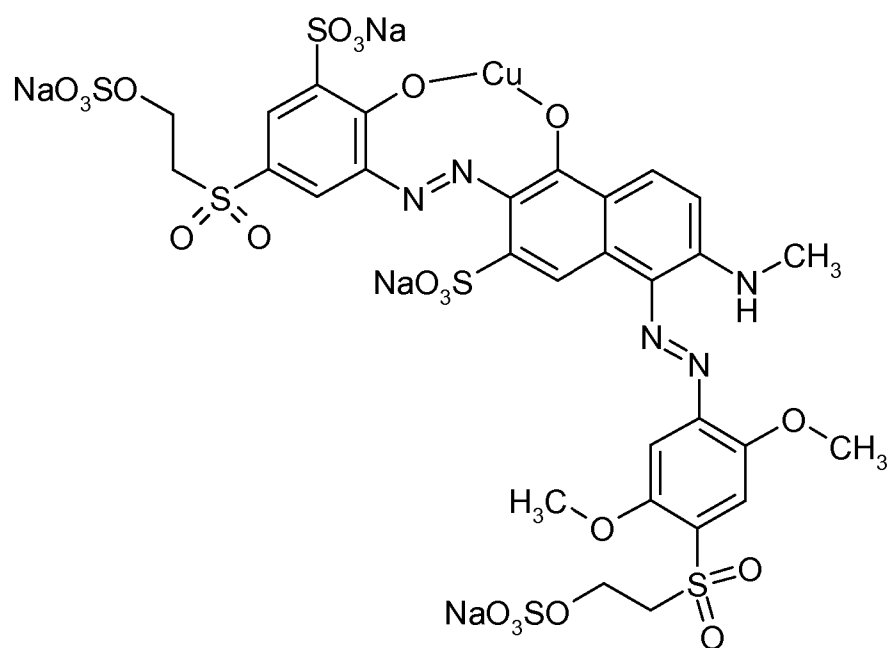
I-13,



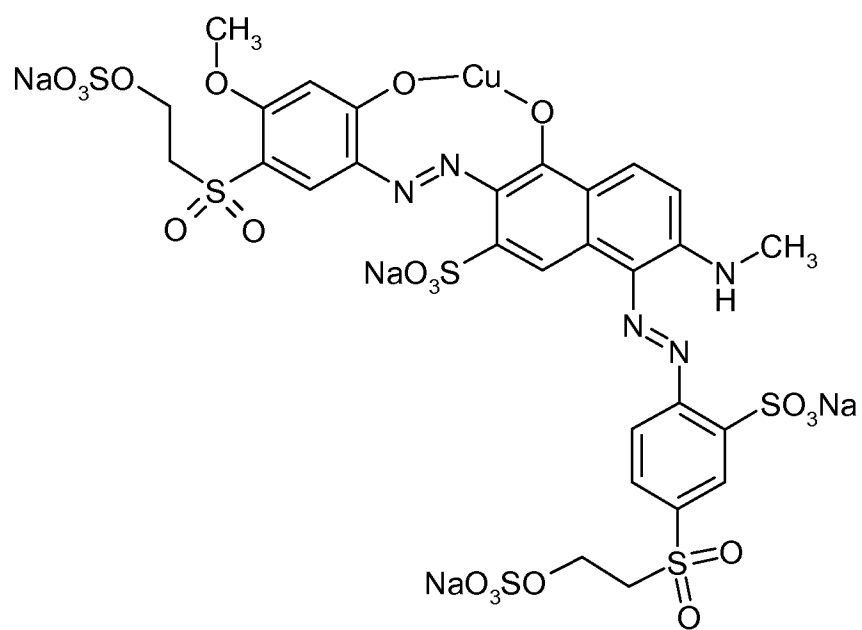
1-14,



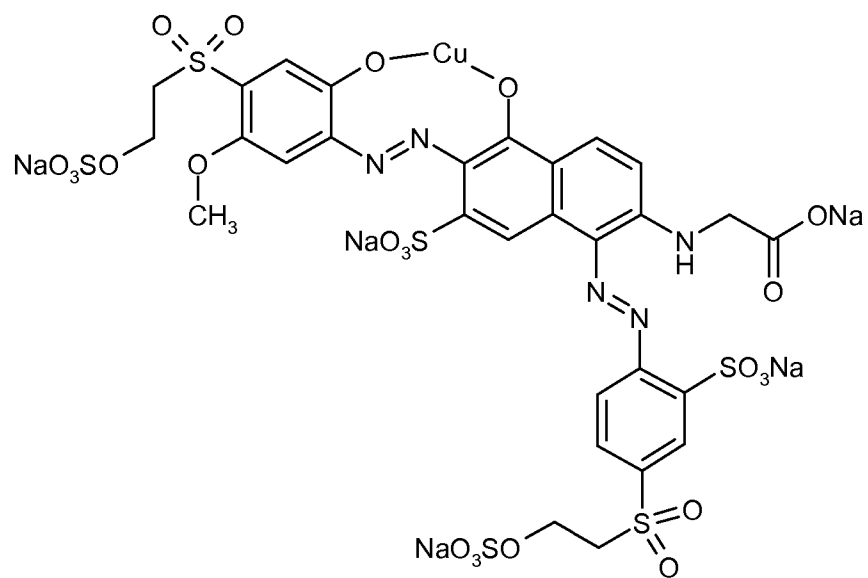
1-15,



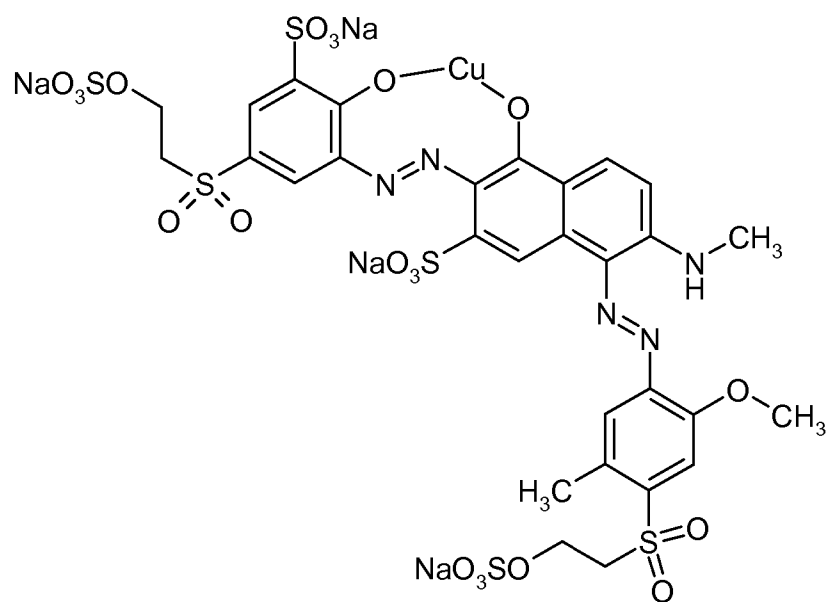
I-16,



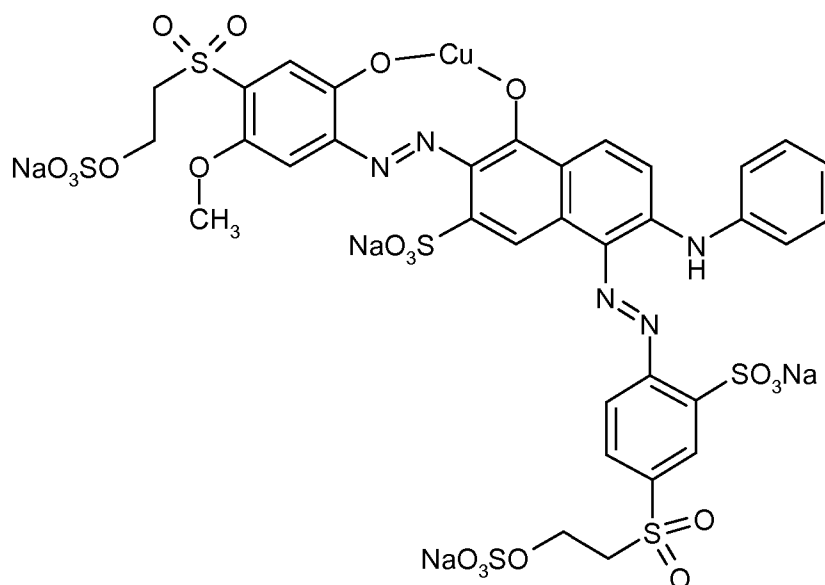
I-17,



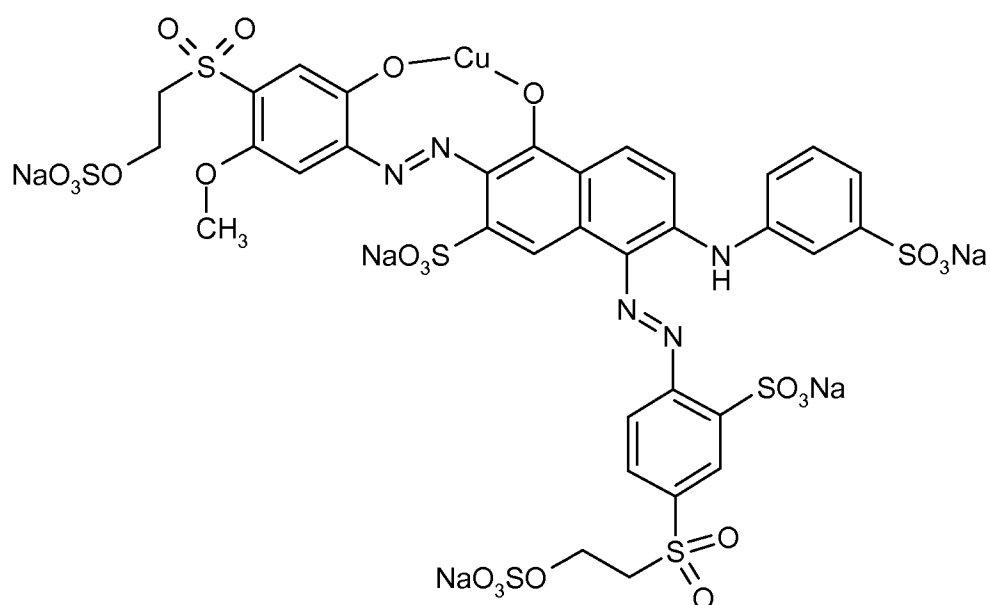
