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Reactive dyes, process for their preparation and the use thereof

The present invention relates to novel reactive dyes, to a process for their preparation and to the use thereof.

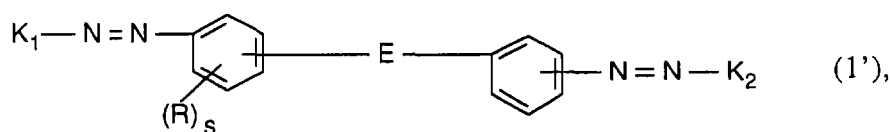
The practice of dyeing with reactive dyes in recent years has led to more exacting demands being made of the quality of the dyeings obtained and to the efficiency of the dying process. Consequently there is a continuing need to provide novel reactive dyes that have enhanced properties, especially with respect to application.

At the present time it is required of reactive dyes that they shall have sufficient substantivity for the substrate to be dyed and at the same time have the property that unfixed dye is easily washed off. They are further required to afford a good tinctorial yield and have high reactivity to give in particular dyeings of good fixation. The known dyes do not meet these requirements in all respects.

It is therefore the object of this invention to provide novel, improved reactive dyes for dyeing and printing fibre materials that have the qualities referred to above to a high degree. The novel dyes shall in particular be distinguished by high fixation yields and high fibre-bond stability, and it shall furthermore be possible to wash-off unfixed dye in the fibre with ease. The novel dyes shall also produce dyeings with good allround fastness properties, preferably light- and wetfastness properties.

It has been found that this object is substantially achieved with the novel reactive dyes defined below.

The invention relates to compounds of formula

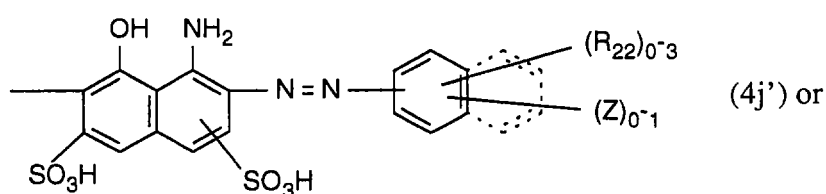
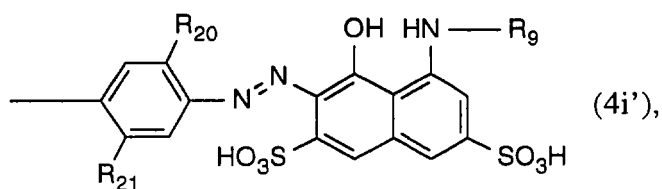
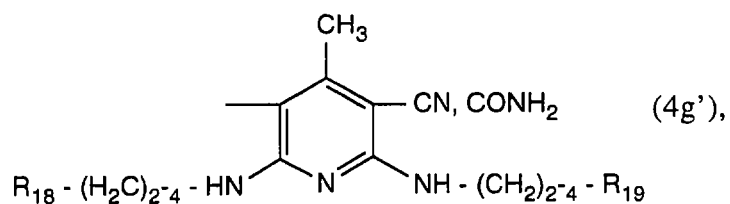
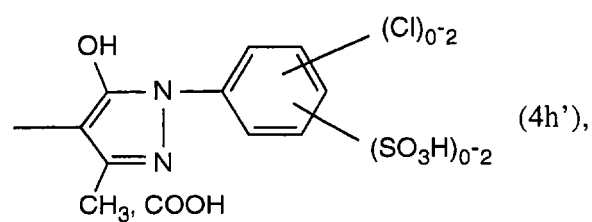
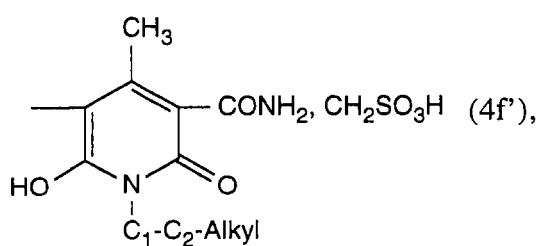
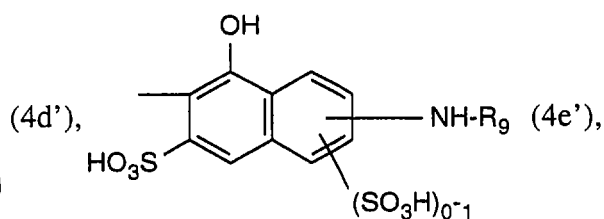
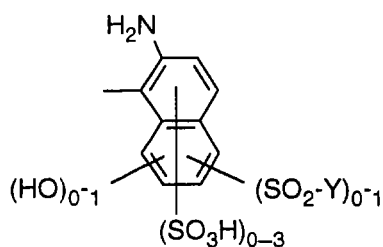
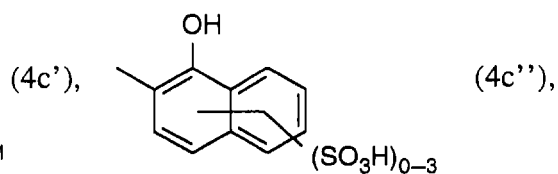
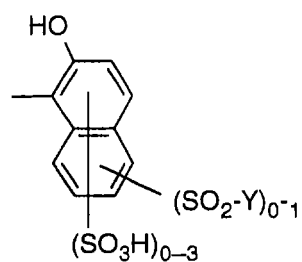


wherein E is the -NH-CO-, -NH-SO₂- or -SO₂-NH-SO₂- group,

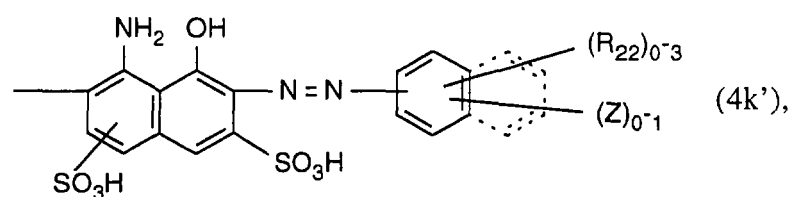
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(R)_s denotes s identical or different substituents selected from the group consisting of sulfo, hydroxy, C₁-C₄alkyl, C₁-C₄alkoxy, halogen and cyano, and s is 0, 1 or 2,

K₁ and K₂ are each independently of the other a radical of the formula



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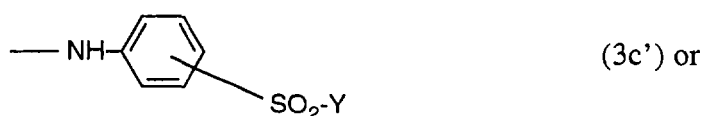


wherein R_9 is acetyl, benzoyl or a radical of formula



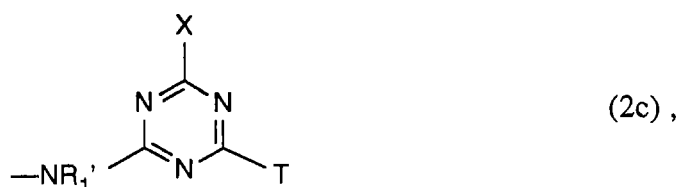
wherein X is halogen, and

T is C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy, amino, N- C_1 - C_4 alkylamino which is unsubstituted or substituted in the alkyl moiety by hydroxy, sulfato or sulfo; morpholino, phenylamino or N- C_1 - C_4 alkyl-N-phenylamino, wherein alkyl is unsubstituted or substituted by hydroxy, sulfo or sulfato, and phenyl is unsubstituted or substituted by sulfo, carboxy, acetylamino, methyl or methoxy, or T is a fibre-reactive radical of formula



R_{18} is hydrogen, hydroxy or sulfato,

R_{19} independently has the meaning of R_{18} , or is a radical of formula



wherein $R_{1'}$ is hydrogen or C_1 - C_4 alkyl and X and T are as defined above,

R_{20} and R_{21} are each independently of the other hydrogen, methyl, methoxy, 2-hydroxyethoxy, 2-sulfatoethoxy, acetylamino, propionylamino, ureido or sulfo,

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$(R_{22})_{0-3}$ is 0 to 3 identical or different radicals R_{22} selected from the group consisting of sulfo, chloro, C_1 - C_4 alkyl and C_1 - C_4 alkoxy,

Y is vinyl, β -bromoethyl or β -chloroethyl, β -acetoxyethyl, β -benzoyloxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl and, preferably, vinyl or β -sulfatoethyl,

Z is a radical of the formula



wherein R_2 is hydrogen or C_1 - C_4 -alkyl,

n is an integer from 1 to 6, and

Y is as defined above,

with the proviso that at least one of K_1 and K_2 carries a fibre-reactive group, and

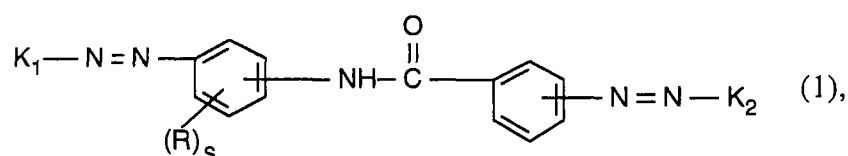
with the proviso that the compound of formula (1') contain at least one sulfo or sulfato group.

Sulfo will be understood as broadly embracing the free $-\text{SO}_3\text{H}$ acid as well as any form of salt, typically an alkali metal salt, alkaline earth metal salt or ammonium salt, or the salt of an organic amine. Typical examples are the sodium, potassium, lithium or ammonium salt, or the salt of triethanolamine.

C_1 - C_4 Alkyl is typically methyl, ethyl, n-propyl or isopropyl, or n-, iso-, sec- or tert-butyl.

C_1 - C_4 Alkoxy is typically methoxy, ethoxy, n-propoxy or isopropoxy, or n-, iso-, sec- or tert-butoxy. Methoxy or ethoxy are preferred. Halogen is typically bromo or chloro.

The novel reactive dyes are preferably those of formula



wherein K_1 , K_2 and $(R)_s$ each have the meanings given above.

R is preferably sulfo, hydroxy, methyl or methoxy. Sulfo is particularly preferred.

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s is preferably 1 or 2.

Y is preferably vinyl or β -sulfatoethyl.

R_2 is hydrogen or C_1 - C_4 alkyl, typically methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl and, preferably, hydrogen, methyl or ethyl. R_2 is most preferably hydrogen.

n is preferably 2, 3 or 4 and, more particularly, 2 or 3.

Illustrative examples of suitable non-reactive amino radicals T are amino, methylamino, ethylamino, β -hydroxyethylamino, N,N-di- β -hydroxyethylamino, β -sulfoethylamino, morpholino, o-, m- or p-methylphenylamino, o-, m- or p-methoxyphenylamino, o-, m- or p-sulfophenylamino, disulfophenylamino, o-carboxyphenylamino, N-ethyl-N-phenylamino, N-methyl-N-phenylamino, methoxy, ethoxy, n- or isopropoxy as well as hydroxy.

T in the significance of a non-reactive radical is preferably C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy, amino, N- C_1 - C_4 alkylamino which is unsubstituted or substituted in the alkyl moiety by hydroxy, sulfato or sulfo; morpholino, phenylamino or N- C_1 - C_4 alkyl-N-phenylamino in which phenyl is unsubstituted or substituted by sulfo, carboxy, acetylamino, methyl or methoxy.

Particularly preferred non-reactive radicals T are amino, N-methylamino, N-ethylamino, morpholino, phenylamino, 2-, 3- or 4-sulfophenylamino or N- C_1 - C_4 alkyl-N-phenylamino.

X is halogen, typically fluoro, chloro or bromo. Chloro or fluoro are preferred.

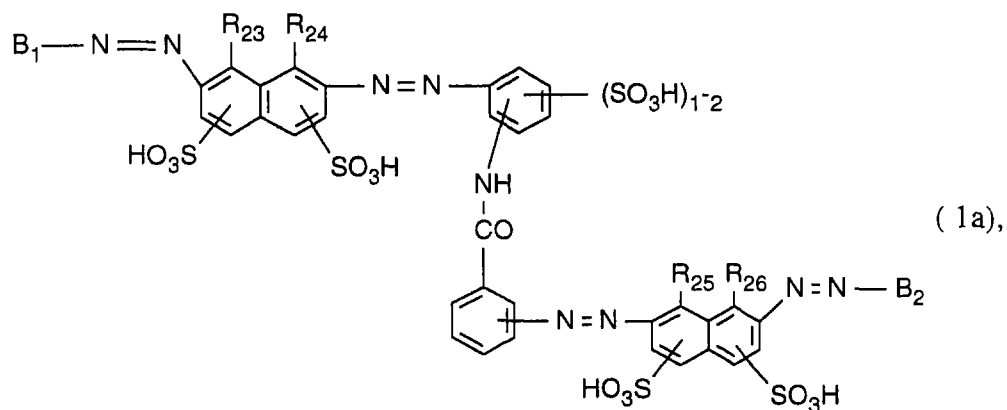
R_1' is preferably hydrogen, methyl or ethyl. Hydrogen is particularly preferred.

