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(54) REACTIVE DYES CONTAINING A HALOBENZENE NUCLEUS

(75) Inventors: **Warren James Ebenezer**, Stockport (GB); **David Greenwood**, Oldham (GB); **Michael Gordon Hutchings**, Bury (GB); **Michael Alan Rabjohns**, Manchester (GB); **Andrea Maria Zamponi**, Mannheim (DE)

Correspondence Address:
OBLON SPIVAK MCCLELLAND MAIER &
NEUSTADT PC
FOURTH FLOOR
1755 JEFFERSON DAVIS HIGHWAY
ARLINGTON, VA 22202 (US)

(73) Assignee: **BASF Akiengesellschaft**, Ludwigshafen (DE)

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(57) **ABSTRACT**

The invention relates to reactive dyes containing a halobenzene nucleus and, in particular, reactive dyes containing a halobenzene nucleus and two or more reactive components.

REACTIVE DYES CONTAINING A HALOBENZENE NUCLEUS

[0001] This invention relates to reactive dyes containing a halobenzene nucleus and, in particular, reactive dyes of this type containing two or more reactive components.

[0002] Dyes are known which contain a halobenzene nucleus linked via an azo group to another aromatic nucleus such that the halobenzene nucleus forms part of the chromophoric chain (see for example GB-A-882001). Dyes of this type which contain two such halobenzene nuclei are disclosed in CA64,14316d (1966), which is an English language abstract of an article by Matsui et al, Yuki Gosei Kagaku Kyokai Shi(1966), 24-(2), 132-136.

[0003] Dyes are also known in which the halobenzene nucleus is attached to a chromophoric group by a sulphonamide or amide linkage; see, for example, GB-A-978162 and CA59,12949g (1963), which is an English language abstract of an article by Matsui et al in Yuki Gosei Kagaku Kyokai Shi (1962), 20,1100-1112. Again dyes of this type may contain two such halobenzene nuclei; see GB-A-978162.

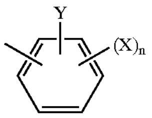
[0004] In other known dyes the halobenzene nucleus is linked to a chromophoric group by an amine linkage; see U.S. Pat. No. 3,301,847 and CA61,16193f (1964) which is an English language abstract of an article by Matsui et al in Kogyo Kagaku Zasshi, (1964), 67(1), 94-97. However, such dyes contain only one reactive group.

[0005] We have now found surprisingly that dyes having at least one halobenzene nucleus linked to a chromophoric group via an amino linkage and additionally containing a second reactive group have particularly high build up, especially in warm dyeing applications.

[0006] According to the invention there is provided a dye containing

[0007] at least one chromophore D;

[0008] at least a first, halobenzene, reactive group Z^1, of the formula (I)



(I)

[0009] in which:

[0010] n is 1 or 2

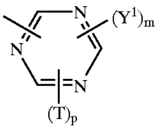
[0011] X, or each X independently, is an electron withdrawing group; and

[0012] Y is a halogen atom;

[0013] at least a second reactive group Z^2 selected from

[0014] (1) a group of the formula (I), given and defined above, but selected independently thereof;

[0015] (2) a group of the formula (II)



(II)

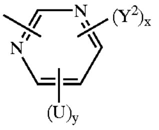
[0016] wherein

[0017] m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

[0018] Y^1 or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

[0019] T is C_{1-4}alkoxy, C_{1-4}thioalkoxy or $N(R^1)(R^2)$, in which each of R^1 and R^2 independently is hydrogen, optionally substituted C_{1-4}alkyl or optionally substituted aryl;

[0020] (3) a group of the formula (III)



(III)

[0021] wherein:

[0022] x is 1, 2 or 3; y is zero, 1 or 2; and

[0023] $x+y \leqq 3$;

[0024] Y^2, or each Y^2 independently, is a halogen atom or an optionally substituted pyridinium group; and

[0025] U or each U independently, is C_{1-4}alkyl or C_{1-4}alkylsulphonyl;

[0026] (4) a group of the formula (IV)

$$—SO_2CH_2CH_2X^1 \qquad (IV)$$

[0027] wherein

[0028] X^1 is an eliminatable group;

[0029] (5) a group of the formula (V)

$$—SO_2(CH_2)_zCH{=}CH_2 \qquad (V)$$

[0030] wherein

[0031] z is zero or 1; and

[0032] (6) a group of formula (VI)

$$—W—C(R^{10}){=}CH_2 \qquad (VI)$$

[0033] wherein:

[0034] R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

[0035] W is —OC(=O)— or $—N(R^{11})C(=O)—$ in which R^{11} is hydrogen or C_{1-4} alkyl;

[0036] at least a first linking group L^1, linking the said first, halobenzene, reactive group Z^1 to one of components (i) the or a chromophore D and (ii) the second reactive group Z^2, which said first linking group L^1 presents an amino nitrogen to the reactive group Z^1 and to the component (i) or (ii) or, when component (i) contains a heterocyclic nitrogen atom, is linked directly to the nitrogen atom and which said first linking group L^1 optionally includes a hydrocarbon bridging group, which hydrocarbon bridging group B has at least two carbon atoms, is optionally substituted, optionally includes at least one hetero atom and is optionally a chromophore; and

[0037] when Z^2 is selected from the said groups (I)-(III), at least a second linking group L^2 linking the second reactive group Z^2 to one of (i) the or a chromophore D and (ii) the said first reactive group Z^1, which said linking group L^2 is selected from

[0038] (1) a linking group L^1, but selected independently thereof; or

[0039] (2) an amide linkage; and

[0040] (3) a sulphonamide linkage; and

[0041] optionally at least one aromatic group Ar which, when Z^2 is selected from the said groups (IV)-(VI), may carry the said reactive group Z^2.

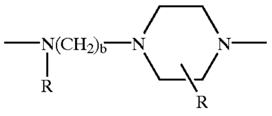
[0042] Preferably, the linking group L^1 has the formula $(VII)^1$

$$N(R) \qquad (VII)^1$$

[0043] wherein R is hydrogen or optionally substituted C_{1-4}alkyl, such that the same amino group presents itself to each of the reactive group Z^1 and the component (i) or (ii), as defined above; or

[0044] is a piperazinoalkylamino group of the formula $(VII)^2$

$(VII)^2$



[0045] wherein each R, independently, is as defined above, such that respective amino nitrogens, one of the piperazine group and the other of the alkylamino group, present themselves respectively, to the reactive group Z^1 and to the component (i) or (ii), as defined above; or

[0046] has the formula $(VII)^3$

$$—N(R)BN(R)— \qquad (VII)^3$$

[0047] wherein B is a hydrocarbon bridging group as defined above, each R, independently , is as defined above and B is optionally linked additionally to at least one additional group —N(R).

[0048] The hydrocarbon bridging group B may be a straight or branched, optionally substituted, C_{2-6}alkylene group optionally interrupted by at least one hetero atom, for example, O,S or N. Optional substituents are OH alkoxy, carboxy, carboxylic ester or carboxamide. Alternatively the bonding group B may be an optionally substituted arylene especially phenylene group. Optional substituents are SO_3H and salts thereof, C_{1-4}alkyl, C_{1-4}alkoxy and chloro. The bridging group B is is especially preferably an optionally substituted aryl group.

[0049] An especially preferred dye embodying the invention has the formula (VIII)

$$Z^1\text{-}L^1\text{-}D\text{-}(L^2)_aZ^2 \qquad (VIII)$$

[0050] wherein:

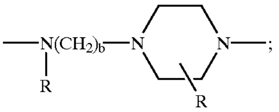
[0051] D is a chromophore;

[0052] each of L^1 and L^2 is an amine or piperazine linkage of the formula

$$—N(R)— \qquad (VII)^1;$$

[0053]

$(VII)^2$



or

$$—N(R)BN(R)— \qquad (VII)^3$$

[0054] wherein:

[0055] R, or each R independently, is hydrogen or C_{1-4} alkyl;

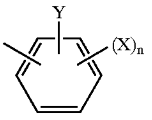
[0056] B is a hydrocarbon bridging group which has at least two carbon atoms, is optionally substituted, optionally includes at least one hetero atom and is optionally a chromophore;

[0057] a is zero or 1; and

[0058] b is from 2 to 6 inclusive;

[0059] Z^1 is a group

(I)



[0060] in which:

[0061] n is 1 or 2;

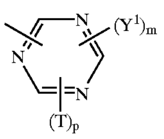
[0062] X, or each X independently, is an electron withdrawing group; and

[0063] Y is a halogen atom; and

[0064] when a is 1, Z^2 is:

[0065] a group of the formula (1), given and defined above but selected independently thereof; or

[0066] a group of the formula (II)



(II)

[0067] wherein:

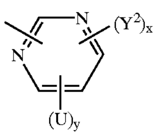
[0068] m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

[0069] Y^1, or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

[0070] T is C_{1-4} alkoxy, thioalkoxy or $N(R^1)$ (R^2) in which R^1 is hydrogen, optionally substituted C_{14} alkyl or optionally substituted aryl and

[0071] R^2 is hydrogen or optionally substituted C_{14} alkyl; or

[0072] a group of the formula (III)



(III)

[0073] wherein:

[0074] x is 1, 2 or 3; y is zero, 1 or 2; and $x+y \leqq 3$;

[0075] Y^2, or each Y^2 independently, is a halogen atom; and

[0076] U, or each U independently, is C_{1-4} alkyl or C_{1-4} alkylsulphonyl; and

[0077] when a is zero, Z^2 is:

$—SO_2CH_2CH_2X^1$ (IV)

[0078] in which X^1 is an eliminatable group; or

$—SO_2(CH_2)_zCH{=}CH_2$ (V)

[0079] wherein z is zero or 1; or

[0080] a group of formula (VI)

$—W—C(R^{10}){=}CH_2$ (VI)

[0081] wherein:

[0082] R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

[0083] W is $—OC({=}O)—$ or $—N(R^{11})C({=}O)—$ in which R^{11} is hydrogen or C_{1-4} alkyl.

