



- (51) International Patent Classification: Not classified
- (21) International Application Number:
PCT/EP2009/055525
- (22) International Filing Date:
7 May 2009 (07.05.2009)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0808875.9 15 May 2008 (15.05.2008) GB
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

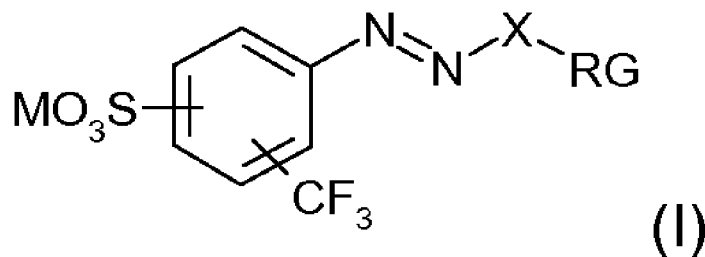
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: FIBRE-REACTIVE DYESTUFFS CONTAINING A TRIFLUOROMETHYL GROUP



(57) Abstract: The present invention claims dyestuffs of the formula (I) wherein X, RG and M are defined as given in claim 1, a method for their preparation and their use.



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Fibre-reactive dyestuffs containing a trifluoromethyl group

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This invention relates to the technical field of fibre-reactive azo dyes.

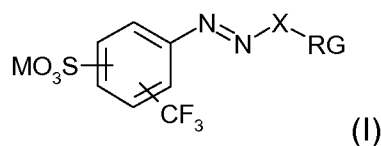
Dyestuffs and colorants, respectively, containing a trifluoromethyl group are known and described in literature.

- 10 For example, GB732121 discloses monoazo acid dyestuffs comprising a trifluoromethyl-benzenesulfonic acid. Azo pigments derived from trifluoromethyl-anilinesulfonic acid are known from CAN 61:33096, CAN 66:96276 and CAN 67:100981.

- As regards fibre-reactive dyestuffs, trifluoromethyl groups are within the generic
15 teaching of for example GB 2 259 710 A, EP 0 094 020 A1, EP 0 354 409 A1, EP 0 385 426 A1, EP 0 433 764 A1, EP 470 930 A1, EP 0 603 116 A1 and EP 0 872 523 A2. However, all these references lack any specific teaching of such dyestuffs.

- It has been surprisingly found that fibre-reactive dyestuffs obtained from
20 trifluoromethyl containing anilinesulfonic acids as diazo components show particularly advantageous fastness profiles when reactively applied to cotton especially in relation to fastness to light, chlorine and perspiration light fastness. Also, the dyestuffs give level shades with good contact fastness after wash off.

- 25 Accordingly, the present invention provides dyestuffs of the formula (I)

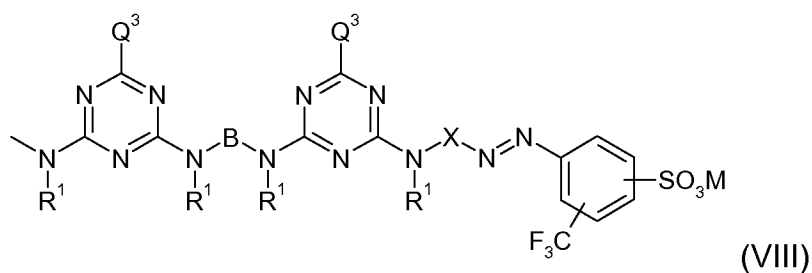


wherein

X is an aromatic or heteroaromatic divalent group;

- 30 RG is a reactive group capable of forming a covalent bond to cellulose under dyeing conditions or a group comprising a reactive group capable of forming a covalent bond to cellulose under dyeing conditions; or

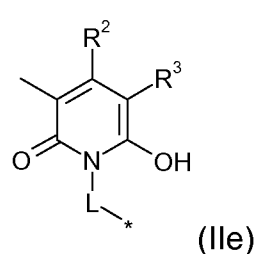
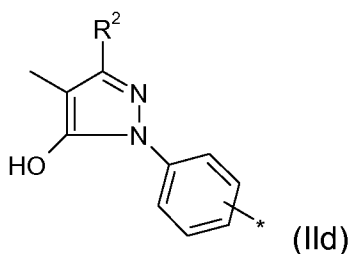
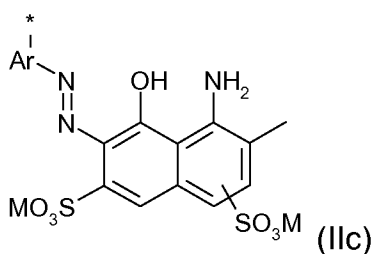
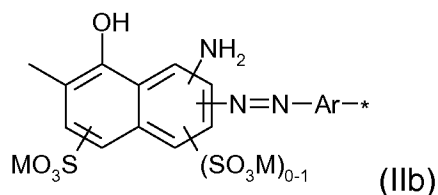
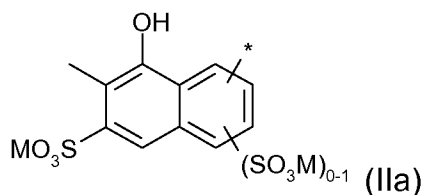
is a group of the formula (VIII)

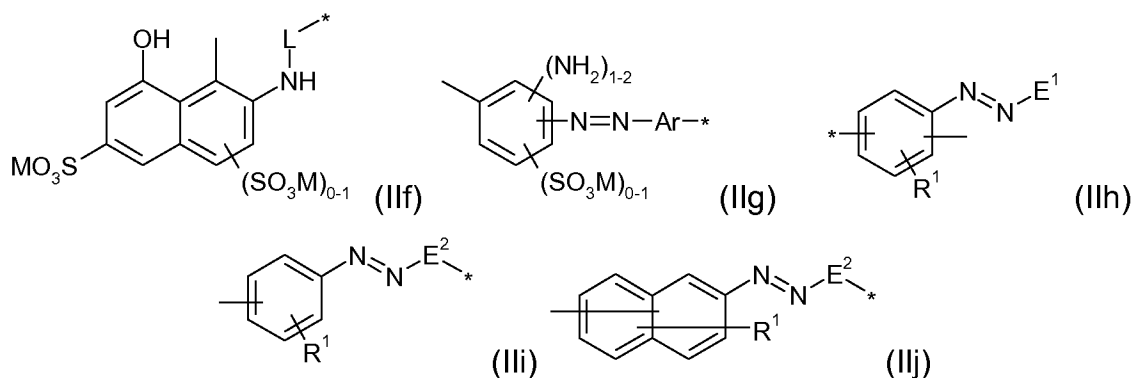


wherein

- B is 1,2-phenylene, 1,3-phenylene or 1,4 phenylene, which are unsubstituted or substituted by $-\text{SO}_3\text{M}$, $-\text{COOM}$ or R^1 , or is $(\text{C}_2\text{-C}_6)$ -alkylene or $(\text{C}_1\text{-C}_4)$ -alkylene-phenylene which are unsubstituted or substituted by R^1 ;
- Each R^1 independently is hydrogen, $(\text{C}_1\text{-C}_6)$ -alkyl, sulfo- $(\text{C}_1\text{-C}_6)$ -alkyl, phenyl or phenyl substituted by $(\text{C}_1\text{-C}_4)$ -alkyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, hydroxyl, $-\text{SO}_3\text{M}$, halogen-, $-\text{COOM}$, acetamido or ureido;
- Q^3 is chlorine, fluorine, cyanamido, hydroxyl, $(\text{C}_1\text{-C}_6)$ -alkoxy, phenoxy, sulfophenoxy, mercapto, $(\text{C}_1\text{-C}_6)$ -alkylmercapto, pyridino, carboxypyridino or carbamoylpyridino; and
- M is hydrogen, an alkali metal or an equivalent of an alkaline earth metal.

- Preferred aromatic or heteroaromatic divalent groups standing for X correspond to one of the formulae (IIa) to (IIj)



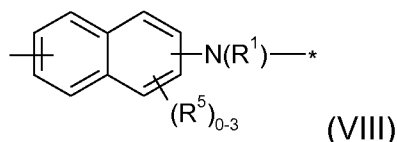


wherein

Ar is phenyl or phenyl which is substituted by 1, 2 or 3 substituents selected from the group comprising (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy and $-SO_3M$;

E^1 has one of the meanings of Ar , is naphthyl or naphthyl which is substituted by 1, 2 or 3 substituents selected from the group comprising (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, $-SO_3M$, amino, acetylamino or hydroxy; or is a 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, or is a 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, which is substituted by 1, 2 or 3 substituents selected from the group comprising (C_1-C_4) -alkyl and (C_1-C_4) -alkoxy;

E^2 is phenylene or naphthylene which are unsubstituted or substituted by 1, 2 or 3 substituents selected from the group comprising (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy $-SO_3M$, amino, acetylamino or hydroxy; or is a divalent 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, or is a divalent 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, which is substituted by 1, 2 or 3 substituents selected from the group comprising (C_1-C_4) -alkyl and (C_1-C_4) -alkoxy; or is a group of the formula (VIII)



wherein

R^5 is (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy $-SO_3M$ or hydroxy;

R^1 is defined as given above;

R^2 is (C_1-C_4) -alkyl or $-COOM$;