K_1 and K_2 are each independently of the other preferably a radical of the above formula (4j') or (4k').

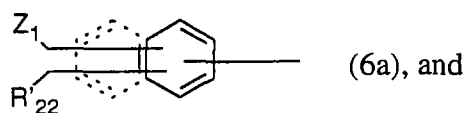
K_1 and K_2 may be different or, preferably, identical.

A preferred embodiment of this invention relates to compounds of formula

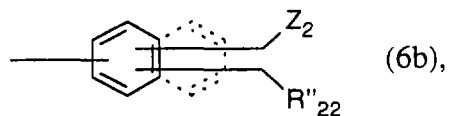
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wherein B_1 is a radical of formula

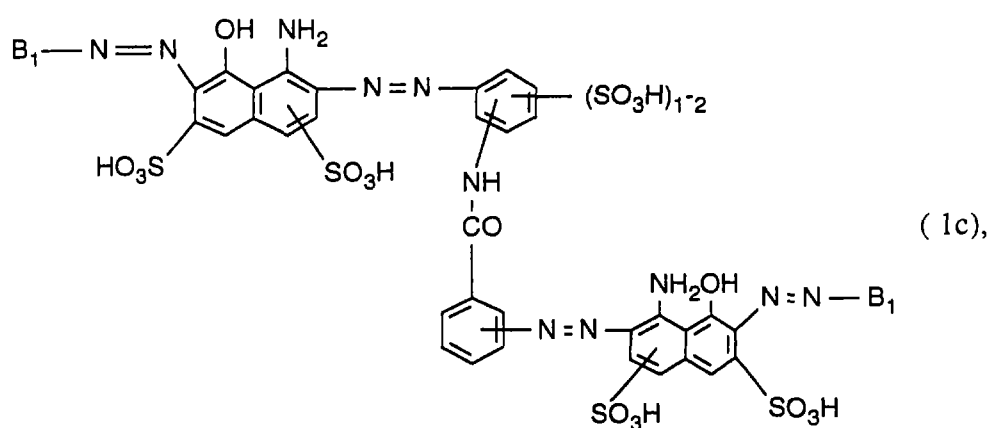
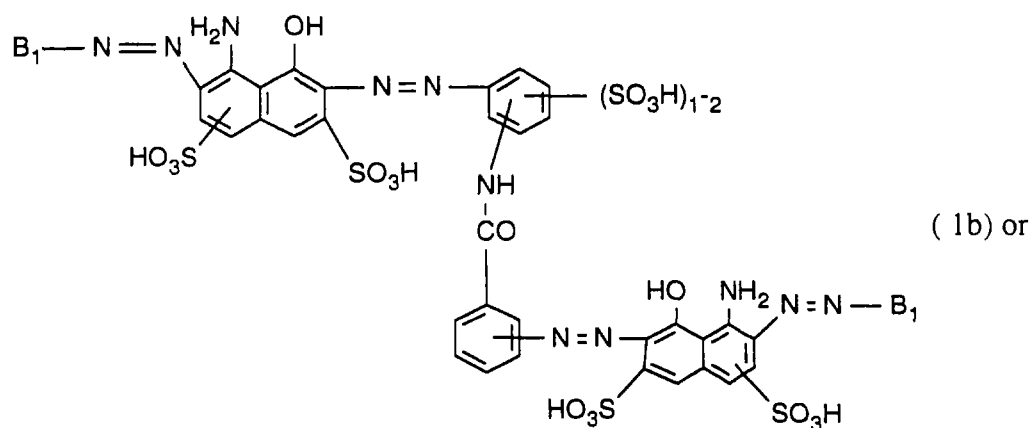


B_2 is a radical of formula

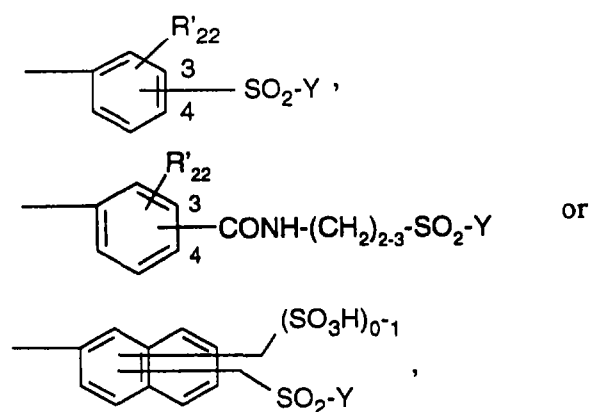


R'_{22} and R''_{22} are each independently of the other hydrogen, sulfo, chloro, C_1 - C_4 alkyl or C_1 - C_4 alkoxy; one of R_{23} and R_{24} is hydroxy and the other is amino; one of R_{25} and R_{26} is hydroxy and the other is amino, and Z_1 and Z_2 are each independently of the other a radical of the above formula (2a) or (2b).

A particularly preferred embodiment of this invention relates to compounds of formula



wherein B₁ is a radical of formula

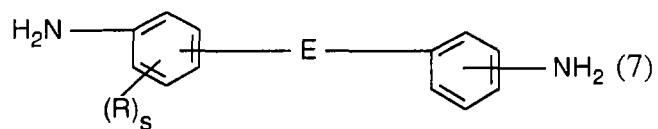


R'₂₂ is hydrogen, sulfo, methyl or methoxy, and Y has the meanings and preferred meanings given above.

The compounds of formula (1') can be obtained by e.g. tetrazotising about 1 molar

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equivalent of the compound of formula



in conventional manner, typically with nitrite such as sodium nitrite in acid medium, typically a medium containing hydrochloric acid, and then coupling the tetrazotised compound with about 1 molar equivalent of a coupling component of formula

$\text{K}_1 - \text{H}$ (8) and

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about 1 molar equivalent of a coupling component of formula



in acid, neutral or alkaline medium, E, R, K_1 , K_2 and s having the meanings and preferred meanings given above.

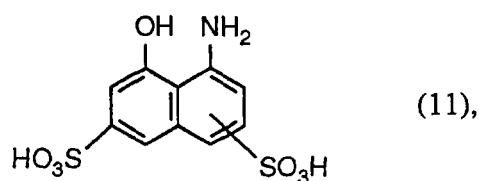
If K_1-H and K_2-H are identical coupling components then it is advantageous to react about 1 molar equivalent of the tetrazotised compound of formula (7) with about 2 molar equivalents of a compound of formula (8).

The synthesis of the compounds of formula (1') can also be carried out by first coupling the tetrazotised compound of formula (7) with a precursor of K_1-H or K_2-H and then converting the resultant disazo compound into the final compound, typically by coupling with a further diazotised diazo component.

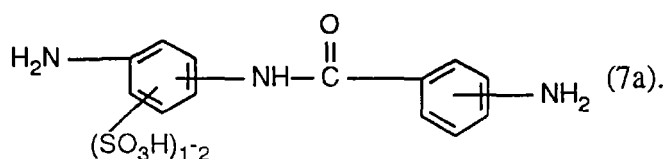
The preferred compounds of formula (1b) and (1c) are conveniently prepared by coupling about 1 molar equivalent of a diazotised compound of formula



wherein B_1 has the meaning given above, with about 1 molar equivalent of a coupling component of formula



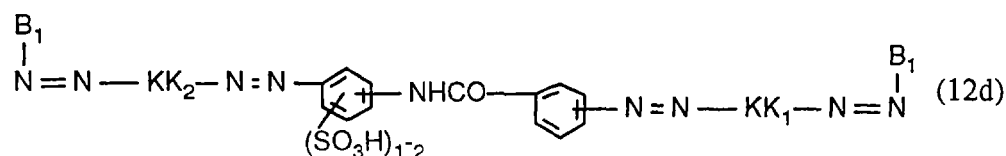
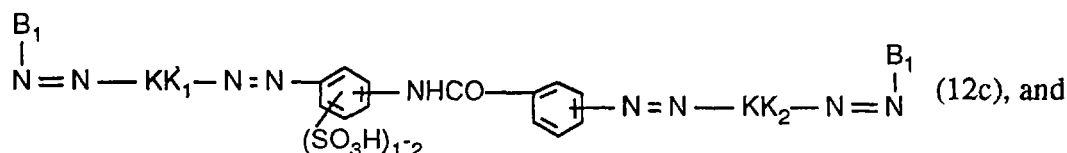
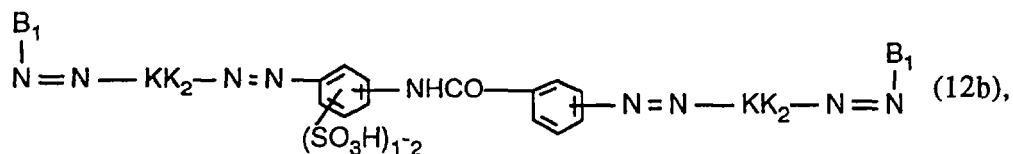
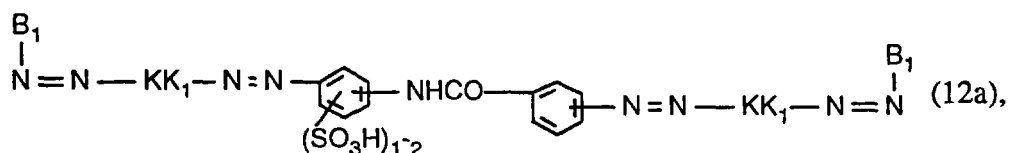
and coupling the monoazo compound so obtained with about 0.5 molar equivalent of a tetrazotised compound of formula



The first coupling is carried out in acid medium to prepare the compounds of formula (1b), and in alkaline medium to prepare the compounds of formula (1c). This process, in which the pH in the first coupling is in the acid range, is particularly preferred for the preparation of the compounds of formula (1b).

The compounds of formula (1b) and (1c) can also be prepared by coupling about 0.5 molar equivalent of a previously tetrazotised compound of formula (7a) with about 1 molar equivalent of a compound of the above formula (11) and then coupling the disazo compound so obtained with a diazotised compound of the above formula (10). It is particularly preferred to use this process, in which the pH in the first coupling is in the acid range, for the preparation of the compounds of formula (1c).

Replacing 1 molar equivalent of a compound of formula (11) in the above process for the preparation of the compounds of formulae (1b) and (1c) with c. 0.5 molar equivalent of each of two different compounds of formula (11), typically c. 0.5 molar equivalent of an aminonaphtholdisulfonic acid KK1 and c. 0.5 molar equivalent of an aminionaphtholdisulfonic acid KK2, gives mixtures of two symmetrical and two asymmetrical compounds, e.g. of formula



which constitute a further object of this invention. The variable B_1 in formulae (12a) to (12d) has the meanings and preferred meanings given above, and KK1 is preferably the radical of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid), and KK2 is preferably the radical of 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid (K-acid).

The compounds of formula (7) or (7a), (8), (9), (10) and (11) are known or can be prepared in *per se* known manner. Accordingly, the compounds of formula (7) may conveniently be prepared by simple reaction in conventional manner of an aminobenzoyl chloride or an aminobenzenesulfoyl chloride with the corresponding diaminobenzene or aminobenzene-sulfonamide.

The novel compounds of formula (1') as well as the mixtures of compounds of formulae (12a) to (12d) are fibre-reactive, i.e. they are capable of reacting with the hydroxyl groups of cellulose or with the reactive centres of natural and synthetic polyamides to form covalent chemical bonds.

The reactive dyes of formula(1') as well as of the mixtures of compounds of formula (12a) to (12d) are suitable for dyeing and printing a wide range of materials, preferably hydroxyl group-containing or nitrogen-containing fibre materials. Illustrative examples of such materials are silk, leather, wool, polyamide fibres and polyurethanes, and, in particular, cellulosic fibre materials of all kinds. Typical examples of such materials are natural cellulose fibres such as cotton, linen and hemp, as well as cellulose and regenerated cellulose. The reactive dyes of formula (1) are also suitable for dyeing or printing hydroxyl group-containing fibres which are components of blended fabrics, typically blends of cotton and polyester or polyamide fibres.