[0084] In the halobenzene nucleus of the formula (I), X or each X independently, may be selected from nitro, cyano, alkylsulphonyl, dialkylaminosulphonyl and sulphonic acid groups and salts thereof. Preferably, X or each X independently, is selected from nitro and cyano.

[0085] The halogen atom in the halobenzene nucleus of formula (I) is preferably fluorine or chlorine.

[0086] The group R in the linking group L^1 of formulae (1)-(3) may be any of hydrogen, methyl, ethyl, n- or i-propyl or n-, s- or t-butyl, but is preferably hydrogen.

[0087] In the dye of formula (VII), each of Z^1 and Z^2, independently, is preferably a group of the above mentioned formula (I). Moreover, it is even more preferred that each of Z^1 and Z^2 is the same group as the other.

[0088] However, alternatively, Z^1 may be a halobenzene nucleus of the formula (I), A may be zero and Z^2 a group of the formula

$—SO_2CH_2CH_2X^1$ (IV)

[0089] in which X^1 is an eliminatable group such as OSO_3H, OPO_3H_2 and salts of any of these, and Cl, a preferred group (IV) being

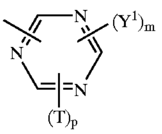
$—SO_2CH_2CH_2OSO_3H$ (or a salt thereof)

[0090] or

$—SO_2(CH_2)_zCH{=}CH_2$ (V)

[0091] wherein z is zero or 1.

[0092] In an other alternative range of dyes, Z^1 is a halobenzene nucleus of the formula (I) above and Z^2 is a halotriazine nucleus of the formula (II)



(II)

[0093] wherein m is 1 or 2, p is 0 or 1,

[0094] when m is 1, p is 1 and

[0095] when m is 2, p is 0;

[0096] Y^1_1 or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

[0097] T is C_{1-4} alkoxy, C_{1-4}thioalkoxy or $N(R^1)$ (R^2) in which R^1 is hydrogen, optionally substituted C_{1-4} alkyl or optionally substituted aryl; and

[0098] R^2 is hydrogen or optionally substituted C_{1-4}alkyl.

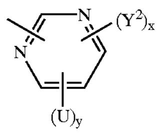
[0099] In the above formula (II), Y^1 is preferably fluorine, chlorine or optionally substituted pyridinium which may be derived from, for example, nicotinic or isonicotinic acid or their carboxamides.

[0100] Each of R^1 and R^2 is preferably hydrogen, but at least one of R^1 and R^2 may be a C_{1-4} alkyl group and indeed R^1 may additionally be an optionally substituted aryl, preferably phenyl, group.

[0101] When such a C_{1-4} alkyl or aryl group is substituted, a preferred substituent is hydroxyl, amino, halo, carboxy or sulpho.

[0102] In yet another alternative dye in accordance with the invention, Z^1 is a halobenzene nucleus of the formula (I) and Z^2 is a halopyrimidine nucleus of the formula

(III)



[0103] wherein

[0104] x is 1, 2 or 3; y is 0, 1 or 2; and $x+y \leqq 3$;

[0105] Y^2_1 or each Y^2 independently, is halogen atom; and

[0106] U, or each U independently, is C_{1-4}alkyl or C_{1-4}alkylsulphonyl.

[0107] In the above formula (III) Y^2 is preferably fluorine or chlorine.

[0108] A preferred range of dyes embodying the invention has the formula (XXX)

$$Z^1\text{-}L^1\text{-}D[L^3]_q\text{-}[Z^3\text{-}L^4{}_r[J^1]_s[L^2]_aZ^2[L^5\text{-}J^2]_t \qquad \text{(XXX)}$$

[0109] wherein:

[0110] Z^3 is a third reactive group selected from the groups of the formulae (I)-(III), given and defined above;

[0111] each of J^1 and J^2, independently, is an optionally substituted aryl group or a chromophore;

[0112] L^3 is a linking group linking Z^3 and D;

[0113] L^4 is a linking group linking Z^3 and J^1;

[0114] L^1 is a linking group linking Z^2 and J^2;

[0115] each of q, r, s and t independently, is zero or 1;

[0116] each of Z^1, Z^2, L^1, L^2 and a is as defined above; and

[0117] when at least one of a and t is 1, Z^2 is selected from the groups of the formulae (I)-(III), given and defined above.

[0118] In one such range of dyes, q is 1, r is 1, s is 1, each of a and t is zero and Z^2 is selected from the groups of the formulae (IV)-(VI), given and defined above.

[0119] In another such range, q is 1, r is 1, s is zero, a is zero and t is 1.

[0120] In a dye of the formula (XXX), each of L^3 and $L^4{}_1$ independently, is preferably selected from one of the groups of the formulae $(VII)^1$, $(VII)^2$ and $(VII)^3$, given and defined above;

[0121] each of L^3 and L^4 is preferably a group of the formulae $(VII)^1$, given and defined above.

[0122] In one preferred range of dyes of the formula (XXX), q is 1, r is zero, s is 1, a is zero and t is zero and in such a range L^3 is preferably a group of the formula $(VII)^3$

$$\text{—N(R)BN(R)—} \qquad (VII)^3$$

[0123] wherein B is a triazine group substituted by a non-reactive group.

[0124] In a dye of the formula (XXX), the chromophore D is preferably an azo chromophore derived from 1-hydroxy-8-aminonaphthalene substituted by at least one sulphonic acid group.

[0125] Yet another range of dyes embodying the invention has the formula

$$z^1\text{-}L^1\text{-}D^1[L^3\text{-}Z^3(L^4\text{-}Z^4)_lL^5\text{-}D^2]_k[L^2]_aZ^2$$

[0126] wherein:

[0127] D^1 is a first chromophore;

[0128] D^2 is a second chromophore;

[0129] Z^3, when present, is a third reactive group selected from the groups of the formulae (I)-(III), given and defined in claim 1;

[0130] Z^4, when present, is a fourth reactive group selected from the groups of the formulae (I)-(III), given and defined in claim 1;

[0131] L^3 is a linking group linking Z^3 to D^1;

[0132] L^4 is a linking group linking Z^3 to Z^4;

[0133] L^1 is a linking group linking D^2 to one of Z^3 and Z^4;

[0134] each of k and l, independently, is zero or 1; and

[0135] each of Z^1, Z^2, L^1, L^2 and a is as defined in claim 1.

[0136] In one range of such dye of formula (XXXI), a is 1, Z^2 is a group of the formula (I), given and defined above, k is zero and D^1 is a tetrakisazo chromophore containing two residues of H-acid linked together by a group forming part of the chromophore.

[0137] In another such range, a is 1, each of Z^1 and Z^2 is a group of the formula (I), given and defined above, each of k and l is 1;

[0138] each of D^1 and D^1 is a disazo chromophore containing a respective residue of H-acid,

[0139] each of Z^3 and Z^4 is a group of the formula (II), given and defined above, and

[0140] L^4 is a linking group of the formula $(VII)^2$ or $(VII)^3$, given and defined above.

[0141] In still further such ranges

[0142] (i) a is 1, Z^2 is a group of the formula (I), given and defined above, k is 1 and l is 1; or

[0143] (ii) a is 1, Z^2 is a group of the formula (I), given and defined above, k is 1 and l is zero.