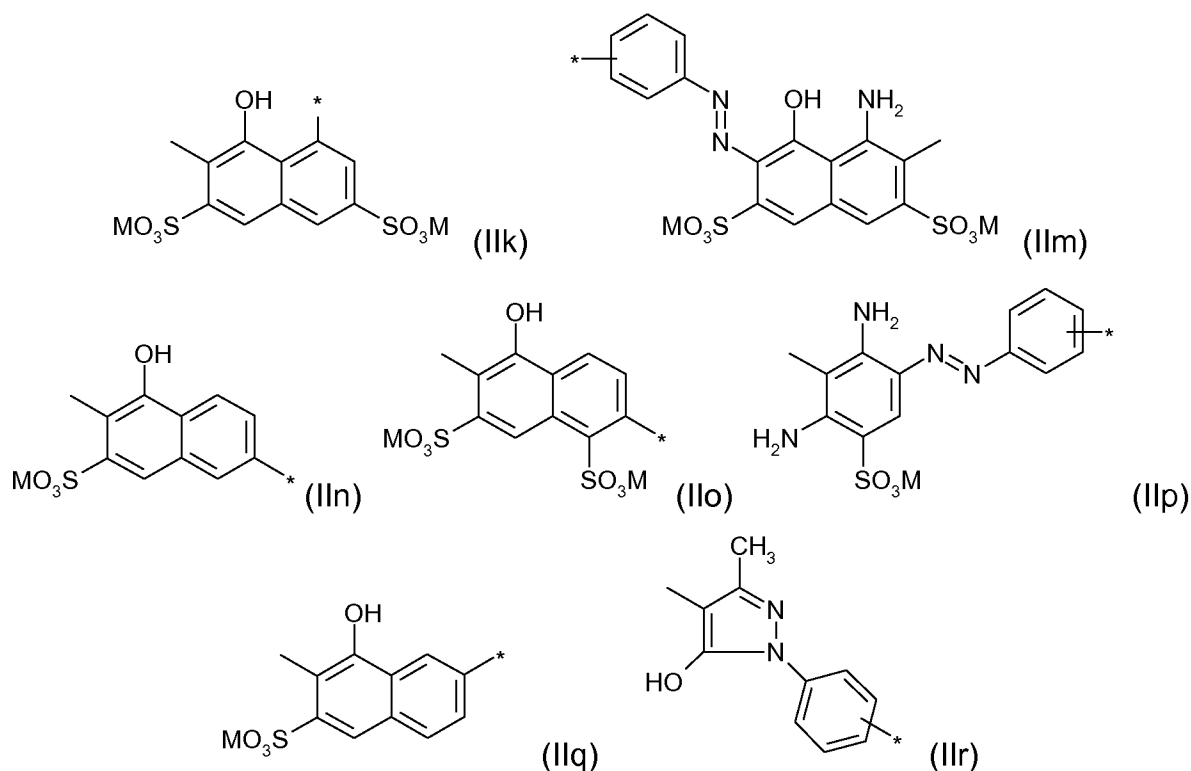
R^3 is hydrogen, CN or $-CONH_2$;

L has one of the meanings of B;
 M is defined as given above; and
 * is the bond to the group RG.

- 5 Examples of 5- or 6-membered heterocyclic residues comprising one or two heteroatoms standing for E¹ are pyridones, pyrazolones and diaminopyridines. Similarly, examples of divalent 5- or 6-membered heterocyclic residues comprising one or two heteroatoms standing for E² are divalent pyridone, pyrazolone and diaminopyridine residues.

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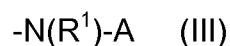
Especially preferred aromatic or heteroaromatic divalent groups standing for X correspond to the formulae (IIk) to (IIr)



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wherein M and * are defined as given above.

- Preferred reactive groups capable of forming a covalent bond to cellulose under
 20 dyeing conditions standing for RG are -SO₂-CH=CH₂, -SO₂-CH₂CH₂Z¹ or a group of the formula (III)

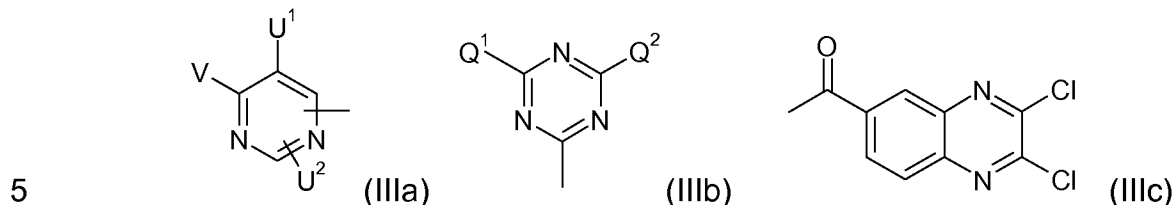


wherein

Z^1 is an alkali-eliminatable group;

R^1 is defined as given above;

A is a group of the formula (IIIa), (IIIb) or (IIIc)

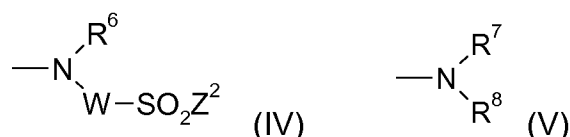


V is fluorine or chlorine;

U^1 and U^2 are independently fluorine, chlorine or hydrogen; and

Q^1 and Q^2 are independently chlorine, fluorine, cyanamido, hydroxyl, (C_1-C_6) -alkoxy, phenoxy, sulfophenoxy, mercapto, (C_1-C_6) -alkylmercapto, pyridino,

10 carboxypyridino, carbamoylpyridino or a group of the formula (IV) or (V)



where

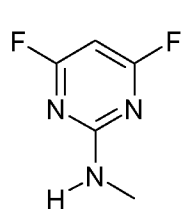
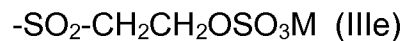
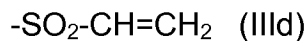
R^6 has one of the meanings of R^1 ;

15 R^7 and R^8 independently have one of the meanings of R^1 or combine to form a group of the formula $-(CH_2)_j-$ or of the formula $-(CH_2)_2-B^1-(CH_2)_2-$, where j is 4 or 5, B^1 is oxygen, sulfur, sulfonyl or $-NR^9-$ and R^9 is (C_1-C_6) -alkyl;

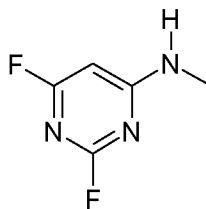
W is phenylene which is unsubstituted or substituted by 1 or 2 substituents selected from the group consisting of (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, carboxyl, sulfo, chlorine and bromine, or is (C_1-C_4) -alkylenephénylene, (C_2-C_6) -alkylene, which may be
20 interrupted by oxygen, sulfur, sulfonyl, amino, carbonyl or carboxamido, or is phenylene CONH phenylene which is unsubstituted or substituted by 1 or 2 substituents selected from the group consisting of (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido and halogen, or is naphthylene which is unsubstituted or substituted by one or two sulfo groups; and

25 Z^2 is $-CH=CH_2$ or $-CH_2CH_2Z^1$.

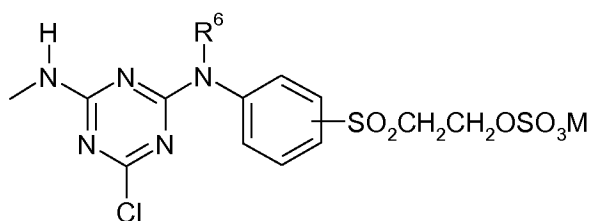
Especially preferred reactive groups capable of forming a covalent bond to cellulose under dyeing conditions standing for RG are the groups of the formulae (IIIId) to (IIIi)



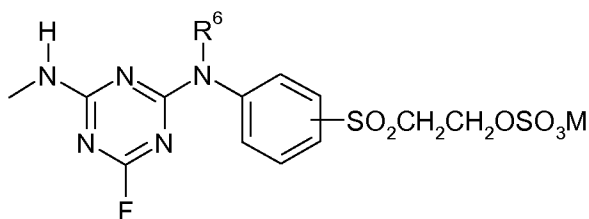
(III f)



(III g)



(III h)



(III i)

wherein R^6 and M are defined as given above.

In the formulae disclosed in this specification alkyl groups may be straight chain or branched and are in particular methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl and tert-butyl. (C₁-C₆)-alkyl groups may in addition be n-pentyl or n-hexyl.

Methyl and ethyl are preferred. The same logic applies to alkoxy groups, which accordingly are preferably methoxy and ethoxy and to alkylene groups, which are in particular ethylene, propylene and butylene.

Halogen is preferably bromine, chlorine and fluorine.

Alkali M is in particular lithium, sodium or potassium; an alkaline earth metal equivalent M is in particular the equivalent of calcium. M is preferably hydrogen or sodium.

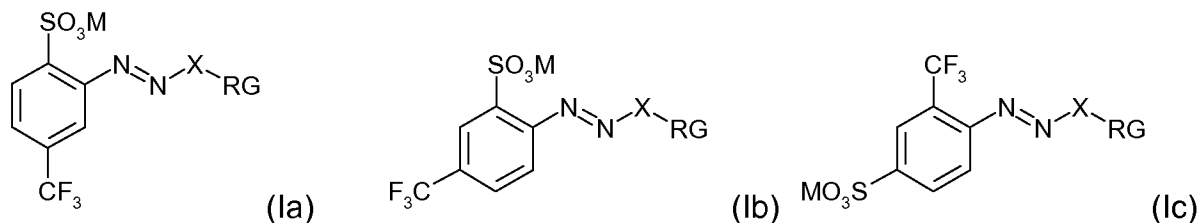
Alkali-eliminatable groups standing for Z^1 are for example halogen, such as chlorine and bromine; ester groups of organic carboxylic and sulfonic acids, for example alkylcarboxylic acids, substituted or unsubstituted benzenecarboxylic acids and substituted or unsubstituted benzenesulfonic acids, in particular alkanoyloxy of 2 to 5 carbon atoms such as acetyloxy, benzoyloxy, sulfobenzoyloxy, phenylsulfonyloxy and toluylsulfonyloxy; also acidic ester groups of inorganic acids, as of phosphoric

acid, sulfuric acid and thiosulfuric acid (phosphato, sulfato and thiosulfato groups) and dialkylamino groups having alkyl groups of 1 to 4 carbon atoms each, such as dimethylamino and diethylamino.

Z¹ is preferably chloro and more preferably sulfato.