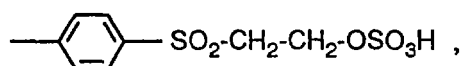
The novel dyes can be applied to, and fixed on, the fibre material by different methods, preferably in the form of aqueous dye solutions and printing pastes. They are suitable for dyeing by the exhaust process as well as by the pad dyeing process, and they can be used at low dyeing temperatures and require only short steaming times in the pad-steam process. Fixation is good and unfixed dye can be easily washed off, the difference between degree of exhaustion and degree of fixation being remarkably small, i.e. the soap loss is very insignificant. The reactive dyes of formula (1') and (12a) to (12d) are also suitable for printing, especially on cotton, but also for printing nitrogen-containing fibres such as wool, silk or blends which contain wool.

The dyeings and prints obtained with the dyes of this invention have superior tinctorial strength and high fibre-dye bonding stability in the acid as well as in the alkaline range. In addition, they have good lightfastness and very good wetfastness properties such as fastness to washing, water, seawater, cross-dyeing and perspiration, as well as good fastness to pleating, ironing, rubbing and, in particular, chlorine.

The invention is illustrated by the following Examples in which, unless otherwise stated, parts and percentages are by weight. The ratio of parts by weight to parts by volume is the same as that of the kilogram to the litre.

Preparation of the diazotised amines of formula (10)

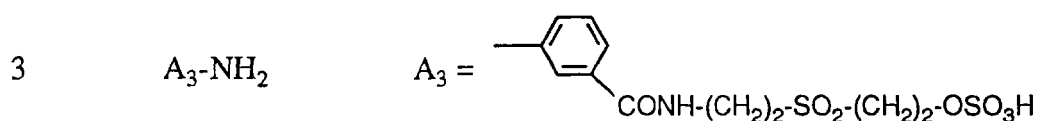
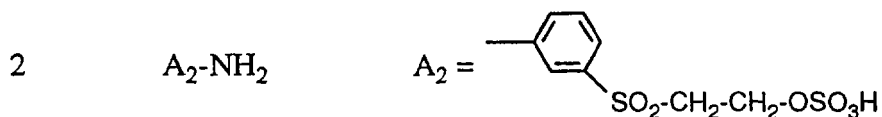
Example 1: 28 parts of the amine of formula A_1-NH_2 , wherein A_1 is the radical of formula



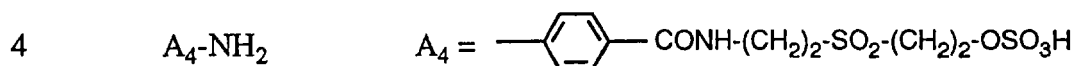
are thoroughly stirred in 150 parts of water. 16 parts of concentrated hydrochloric acid are added to the suspension so obtained. After cooling to 0-5°C, 7 parts of sodium nitrite, dissolved in 25 parts of water, are slowly added dropwise. When the reaction of the amine to the corresponding diazo compound is complete, excess nitrite is destroyed by addition of sulfamic acid.

Examples 2-4: In general accordance with the procedure of Example 1, the diazo compounds of the following amines can be prepared:

Example Amine

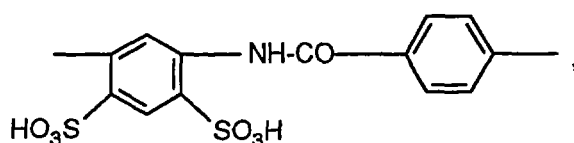


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Preparation of the tetrazotised compounds of formula (7) or (7a)

Example 5: 19 parts of the diamine of formula $H_2N-E_1-NH_2$, wherein E_1 is the radical of formula

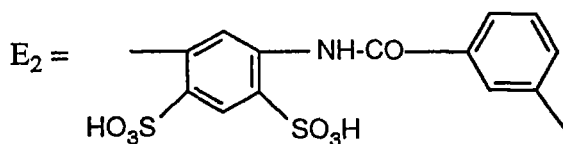


are dissolved in 190 parts of water to form a neutral solution. After cooling to c. $0^{\circ}C$, 16 parts of concentrated hydrochloric acid are added to this solution, and then a solution of 7 parts of sodium nitrite in 25 parts of water is slowly added dropwise. When the reaction of the diamine to the corresponding tetrazo compound is complete, excess nitrite is destroyed by addition of sulfamic acid.

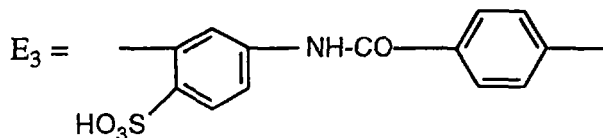
Examples 6-10: In general accordance with the procedure of Example 5, the tetrazo compounds of the following diamines can be prepared:

Example Diamine

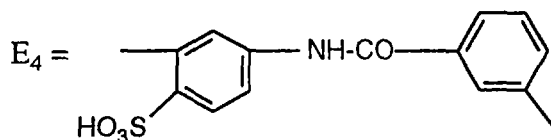
6 $H_2N-E_2-NH_2$



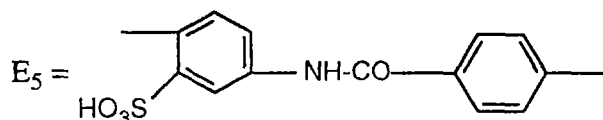
7 $H_2N-E_3-NH_2$

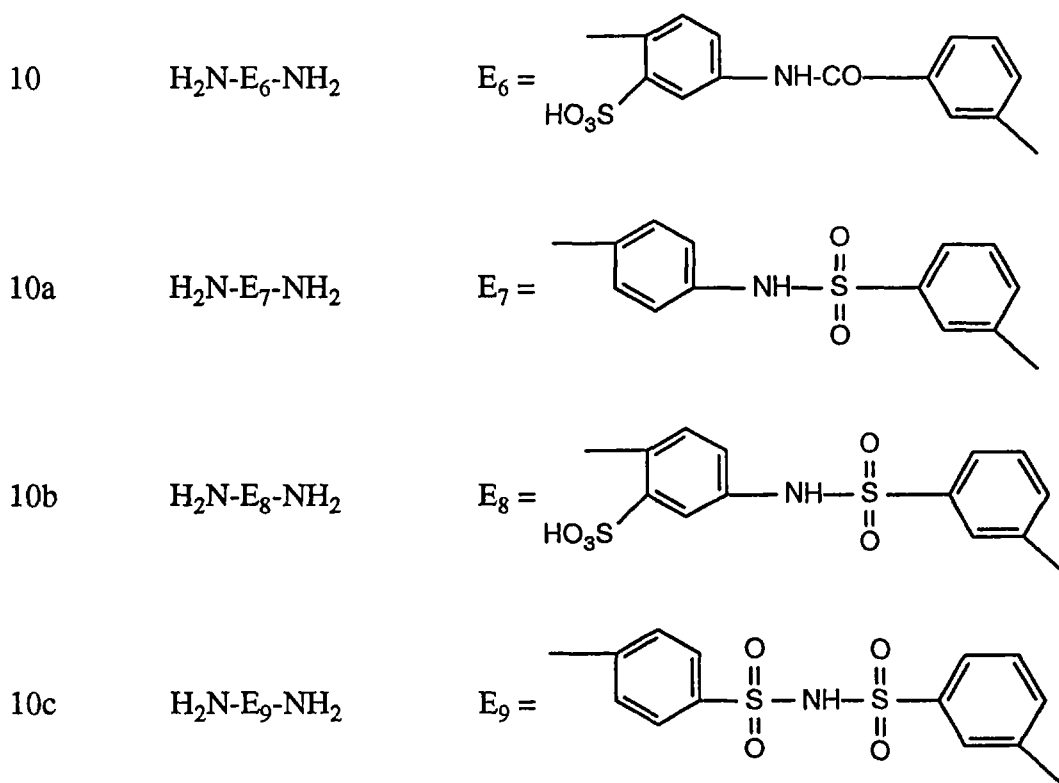


8 $H_2N-E_4-NH_2$



9 $H_2N-E_5-NH_2$

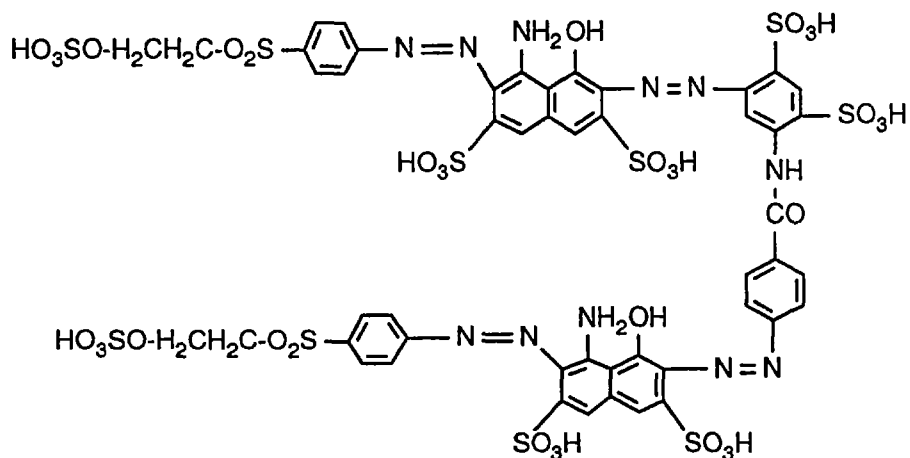




Preparation of the compounds of formula (1)

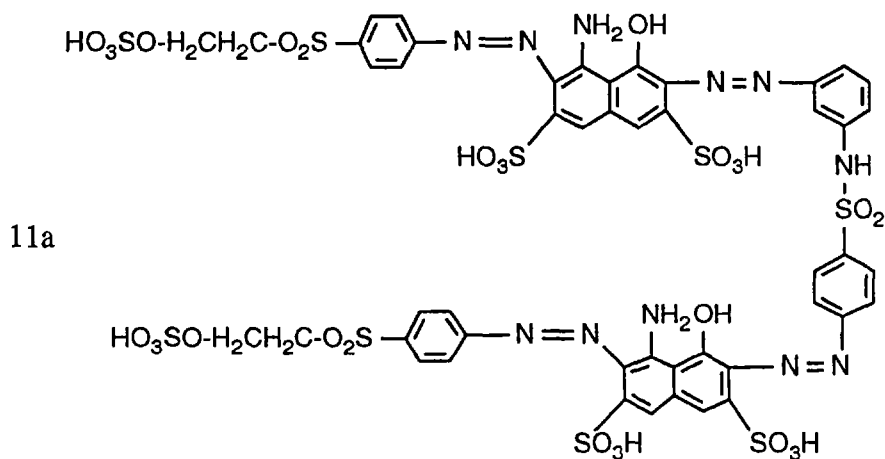
Example 11: The solution of the diazo compound of the amine of formula $\text{A}_1\text{-NH}_2$ obtained according to Example 1 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the tetrazo compound of the amine of formula $\text{H}_2\text{N-E}_1\text{-NH}_2$ obtained according to Example 5 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula

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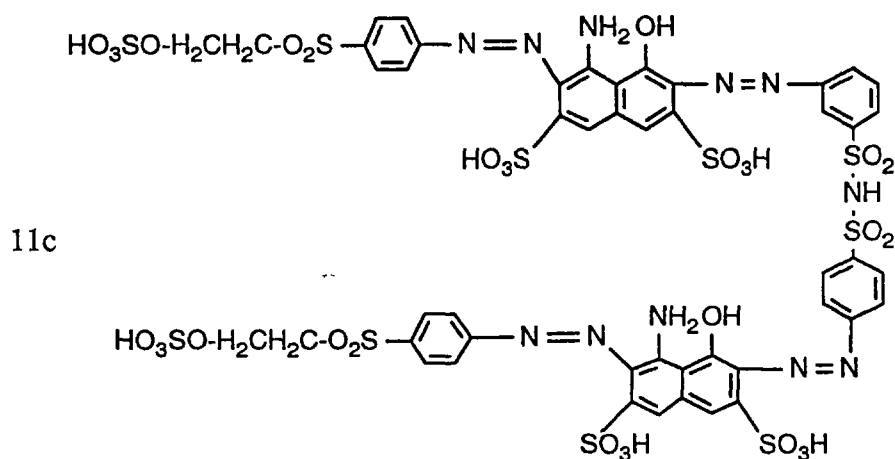
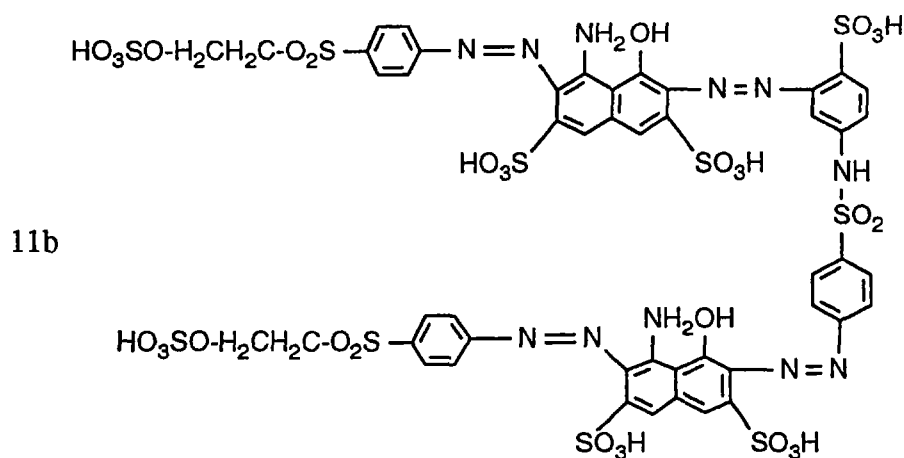


in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

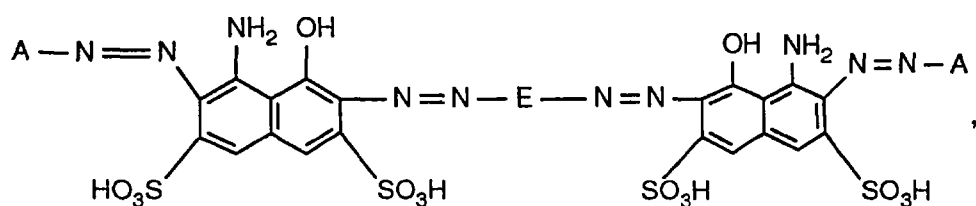
Examples 11a-11c: The procedure of Example 11 is repeated, but replacing the solution of the tetrazo compound of the amine of formula $\text{H}_2\text{N-E}_1\text{-NH}_2$ with an equivalent amount of the solution of the tetrazo compound according to Example 10a, 10b or 10c, to give the following compounds which also dye cellulose in a navy blue shade of good allround fastness properties.



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Example 12-34: In general accordance with the procedure of Example 11, the dyes of the general formula



wherein the variables have the meanings indicated in Table 1, can be obtained from the diazo compounds of Examples 1 to 4 and the tetrazo compounds of Examples 5 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 1:

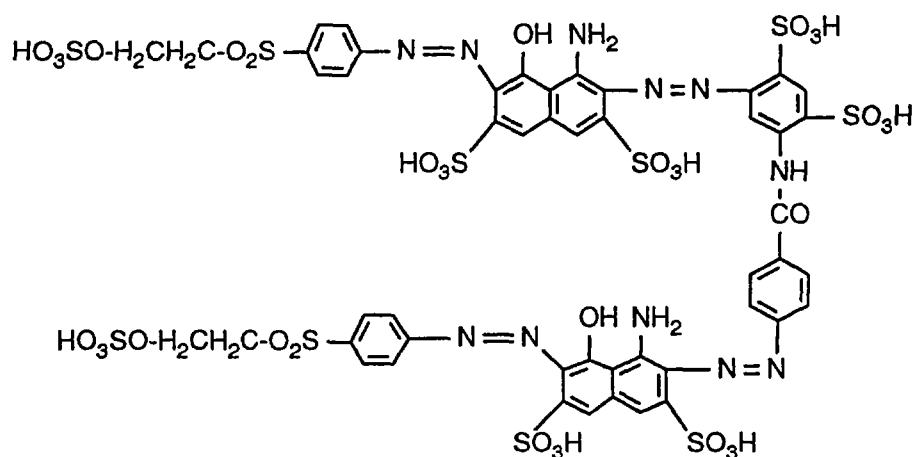
<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
12	A ₁	E ₂
13	A ₁	E ₃
14	A ₁	E ₄
15	A ₁	E ₅
16	A ₁	E ₆
17	A ₂	E ₁
18	A ₂	E ₂
19	A ₂	E ₃
20	A ₂	E ₄
21	A ₂	E ₅
22	A ₂	E ₆
23	A ₃	E ₁
24	A ₃	E ₂
25	A ₃	E ₃
26	A ₃	E ₄
27	A ₃	E ₅
28	A ₃	E ₆
29	A ₄	E ₁
30	A ₄	E ₂
31	A ₄	E ₃
32	A ₄	E ₄
33	A ₄	E ₅
34	A ₄	E ₆

A₁-A₄ and E₁-E₆ in this Table have the meaning given in the Examples 1 to 10.

Example 35: The solution of the tetrazo compound of the amine of formula H₂N-E₁-NH₂ obtained according to Example 5 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to

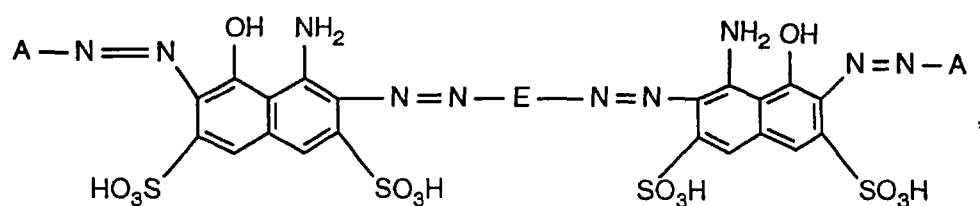
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3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine of formula A_1-NH_2 obtained according to Example 1 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

Examples 36-58: In general accordance with the procedure of Example 35, the dyes of the general formula



wherein the variables have the meaning indicated in Table 2, can be obtained from the diazo compounds of Examples 1 to 4 and the tetrazo compounds of Examples 5 to 10, These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 2:

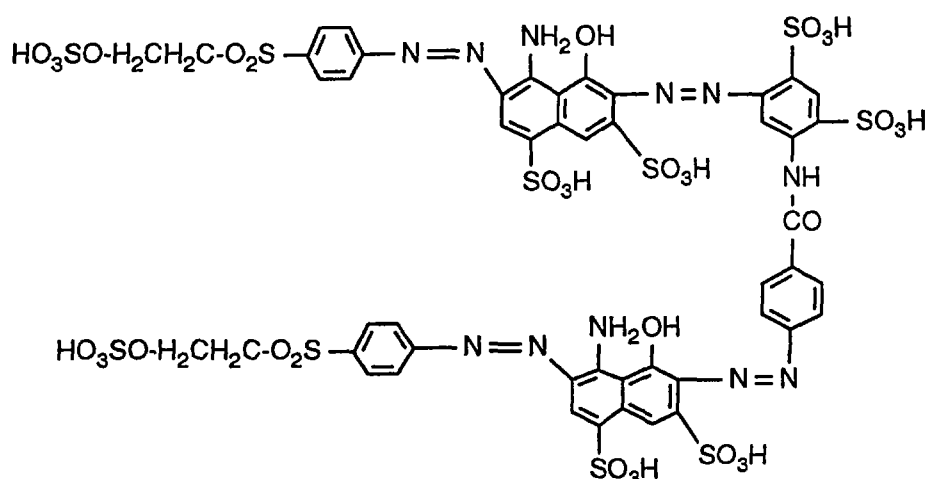
<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
36	A ₁	E ₂
37	A ₁	E ₃
38	A ₁	E ₄
39	A ₁	E ₅
40	A ₁	E ₆
41	A ₂	E ₁
42	A ₂	E ₂
43	A ₂	E ₃
44	A ₂	E ₄
45	A ₂	E ₅
46	A ₂	E ₆
47	A ₃	E ₁
48	A ₃	E ₂
49	A ₃	E ₃
50	A ₃	E ₄
51	A ₃	E ₅
52	A ₃	E ₆
53	A ₄	E ₁
54	A ₄	E ₂
55	A ₄	E ₃
56	A ₄	E ₄
57	A ₄	E ₅
58	A ₄	E ₆

A₁-A₄ and E₁-E₆ in Table 2 have the meanings given in the Examples 1 to 10.

Example 59: The solution of the diazo compound of the amine of formula A₁-NH₂ obtained according to Example 1 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid (K-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the tetrazo compound of the

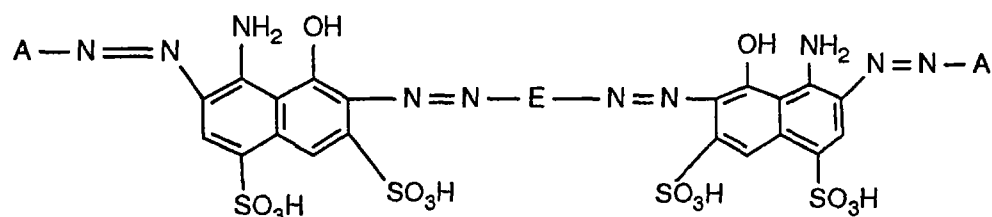
- 20 -

amine of formula $H_2N-E_1-NH_2$ obtained according to Example 5 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

Examples 60-82: In general accordance with the procedure of Example 59, the dyes of the general formula



wherein the variables have the meaning indicated in Table 3, can be obtained from the diazo compounds of Examples 1 to 4 and the tetrazo compounds of Examples 5 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 3:

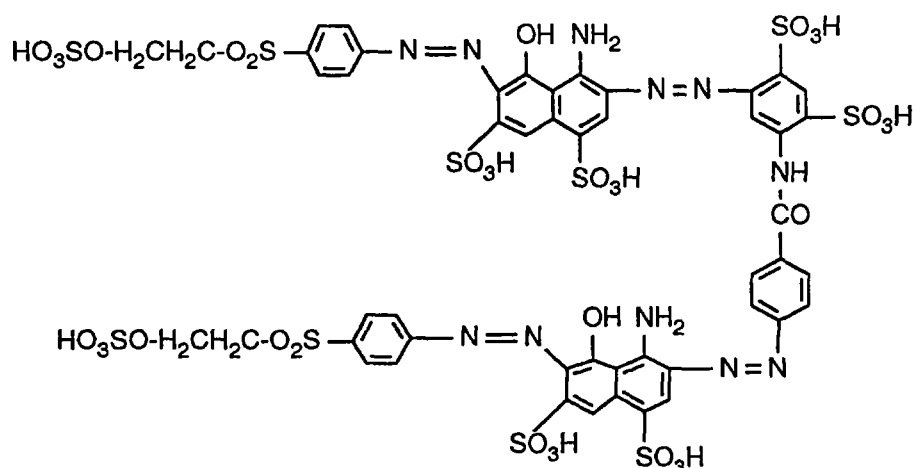
<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
60	A ₁	E ₂
61	A ₁	E ₃
62	A ₁	E ₄
63	A ₁	E ₅
64	A ₁	E ₆
65	A ₂	E ₁
66	A ₂	E ₂
67	A ₂	E ₃
68	A ₂	E ₄
69	A ₂	E ₅
70	A ₂	E ₆
71	A ₃	E ₁
72	A ₃	E ₂
73	A ₃	E ₃
74	A ₃	E ₄
75	A ₃	E ₅
76	A ₃	E ₆
77	A ₄	E ₁
78	A ₄	E ₂
79	A ₄	E ₃
80	A ₄	E ₄
81	A ₄	E ₅
82	A ₄	E ₆

A₁-A₄ and E₁-E₆ in Table 3 have the meaning given in Examples 1 to 10.

Example 83: The solution of the tetrazo compound of the amine of formula H₂N-E₁-NH₂ obtained according to Example 5 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid (K-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine

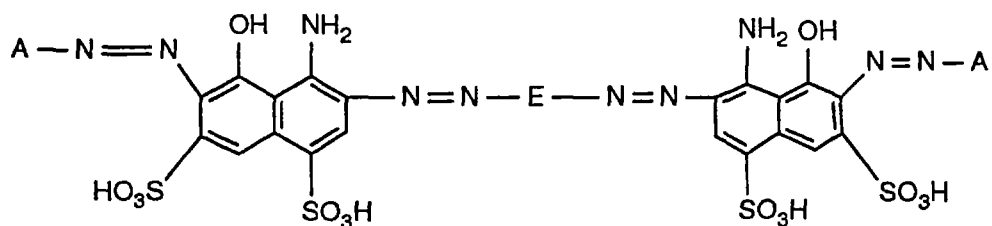
- 22 -

of formula A_1-NH_2 obtained according to Example 1 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



in the form of the free acid as a dark powder, which dyes cellulose is a navy blue shade of good allround fastness properties.