[0144] Yet another preferred range of dyes embodying the invention has the formula (XXXII)

$$Z^1\text{-}L^1\text{-}Z^3\text{-}L^3\text{-}D\text{-}Z^2 \qquad \text{(XXXII)}$$

[0145] wherein:

[0146] Z^3 is a third reactive group selected from the groups (I)-(III), given and defined above; and

[0147] L^3 is a third linking group selected from the groups $(VII)^1$, $(VII)^2$ and (VII),^{3} given and defined above;

[0148] Z^2 is a second reactive group selected from the groups (IV)-(VI), given and defined above; and

[0149] each of Z^1 and L^1 is as defined above.

[0150] In such dyes of the formula (XXXII), L^1 is preferably a linking group of the formula $(VII)^2$ or $(VII)^3$, given and defined above and Z^3 is preferably a group of the formula (II), given and defined above.

[0151] Another range of dyes embodying the invention has the formula (XXXIII)

$$D\text{-}L^2\text{-}Z^2\text{-}L^1\text{-}Z^1 \qquad \text{(XXXIII)}$$

[0152] wherein:

[0153] Z^2 is selected from groups of the formulae I-(III), given and defined above; and

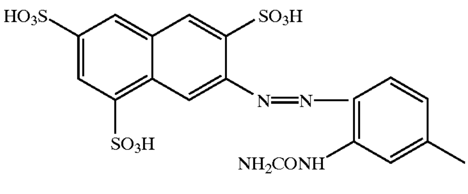
[0154] each of D, Z^1, L^1 and L^1 is as defined above.

[0155] In such dyes of the formula (XXXIII), Z^2 is preferably a group of the formula (II), given and defined above and L^2 is preferably a linking group selected from the groups $(VII)^1$, $(VII)^2$ and $(VII)^3$, given and defined above, more preferably a group of the formula $(VII)^2$ or $(VII)^3$, given and defined above; and

[0156] L^1 is a group of the formula $(VII)^3$, given and defined above, in which B is an optionally substituted aryl group, or is alternatively a chromophoric bridging group.

[0157] In the range of dyes of formulae (XXXII), a preferred chromophore D is a disazo dye containing a residue derived from H-acid and having azo groups at the 2- and 7- positions.

[0158] Another preferred chromophore D is a group of the formula



[0159] Other ranges of dyes embodying the invention are of the respective formulae

$$D^2\text{-}L^2\text{-}Z^2\text{-}L^3\text{-}D^1\text{-}L^1\text{-}Z^1 \qquad \text{(XXXIV)}$$

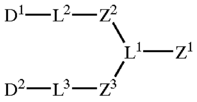
[0160] wherein:

[0161] each of D^1 and D^2, independently, is a chromophore;

[0162] L^3 is a linking group selected from groups of the formula (I)-(III), given and defined above; and

[0163] each of Z^1, Z^2_1 L^1 and L^2 is as defined above; and

(XXXV)



$$\begin{array}{l} D^1—L^2—Z^2 \\ \qquad\qquad\quad \backslash \\ \qquad\qquad\quad L^1—Z^1 \\ \qquad\qquad\quad / \\ D^2—L^3—Z^3 \end{array}$$

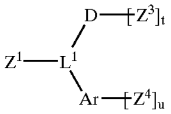
[0164] wherein:

[0165] each of D^1 and D^2_1 independently, is a chromophore;

[0166] L^3 is a linking group selected from the groups of the formulae (I)-(III), given and defined above; and

[0167] each of Z^1, Z^2, L^1 and L^2 is as defined above; and

(XXXVI)



$$\begin{array}{l} \qquad\quad D—[Z^3]_t \\ \qquad\ / \\ Z^1—L^1 \\ \qquad\ \backslash \\ \qquad\quad Ar—[Z^4]_u \end{array}$$

[0168] wherein:

[0169] one of Z^3 and Z^4 is a reactive group Z^2;

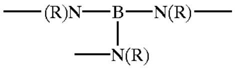
[0170] each of Z^3 and Z^4, independently, is a reactive group selected from the formulae (IV)-(VI), given and defined above;

[0171] each of t and u, independently, is zero or 1 and at least one of t and u is 1;

[0172] D is a chromophore;

[0173] Ar is an optionally substituted aryl group;

[0174] L^1 is a group of the formula



$$\begin{array}{c} —(R)N—\underset{\substack{| \\ —N(R)}}{B}—N(R)— \end{array}$$

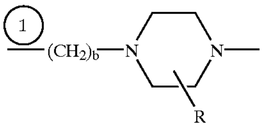
[0175] wherein each R, independently, is as defined in claim; and

[0176] Z^1 is as defined above.

[0177] In such dyes of formulae (XXXVI), D is preferably a disazo dye containing a residue derived from H-acid.

[0178] In a dye embodying the invention, the or a chromophore D may contain a heterocyclic nitrogen atom, in which case the linking group may have the formula

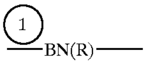
$(VII)^4$



or

-continued

(VII)^5



$$\overset{\textcircled{1}}{—}\mathrm{BN(R)}—$$

[0179] wherein each of B,R and b is as defined above and the bond ① is linked to the heterocyclic nitrogen atom of the chromophore.

[0180] Such dyes, may have the formula

$$Z^1\text{-}L^1\text{-}D^N[L^2]_a Z^2\,[L^5—Ar]_t$$

[0181] wherein:

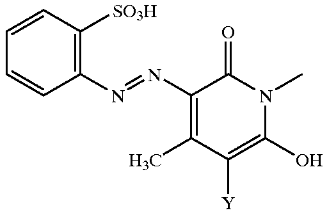
[0182] D^N is a chromophore containing a heterocyclic group including a nitrogen atom;

[0183] L^1 is a group of the formula (VII)^4 or (VII)^5, given and defined above, directly attached via the bond ①, to the nitrogen atom of the said chromophore D^N;

[0184] Ar is an optionally substituted aryl group;

[0185] and each of Z^1, Z^2, L^2, L^5, a and t is as defined above.

[0186] A typical chromophore D containing a heterocyclic nitrogen atom has the formula



[0187] In the above formulae, wherever L^1-L^5, J^1, J^2 or B is or has an optionally substituted phenyl group, optional substituents are SO_3H or a salt thereof, C_{1-4}alkyl, especially methyl and chloro, especially SO_3H.

[0188] Again, in all of the above formulae, where the groups Z^2 is any of the groups of the formulae (I)-(III), it is most preferably of the formula (II).

[0189] Likewise in all such formulae, where Z^2 i s any of the groups (IV)(VI), it is most preferably of the formula (IV) or (V), wherein Z is zero.

[0190] In a dye according to the invention, in general, the or each chromophoric group independently preferably comprises an azo (which may be a monoazo, polyazo or metal complex azo), anthraquinone, hydrazone, phthalocyanine, triphenodioxazine or formazan group. Examples of chromophoric groups which may be present are those given as types (a)-(g) of the group "D_1" in formula (I) of U.S. Pat. No. 5,484,899, which is incorporated herein by reference.

[0191] Preferred azo groups are monoazo and disazo groups. Preferred monoazo groups have the formula

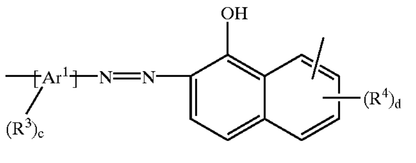
$$—Ar^1—N{=}N—Ar^2—$$

[0192] wherein Ar^1 is an aryl or heteroaryl group and Ar^2 is an aryl group.

[0193] It is preferred that each aryl group independently is a mono- or di-cyclic aryl group. Preferred aryl groups are optionally substituted phenyl and optionally substituted naphthyl. Preferred heteroaryl groups are pyridonyl and pyrazolonyl.

[0194] A first preferred monoazo group is of the Formula (IX) (or salt thereof):

(IX)



[0195] wherein:

[0196] Ar^1 is an aryl group, preferably a benzene or naphthalene nucleus;

[0197] R^3, or each R^3 independently, is C_{1-4} alkyl, nitro, halo or sulphonic acid or a salt thereof;

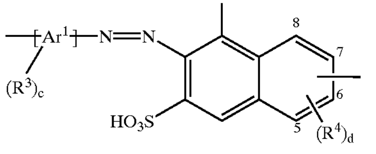
[0198] c is zero or 1 to 4;

[0199] R^4, or each R^4 independently, is a sulphonic acid or a salt thereof; and

[0200] d is 1 or 2;

[0201] and is more preferably of the formula:

(X)^1



[0202] wherein each of Ar^1R^3 and a are as defined above, R^4 is sulpho and c is zero or 1.

[0203] Ar^1 is preferably optionally substituted phenyl or naphthyl, especially a phenyl or naphthyl group having at least one sulpho substituent. Further optional substituents which may be present on Ar include a halogen atom, especially chlorine; an alkyl radical, especially C_{1-4} alkyl, more especially methyl; an acylamido radical, especially acetylamino, benzamido or sulphonated benzamido; amino; hydroxy; and an alkoxy radical, especially C_{1-4} alkoxy, more especially methoxy.