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Preferred dyestuffs of the formula (I) correspond to the formulae (Ia) to (Ic)

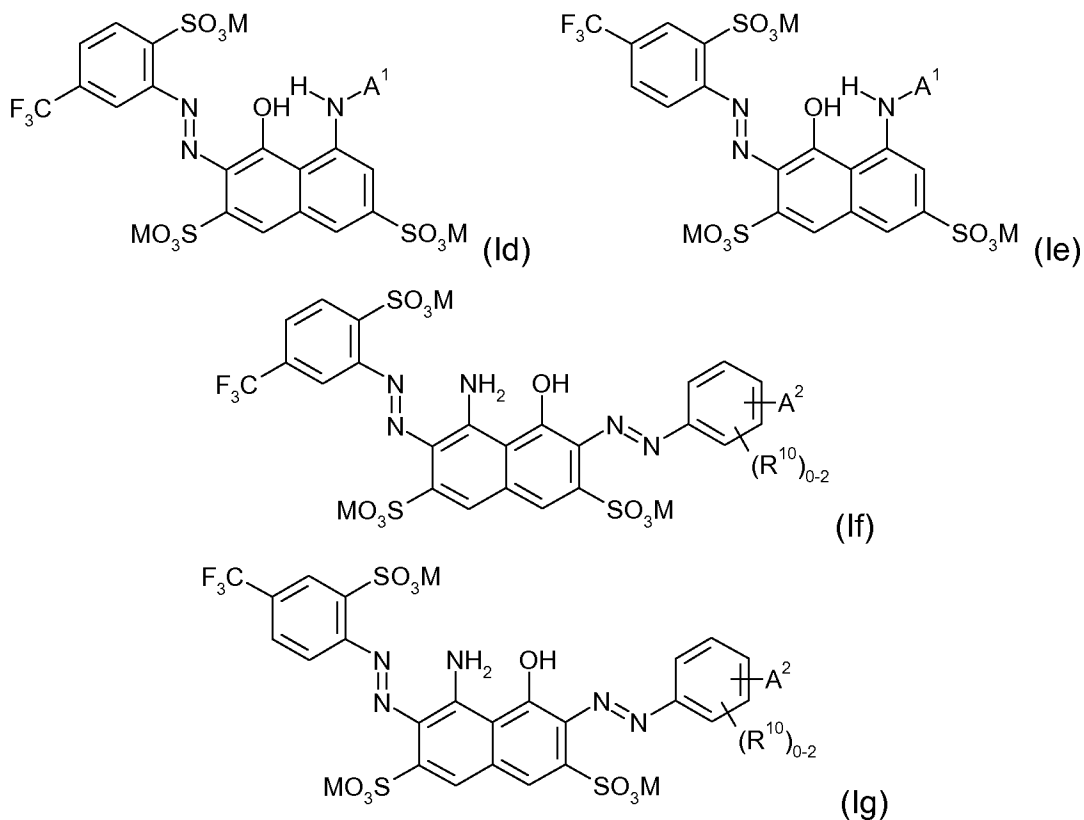


wherein X, RG and M are defined as given above.

10 Especially preferred dyestuffs of the formula (I) correspond to the formulae (Ia) to (Ic), wherein X, RG and M have preferred meanings as defined above.

Exceptionally preferred dyestuffs of the formula (I) correspond to the formulae (Ia) to (Ic), wherein X, RG and M have especially preferred meanings as defined above.

15 Accordingly, exceptionally preferred dyestuffs of the formula (I) are for example the dyestuffs of the formulae (Id) to (Ig)



wherein

A¹ is a group of the formula (III_f), (III_g), (III_h) or (III_i);

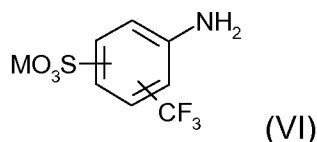
A² is a group of the formula (III_d) or (III_e);

R¹⁰ is methyl, methoxy or -SO₃M; and

5 M is defined as given above.

The dyestuffs of the formula (I) can be prepared by synthesis steps which are known to a skilled person.

In a preferred method, a compound of the formula (VI)



wherein M is defined as given above,

is diazotized and coupled onto a compound of the formula (VII)



wherein X and RG are defined as given above.

The compounds of formula (VI) are known and can be prepared in line with the teachings given in DE 629257. The compounds of formula (VII) are known as well and can be prepared by known methods.

The present invention's dyes of the formula (I) have useful application properties and can be used for dyeing and printing carboxamido- and/or hydroxyl-containing materials. The materials mentioned can be present for example in the form of sheetlike constructions such as paper and leather, in the form of films, as for example polyamide films, or in the form of a bulk composition, for example composed of polyamide or polyurethane. In particular, however, they are present in the form of fibres of the materials mentioned.

Thus, the present invention's dyes of the formula (I) are used for dyeing and printing cellulosic fibrous materials of any kind. They are preferably also useful for dyeing or printing polyamide fibres or of blend fabrics of polyamide with cotton or with polyester fibres.

It is also possible to use the present invention's dyes of the formula (I) to print textiles or paper by the ink jet process.

The present invention thus also provides for the use of the present invention's dyes of the formula (I) for dyeing or printing carboxamido- and/or hydroxyl-containing materials, or as the case may be for processes for dyeing or printing such materials in a conventional manner wherein one or more dyes of the formula (I) according to
5 the present invention are utilized as a colorant.

Advantageously, the as-synthesized solutions of the present invention's dyes of the formula (I), if appropriate after addition of a buffer substance, and if appropriate also after concentrating or diluting, can be directly used for dyeing as a liquid preparation.

10 Fibrous materials or fibres herein refers in particular to textile fibers which can be present as wovens, yarns or in the form of hanks or wound packages.

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

Hydroxyl-containing materials are those of natural or synthetic origin, for example cellulosic fibre materials or their regenerated products and polyvinyl alcohols.

Cellulosic fibre materials are preferably cotton, but also other vegetable fibres, such
20 as linen, hemp, jute and ramie fibers. Regenerated fibres of cellulose are for example staple viscose and filament viscose.

The present invention's dyes of the formula (I) can be applied to and fixed on the materials mentioned, in particular on the fibrous materials mentioned, by the
25 application techniques known for water-soluble dyes, in particular known for fibre-reactive dyes.

Wool which has been given a nonfelting or low-felting finish (cf. for example H. Rath, Lehrbuch der Textilchemie, Springer-Verlag, 3rd edition (1972), pp. 295-299, in
30 particular the finish by the so-called 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 is here carried out in a conventional manner from an acidic medium. For instance, acetic acid and/or ammonium sulfate or acetic acid and ammonium acetate or sodium acetate may be added to the dyebath

to obtain the desired pH. To obtain a dyeing of acceptable levelness, it is advisable to add a customary leveling agent, for example on the basis of a reaction product of cyanuric chloride with 3 times the molar amount of an aminobenzenesulfonic acid and/or of an aminonaphthalenesulfonic acid or on the basis of a reaction product of for example stearylamine with ethylene oxide. For instance, the dyes of the present invention are preferably subjected to the exhaust process initially from an acidic dyebath having a pH of about 3.5 to 5.5 under pH control and the pH is then, toward the end of the dyeing time, shifted into the neutral and optionally weakly alkaline range up to a pH of 8.5 to bring about, especially for very deep shades, the full reactive bond between the dyes of the present invention and the fibre. At the same time, the dye portion not reactively bound is removed.

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

The dyeing liquors and print pastes, as well as the dyes of the formula (I) may contain further additions. Additions are for example wetting agents, antifoam agents, leveling agents and agents which influence the properties of the textile material, such as softeners, additions for a flameproof finish and soil-, water- and oil-rejecting or water-softening agents. Print pastes in particular may also contain natural or synthetic thickeners, such as for example alginates and cellulose ethers. The dye quantities in the dyebaths and print pastes can vary within wide limits according to the desired depth of shade. Generally, the dyes of the formula (I) are present in amounts of 0.01% to 15% by weight and in particular in amounts of 0.1% to 10% by weight based respectively on the material to be dyed and on the print paste.

30

On cellulose fibres they produce by the exhaust method from a long liquor using a wide variety of acid-binding agents and if appropriate neutral salts, such as sodium chloride or sodium sulfate, dyeings having very good color yields. Application of the dye is preferably at a pH of 3 to 7, and in particular at a pH of 4 to 6 for the exhausts

method. The liquor ratio can be chosen within a wide range and is for example between 3:1 and 50:1, preferably between 5:1 and 30:1. Dyeing is preferably carried out in an aqueous bath at temperatures between 40 and 105°C, if appropriate at a temperature of up to 130°C under pressure, and if appropriate in the presence of customary dyeing auxiliaries. To increase the wetfastnesses of the dyed material, unfixed dye can be removed in an aftertreatment. This aftertreatment is carried out in particular at a pH of 8 to 9 and temperatures of 75 to 80°C.

One possible procedure here is to introduce the material into the warm bath and to gradually heat the bath to the desired temperature and complete the dyeing process at that temperature. The neutral salts which accelerate the exhaustion of the dyes may also if desired only be added to the bath after the actual dyeing temperature has been reached.

Padding processes likewise provide excellent color yields and a very good color buildup on cellulose fibres, the dyes being fixable in a conventional manner by batching at room temperature or elevated temperature, for example at up to about 60°C, by steaming or using dry heat.

Similarly, the customary printing processes for cellulose fibers, which can be carried out in one step, for example by printing with a print paste containing sodium bicarbonate or some other acid-binding agent and by subsequent steaming at 100 to 103°C, or in two steps, for example by printing with a neutral or weakly acidic print color and then fixing either by passing the printed material 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, produce strong color prints with well-defined contours and a clear white ground. The outcome of the prints is affected by variations in the fixing conditions.

When fixing by means of dry heat in accordance with the customary thermofix processes, hot air at 120 to 200°C is used. In addition to the customary steam at 101 to 103°C, it is also possible to use superheated steam and high-pressure steam at temperatures of up to 160°C.

The acid-binding agents which effect the fixation of the dyes on the cellulose fibers are for example water-soluble basic salts of alkali metals and likewise alkaline earth metals of inorganic or organic acids or compounds which liberate alkali in the heat. Especially suitable are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids, the preferred alkali metal compounds being the sodium and potassium compounds. Such acid-binding agents are for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate, disodium hydrogenphosphate, sodium trichloroacetate, waterglass or trisodium phosphate.