Examples 84-106: In general accordance with the procedure of Example 83, the dyes of the general formula



wherein the variables have the meaning indicated in Table 4, can be obtained from the diazo compounds of Examples 1 to 4 and the tetrazo compounds of Examples 5 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 4:

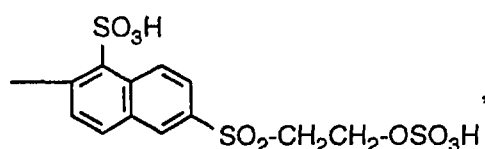
<u>Example</u>	<u>A</u>	<u>E</u>
<u>No.</u>		
84	A_1	E_2
85	A_1	E_3

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86	A ₁	E ₄
87	A ₁	E ₅
88	A ₁	E ₆
89	A ₂	E ₁
90	A ₂	E ₂
91	A ₂	E ₃
92	A ₂	E ₄
93	A ₂	E ₅
94	A ₂	E ₆
95	A ₃	E ₁
96	A ₃	E ₂
97	A ₃	E ₃
98	A ₃	E ₄
99	A ₃	E ₅
100	A ₃	E ₆
101	A ₄	E ₁
102	A ₄	E ₂
103	A ₄	E ₃
104	A ₄	E ₄
105	A ₄	E ₅
106	A ₄	E ₆

A₁-A₄ and E₁-E₆ in Table 4 have the meaning given in the Examples 1 to 10.

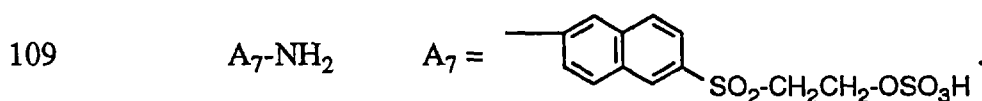
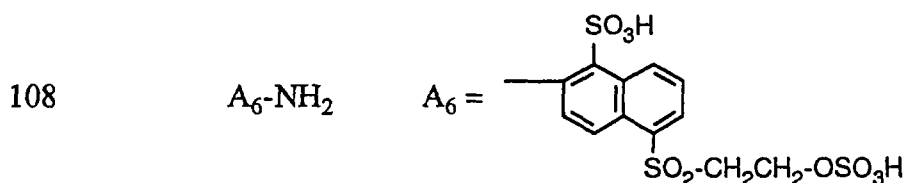
Example 107: 35 parts of the amine of formula A₅-NH₂, wherein A₅ is the radical of formula



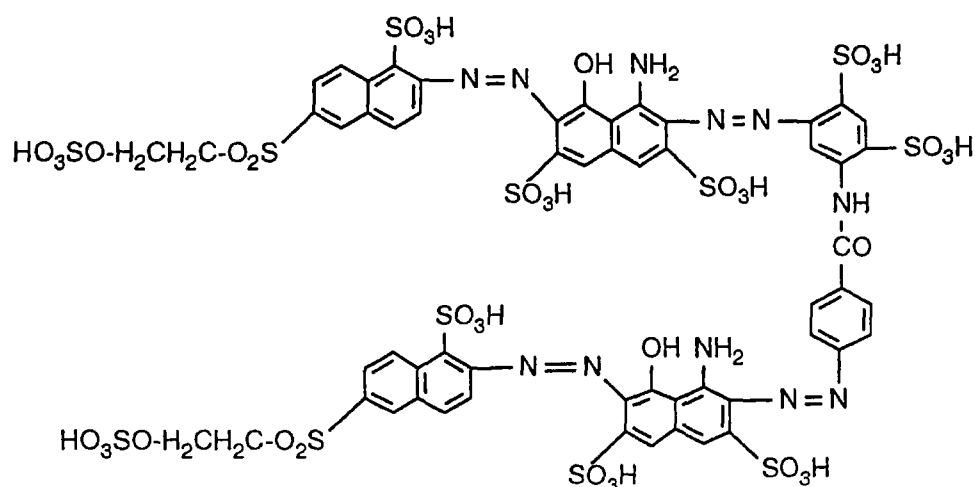
are thoroughly stirred in 200 parts of water. 16 parts of concentrated hydrochloric acid are added to the suspension. After cooling to 0-5°C, 7 parts of sodium nitrite dissolved in 25 parts of water are slowly added dropwise. When the reaction of the amine to the corresponding diazo compound is complete, excess nitrite is destroyed by addition of sulfamic acid.

Examples 108-109: In general accordance with the procedure of Example 107, the diazo compounds of the following amines can be prepared:

Example Amine



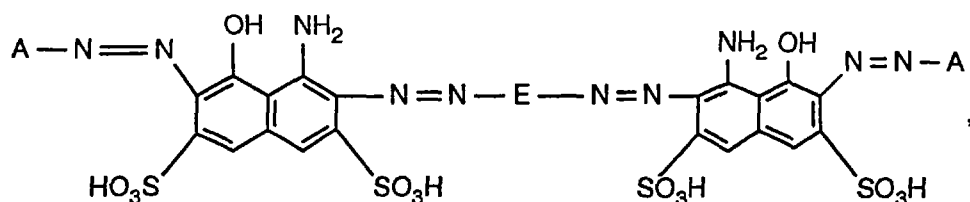
Example 110: The solution of the tetrazo compound of the amine of formula $H_2N-E_1-NH_2$ obtained according to Example 5 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine of formula A_5-NH_2 obtained according to Example 107 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



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in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

Examples 111-115: In general accordance with the procedure of Example 110, the dyes of the general formula



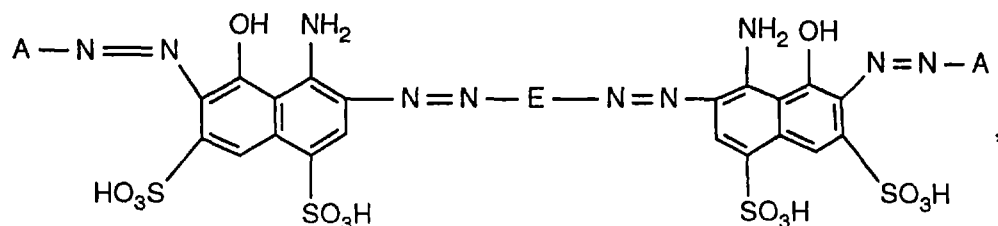
wherein the variables have the meaning indicated in Table 5, can be obtained from the diazo compound of Example 107 and the tetrazo compounds of Examples 6 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 5:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
111	A ₅	E ₂
112	A ₅	E ₃
113	A ₅	E ₄
114	A ₅	E ₅
115	A ₅	E ₆

A₅ and E₂-E₆ in Table 5 have the meaning given in the Examples 6 to 10 and 107.

Examples 116-121: The procedure of Examples 110 to 115 is repeated, but replacing the H-acid with the equivalent amount of K-acid, to give the compounds of the general formula



wherein the variables have the meaning indicated in Table 6 and which also dye cellulose in a navy blue shade of good allround fastness properties.

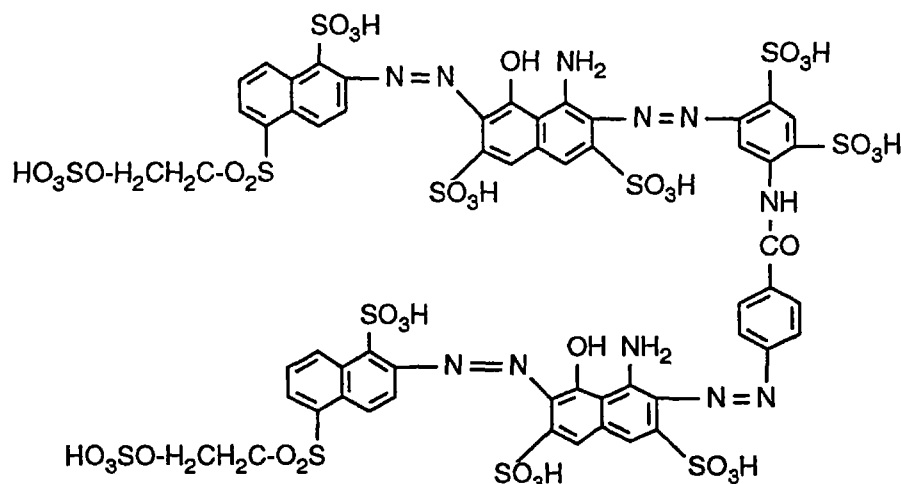
Table 6:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
116	A ₅	E ₁
117	A ₅	E ₂
118	A ₅	E ₃
119	A ₅	E ₄
120	A ₅	E ₅
121	A ₅	E ₆

A₅ and E₁-E₆ in Table 6 have the meaning given in Examples 5 to 10 and 107.

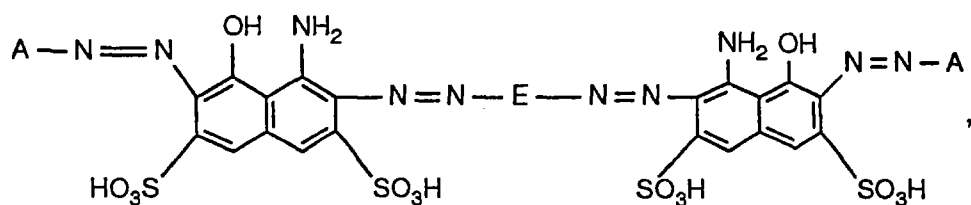
Example 122: The solution of the tetrazo compound of the amine of formula H₂N-E₁-NH₂ obtained according to Example 5 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine of formula A₆-NH₂ obtained according to Example 108 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula

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in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

Examples 123-127: In general accordance with the procedure of Example 122, the dyes of the general formula



wherein the variables have the meaning indicated in Table 7, can be obtained from the diazo compound of Example 108 and the tetrazo compounds of the Examples 6 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

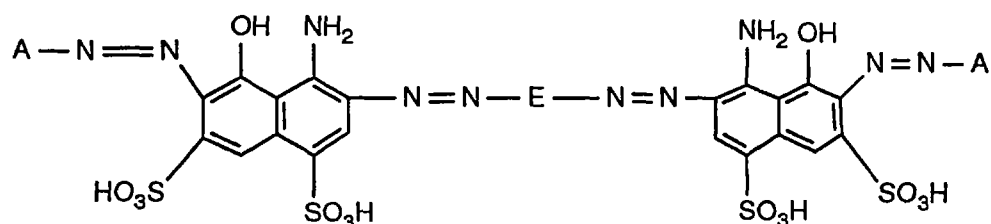
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Table 7:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
123	A ₆	E ₂
124	A ₆	E ₃
125	A ₆	E ₄
126	A ₆	E ₅
127	A ₆	E ₆

A₆ and E₂-E₆ in Table 7 have the meaning given in Examples 6 to 10 and 108.

Examples 128-133: The procedure of Examples 122 to 127 is repeated, but replacing the H-acid with the equivalent amount of K-acid, to give the compounds of the general formula



wherein the variables have the meaning indicated in Table 8 and which also dye cellulose in a navy blue shade of good allround fastness properties.

Table 8:

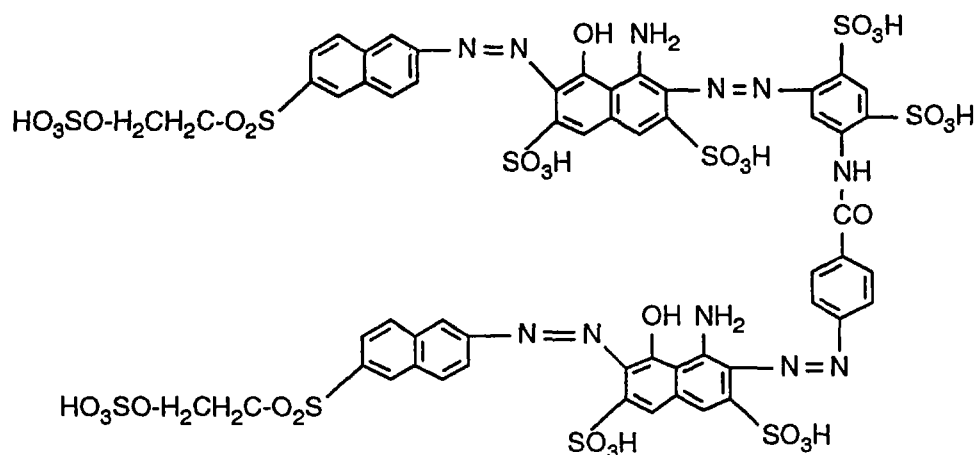
<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
128	A ₆	E ₁
129	A ₆	E ₂
130	A ₆	E ₃
131	A ₆	E ₄
132	A ₆	E ₅

133

 A_6 E_6

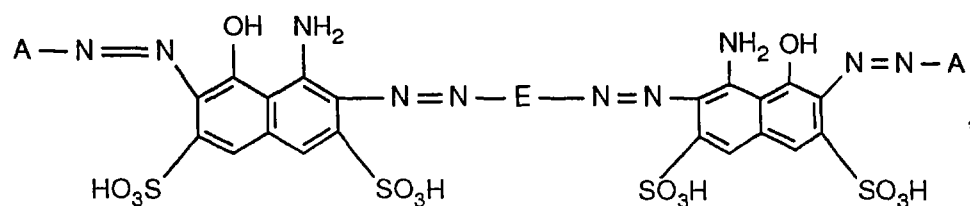
A_6 and E_1 - E_6 in Table 8 have the meaning given in Examples 5 to 10 and 108.