[0204] As examples of phenyl groups having at least one sulpho substituent there may be mentioned 2-, 3- or 4-sulphophenyl; 2-sulpho-4-nitrophenyl; 2-sulpho-5-nitrophenyl; 4-sulpho-2-methylphenyl; 5-sulpho-2-methylphenyl; 2-sulpho-4-methylphenyl; 5-sulpho-2-methoxyphenyl; 2-sulpho-4-methoxyphenyl; 4-sulpho-2-chlorophenyl; 5-acetamido-2-sulphophenyl; 5-sulpho-2-carboxyphenyl; 2,4-disulphophenyl; 2,5-disulphophenyl; and 3,5-disulphophenyl.

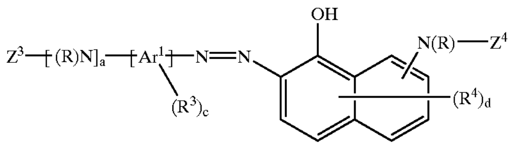
[0205] As examples of naphthyl groups having at least one sulpho substituent there may be mentioned 1-sulphonaphth-2-yl; 1,5-disulphonaphth-2-yl; 1,5,7-trisulphonaphth-2-yl; 3,6,8-trisulphonaphth-2-yl; 5,7-disulphonaphth-2-yl; 6-sulphonaphth-2-yl; 4-, 5-, 6-, or 7-sulphonaphth-1-yl; 4,8-disulphonaphth-1-yl; 3,8-disulphonaphth-1-yl; 2,5,7-trisulphonaphth-1-yl; and 3,5,7-trisulphonaphth-1-yl.

[0206] Preferred optional substituents which may be present on the naphthalene nucleus of Formula (IX) are those mentioned above for Ar^1.

[0207] Groups of the Formula (IX) are preferably linked to a group L^1 or L^2 at the 6-, 7- or 8-position, especially the 6- or 8-position. When L^1 or L^2 is to be linked at the 8-position, it is preferred that R^5 is a sulpho group at the 5- or 6-position.

[0208] Thus a preferred monoazo dye embodying the invention has the formula (XVII)

(XVII)



[0209] wherein:

[0210] each R independently and a is as defined above;

[0211] one of Z^3 and Z^4 is a group Z^1 and the other is a group Z^2;

[0212] the group Z^4 is selected from the groups of the formulae (I)-(III), given and defined above.

[0213] Ar^1 is a benzene or naphthalene nucleus;

[0214] R^3, or each R^3 independently, is C_{1-4} alkyl, nitro, halo or sulphonic acid or salt thereof;

[0215] c is zero or 1-4;

[0216] R^4, or each R^4 independently, is a sulphonic acid or a salt thereof; and

[0217] d is 1 or 2.

[0218] A preferred disazo group is of the Formula (XI) (or salt thereof):

$$Ar^1\text{—N=N—M—N=N—E} \qquad \text{(XI)}$$

[0219] wherein:

[0220] M and E are each independently optionally substituted phenylene or naphthalene; and

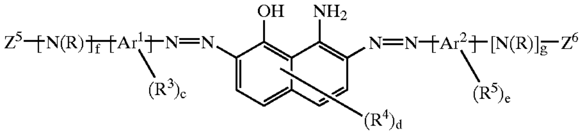
[0221] Ar^1 is as defined above.

[0222] It is preferred that E is optionally substituted naphthalene and M is optionally substituted phenylene. The optional substituents which may be present on M or E are preferably independently selected from halo, especially chloro; alkoxy, especially C_{1-4} alkoxy; alkyl, especially methyl; sulpho; carboxy; hydroxy; amino; acylamino, especially acetamido, benzamido and sulphonated benzamido, and pyrimidinylamino or triazinylamino cellulose-reactive groups.

[0223] As Examples of groups represented by M and E, there may be mentioned phenylene, 2-methyl-1,4-phenylene, sulphophenylene, ureidophenylene, 7-sulpho-1,4-naphthalene, 6-sulpho-1,4-naphthalene; 8-sulpho-1,4-naphthalene and 6-hydroxy-4-sulpho-1,5-naphthalene.

[0224] An especially preferred range of disazo-dyes has the formula (XVIII)

(XVIII)



[0225] wherein:

[0226] one of Z^5 and Z^6 is a group Z^1 and the other is a group Z^2;

[0227] each of f and g independently is zero or 1;

[0228] when Z^5 or Z^6 is any of the groups of the formulae (I)-(III), given and defined above, f or g respectively is 1 and when Z^5 or Z^6 is any of the groups of the formulae (IV)-(VI), given and defined above, f or g respectively is zero;

[0229] each of c and e, independently, is zero or 1-4;

[0230] d is 1 or 2;

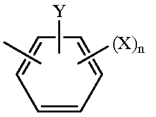
[0231] each R independently is as defined above;

[0232] each of Ar^1 and Ar^2 independently is an optionally substituted aryl group; and

[0233] each of R^3 and R^4 is as defined above.

[0234] In a dye of the formula (XVIII), each of Z^5 and Z^6 may be the same group

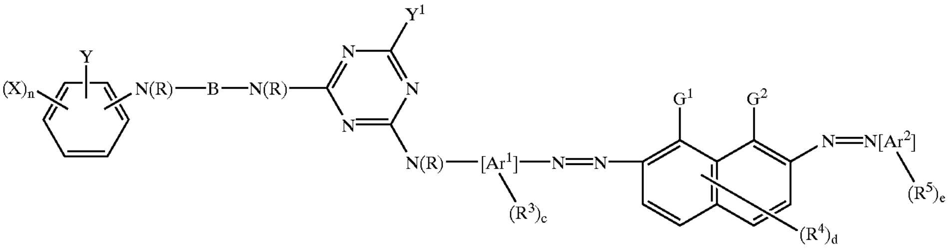
(I)



[0235] wherein X, Y and n are as defined above.

[0236] Alternatively, one of Z^5 and Z^6 may be a group of the formula (I), given and defined above, and the other of Z^5 and Z^6 may be selected from groups of the formulae (II) and (III), given and defined above. In such a dye it is preferred that one of Z^5 and Z^6 is a group of the formula (I), given and defined above, and the other of Z^5 and Z^6 is a group of the formula (II).

[0237] Another especially preferred range of disazo dyes has the formula



[0238] wherein:

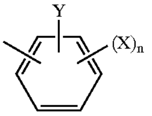
[0239] B is a hydrocarbon bridging group as defined above, and preferably an optionally substituted aryl group;

[0240] one of G^1 and G^2 is OH and the other is NH_2;

[0241] each of X, Y, Y^1, Ar^1Ar^2, R^3, R^4, R^5, c, d and e is as defined above.

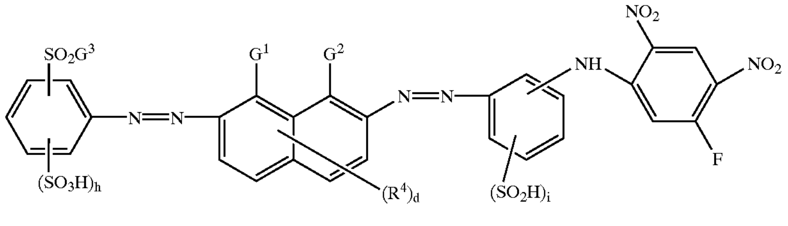
[0242] In a dye of the formula (XVIII), one of Z^5 and Z^6 may be a group

(I)



[0243] wherein: X, Y and n are as defined in claim **1** and the other of Z^5 and Z^6 is the group $—SO_2CH_2CH_2OSO_3H$ or $—SO_2CH{=}CH_2$.

[0244] Typically such a dye has the formula



[0245] wherein

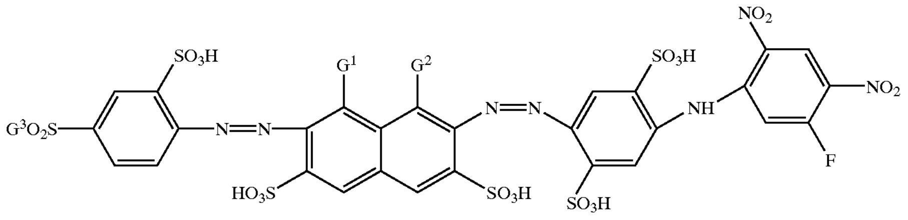
[0246] G^3 is $C_2H_4OSO_3H$ or a salt thereof or $—CH{=}CH_2$;

[0247] G^1 and G^2 are as defined above;

[0248] R^4 and d are as defined above; and

[0249] each of h and i, independently, is zero, 1 or 2.