The present invention's dyes of the formula (I) are notable for high reactivity, good fixing ability, very good build-up ability and also high light and perspiration light fastness. They can therefore be applied by the exhaust dyeing process at low dyeing temperatures and require only short steam times in the pad-steam process. The degrees of fixation are high and unfixed portions are readily washed off with the difference between the degree of exhaustion and the degree of fixation being remarkably small, i.e., the loss on soaping is very low. They are also particularly useful for printing, particularly on cotton, but also for printing nitrogenous fibers, for example wool or silk or blend fabrics containing wool or silk.

The present invention's dyes of the formula (I) are notable for unfixed portions of dye being readily washed off the fibrous material after the dyeing operation without whites included in the washing operation being stained or tainted by the dye which comes off. This results in advantages for the dyeing operation, in which washing cycles and hence costs are saved.

The dyeings and prints produced using the present invention's dyes of the formula (I) possess a high color strength and a high fibre-dye bond stability not only in the acidic region but also in the alkaline region, and also good light fastness and very good wet fastness properties, such as wash, water, seawater, cross-dyeing and perspiration fastnesses and also good fastness to pleating, hotpressing and crocking.

The present invention also provides inks for digital textile printing by the ink jet process, the inks comprising a present invention's dye of the formula (I).

The present invention's inks contain one or more of the present invention's dyes of the formula (I), for example in amounts from 0.1% by weight to 50% by weight, preferably in amounts from 1% by weight to 30% by weight and more preferably in amounts from 1% by weight to 15% by weight, based on the total weight of the ink.

- 5 For the inks to be used in the continuous flow process, a conductivity of 0.5 to 25 mS/m can be set by adding an electrolyte. Useful electrolytes include for example lithium nitrate and potassium nitrate. The inks of the present invention may include organic solvents at a total level of 1-50% and preferably 5-30% by weight. Suitable organic solvents are for example alcohols, for example methanol, ethanol, 1-
10 propanol, isopropanol, 1-butanol, tert-butanol, pentyl alcohol, polyhydric alcohols for example: 1,2-ethanediol, 1,2,3-propanetriol, butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-propanediol, 2,3-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, for example: polyethylene glycol, polypropylene
15 glycol, alkylene glycols having 2 to 8 alkylene groups, for example: monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, thioglycol, thiodiglycol, butyltriglycol, hexylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, low alkyl ethers of polyhydric alcohols, for example: ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl
20 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
25 ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, tripropylene glycol isopropyl ether, polyalkylene glycol ethers, such as for example: polyethylene glycol monomethyl ether, polypropylene glycol glycerol ether, polyethylene glycol tridecyl ether, polyethylene glycol nonylphenyl ether, amines, such as for example: methylamine, ethylamine, triethylamine, diethylamine,
30 dimethylamine, trimethylamine, dibutylamine, diethanolamine, triethanolamine, N-formylethanolamine, ethylenediamine, urea derivatives, such as for example: urea, thiourea, N-methylurea, N,N'-epsilon dimethylurea, ethyleneurea, 1,1,3,3-tetramethylurea, N-acetyethanolamine, amides, such as for example: dimethylformamide, dimethylacetamide, acetamide, ketones or keto alcohols, such

as for example: acetone, diacetone alcohol, cyclic ethers, such as for example:

tetrahydrofuran, trimethyloethane, trimethylolpropane, 2-butoxyethanol, benzyl alcohol, 2-butoxyethanol, gamma butyrolactone, epsilon-caprolactam, further sulfolane, dimethylsulfolane, methylsulfolane, 2,4-dimethylsulfolane, dimethyl

5 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, 10 2-(2-propoxyethoxy)ethanol, pyridine, piperidine, butyrolactone, trimethylpropane, 1,2-dimethoxypropane, dioxane ethyl acetate, ethylenediaminetetraacetate ethyl pentyl ether, 1,2-dimethoxypropane and trimethylpropane.

The inks of the invention may further include customary additives, for example viscosity moderators to set viscosities in the range from 1.5 to 40.0 mPas in a 15 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.

Useful viscosity moderators include rheological additives, for example polyvinylcaprolactam, polyvinylpyrrolidone and their copolymers polyetherpolyol, 20 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 to set surface tensions of 20 to 65 mN/m, which are adapted if necessary as a 25 function of the process used (thermal or piezo technology). Useful surface-active substances include for example all surfactants, preferably nonionic surfactants, butyldiglycol and 1,2-hexanediol.

The inks may further include customary additives, for example substances to inhibit 30 fungal and bacterial growth in amounts from 0.01 to 1% by weight based on the total weight of the ink.

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

The inks of the invention are particularly useful in inkjet printing processes for printing a wide variety of pretreated materials, such as silk, leather, wool, cellulosic fibre materials of any kind, polyurethanes and polyamide fibres. The printing inks of the invention are also suitable for printing pretreated hydroxyl-containing and/or amino-
5 containing fibers present in blends, examples being blends of cotton, silk, wool with polyester fibres or polyamide fibres.

In contrast to conventional textile printing, where the printing ink already contains all the fixing chemicals and thickeners for a reactive dye, in inkjet printing the auxiliaries
10 have to be applied to the textile substrate in a separate pretreatment step.

The pretreatment of the textile substrate, for example cellulose and regenerated cellulose fibres and also silk and wool, is effected with an aqueous alkaline liquor prior to printing. To fix reactive dyes there is a need for alkali, for example sodium
15 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, for example sodium nitrobenzenesulfonates, and also thickeners to prevent flowing of the motives when the printing ink is applied, for example sodium
20 alginates, modified polyacrylates or highly etherified galactomannans.

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

After printing, the textile fiber material is dried at 120 to 150°C and subsequently fixed.

The fixing of the inkjet prints prepared with reactive dyes may be effected at room
30 temperature or with saturated steam, with superheated steam, with hot air, with microwaves, with infrared radiation, with laser or electron beams or with other suitable energy transfer techniques.

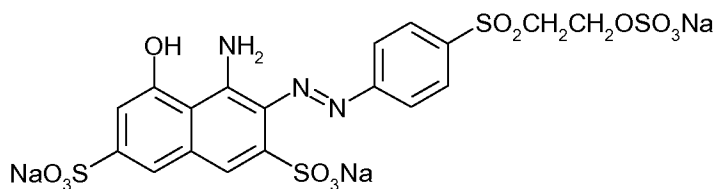
A distinction is made between one- and two-phase fixing processes. In one-phase fixing, the necessary fixing chemicals are already on the textile substrate. In two-phase fixing, this pretreatment is unnecessary. Fixing only requires alkali, which, following inkjet printing, is applied prior to the fixing process, without intermediate drying. There is no need for further additives such as urea or thickener.

Fixing is followed by the print aftertreatment, which is the prerequisite for good fastnesses, high brilliance and an impeccable white ground.

The prints produced with the inks of the present invention possess high color strength and a high fiber-dye bond stability not only in the acidic but also in the alkaline region, also good lightfastness and very good wet fastness properties such as fastness to washing, water, seawater, crossdyeing and perspiration, and also good fastness to pleating, hotpressing and crocking.

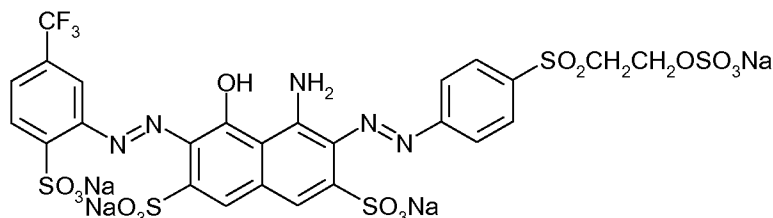
Example 1

2-Amino-4-trifluoromethylbenzenesulphonic acid (3.29g, 0.014mol) was added to water (50mls) with stirring and the pH adjusted to 7.0 with 10% sodium carbonate solution to effect solution. Sodium nitrite (1.1g, 0.016mol) was added to the solution and after 10mins stirring the solution was added dropwise to a stirred mixture of ice (100g) and conc. HCl (15mls) ensuring the temperature remained $<5^{\circ}\text{C}$ by the use of external cooling. After a further 30mins the diazotization was complete and the excess nitrite was destroyed by the addition of sulphamic acid. The monoazo dye of the formula



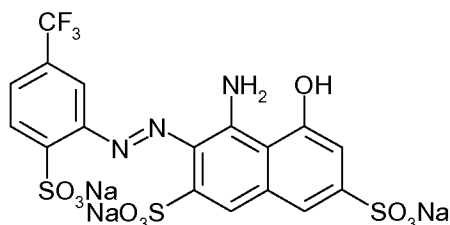
(12.09g, 0.014mol) prepared according to the art was dissolved in water (150mls) before adding the solution of the diazonium salt portionwise over 15mins maintaining the pH at 5.0-6.0 throughout *via* the addition of 2N sodium carbonate solution. After stirring for a further hour, the reaction mixture was dialysed to remove salt before evaporation *in vacuo* to give the expected product as a dark solid (20.02g) which

exhibited analytical data consistent with the expected structure λ_{max} 592nm ϵ_{max} 38900.