1-18,



1-19,



I-20 and



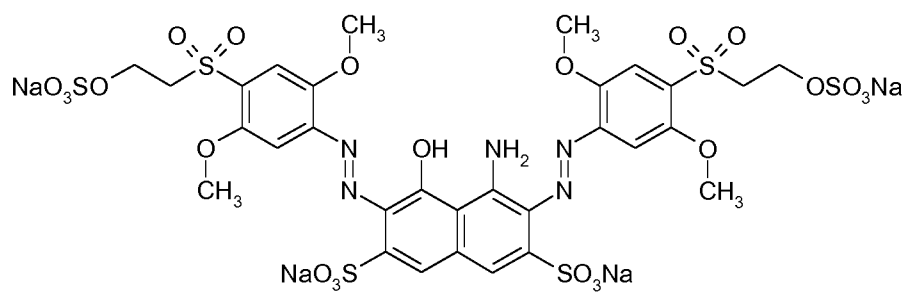
I-21.

5

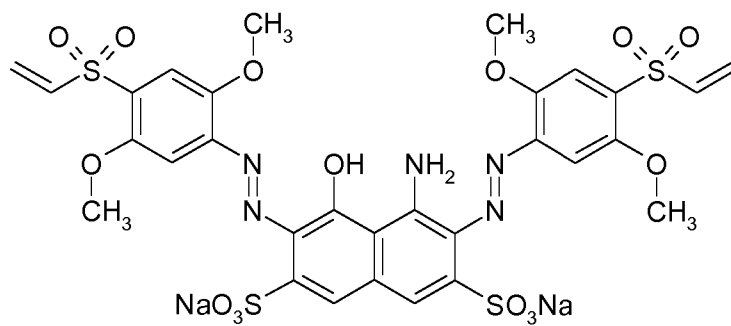
5. Mixtures according to any one of claims 1 to 4 wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21.

- 10 6. Mixtures according to any one of claims 1 to 5, wherein the dye of general structure (I) is selected from the group consisting of: I-1, I-2 and I-4.

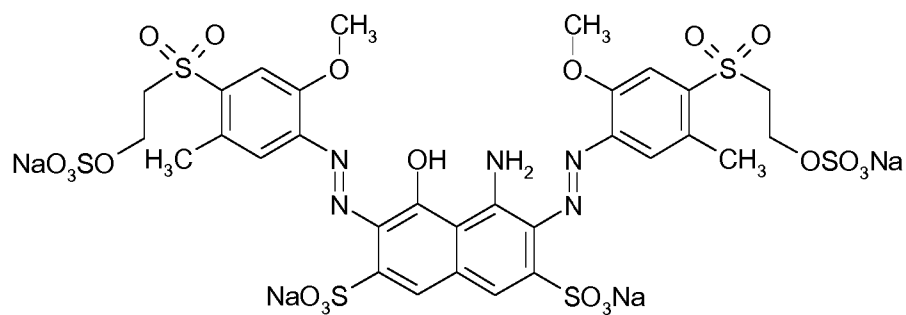
7. Mixtures according to any one of calims 1 to 6, wherein the dye of general structure (II) is selected from the group consisting of:



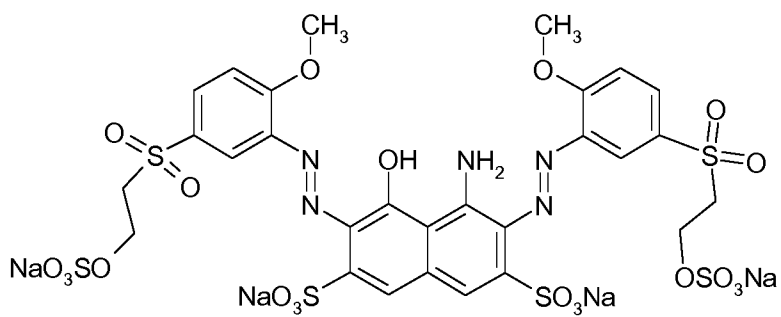
II-1,



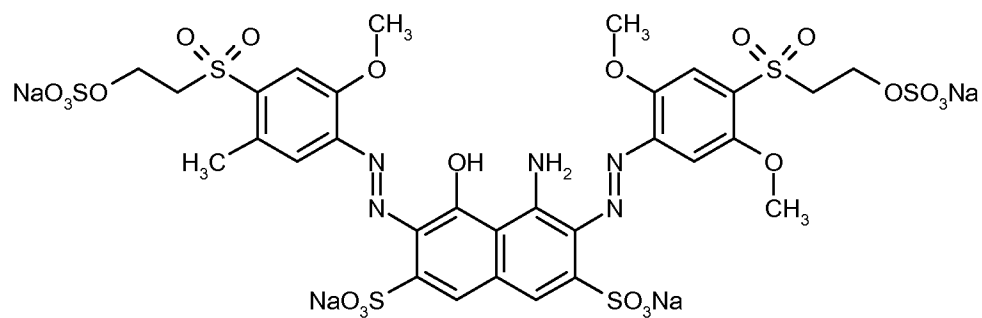
II-2,



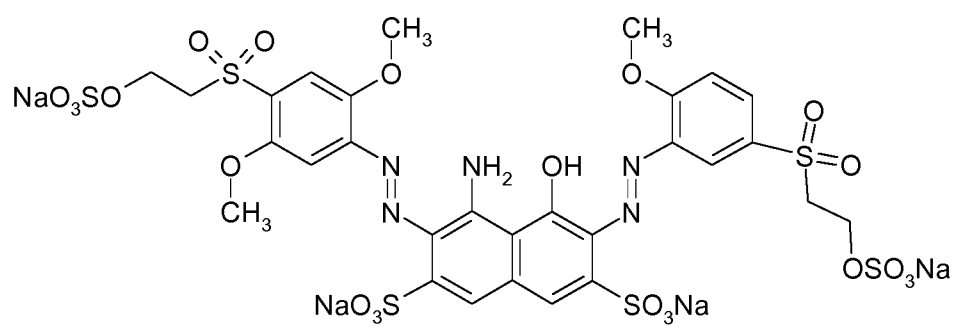
II-3,



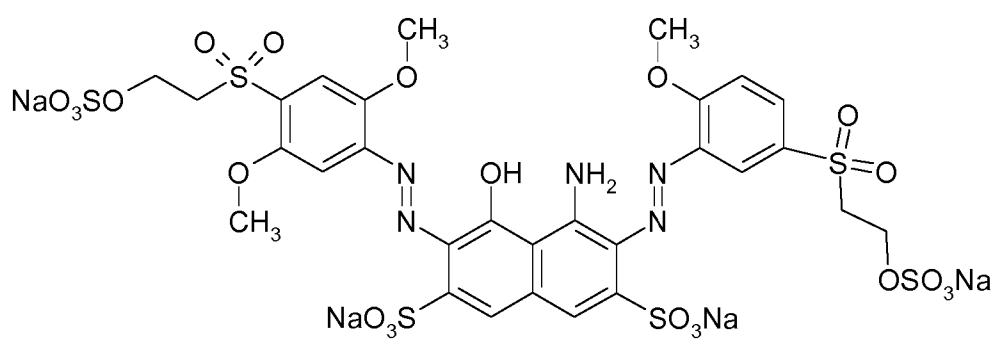
II-4,



II-5,

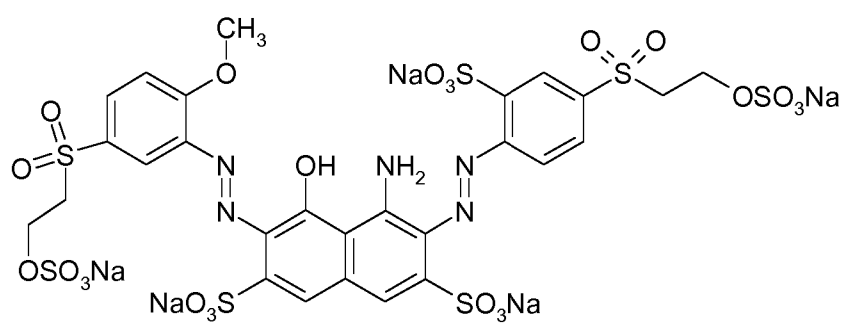


II-6,

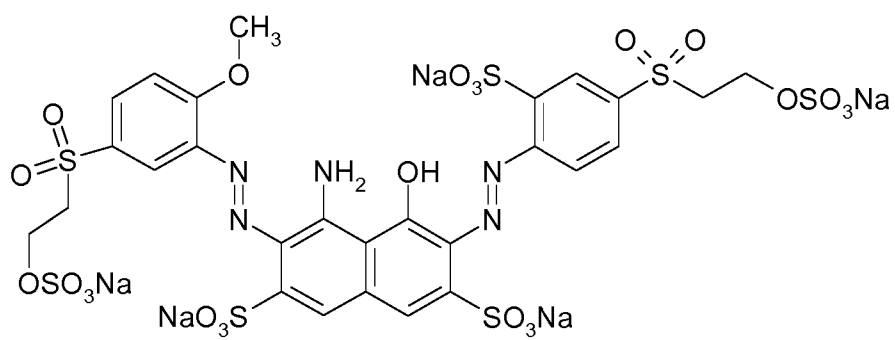


5