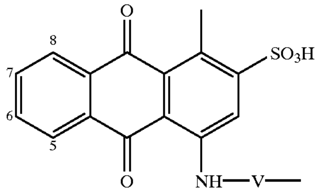
[0250] A more preferred range of such dyes has the formula



[0251] where each of G^1 G^2 and G^3 is as defined above.

[0252] When the chromophore D is an anthraquinone, a preferred anthraquinone group is of the Formula (XII) (or a salt thereof).

(XII)



[0253] wherein the anthraquinone nucleus optionally contains a sulphonic acid group in the 5-, 6-, 7-, or 8-position and V is a divalent organic linking group, preferably of the benzene series.

[0254] V is a bridging group B, preferably phenylene, diphenylene, or 4,4'-divalent stilbene or azobenzene radicals which are optionally sulphonated. It is preferred that V contains one sulphonic acid group for each benzene ring present therein.

[0255] A preferred anthraquinone dye of has the formula

$D^A\text{-}L^3\text{-}Ar\text{-}\ L^2\text{-}Z^2\text{-}\ L^1\text{-}Z^1$

[0256] wherein:

[0257] D^A is an anthraquinone chromophore;

[0258] L^3 is a linking of the formula $(VII)^1$, given and defined above;

[0259] Ar is an optionally substituted aryl group;

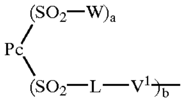
[0260] and

[0261] each of Z^1, Z^2, L^1 and L^2 is as defined above.

[0262] More preferably each of L^1 and L^2, independently, is a linking group of the formula $(VII)^1$, $(VII)^2$ or $(VII)^3$, given and defined above; and still more preferably, each of L^1 and L^2_1 independently is a group of the formula $(VII)^3$, given and defined above, in which B is an optionally substituted aryl group.

[0263] When the chromophore D is a phthalocyanine, a preferred phthalocyanine group is of the Formula (XIII) (or a salt thereof).

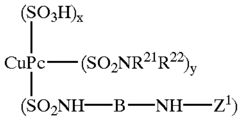
(XIII)



$$\mathrm{Pc}\begin{array}{l}(\mathrm{SO_2{-}W})_a\\(\mathrm{SO_2{-}L{-}V^1})_b{-}\end{array}$$

[0264] wherein Pc is a metallo-phthalocyanine nucleus, preferably copper or nickel phthalocyanine; L is as hereinbefore defined; each W independently is a hydroxy or a substituted or unsubstituted amino group, V^1 is a divalent organic linking group, preferably a C_{1-4}-alkylene or phenylene linking group; and a and b are each independently 1, 2 or 3 provided that a+b is not greater than 4.

[0265] Preferably such a metal phthalocyanine dye has the formula



$$\begin{array}{l}(\mathrm{SO_3H})_x\\ |\\ \mathrm{CuPc{-}(SO_2NR^{21}R^{22})_y}\\ |\\ (\mathrm{SO_2NH{-}B{-}NH{-}Z^1})_z\end{array}$$

[0266] wherein:

[0267] Cu Pc is a copper phthalocyanine chromophore;

[0268] $X+Y+Z \leqq 4$;

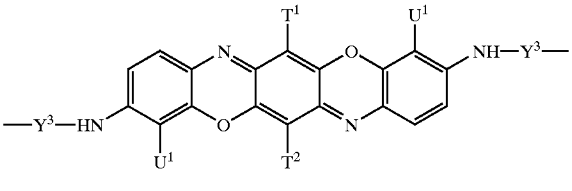
[0269] each of R^{21} and R^{22}, independently, is hydrogen or optionally substituted C_{1-4}alkyl;

[0270] B is a hydrocarbon bridging group; and

[0271] Z^1 is as defined above.

[0272] When the chromophore D is a triphenodioxazine a preferred triphenodioxazine group is of the Formula (XIV) (or a salt thereof).

(XIV)



[0273] wherein:

[0274] each Y^3 independently is a covalent bond, C_{2-4}-alkylene, phenylene or sulphophenylene;

[0275] U^1 is H or SO_3H; and

[0276] T^1 and T^2 are halo, especially chloro, C_{1-4}-alkyl, or C_{1-4} alkoxy.

[0277] Each Y^3 is preferably —CH_2H_4— or —C_3H_6—, U^1 is preferably SO_3H and T^1 and T^2 are preferably Cl, methyl or ethyl.

[0278] Preferably such a triphendioxazine dye has the formula

Z^1-L^1-$[Z^3$-$L^3]_q$-D^T-$[Z^4]_r$-L^2-Z^2

[0279] wherein:

[0280] D^T is a triphendioxazine chromophore;

[0281] each of L^2, L^3 and L^4, independently, is a linking group of the formula $(VII)^1{}_1$ $(VII)^2$ or $(VII)^3$ given and defined above;

[0282] each of Z^2, Z^3 and Z^4 is a reactive group selected from groups of the formulae (I)-(III), given and defined above;

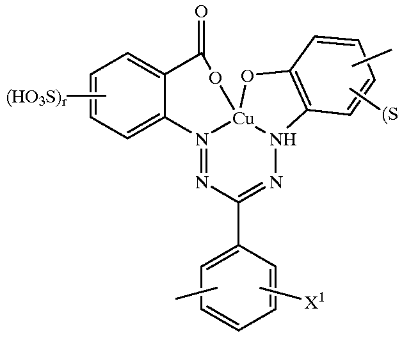
[0283] each of q and r is zero or 1; and

[0284] each of Z^1 and L^1 is as defined above.

[0285] In such a dye, Z^2 is preferably a group of the formula (I), given and defined above and each of Z^3 and Z^4 is a group of the formula (II), given and defined above; and each of L^1, L^2, L^3 and L^4 is preferably a group of the formula $(VII)^3$, given and defined above.

[0286] When the chromophore D is a formazan, a preferred group is of the Formula (XV) (or a salt thereof).

(XV)



[0287] wherein:

[0288] X^1 is H, SO_3H or Cl; and

[0289] each r independently has a value of 0, 1 or 2.

[0290] provided that the formazan group has at least one, and preferably at least two, sulpho groups.

[0291] It is preferred that each r has a value of 1.

[0292] Preferably such a formazan dye has the formula

$[Z^A]_a$-D^F-L-Z^B-L^1-Z^1

[0293] wherein:

[0294] D^F is a formazan chromophore;

[0295] one of Z^A and Z^B is a group Z^2, given and defined above;

[0296] each of L^3 and L^4 is a linking group of the formula $(VII)^1$, $(VII)^2$ or $(VII)^3$, given and defined above;

[0297] each of Z^1 and L^1 is as defined above;

[0298] a is zero or 1;

[0299] Z^A is selected from groups of the formulae (IV)-(VI), given and defined above; and

[0300] Z^8 is selected from groups of the formulae (I)-(III),given and defined above.

[0301] According to one process aspect, the invention provides a process for preparing a dye of the formula $(VIII)^1$

Z^1 -L^1-D-L^2-Z^2 $(VIII)^1$

[0302] wherein:

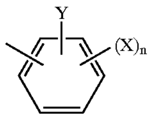
[0303] D is a chromophore;

[0304] each of L^1 and L^2 independently, is N(R);

[0305] each R, independently, is hydrogen or C_{1-4}-alkyl;

[0306] each of Z^1 and Z^2 is a group

(I)



[0307] in which:

[0308] n is 1 or 2

[0309] X, or each X independently, is an electron withdrawing group; and

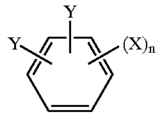
[0310] Y is a halogen atom,

[0311] which process comprises reacting a chromophoric compound of the formula (XX)

H(R)N-D-N(R)H (XX)

[0312] wherein each of D and R is as defined above, with at least two moles, per mole of the chromophoric compound of the formula (XX), of a dihalobenzene component comprising at least one dihalobenzene compound of the formula (XXI)

(XXI)



[0313] wherein each of X, Y and n is as defined above, to obtain the dye of the formula $(VIII)^1$.

[0314] When the dye is of the formula (XVIII) given above, the chromophoric compound of the formula (XX) can be prepared by protecting one amino group of a phenylene diamine sulphonic acid and then diazotising this and coupling a first portion of the diazotised phenylene diamine sulphonic acid to the naphthalene nucleus under acid conditions so as to couple on to the benzene ring of the naphthalene nucleus containing an amino group and then taking a second portion of the same diazotised and protected phenylene diamine sulphonic acid compound referred to above (or a different such compound) and coupling this under neutral or alkaline conditions to the benzene ring of the naphthalene nucleus containing a hydroxyl group to obtain a diamine dyestuff having respective protected amino groups. The protective group can then be removed by hydrolysis.