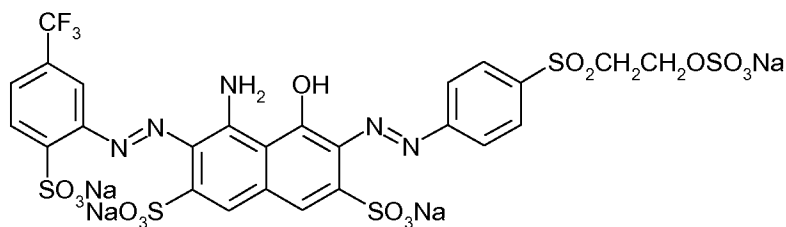


5 Example 2

a) 2-Amino-4-trifluoromethylbenzenesulphonic acid (5.0g, 0.02mol) was added to water (100mls) with stirring and the pH adjusted to 6.0 with sodium bicarbonate solution to effect solution. Sodium nitrite (1.4g, 0.02mol) was added to the solution and after 10mins stirring the solution was added dropwise to a stirred mixture of ice (25g), water (25g) and conc. HCl (15mls) ensuring the temperature remained $<5^{\circ}\text{C}$ by the use of external cooling. After a further 30mins the diazotization was complete and the excess nitrite was destroyed by the addition of sulphamic acid before adding H-acid (8.09g, 0.02mol) and stirring while the pH was raised and held at 2.0 by the addition of sodium bicarbonate. After 2hrs the temperature had reached ambient and chromatography showed the coupling to be complete. The dye obtained has the formula



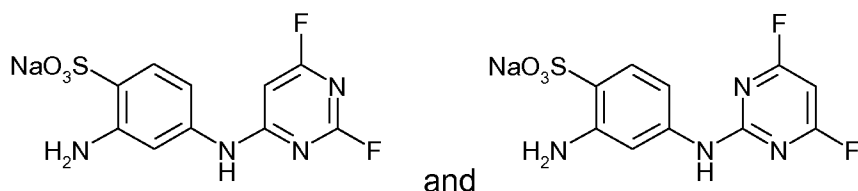
b) To the solution according to step a) above was added a cold suspension of the diazonium salt of 4-sulphatoethylsulphonylaniline (0.02mol) portionwise before adjusting the pH to 4.0 with sodium bicarbonate. The mixture was then allowed to warm to ambient temperature overnight holding the pH at 4.0. The solution was then concentrated *in vacuo* before precipitating the product by the controlled addition of methylated spirits. The solid was isolated by filtration and dried in a fan oven at 40°C to give the expected product as a dark solid (30.5g) which exhibited analytical data consistent with the expected product λ_{max} 601nm ϵ_{max} 45000.



Example 3

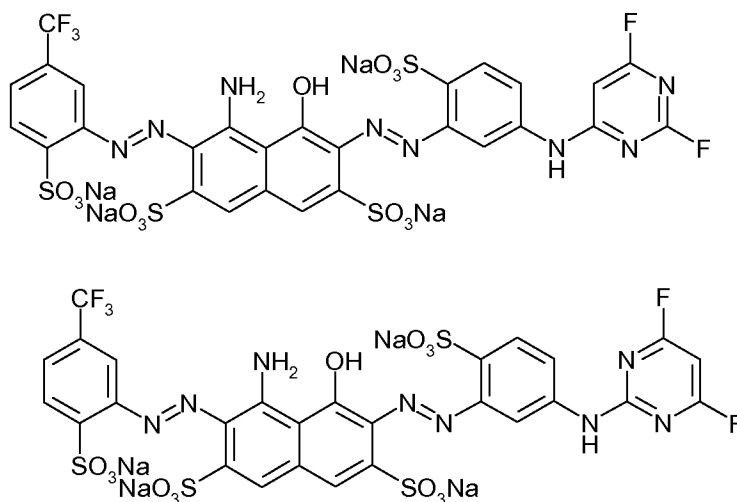
a) The dye according to Example 2a) was isolated before determining its strength by combustion analysis.

b) A mixture of sulphonated anilines of the formulae



is prepared according to the art by the condensation of 2,4,6-trifluoropyrimidine and 2,4-diaminobenzenesulphonic acid and consists of an approximate 2:1 mixture of the positional isomers indicated.

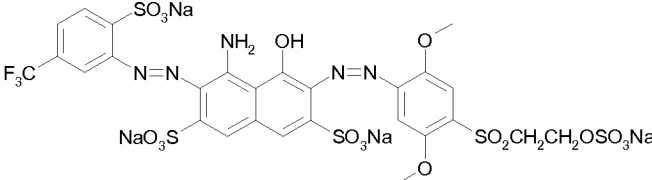
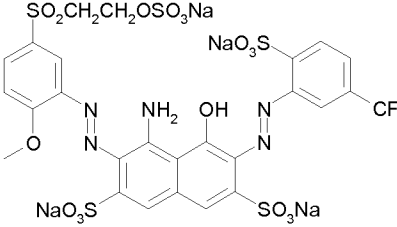
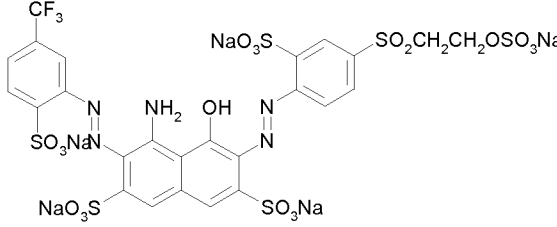
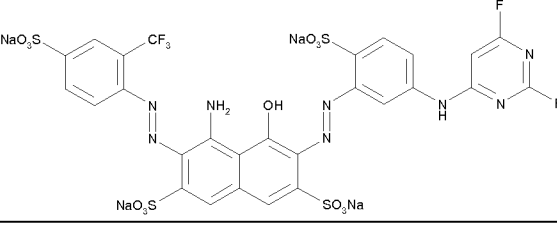
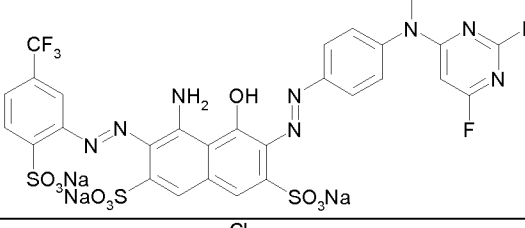
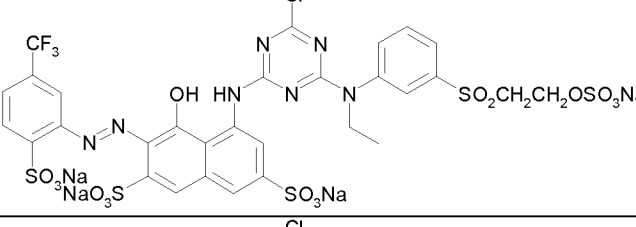
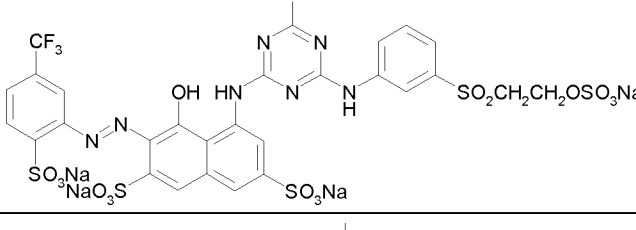
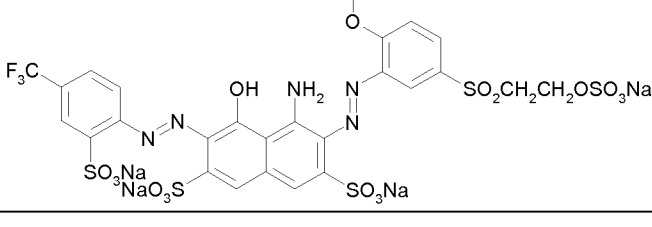
c) The mixture of sulphonated anilines according to step b) above (53.45g, 0.70mol) was dissolved in water (200mls) at pH 6.0 by the addition of 10% aqueous sodium bicarbonate solution. To this solution was added sodium nitrite (4.82g, 0.70mol) and the mixture stirred for 10minutes. This solution was then added dropwise to a stirred mixture of ice (50g) and conc. HCl (80mls) ensuring the temperature remained $<5^{\circ}\text{C}$ by the use of external cooling. After a further 30mins the diazotization was complete and the excess nitrite was destroyed by the addition of sulphamic acid before adding the dye according to step a) above (60.0g, 0.58mol) as a solid and stirring while the pH was raised and held at 6.0 by the addition of sodium bicarbonate. After stirring overnight at ambient temperature the product had precipitated and was isolated by filtration before drying in a fan oven at 40°C to give a dark solid (36.6g) which exhibited analytical data consistent with the expected mixture of isomeric products. λ_{max} 607nm ϵ_{max} 50250.

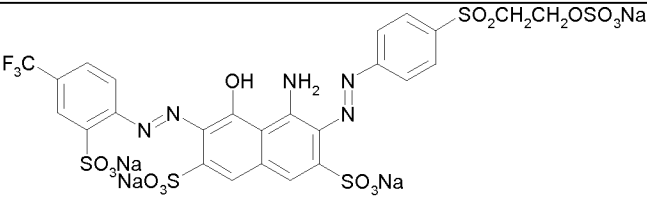
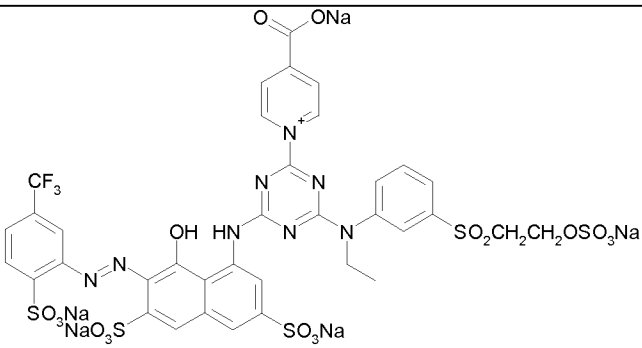
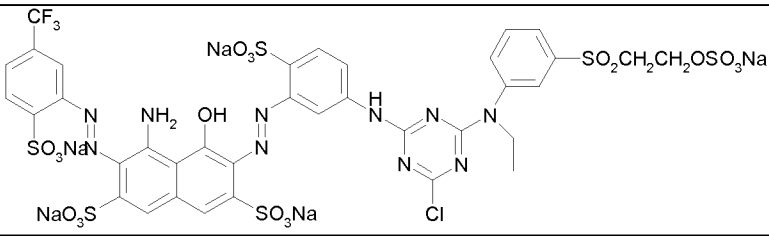
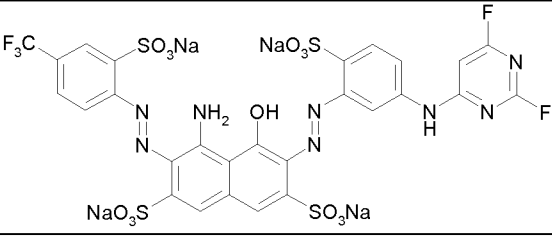
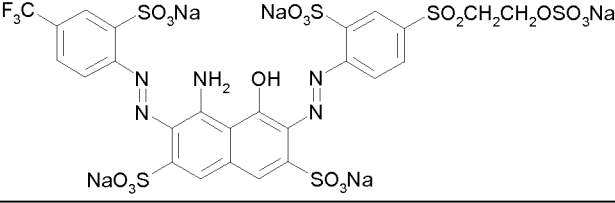
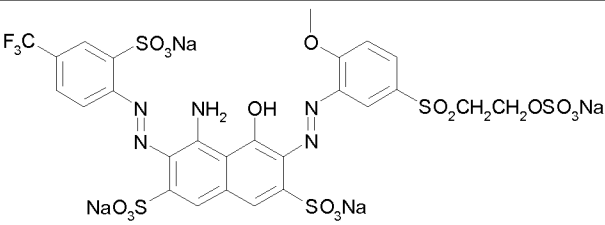
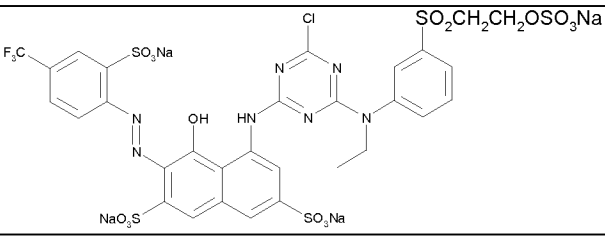