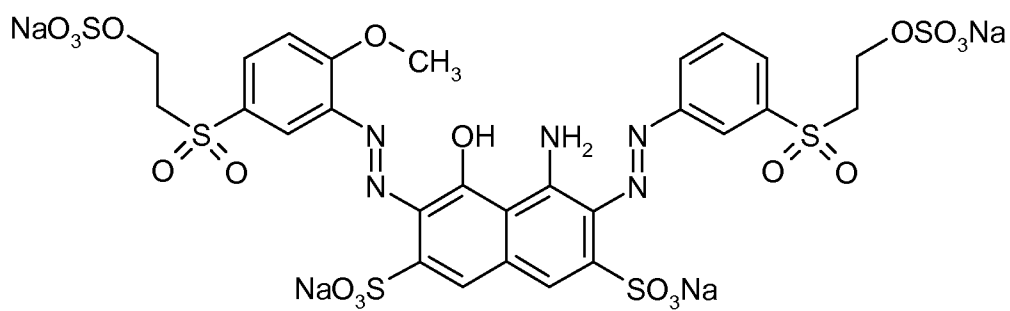
II-7,



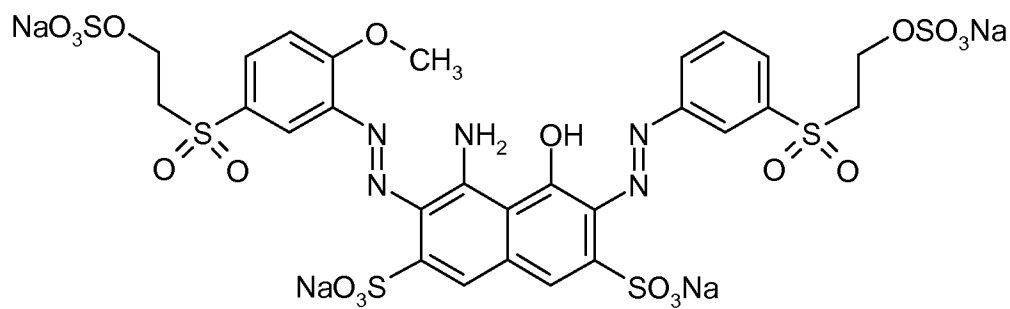
II-8,



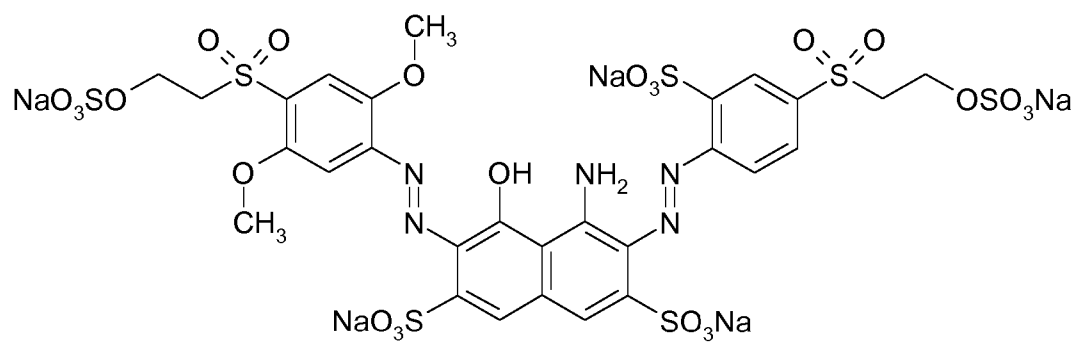
II-9,



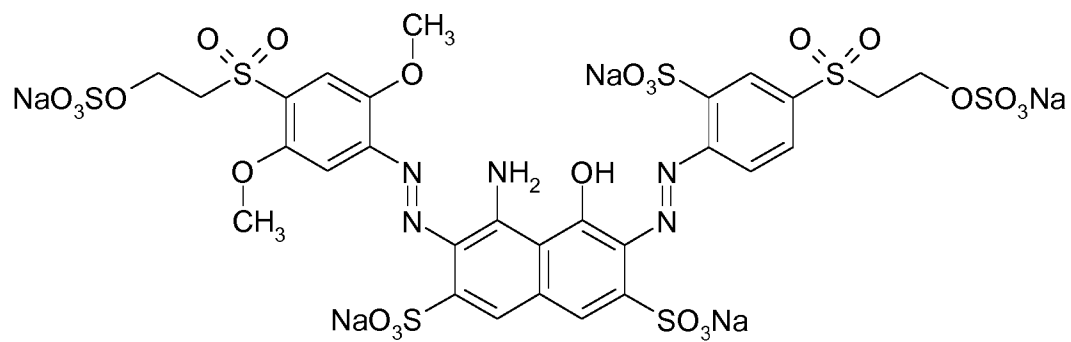
II-10,



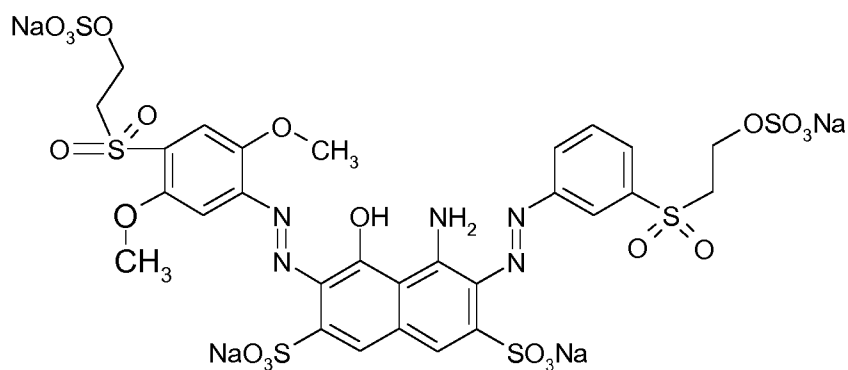
II-11,



II-12,



II-13 and

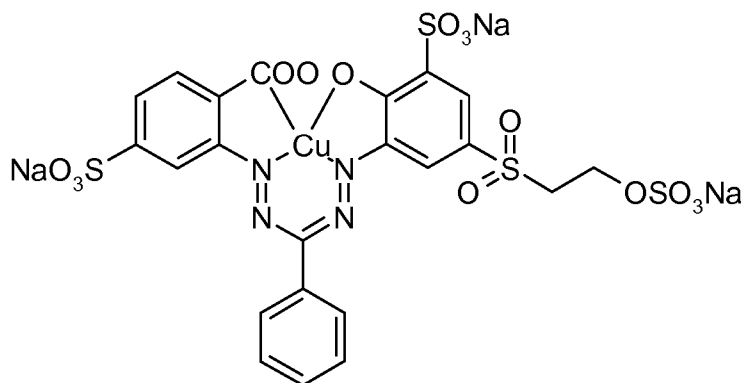


II-14.