[0315] According to another process aspect, the invention provides a process for preparing a dye of the formula $(VIII)^1$

$$Z^1\text{-}L^1\text{-}D\text{-}L^2\text{-}Z^2 \qquad (VIII)^2$$

[0316] wherein:

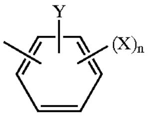
[0317] D is a chromophore;

[0318] each of L^1 and L^2 independently, is N(R);

[0319] each R, independently, is hydrogen or C_{1-4}alkyl;

[0320] Z^1 is a group

(I)



[0321] in which:

[0322] n is 1 or 2

[0323] X, or each X independently, is an electron withdrawing group; and

[0324] Y is a halogen atom; and

[0325] Z^2 is selected from the groups (II) and (III) defined above;

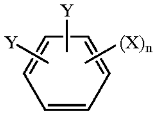
[0326] which process comprises reacting a chromophoric compound of the formula (XX)

$$H(R)N\text{-}D\text{-}N(R)H \qquad (XX)$$

[0327] wherein each of D and R is as defined above, with one mole, per mole of the chromophoric compound of the formula (XX), of each of

[0328] (a) a dihalobenzene compound of the formula (XXI)

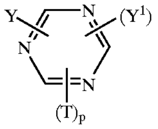
(XXI)



[0329] wherein each of Z, X, Y and n is as defined above; and

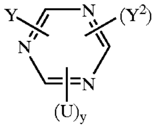
[0330] (b) a compound selected from

(XXII)



and

(XXIII)



[0331] wherein:

[0332] m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

[0333] Y^1, or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

[0334] T is C_{1-4}alkoxy, C_{1-4}thioalkoxy or $N(R^1)(R^2)$, in which each of $R^1$and R^2 independently is hydrogen, optionally substituted C_{1-4}alkyl or optionally substituted aryl;

[0335] x is 1, 2 or 3; y is zero, 1 or 2; and $x+y \leqq 3$;

[0336] Y^2, or each Y^2 independently, is a halogen atom or an optionally substituted pyridinium group;

[0337] U or each U independently, is C_{1-4}alkyl or C_{1-4}alkylsulphonyl; and

[0338] Y is as defined above;

[0339] the said reactions of the compound of the formula (XX) with each of the respective compounds of the formulae (XII) and (XIII) being carried out simultaneously or one before the other, in either order, to obtain a dye of the formula $(VIII)^2$.

[0340] According to yet another process aspect, the invention provides a process for preparing a dye of the formula $(VIII)^3$

$$Z^1\text{-}L^1\text{-}D\text{-}Z^2 \qquad (VIII)^3$$

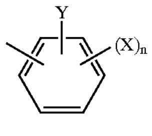
[0341] wherein:

[0342] D is a chromophore

[0343] L^1 is N(R), in which R is hydrogen or C_{1-4}alkyl;

[0344] Z^1 is a group

(I)



[0345] in which n is 1 or 2; X, or each X independently, is an electron withdrawing group; and Y is a hydrogen atom; and Z^2 is a group of the formula (IV)

$$—SO_2CH_2CH_2X^1 \quad (IV)$$

[0346] wherein

[0347] X^1 is an eliminatable group;

[0348] a group of the formula (V)

$$—SO_2(CH_2)_2CH{=}CH_2 \quad (V)$$

[0349] wherein

[0350] z is zero or 1; and

[0351] a group of formula (VI)

$$—W—C(R^{10}){=}CH_2 \quad (VI)$$

[0352] wherein:

[0353] R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

[0354] W is —OC(═O)— or —N(R^{11})C(═O)—

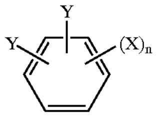
[0355] in which R^{11} is hydrogen or C_{1-4}alkyl;

[0356] which process comprises reacting a chromophoric compound of the formula (XXIV)

$$H(R)N\text{-}D\text{-}Z^2 \quad (XXIV)$$

[0357] wherein D and Z^2 are as defined above, with a dihalobenzene compound of the formula (XXI)

(XXI)



[0358] wherein each of X, Y and n is as defined above, to obtain the dye of the formula $(VIII)^3$.

[0359] Although dye formulae have been shown in the form of their free acid in this specification, the invention also includes dyes and processes using dyes in the salt form, particularly their salts with alkali metals such as the potassium, sodium, lithium or mixed sodium/lithium salt and their salts with tetraalkylammonium ions.

[0360] The dyes may be used for dyeing, printing or ink-jet printing, for example, of textile materials and paper.

[0361] The process for colouration is preferably performed at a pH of 7.1 to 13, more preferably 10 to 12. pH levels above 7 can be achieved by performing the process for colouration in the presence of an acid-binding agent.

[0362] The substrate may be any of a textile material, leather, paper, hair or film, but is preferably a natural or artificial textile material containing amino or hydroxyl groups, for example textile material such as wool, silk, polyamides and modified polyacrylonitrile fibres, and more preferably a cellulosic material, especially cotton, viscose and regenerated cellulose, for example, that commercially available as Tencel. For this purpose the dyes can be applied to the textile materials at a pH above 7 by, for example, exhaust dyeing, padding or printing, including ink-jet printing. Textile materials are coloured bright shades and possess good fastness to light and wet treatments such as washing.

[0363] The new dyes are particularly valuable for colouring cellulosic textile materials. For this purpose, the dyes are preferably applied to the cellulosic textile material at a pH above 7 in conjunction with a treatment with an acid binding agent.

[0364] Preferred acid-binding agents include alkali metal carbonates, bicarbonates, hydroxides, metasilicates and mixtures thereof, for example sodium bicarbonate, sodium carbonate, sodium metasilicate, sodium hydroxide and the corresponding potassium salts. The dyes benefit from the excellent build-up and high fixation.

[0365] At least for cellulosic materials, exhaust dyeing can be carried out at a relatively low temperature of about 50-70° C., especially about 60° C.

[0366] The new dyes can be applied to textile material containing amine groups, such as wool and polyamide textile materials, from a neutral to mildly alkaline dyebath. The dyeing process can be carried out at a constant or substantially constant pH, that is to say that the pH of the dyebath remains constant or substantially constant during the dyeing process, or if desired the pH of the dyebath can be altered at any stage of the dyeing process.

[0367] The dyes may be in a liquid form, or solid form, for example in granular or powdered form.

[0368] We find surprisingly that such dyes give a much higher build up, as compared with known dyestuffs, particularly in warm dyeing applications at about 60° C.

[0369] In addition, a wide selection of dye backbones is possible, giving the potential to provide high fastness dyes.

[0370] Dyes embodying the invention are especially useful for application to substrates by ink-jet technologies. Substrates which are particularly useful are cellulosic textiles and paper.

[0371] The dye used in the ink is preferably purified by removal of substantially all the inorganic salts and by-products which are generally present in a commercial dye at the end of its synthesis. Such purification assists in the preparation of a low viscosity aqueous solution suitable for use in an ink jet printer.

[0372] To assist in the achievement of heavy depths of shades the dye should preferably have a water-solubility of at least 5%, and more preferably from 5% to 25%, by weight. Solubility of the dye can be enhanced by converting the sodium salt, in which form it is normally synthesised, either partially or wholly, into the lithium or ammonium salt. Purification and ion exchange can conveniently be effected by use of membrane separation processes which permit the separation of unwanted inorganic materials and by-products directly from an aqueous solution or dispersion of the dye followed by partial or complete exchange of the counter-ion. The ink preferably contains up to 20% by weight of dye and more preferably from 2% to 10%, especially from 3% to 8%.

[**0373**] The ink may also contain a humectant, which may also function as a water miscible solvent, which preferably comprises a glycol or dihydroxyglycolether, or mixture thereof, in which one or both hydroxy groups are secondary hydroxy groups, such as propane-1,2-diol,butane-1,3-diol and 3-(3-hydroxy-prop-2-oxy)propan-2-ol.

[**0374**] Where the humectant has a primary hydroxy group this is prefereably attached to a carbon atom adjacent to a carbon atom carrying a secondary or tertiary hydroxy group. The humectant may comprise up to a total of 10% by weight of a polyol, especially a glycol or dihydroxyglycolether, having two or more primary hydroxy groups, such as ethyleneglycol, propane-1,3-diol,butane-1,4-diol, 2-(2-hydroxyethoxy)ethanol and 2-(2-[2-hydroxyethoxy)ethanol and/or an alcohol with a primary hydroxy group, such as ethanol,n-propanol and n-butanol. However, it preferably contains not more than 5% by weight, and is more preferably free from, such compounds. In the context of the humectant, the term "alcohol" means a compound having only one hydroxy group attached to an aliphatic carbon atom. The ink preferably contains from 5% to 25%, by weight, more especially from 10% to 20%, of humectant.