Example 134: The solution of the tetrazo compound of the amine of formula $H_2N-E_1-NH_2$ obtained according to Example 5 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine of formula A_7-NH_2 obtained according to Example 109 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of good allround fastness properties.

Examples 135-139: In general accordance with the procedure of Example 134, the dyes of the general formula



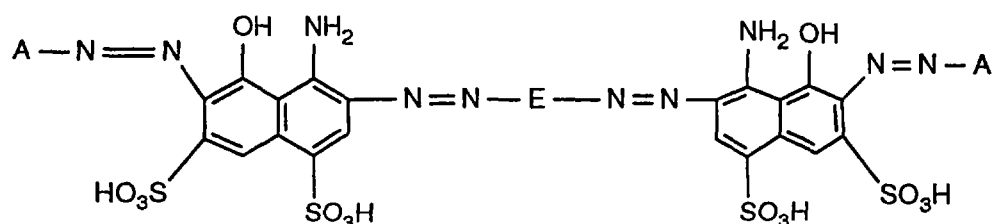
wherein the variables have the meaning indicated in Table 9, can be obtained from the diazo compound of Example 109 and the tetrazo compounds of Examples 6 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Table 9:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
135	A ₇	E ₂
136	A ₇	E ₃
137	A ₇	E ₄
138	A ₇	E ₅
139	A ₇	E ₆

A₇ and E₂-E₆ in Table 9 have the meaning given in the Examples 6 to 10 and 109.

Examples 140-145: The procedure of Examples 134 to 139 is repeated, but replacing the H-acid with the equivalent amount of K-acid, to give the compounds of the general formula



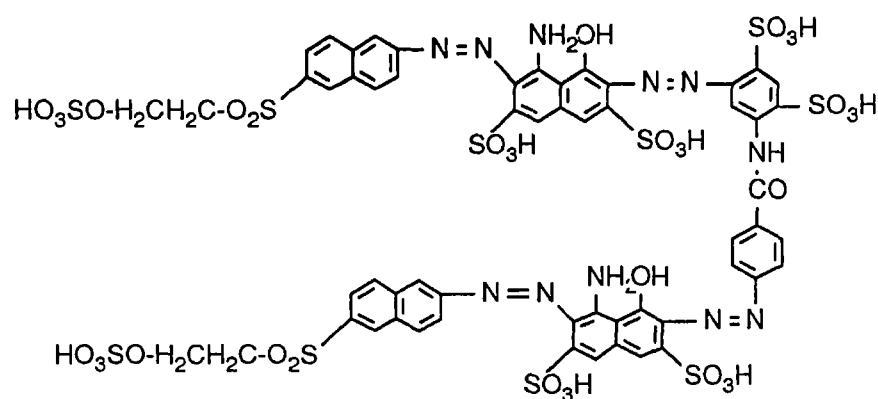
wherein the variables have the meaning indicated in Table 10 and which also dye cellulose in a navy blue shade of good allround fastness properties.

Table 10:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
140	A ₇	E ₁
141	A ₇	E ₂
142	A ₇	E ₃
143	A ₇	E ₄
144	A ₇	E ₅
145	A ₇	E ₆

A₇ and E₁-E₆ in Table 10 have the meaning given in the Examples 5 to 10 and 109.

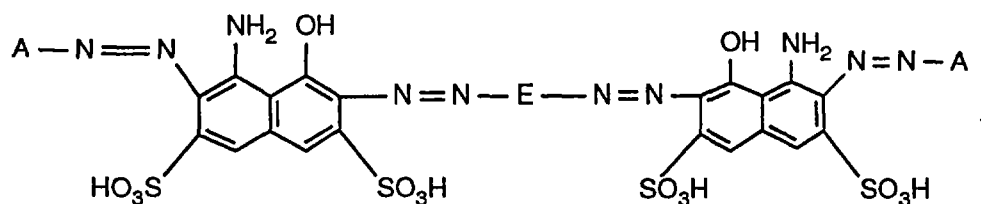
Example 146: The solution of the diazo compound of the amine of formula A₇-NH₂ obtained according to Example 109 is added dropwise to a suspension of 32 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (H-acid) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the tetrazo compound of the amine of formula H₂N-E₁-NH₂ obtained according to Example 5 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording the compound of formula



in the form of the free acid as a dark powder, which dyes cellulose in a navy blue shade of

good allround fastness properties.

Examples 147-151: In general accordance with the procedure of Example 146, the dyes of the general formula



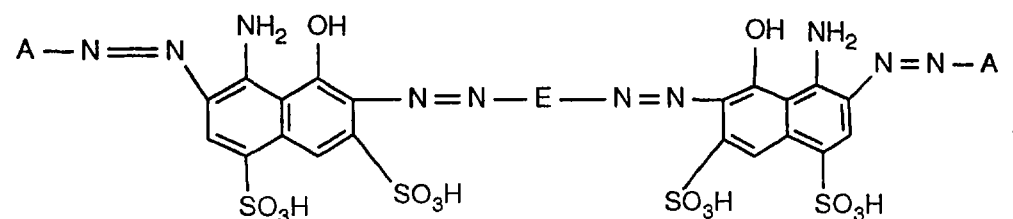
wherein the variables have the meaning indicated in Table 11, can be obtained from the diazo compound of Example 109 and the tetrazo compounds of Examples 6 to 10. These dyes also dye cellulose in a navy blue shade of good allround fastness properties.

Tabelle 11:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
147	A ₇	E ₂
148	A ₇	E ₃
149	A ₇	E ₄
150	A ₇	E ₅
151	A ₇	E ₆

A₇ and E₂-E₆ in Table 11 have the meaning given in the Examples 6 to 10 and 109.

Examples 152-157: The procedure of Examples 146 to 151 is repeated, but replacing the H-acid with the equivalent amount of K-acid, to give the compounds of the general formula



wherein the variables have the meaning indicated in Table 12 and which also dye cellulose in a navy blue shade of good allround fastness properties.

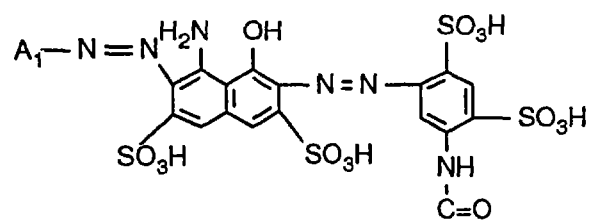
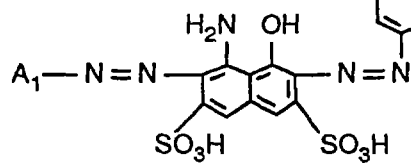
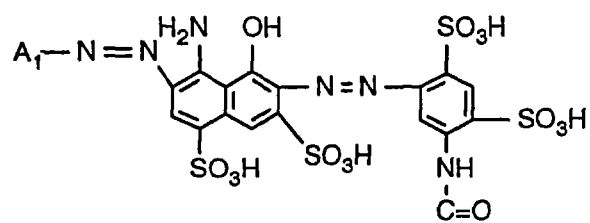
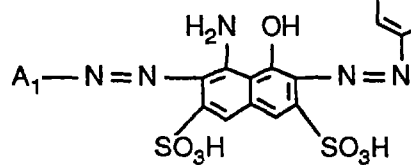
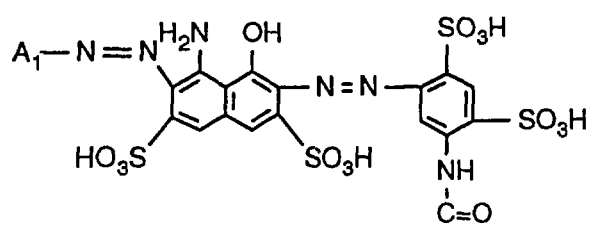
Table 12:

<u>Example</u> <u>No.</u>	<u>A</u>	<u>E</u>
152	A ₇	E ₁
153	A ₇	E ₂
154	A ₇	E ₃
155	A ₇	E ₄
156	A ₇	E ₅
157	A ₇	E ₆

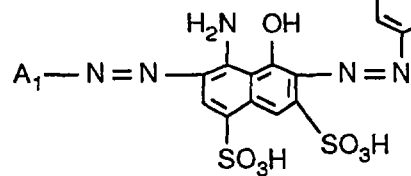
A₇ and E₁-E₆ in Table 12 have the meaning given in the Examples 5 to 10 and 109.

Example 158: The solution of the diazo compound of the amine of formula A₁-NH₂ obtained according to Example 1 is added dropwise to a suspension of (32 - n) parts of H-acid and n parts of K-acid (n = 1-31) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the tetrazo compound of the amine of formula H₂N-E₁-NH₂ obtained according to Example 5 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording a mixture of the compounds of formulae