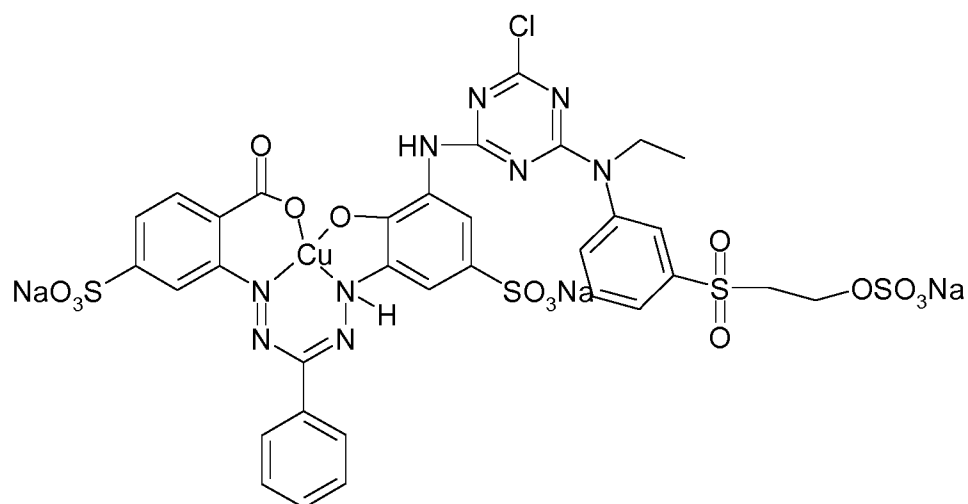
8. Mixtures according to any one of claims 1 to 7, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

9. Mixtures according to any one of claims 1 to 8, wherein the dye of general structure (II) is selected from the group consisting of: II-1, II-2, II-6, II-7, II-12 and II-13.

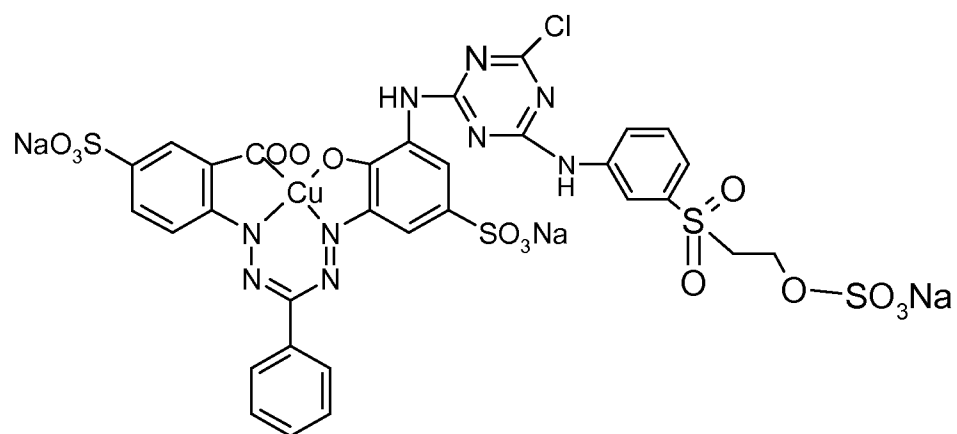
10. Mixtures according to any one of claims 1 to 9, wherein a dye of general structure (III) is present and said dye is selected from the group consisting of:



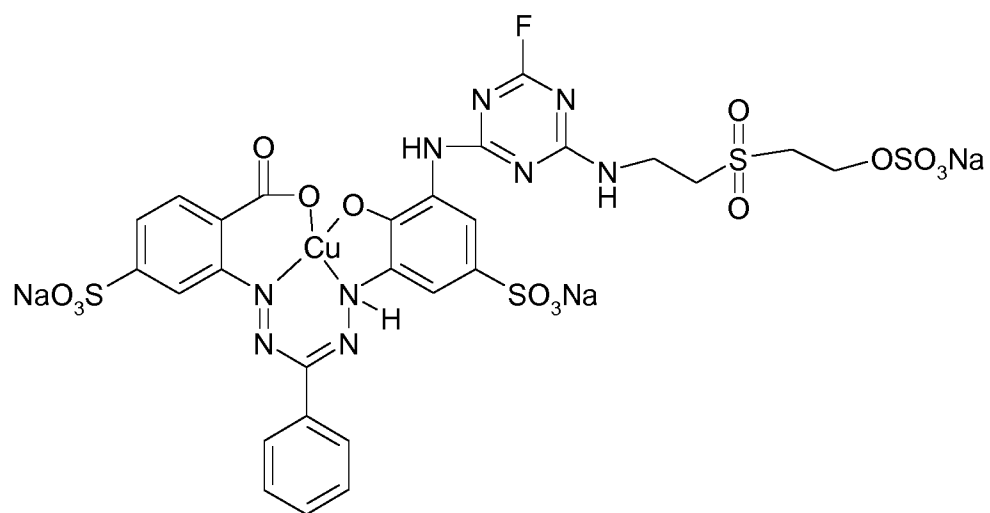
III-1,



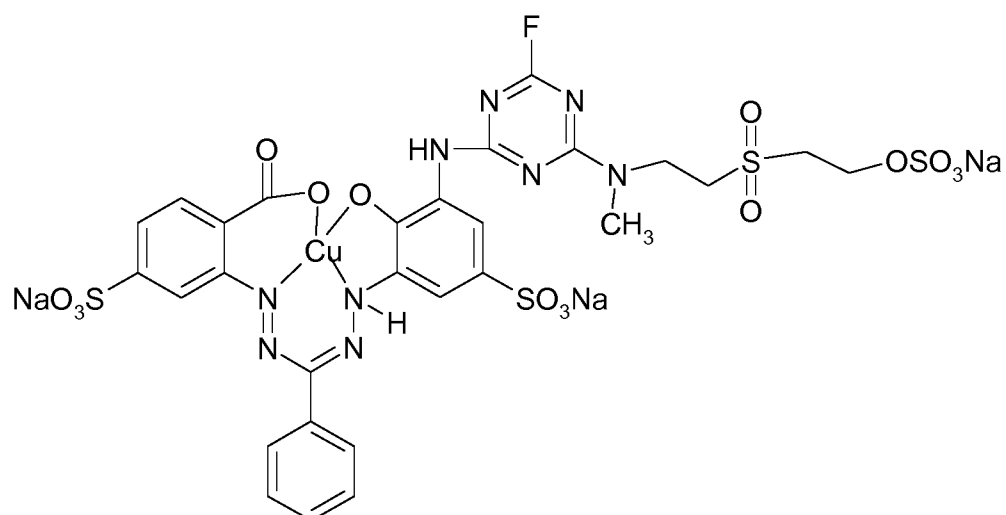
III-2,



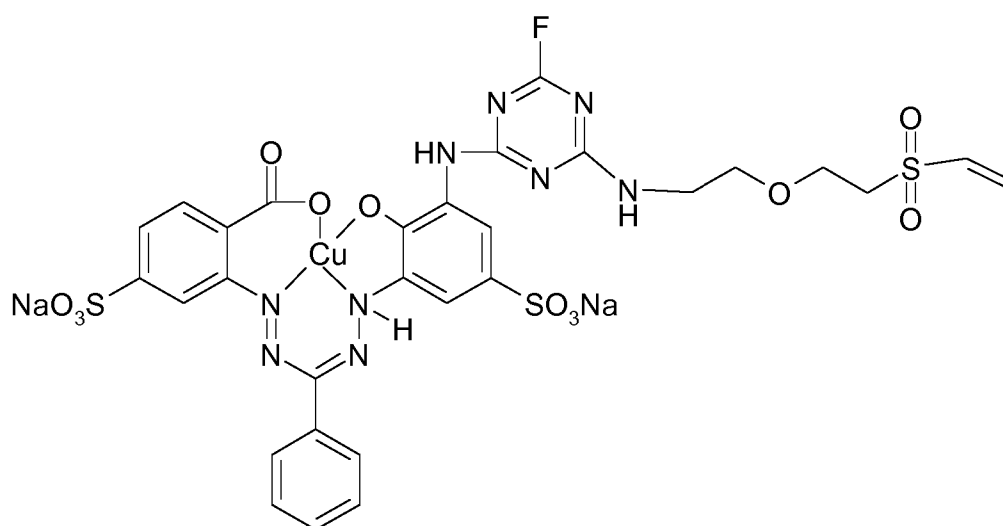
III-3,



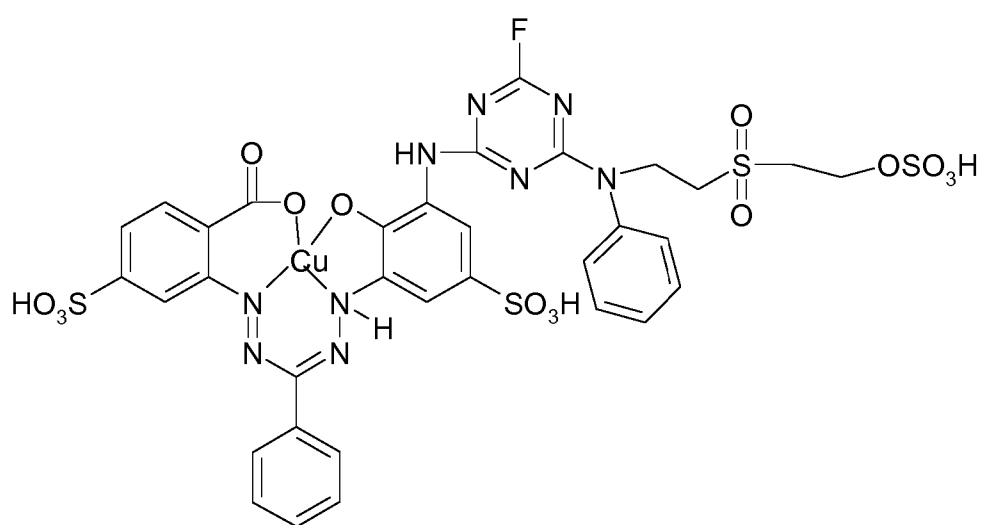
III-4,



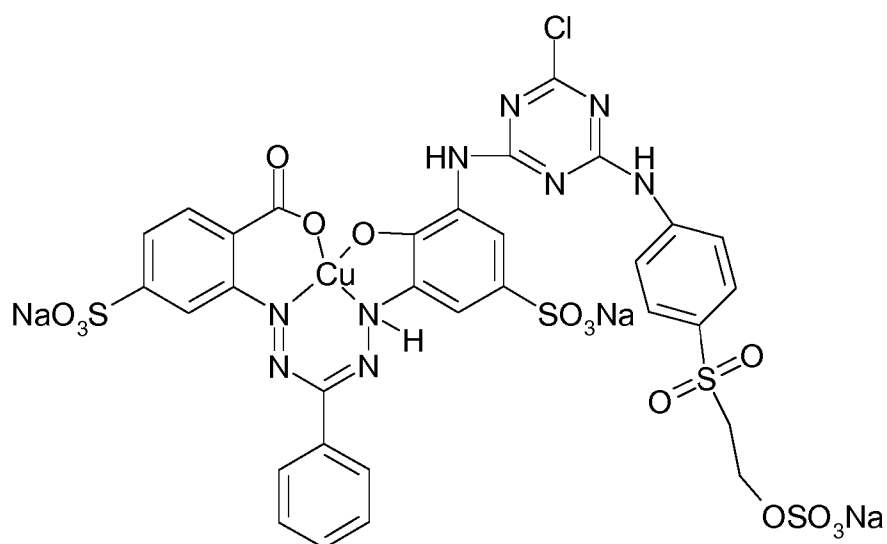
III-5,



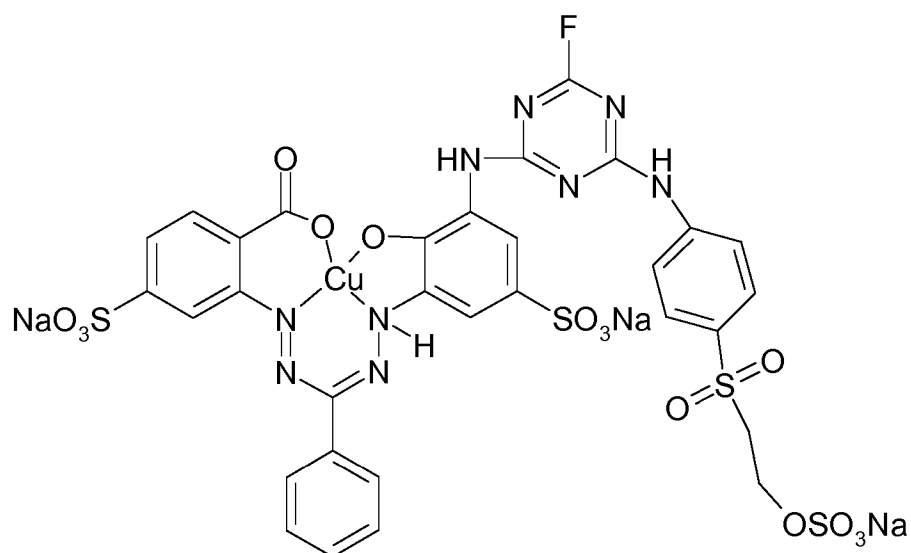
III-6,



III-7



III-8 and



III-9.

5

11. Mixtures according to any one of claims 1 to 10, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-4, III-6, III-7 and III-8.

10 12. Mixtures according to any one of claims 1 to 11, wherein the dye of general structure (III) is selected from the group consisting of: III-1, III-2, III-6, III-7 and III-8.

13. Mixtures according to any one of claims 1 to 12, wherein the dye of the formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13.

15

14. Mixtures according to any one of claims 1 to 13, wherein the dye of the formula (I) is selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13.

5

15. Mixtures according to any one of claims 1 to 14, a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8.

10

16. Mixtures according to any one of claims 1 to 15, a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2 and I-4 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

15

17. Mixtures according to any one of claims 1 to 16, wherein a dye of structure (III) is present and wherein the dye of formula (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-4, III-6, III-7 and III-8.

20

18. Mixtures according to any one of claims 1 to 17, wherein a dye of structure (III) is present and wherein the dye of formula (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of formula (III) is selected from the list consisting of III-1, III-2, III-6, III-7 and III-8.

25

19. Mixtures according to any one of claims 1 to 18, wherein a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2, I-3, I-4, I-5, I-6, I-12, I-13, I-17, I-18, I-20 and I-21, the dye of structure (II) is selected from the list consisting of II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-10, II-11, II-12 and II-13 and the dye of structure (III) is selected from the group consisting of III-1, III-2, III-4, III-6, III-7 and III-8.

30

20. Mixtures according to any one of claims 1 to 18, wherein a dye of structure (III) is present and wherein the dye of formula (I) is selected from the list consisting of I-1, I-2 and I-4, the dye of structure (II) is selected from the list consisting of II-1, II-2, II-6, II-7, II-12 and II-13 and the dye of structure (III) is selected from the group consisting of III-1, III-2, III-6, III-7 and III-8.

35

Abstract:

Mixtures of fibre reactive dyes and their use of for the dyeing of hydroxyl- and carboxamide-containing material in blue and navy shades.