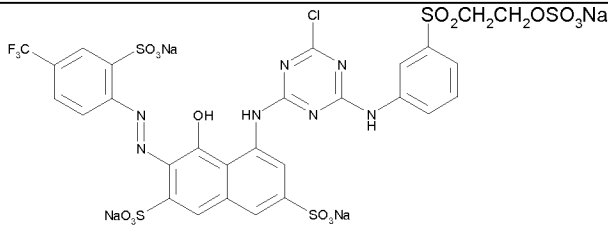
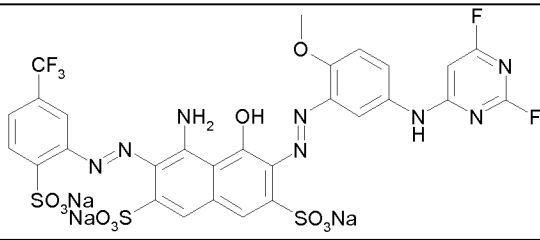
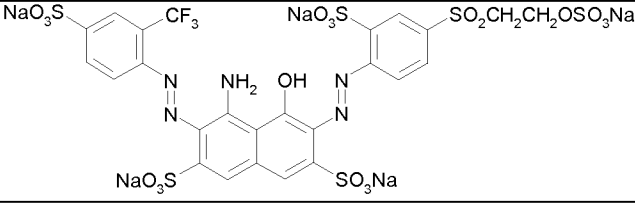
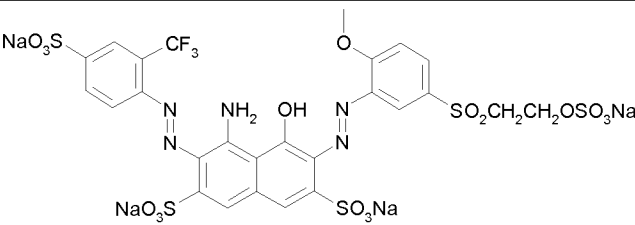
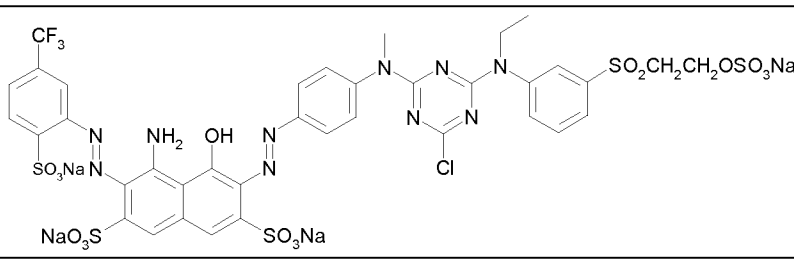
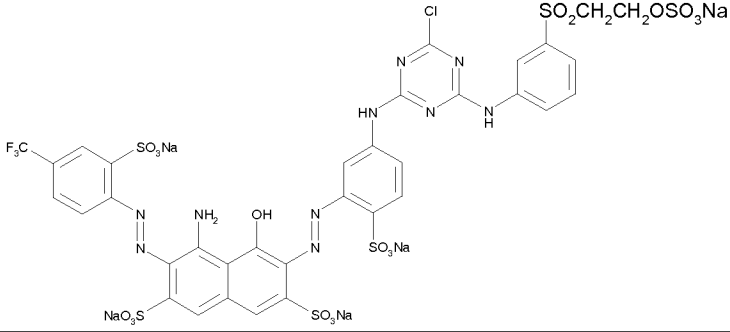
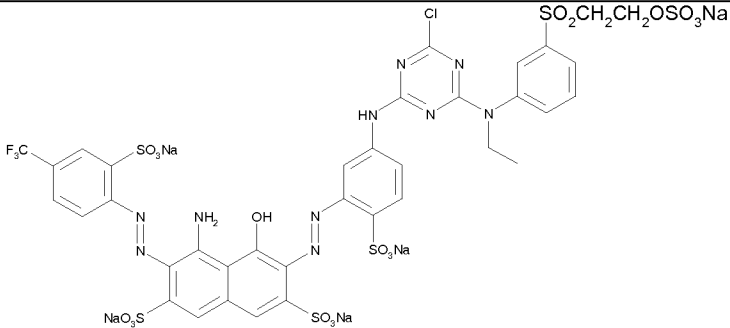
Examples 4 to 43

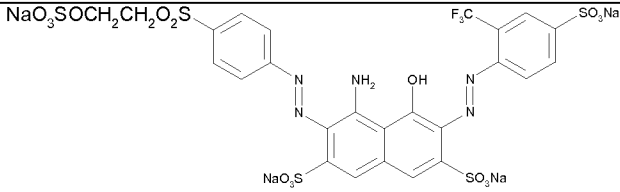
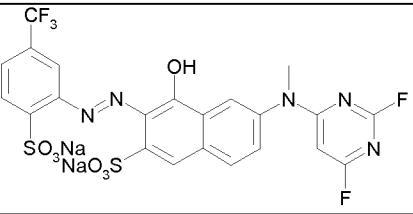
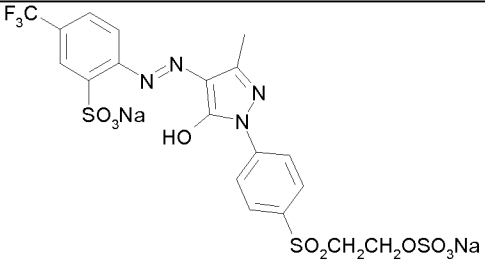
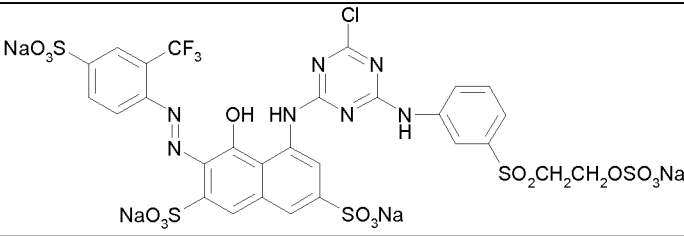
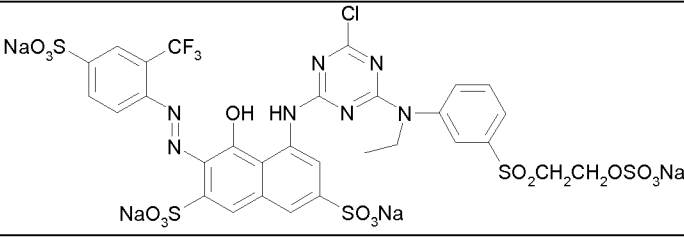
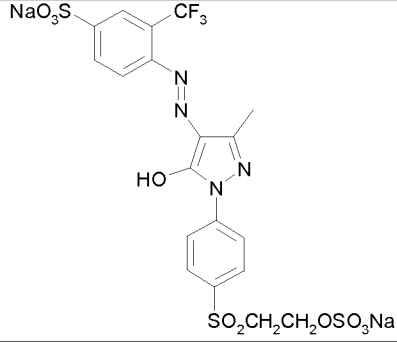
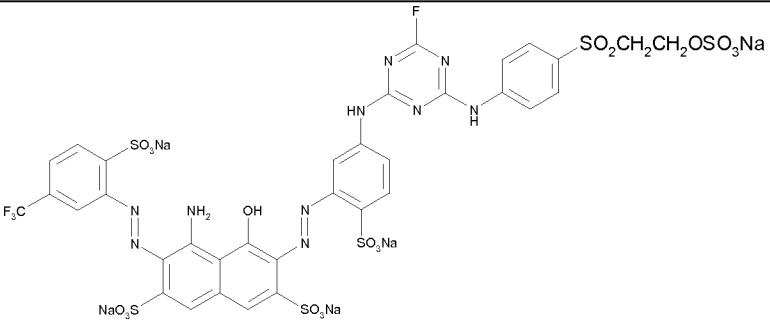
- 5 The dyestuffs according to Examples 4 to 43 were prepared in line with the methods described in Examples 1 to 3

	Structure	$\lambda_{\max}$
4		603nm
5		613nm
6		628nm
7		613nm
8		621nm

9		631nm
10		594nm
11		599nm
12		608nm
13		619nm
14		512nm
15		512nm
16		595nm

17		594nm
18		515nm
19		609nm
20		612nm
21		603nm
22		625nm
23		514nm

24		512nm
25		609nm
26		600nm
27		620nm
28		625nm
29		614nm
30		613nm

31		596nm
32		484nm
33		383nm
34		515nm
35		516nm
36		386nm
37		611nm

38		612nm
39		613nm
40		472nm
41		416nm
42		407nm
43		383nm

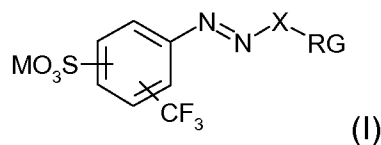
44		502nm
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Example 45

- A textile fabric consisting of mercerized cotton is padded with a liquor containing 35 g/l of anhydrous sodium carbonate, 100 g/l of urea and 150 g/l of a low viscosity sodium alginate solution (6%) and then dried. The wet pick-up is 70%.
- The textile thus pretreated is printed with an aqueous ink containing 2% of the dye obtained according to Example 1, 20% of sulfolane, 0.01% of Mergal K9N and 77.99% of water using a drop-on-demand (bubble jet) ink jet print head. The print is fully dried. Fixation is effected by means of saturated steam at 102°C for 8 minutes.
- The print is subsequently rinsed warm, subjected to a fastness wash with hot water at 95°C, rinsed warm and then dried to obtain a print having excellent service fastnesses.