[**0375**] If desired, the ink may be buffered to a pH from 5 to 8, especially to a pH from 6 to 7, with a buffer such as the sodium salt of metanilic acid or an alkali metal phosphate, or di- or triethanolamine.

[**0376**] The ink preferably also contains one or more preservatives to inhibit the growth of fungi, bacteria and/or algae because these can block the jet of the ink jet printing equipment. Where the ink jet printing technique involves the charging and electrically controlled deflection of drops the solution preferably contains a conducting material such as an ionised salt to enhance the accumulation of charge on the drop. Suitable salts for this purpose are alkali metal salts of mineral acids. The remainder of the ink is preferably water, especially de-ionised water to avoid the introduction of impurities into the ink.

[**0377**] Especially preferred embodiments of the invention will now be described in more detail with reference to the following Examples in which all parts and percentages are by weight unless otherwise stated. Although preparation and dyeing with any single dye is exemplified, particular advantage could be seen when dyeing with mixtures of dyes.

PREPARATIVE EXAMPLES

Example 1

[**0378**] 2-amino-4-(N-acetyl)aminobenzene-1-sulphonic acid (0.5M, 182 g) was dissolved in water (600 ml) at pH 7 and 2M sodium nitrite solution added (0.526M, 263 ml). This solution was added dropwise to a mixture of hydrochloric acid 35% (1.13M, 100 ml, SG=1.18) and ice (1 Kg), maintaining a temperature of 0-5° C. The mixture was stirred for 0.5 hrs with excess nitrous acid at 0-5° C. A solution of sulphamic acid (10%) was added to remove excess nitrous acid to obtain a suspension of a diazotized diamine for coupling.

[**0379**] H-Acid (0.475M, 183 g) was dissolved in water (800 ml) at pH 7.5. This solution was added dropwise to the above diazo suspension with good agitation over 1 hr at 0-2° C. The mixture was then stirred at 0-2° C. for a further 2 hrs at pH 2-3, and allowed to warm to room temperature over 18 hrs.

[**0380**] The viscous suspension was adjusted to pH 6 using sodium hydroxide solution (46/48%) and a solution of a monoazo dye was thereby obtained.

[**0381**] The above monoazo dye solution was cooled to 0-5° C. and a batch of the diazotized diamine prepared as above was added. The mixture was stirred at 0-5° C. and pH 6-7 for 2 hrs and subsequently over 18 hrs at room temperature while maintaining the pH at 6-7 using 2M sodium carbonate solution, thereby obtaining a disazo dye solution.

[**0382**] Hydrolysis was then carried out by adding sodium hydroxide solution (46/48%, 800 g) to the above disazo dye solution (vol=5 L) and heating at 70-75° C. for 1.5 hrs.

[**0383**] The reaction mixture was cooled to 20° C. and neutralised by controlled addition of 35% hydrochloric acid. After screening to remove a small amount of impurity sodium chloride was added (15% w/v) and stirring continued to allow precipitation of the resultant diaminodisazo product. This was collected by filtration and dried at 40° C. (285 g; 0.242M; strength=68.3%).

[**0384**] The above diaminodisazo dye (0.01M, 11.78 g) was dissolved in water/acetone (100 ml, 1:1) at 50° C. A solution of 1,5-difluoro-2,4-dinitrobenzene (0.023M, 4.7 g taken as 100% strength) in acetone (20 ml) was added over 0.25 hr and the mixture heated at 55° C. for 3 hrs. The pH was maintained at 7 throughout the reaction by the addition of 2N sodium carbonate solution.

[**0385**] The reaction mixture was cooled to 20° C. and acetone (150 ml) added to precipitate the dye. The product was collected by filtration and washed with acetone (50 ml) and dried at 40° C. to give a greenish-navy dye(11.12 g; 0.0075M; strength 74.8%) ($\lambda_{Max=}$607 nm; $\epsilon_{Max=}$57,036).

Example 2

[**0386**] The method of Example 1 was followed except that the diaminodisazo was reacted with 1,5-dichloro-2,4-dinitrobenzene in place of 1,5-difluoro-2,4-dinitrobenzene to give a greenish-navy dye(λ_{Max}=607 nm; ϵ_{Max}=48,212).

Example 3

[**0387**] The method of Example 1 was followed except that the diaminodisazo was reacted with 1,5-difluoro-2-cyan-4-nitrobenzene in place of 1,5-difluoro-2,4-dinitrobenzene to give a greenish-navy dye(λ_{Max}=607 nm; ϵ_{Max}=56,416).

Example 4

[**0388**] The method of Example 1 was followed except that the diaminodisazo was reacted with 1,5-difluoro-2-nitrobenzene in place of 1,5-difluoro-2,4-dinitrobenzene to give a greenish-navy dye(λ_{Max}=608 nm; ϵ_{Max}=54,660).

Example 5

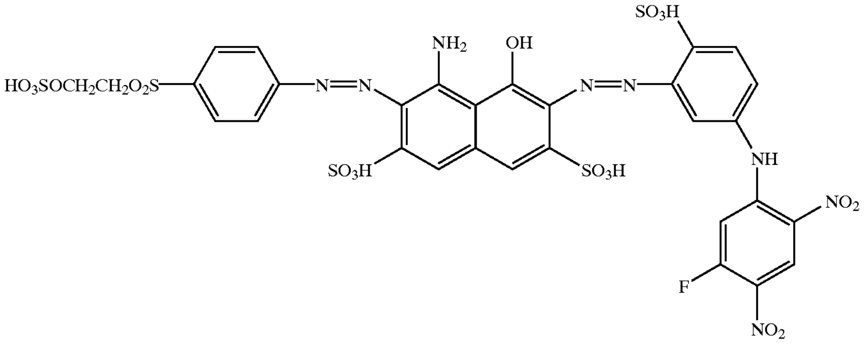
[**0389**] 4-Amino benzene sulphatoethylsulphone (0.1M, 30 g) was stirred in ice/water (400 ml) and hydrochloric acid

35% (0.58M, 52 ml, SG=1.18) and the temperature maintained at below 5° C. 2M Sodium nitrite solution (0.104M, 52 ml) was added dropwise at below 5° C. and the mixture stirred for a further 2 hours. A solution of sulphamic acid was added (10%) to remove excess nitrous acid and provide a diazo suspension for coupling.

[0390] H-Acid (0.103M, 42.6 g) was dissolved in water (300 ml) at pH 6 and the solution cooled to 5° C. This solution was added dropwise to the above diazo suspension with good agitation, while maintaining the temperature below 5° C. The mixture was then stirred for 18 hours, allowing the temperature to rise to 20° C. Sodium chloride (10% w/v) was added and the mixture stirred for 1 hour. The precipitated monoazo dye was collected by filtration and reslurried in ethanol (600 ml) for 1 hour at 20° C. The product was collected by filtration and dried at 40° C. (70 g; 0.0825M; strength=72%).

[0391] 3-Amino-5'-fluoro-2',4'-dinitrodiphenylamine-4-sulphonic acid (0.0068M, 3.2 g) was dissolved in water (100 ml) at 50-60° C. and the solution cooled to 20° C. 2M Sodium nitrite solution (0.008M, 4 ml) was added and the mixture cooled to 0-2° C. and added dropwise to ice (50 g) and hydrochloric acid 35% (0.09M, 8 ml), while maintaining the temperature at 0-2° C. The resulting yellow suspension was stirred at 0-2° C. for 0.5 hour and a solution of sulphamic acid (10%) added to remove excess nitrous acid and provide a diazo suspension for coupling.

[0392] The diazo suspension was then added dropwise to a solution of the above monoazo dye (0.006M, 5.1 g) in water (150 ml) at pH 5 and 0-2° C. The pH of the coupling mixture was maintained at pH 5 by the addition of 2M sodium carbonate solution and stirred at this pH for 18 hours, allowing the temperature to rise to 20° C. Sodium chloride was added (20% w/v) and the product collected by filtration. The solid was reslurried in ethanol (100 ml) for 1 hour at 20° C., collected by filtration and dried at 40° C. to obtain a greenish-navy dye (4.4 g; 0.003M; strength=67%) (λ_{Max}=603 nm; ϵ_{Max}=54,279) of the structure given below:



Examples 6-61

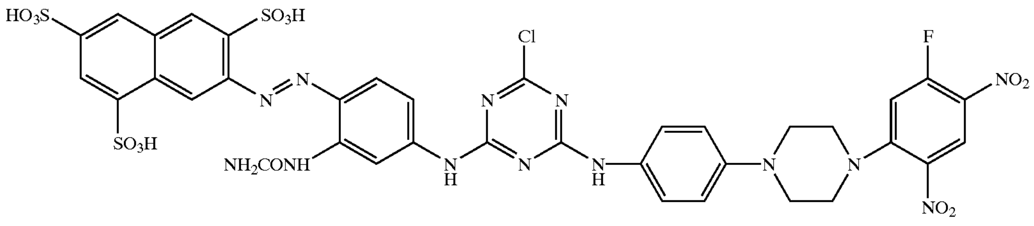
[0393] Other disazo naphthalene structures embodying the invention are shown as Examples 6 to 61 in Table 1. They can be prepared by methods analogous to those outlined in Examples 1 to 5.