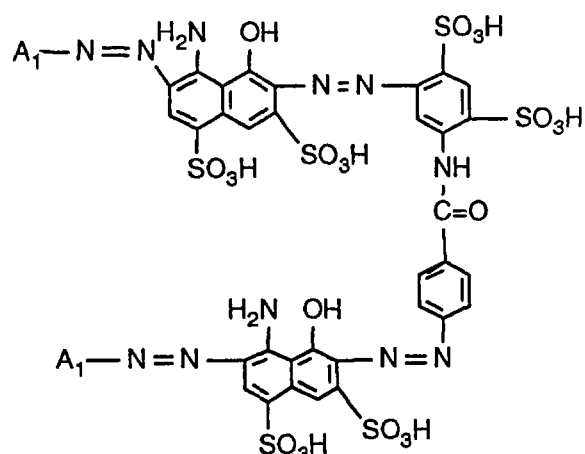
- 34 -



and

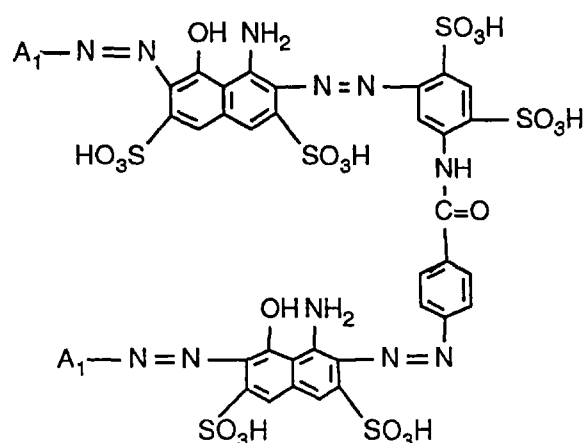


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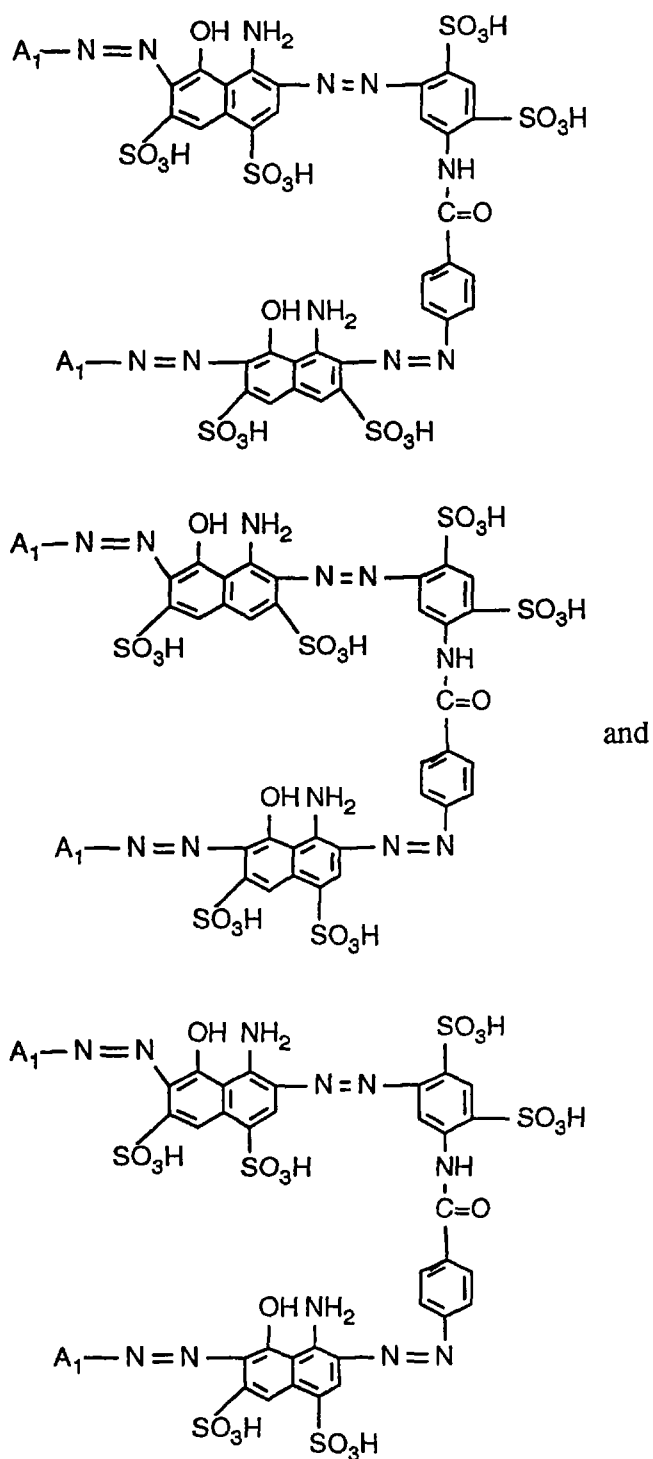


which dyes cellulose in a navy blue shade of good allround fastness properties.

Example 159: The solution of the tetrazo compound of the amine of formula $H_2N-E_1-NH_2$ obtained according to Example 5 is added dropwise to a suspension of (32 - n) parts of H-acid and n parts of K-acid ($n = 1-31$) in 100 parts of water at 0-5°C. The mixture is then allowed to warm to room temperature and is stirred until coupling is complete. The reaction mixture is then cooled to 5-10°C, the pH is raised to 3-4 with sodium hydroxide solution, and the solution of the diazo compound of the amine of formula A_1-NH_2m obtained according to Example 1 is slowly added dropwise, while keeping the pH constant at 3-4 by addition of sodium hydroxide solution. When coupling is complete, the dye solution is freed from salt by dialysis and concentrated by evaporation under vacuum, affording a mixture of the compounds of formulae



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which dyes cellulose in a navy blue shade of good allround fastness properties.

Dyeing Procedure I 2 parts of the reactive dye obtained in Example 11 are dissolved in 400 parts of water. To this solution are added 1500 parts of a solution which contains

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53 g/l of sodium chloride. 100 parts of cotton fabric are put into this dyebath at 40°C and, after 45 minutes, 100 parts of a solution containing 16 g/l of sodium hydroxide and 20 g/l of calcined sodium carbonate are added. The temperature of the dyebath is kept for another 45 minutes at 40°C. The dyed goods are then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

Dyeing Procedure II 2 parts of the reactive dye obtained in Example 11 are dissolved in 400 parts of water. To this solution are added 1500 parts of a solution which contains 53 g/l of sodium chloride. 100 parts of cotton fabric are put into this dyebath at 35°C and, after 20 minutes, 100 parts of a solution containing 16 g/l of sodium hydroxide and 20 g/l of calcined sodium carbonate are added. The temperature of the dyebath is kept for another 15 minutes at 35°C. The temperature is then raised over 20 minutes to 60°C and kept at this temperature for a further 35 minutes. The dyed goods are then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

Dyeing Procedure III 8 parts of the reactive dye obtained in Example 11 are dissolved in 400 parts of water. To this solution are added 1400 parts of a solution which contains 100 g/l of sodium sulfate. 100 parts of cotton fabric are put into this dyebath at 25°C and, after 10 minutes, 200 parts of a solution containing 150 g/l of trisodium phosphate are added. The temperature of the dyebath is then raised over 10 minutes to 60°C and kept at this temperature for a further 90 minutes. The dyed goods are then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

Dyeing Procedure IV 4 parts of the reactive dye obtained in Example 11 are dissolved in 50 parts of water. To this solution are added 50 parts of a solution which contains 5 g/l of sodium hydroxide and 20 g calcined sodium carbonate. A cotton fabric is padded with the solution so obtained to a pick-up of 70 % and rolled up. The cotton fabric is stored in this manner for 3 hours at room temperature. The dyed fabric is then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

Dyeing Procedure V 6 parts of the reactive dye obtained in Example 11 are dissolved in 50 parts of water. To this solution are added 50 parts of a solution which contains 16 g/ of sodium hydroxide and 0.04 l of sodium silicate (38°bé). A cotton fabric is padded with the solution obtained to a pick-up of 70 %, rolled up and stored in this manner for 10 hours at room temperature. The dyed fabric is then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

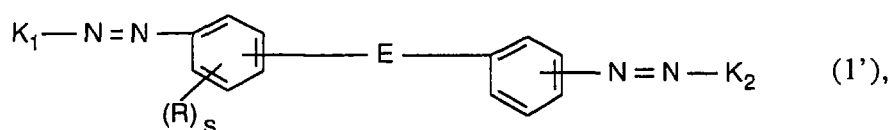
Dyeing Procedure VI 2 parts of the reactive dye obtained in Example 11 are dissolved in 100 parts of water with the addition of 0.5 parts of sodium m-nitrobenzenesulfonate. A cotton fabric is impregnated with the solution so obtained to a pick-up of 75 % and then dried. The fabric is then impregnated with a 20°C solution which contains 4 g/l of sodium hydroxide and 300 g of sodium chloride and then pinched off to a pick-up of 75 %. The dyed fabric is steamed for 30 seconds at 100 to 102°C, rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

Printing Procedure I 3 parts of the reactive dye obtained in Example 11 are sprinkled, with rapid stirring, into 100 parts of a stock thickening which contains 50 parts of 5% sodium alginate thickening, 27.8 parts of water, 20 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 1.2. parts of sodium hydrogen carbonate. A cotton fabric is printed with the printing paste so obtained and dried. The printed fabric is steamed for 2 minutes at 102°C in saturated steam, then rinsed, if necessary soaped at the boil, then rinsed once more and subsequently dried.

Printing Procedure II 5 parts of the reactive dye obtained in Example 11 are sprinkled, with rapid stirring, into 100 parts of a stock thickening which contains 50 parts of 5% sodium alginate thickening, 36.5 parts of water, 10 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 2.5 parts of sodium hydrogen carbonate. A cotton fabric is printed with the printing paste so obtained, the stability of which meets the technical requirements, and dried. The printed fabric is steamed for 8 minutes at 102°C in saturated steam, then rinsed, if necessary soaped at the boil, then rinsed once more and subsequently dried.

What is claimed is

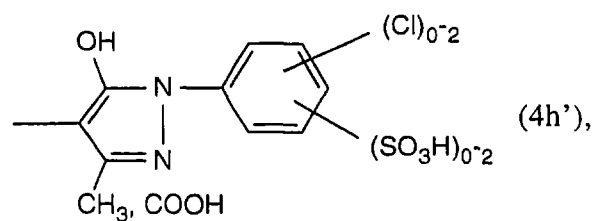
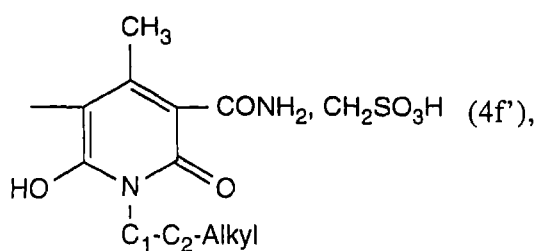
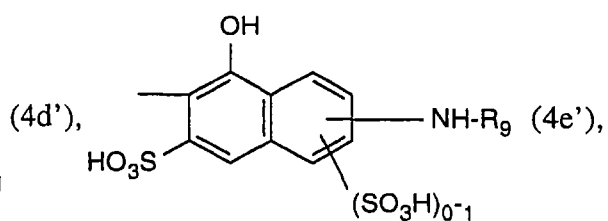
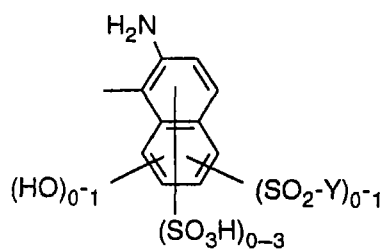
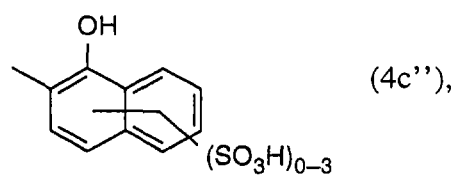
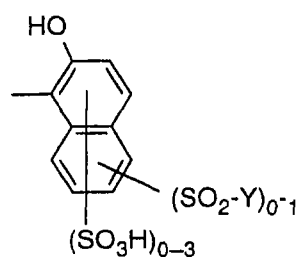
1. A compound of formula



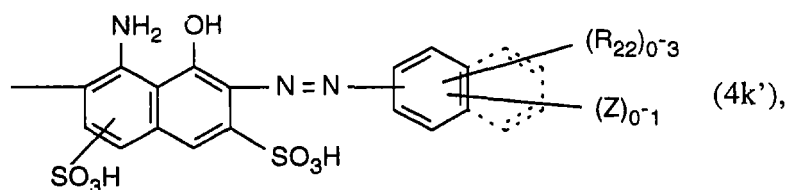
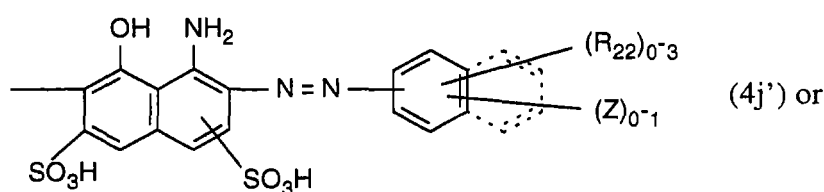
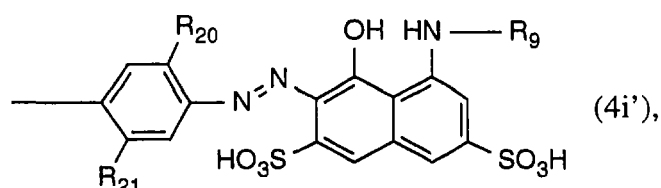
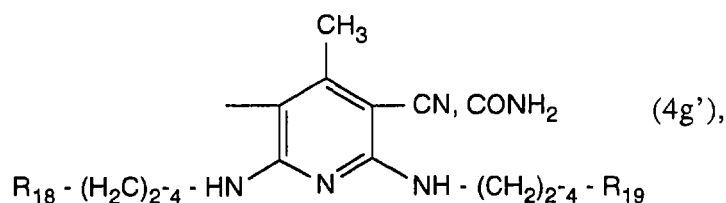
wherein E is the -NH-CO-, -NH-SO₂- or -SO₂-NH-SO₂- group,

(R)_s denotes s identical or different substituents selected from the group consisting of sulfo, hydroxy, C₁-C₄alkyl, C₁-C₄alkoxy, halogen and cyano, and s is 0, 1 or 2,

K₁ and K₂ are each independently of the other a radical of the formula



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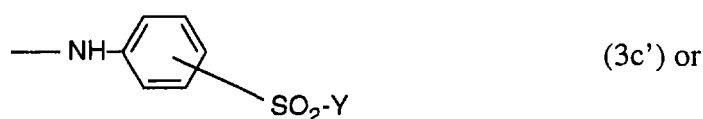


wherein R_9 is acetyl, benzoyl or a radical of formula



wherein X is halogen, and

T is C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy, amino, N- C_1 - C_4 alkylamino which is unsubstituted or substituted in the alkyl moiety by hydroxy, sulfato or sulfo; morpholino, phenylamino or N- C_1 - C_4 alkyl-N-phenylamino, wherein alkyl is unsubstituted or substituted by hydroxy, sulfo or sulfato, and phenyl is unsubstituted or substituted by sulfo, carboxy, acetilamino, methyl or methoxy, or T is a fibre-reactive radical of formula