Patent Claims

1. Dyestuff of the formula (I)

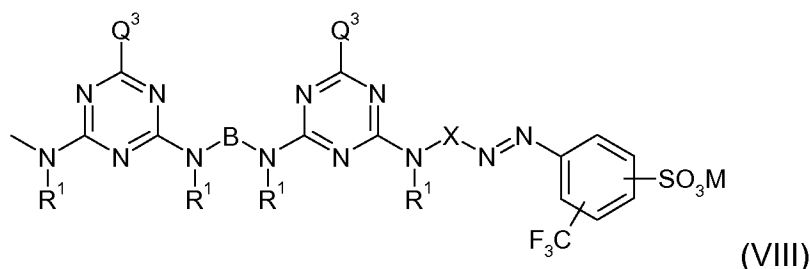


5 wherein

X is an aromatic or heteroaromatic divalent group;

RG is a reactive group capable of forming a covalent bond to cellulose under dyeing conditions or a group comprising a reactive group capable of forming a covalent bond to cellulose under dyeing conditions; or

10 is a group of the formula (VIII)



wherein

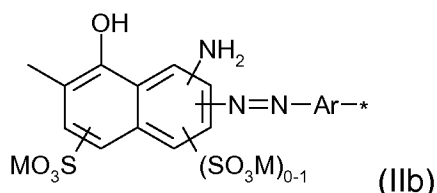
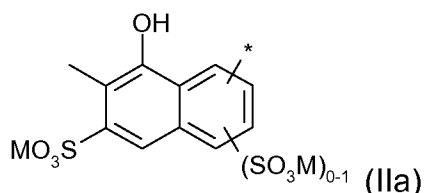
B is 1,2-phenylene, 1,3-phenylene or 1,4 phenylene, which are unsubstituted or substituted by -SO₃M, -COOM or R¹, or is (C₂-C₆)-alkylene or (C₁-C₄)-alkylene-phenylene which are unsubstituted or substituted by R¹;

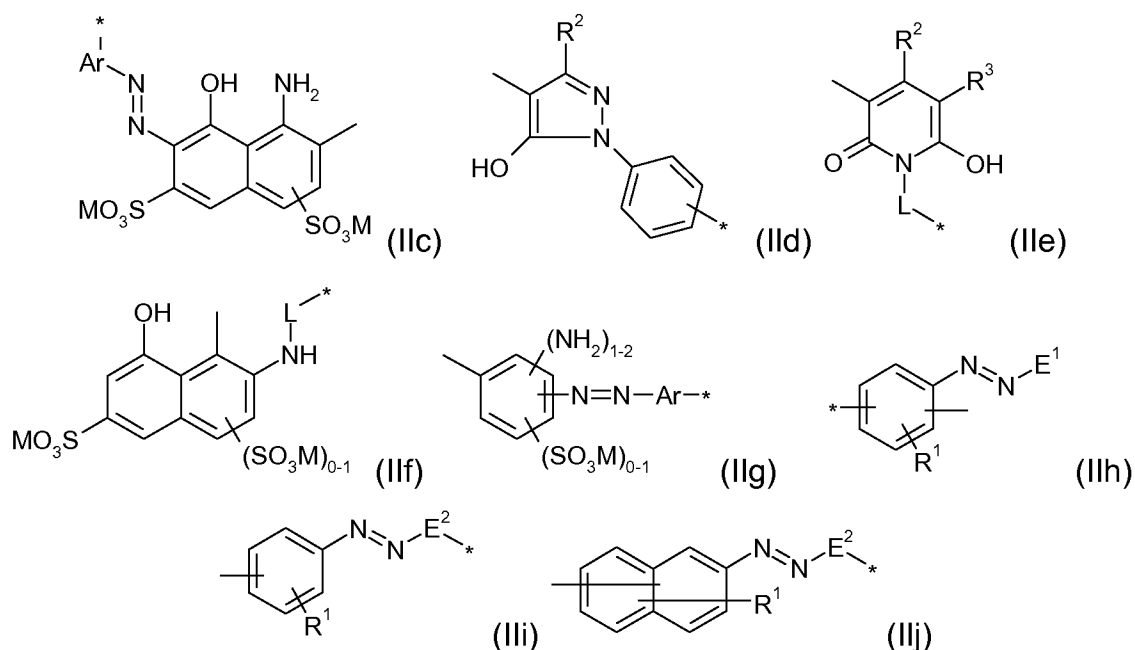
Each R¹ independently is hydrogen, (C₁-C₆)-alkyl, sulfo-(C₁-C₆)-alkyl, phenyl or phenyl substituted by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, hydroxyl, -SO₃M, halogen-, -COOM, acetamido or ureido;

Q³ is chlorine, fluorine, cyanamido, hydroxyl, (C₁-C₆)-alkoxy, phenoxy, sulfophenoxy, mercapto, (C₁-C₆)-alkylmercapto, pyridino, carboxypyridino or carbamoylpyridino; and

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

2. Dyestuff according to claim 1, wherein X is one of the formulae (IIa) to (IIj)



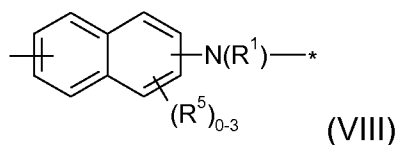


5 wherein

Ar is phenyl or phenyl which is substituted by 1, 2 or 3 substituents selected from the group comprising (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy and -SO₃M;

E¹ has one of the meanings of Ar, is naphthyl or naphthyl which is substituted by 1, 2 or 3 substituents selected from the group comprising (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, -SO₃M, amino, acetylamino or hydroxy; or is a 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, or is a 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, which is substituted by 1, 2 or 3 substituents selected from the group comprising (C₁-C₄)-alkyl and (C₁-C₄)-alkoxy;

E² is phenylene or naphthylene which are unsubstituted or substituted by 1, 2 or 3 substituents selected from the group comprising (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy -SO₃M, amino, acetylamino or hydroxy; or is a divalent 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, or is a divalent 5- or 6-membered heterocyclic residue comprising one or two heteroatoms, selected from the group comprising nitrogen, oxygen and sulphur, which is substituted by 1, 2 or 3 substituents selected from the group comprising (C₁-C₄)-alkyl and (C₁-C₄)-alkoxy; or is a group of the formula (VIII)



wherein

R^5 is (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy -SO₃M or hydroxy;

R^1 is defined as given in claim 1;

5 R^2 is (C₁-C₄)-alkyl or -COOM;

R^3 is hydrogen, CN or -CONH₂;

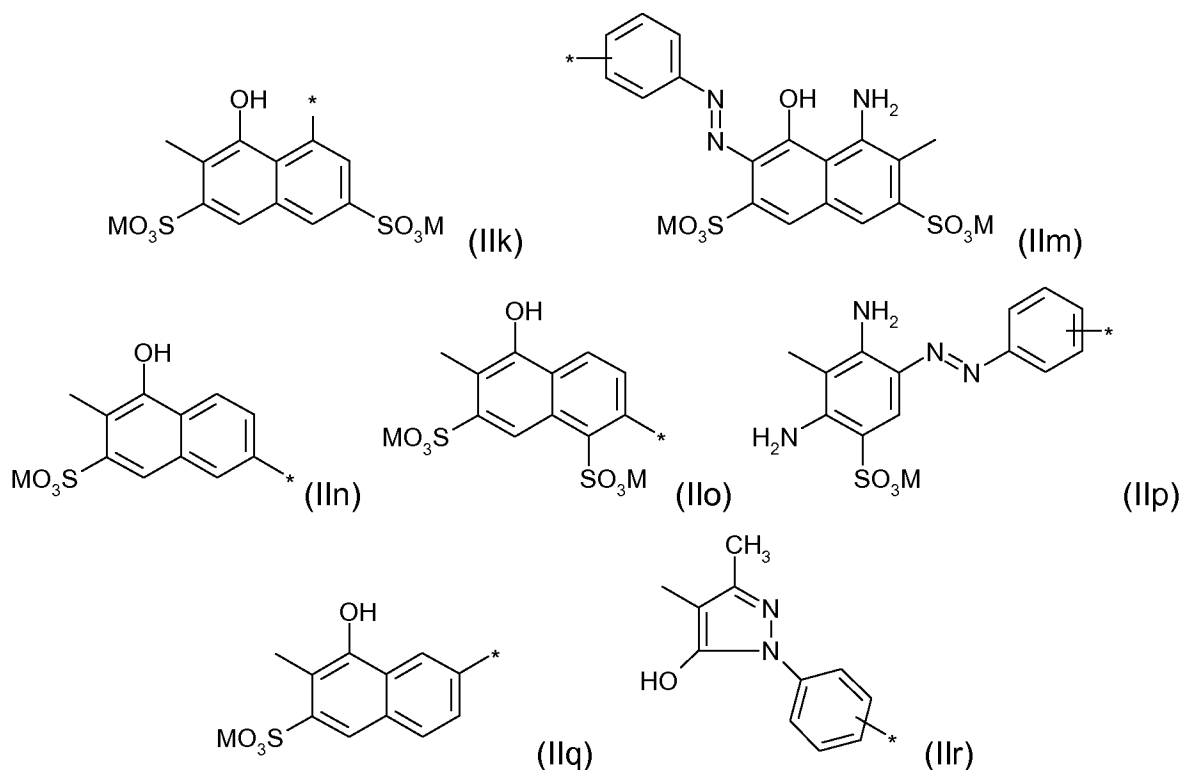
L has one of the meanings of B;

M is defined as given in claim 1; and

* is the bond to the group RG.

10

3. Dyestuff according to claim 2, wherein X corresponds to one of the formulae (IIk) to (IIr)

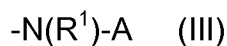


15

wherein M and * are defined as given in claim 1.

4. Dyestuff according to one or more of claims 1 to 3, wherein RG is -SO₂-CH=CH₂,

20 -SO₂-CH₂CH₂Z¹ or a group of the formula (III)

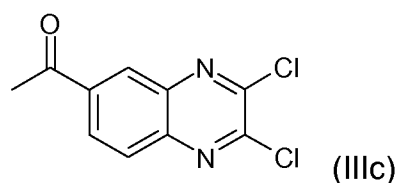
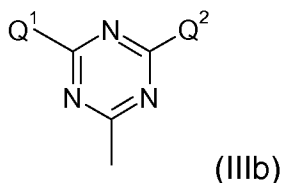
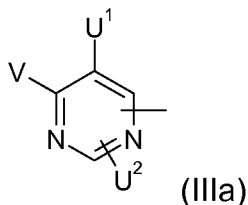


wherein

Z^1 is an alkali-eliminatable group;

R^1 is defined as given above;

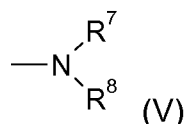
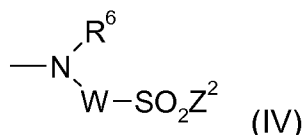
5 A is a group of the formula (IIIa), (IIIb) or (IIIc)



V is fluorine or chlorine;

U^1 and U^2 are independently fluorine, chlorine or hydrogen; and

10 Q^1 and Q^2 are independently chlorine, fluorine, cyanamido, hydroxyl, (C_1-C_6) -alkoxy, phenoxy, sulfophenoxy, mercapto, (C_1-C_6) -alkylmercapto, pyridino, carboxypyridino, carbamoylpyridino or a group of the formula (IV) or (V)



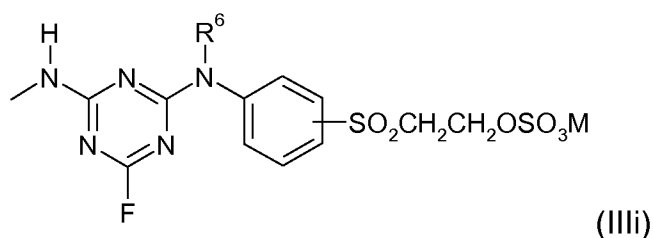
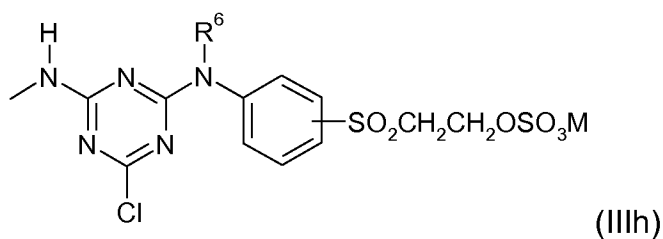
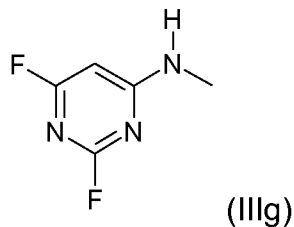
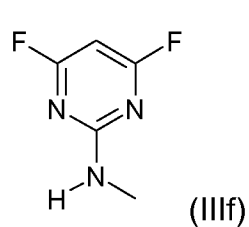
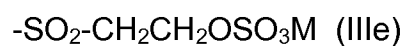
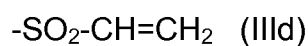
where

R^6 has one of the meanings of R^1 ;

15 R^7 and R^8 independently have one of the meanings of R^1 or combine to form a group of the formula $-(CH_2)_j-$ or of the formula $-(CH_2)_2-B^1-(CH_2)_2-$, where j is 4 or 5, B^1 is oxygen, sulfur, sulfonyl or $-NR^9-$ and R^9 is (C_1-C_6) -alkyl;

W is phenylene which is unsubstituted or substituted by 1 or 2 substituents selected from the group consisting of (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, carboxyl, sulfo, chlorine and bromine, or is (C_1-C_4) -alkylenephénylene, (C_2-C_6) -alkylene, which may be
20 interrupted by oxygen, sulfur, sulfonyl, amino, carbonyl or carboxamido, or is phenylene CONH phenylene which is unsubstituted or substituted by 1 or 2 substituents selected from the group consisting of (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, hydroxyl, sulfo, carboxyl, amido, ureido and halogen, or is naphthylene which is
25 unsubstituted or substituted by one or two sulfo groups; and
 Z^2 is $-CH=CH_2$ or $-CH_2CH_2Z^1$.

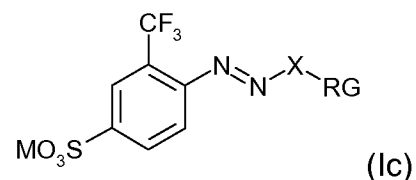
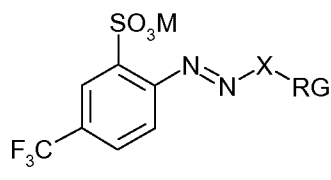
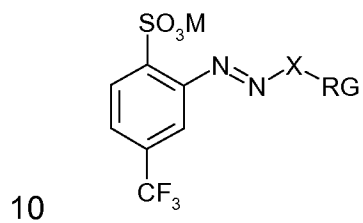
5. Dyestuff according to claim 4, wherein RG is one of the groups of the formulae (IIIId) to (IIIi)



5

wherein R^6 is defined as given in claim 3 and M is defined as given in claim 1.

6. Dyestuff according to one or more of claims 1 to 5, which corresponds to one of the formulae (Ia) to (Ic)

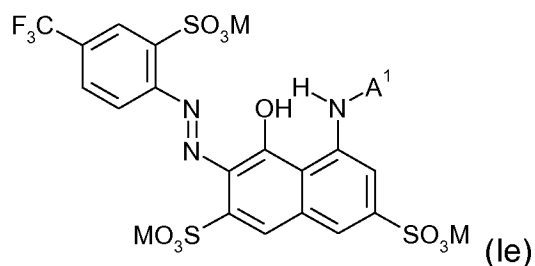
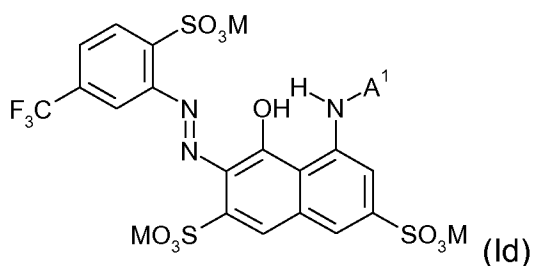


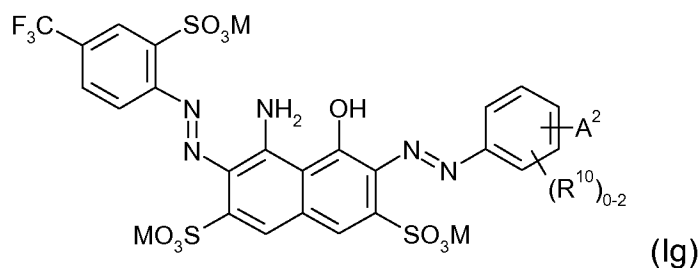
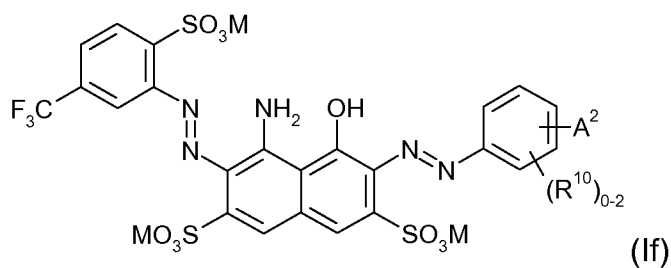
10

wherein X, RG and M are defined as given in claim 1.

7. Dyestuff according to one or more of claims 1 to 6, which corresponds to one of the formulae (Id) to (Ig)

15





wherein

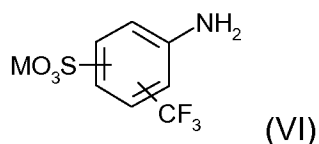
A¹ is a group of the formula (III f), (III g), (III h) or (III i);

5 A² is a group of the formula (III d) or (III e);

R¹⁰ is methyl, methoxy or -SO₃M; and

M is defined as given in claim 1.

8. Method for the preparation of a dyestuff of formula (I) according to claim 1, wherein
10 a compound of the formula (VI)



wherein M is defined is given in claim 1,

is diazotized and coupled onto a compound of the formula (VII)

-X-RG (VII)

15 wherein X and RG are defined as given in claim 1.

9. The use of a dye of the formula (I) according to claim 1 for dyeing or printing carboxamido- and/or hydroxyl-containing materials.

20 10. An ink for digital textile printing by the ink jet process, comprising a dye of the formula (I) according to claim 1.