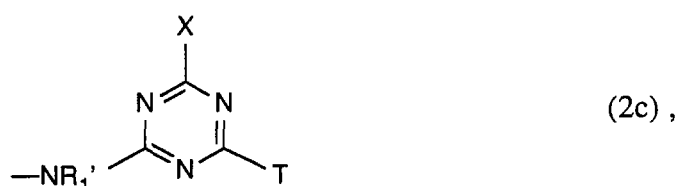


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R_{18} is hydrogen, hydroxy or sulfato,

R_{19} independently has the meaning of R_{18} , or is a radical of formula



wherein $R_{1'}$ is hydrogen or C_1 - C_4 alkyl and X and T are as defined above,

R_{20} and R_{21} are each independently of the other hydrogen, methyl, methoxy,

2-hydroxyethoxy, 2-sulfatoethoxy, acetylamino, propionylamino, ureido or sulfo,

$(R_{22})_{0-3}$ is 0 to 3 identical of different radicals R_{22} selected from the group consisting of sulfo, chloro, C_1 - C_4 alkyl and C_1 - C_4 alkoxy,

Y is vinyl, β -bromoethyl or β -chloroethyl, β -acetoxyethyl, β -benzoyloxyethyl, β -phosphatoethyl, β -sulfatoethyl or β -thiosulfatoethyl and, preferably, vinyl or β -sulfatoethyl,

Z is a radical of the formula



wherein R_2 is hydrogen or C_1 - C_4 -alkyl,

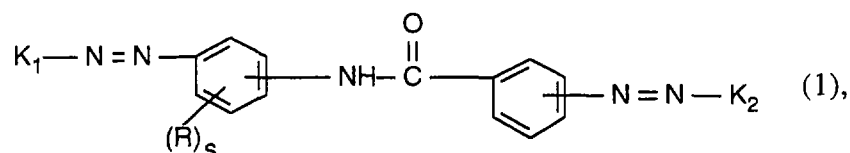
n is an integer from 1 to 6, and

Y is as defined above,

with the proviso that at least one of K_1 and K_2 carries a fibre-reactive group, and

with the proviso that the compound of formula (1') contain at least one sulfo or sulfato group.

2. A compound according to claim 1, of formula



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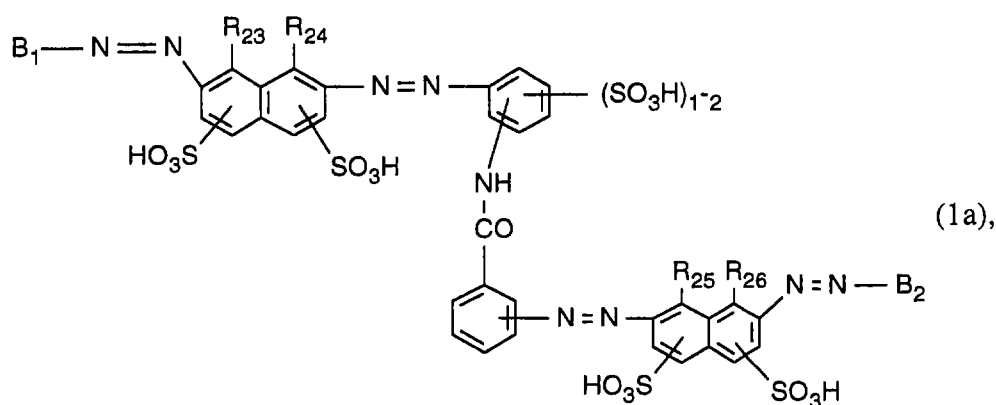
wherein K_1 , K_2 and $(R)_s$ are as defined in claim 1.

3. A compound according to claim 1 or 2, wherein R is hydroxy, methyl, methoxy or sulfo, and s is 1 or 2.

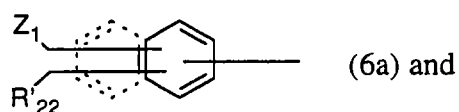
4. A compound according to any one of claims 1 to 3, wherein K_1 and K_2 are each independently of the other a radical of formula (4j') or (4k').

5. A compound according to any one of claims 1 to 4, wherein K_1 and K_2 are identical.

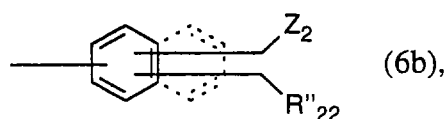
6. A compound according to claim 1, of formula



wherein B_1 is a radical of formula

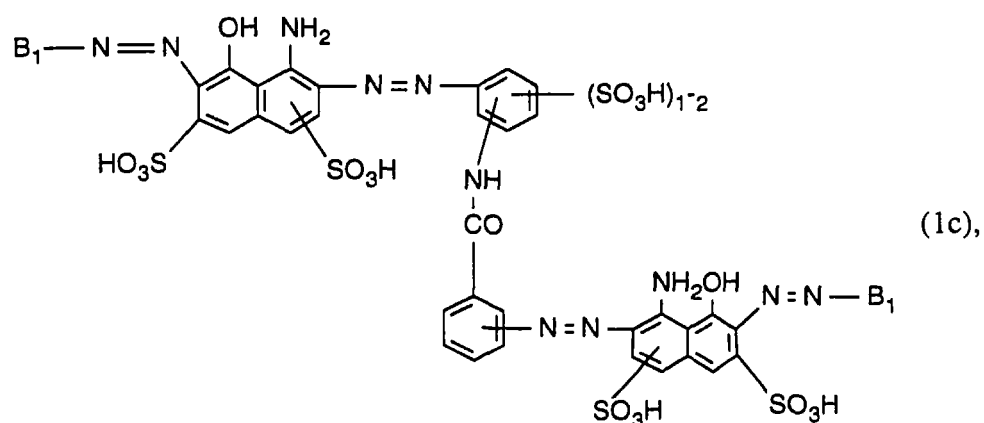
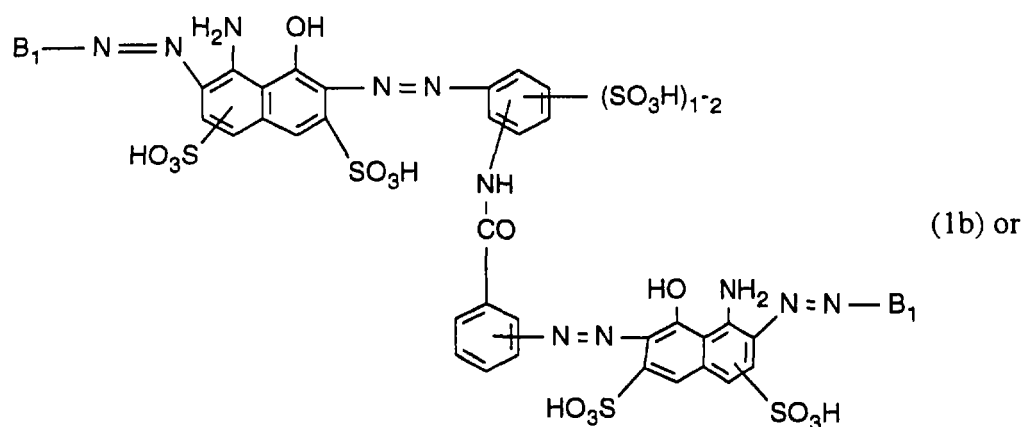


B_2 is a radical of formula

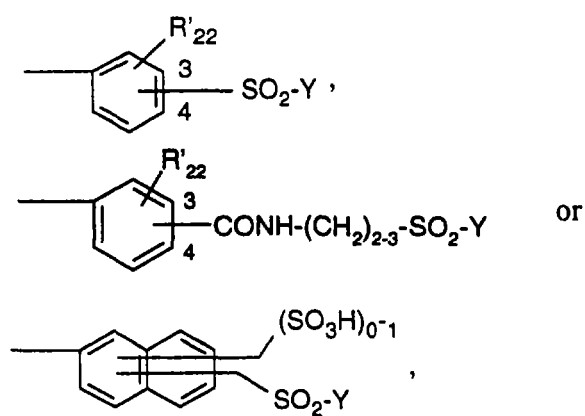


R'_{22} and R''_{22} are each independently of the other hydrogen, sulfo, chloro, C_1 - C_4 alkyl or C_1 - C_4 alkoxy; one of R_{23} and R_{24} is hydroxy and the other is amino; one of R_{25} and R_{26} is hydroxy and the other is amino, and Z_1 and Z_2 are each independently of the other a radical of formula (2a) or (2b) as defined in claim 1.

7. A compound according to claim 1, of formula



wherein B_1 is a radical of formula

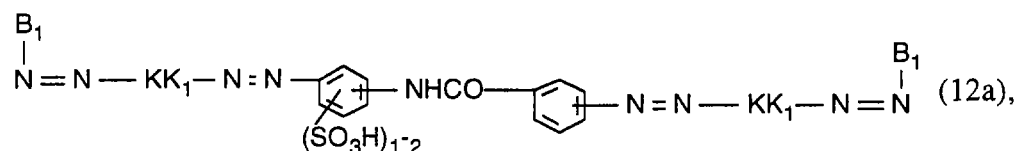


R'_{22} is hydrogen, sulfo, methyl or methoxy, and Y is vinyl or β -sulfatoethyl.

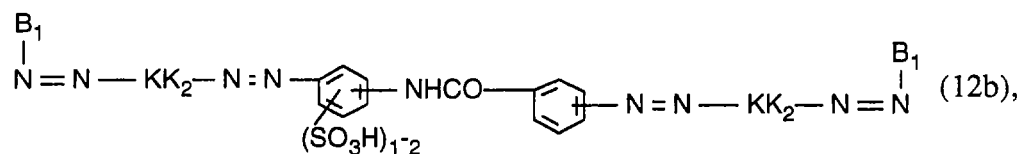
8. A dye mixture comprising two or more than two compounds of formula (1') as claimed in claim 1.

9. A dye mixture according to claim 8, comprising

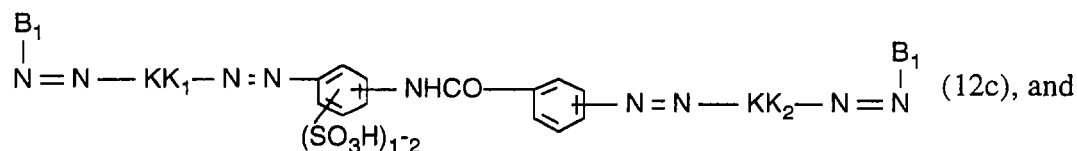
a) a compound of formula



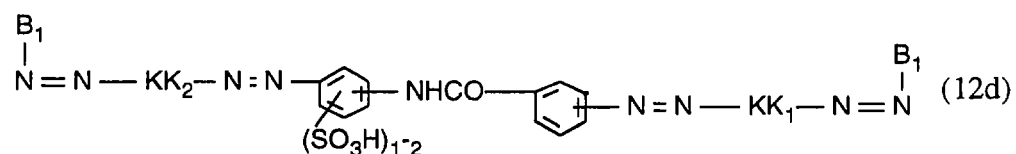
b) a compound of formula



c) a compound of formula



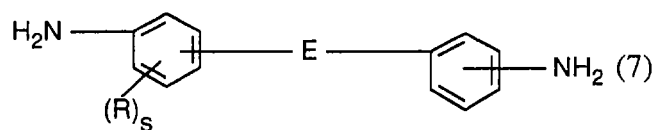
d) a compound of formula



wherein B_1 is as defined in claim 6, KK_1 is the radical of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid, and KK_2 is the radical of 1-amino-8-hydroxynaphthalene-4,6-disulfonic acid.

10. A process for the preparation of a compound of formula (1') as claimed in claim 1, which comprises tetrazotising about 1 molar equivalent of the compound of formula

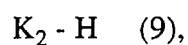
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with a nitrite in acid medium and coupling the tetrazotised compound with about 1 molar equivalent of a coupling component of formula



about 1 molar equivalent of a coupling component of formula



wherein E, R, K₁, K₂ and s have the meanings as claimed in claim 1.

11. Use of the compound of formula (1') as a fibre-reactive dye for dyeing or printing hydroxyl group-containing or nitrogen-containing fibre materials.

12. Use according to claim 11, which comprises dyeing or printing cellulosic fibre materials, preferably cotton-containing fibre materials.