Examples 62-67

[0394] Still further disazo naphthalene dyes embodying the invention, in which the chromophore has been doubled up via a linking group, are shown in Examples 62 to 67 in Table 2.

Example 68

[0395] This Example describes how a dye may be synthesised where the fibre-reactive halobenzene group is attached via a linking diamine to a second fibre-reactive group, and thereby to a chromophore.



[0396] The N-dichlorotriazinyl derivative of the azo dye resulting from azo-coupling 7-aminonaphthalene-1,3,6-trisulphonic acid with m-ureidoaniline was prepared by conventional means. A solution of this dye (35 mmol in 450 ml) was added at room temperature with stirring to N-(4-aminophenyl)piperazine (7.5 g, 42 mmol) dissolved in 50/50 acetone/water (400 ml) maintained at pH 6-6.5 by addition of sodium carbonate solution. After completion of the reaction the solution was concentrated, and the product was precipitated by addition of methylated spirit. To a solution of this intermediate (8.4 mmol) in 50/50 acetone/water (200 ml) was added a solution of 1,5-difluoro-2,4-dinitrobenzene (8.5 mmol) in acetone (20 ml), maintaining the pH at 8.5 by addition of sodium carbonate solution. On completion of the reaction, the pH was adjusted to 6.5 and the solution was concentrated to ca 100 ml. Methylated spirit was added, and the product dye was filtered, washed with meths and dried. λ_{Max}(water)=379 nm, ϵ_{Max}=33000 1 mol^{-1} cm^{-1}, half band width >150 nm. This material dyed cotton a bright golden yellow shade with very good fastness properties.

Examples 69-77

[0397] By following the principles described in Example 68, dyes of a similar nature may be prepared as further exemplified by dyes 69-77 listed in Table 3.

Examples 78-97

[0398] Disazo naphthalene dyes containing two reactive groups attached to the chromophore as described in Example 68 are exemplified by Examples 78 to 97 listed in Table 4.

Examples 98-127

[0399] Further yellow dyes may be prepared by the methods described in Examples 1-6 and 68, and are listed in Tables 5 to 9.

Examples 128-160

[0400] Monoazo naphthalene dyes embodying the invention are listed in Tables 10 to 12.

Examples 161-189

[0401] A variety of dyes embodying the invention, containing blue and green chromophores, are listed in Tables 13 to 16.

Application Examples

Examples 190-192

[0402] Each of the dyes (0.2 parts) of respective Examples 1, 3 and 5 was dissolved in respective amounts of water (50 parts) at 25° C. and pH 9. Cotton fabric (5 parts) and Glaubers salt (2.5 parts) were added. The dyes were fixed to the cotton by raising the temperature to between 50° C.-60° C., basifying to pH 11.0 and maintaining this for 1 hr. The cotton was removed and washed in soapy water to give a dark greenish-navy cotton having high general fastness properties.

Examples 193 and 194

[0403] Each of the dyes (0.2 parts) of respective Examples 2 and 4 was dissolved in water (50 parts) at 25° C. and pH 9. Cotton fabric (5 parts) and salt (4 parts) were added. The dyes were fixed to cotton by raising the temperature to 80-100° C. and maintaining this for 1 hr. The cotton was removed and washed in soapy water to give a deep greenish-navy cotton having good fastness properties.

Examples 195-198

[0404] Methodology for applying dyes embodying the present invention to cotton may be further exemplified by means of the following pad-batch dyeing protocol.

Example 195-198

[0405] Example 195.-Dye from Example 5 (0.5 parts) was dissolved in water (30 parts) at 25° C. and the following agents were added: Primasol NF (1 part of 20% solution) and sodium silicate Q70 (9.5 parts of 50% solution), sodium hydroxide (5.1 parts of 10% solution). The solution was made up to 50 parts by addition of water, and then padded onto woven cotton fabric (70% pick-up). The cloth was wrapped in cling film and batched at room temperature for 24 hours. The cling film was removed and the dyed cloth was rinsed successively with cold water and hot water, then washed with a soap solution, rinsed with water, and dried to give cotton coloured a dull greenish blue shade.

Example 196

[0406] If the amount of dye used in Example 193 is doubled and the procedure repeated, a greenish-navy shade is obtained.

Example 197

[0407] If the amount of dye used in Example 193 is trebled and the procedure repeated, a dark navy shade is obtained.

Example 198

[0408] If six times the amount of dye in Example 193 is used and the procedure repeated, an almost black shade is obtained.

[0409] Other dyes from the above Examples, particularly those containing the 2,4-dinitrofluorobenzene unit and/or a vinyl sulphone group or its sulphate half-ester precursor, can be applied to cotton by the same method.

Example 199

[0410] Dyes embodying the present Invention may be applied to textile substrates, especially cotton, by conventional printing technology, as the following exemplifies.

[0411] A dye from Example 5 (30 parts) was dissolved in a solution containing Manutex F 700 (500 parts of a 10% solution) and Vitexol D (20 parts). The solution was made up to 1000 parts by the addition of water and printed by means of a Zimmer screen printer. The printed cloth was dried and padded through a solution containing sodium silicate (48 degBe, 700 parts) made up to 1000 parts by the addition of water (80% pickup) . Immediately after padding, the printed cotton was steamed in a Roaches Flash-ager steam chamber at 120 deg C. for 45 seconds. The printed cloth was rinsed in cold water, washed with a soap solution at the boil, rinsed again in cold water and dried to give a dull greenish navy print on the cotton.

Example 200

[0412] Dyes embodying the present invention may be used in the preparation of inks specially formulated for application by ink-jet technology. As an Example, the dye from Example 5 (6 parts) was dissolved in a solution of propylene glycol (15 parts) and water (79 parts) . When this solution was applied to cotton which had previously been pretreated (for example, with a pretreatment agent described in EP-A-0534660) by means of commercial ink-jet printing equipment, deep navy shades were obtained.

[**0413**] Other dyes from the above examples as well as others described by the Invention may be used to prepare inks suitable for ink-jet printing.

Example 201

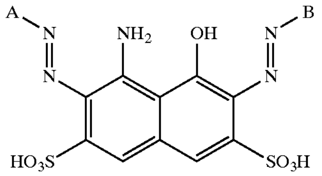
[**0414**] Reactive dyes, including those of Examples 1-189, are usually isolated as their sodium salts, and are contaminated with inorganic impurities resulting from the method of preparation. Dyes free of impurities suitable for ink jet printing, and/or with increased solubility, may be prepared by conventional ion exchange techniques, where for example sodium is replaced by lithium and inorganic impurities are simultaneously removed.

[**0415**] Dye from Example 1 (10 parts) was dissolved in water (100 parts) and treated on a reverse osmosis rig until the permeate conductivity was **10** micro reciprocal ohms. A solution of lithium chloride was added to the dye solution and treatment on the r.o. rig was continued until the permeate conductivity had decreased to **1** micro reciprocal ohm. The sample was concentrated to a volume of about **80** parts, after which the solution was buffered and other formulating agents were added. The dye solution was then diluted to 90 parts by addition of water, at which stage it was suitable for storage. Dye solution prepared in this way could be diluted and applied to cotton by the methods described in any of the Examples 190, 195-198, or formulated into an ink by addition of suitable humectants and/or cosolvents, and applied by ink-jet methodology to cotton, for example by the method described in Example 200. In all these cases, dull blue, greenish navy or black shades were imparted to the substrate, depending on the amount of dye applied.

Example 202

[**0416**] Dye from Example 1 was ion exchanged to the lithium form as in Example 201, and formulated into an ink with the composition: dye (5 parts), propylene glycol (12 parts), diethanolamine (sufficient to buffer the final pH to 7-8.5), and water (to bring the total to 100 parts). The ink was added to the ink reservoir of an ink jet printer (e.g. HP Desk Jet 500) and printed onto paper (Logic 300), to give a black print of generally good fastness properties.

TABLE 1



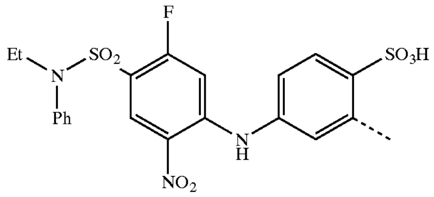
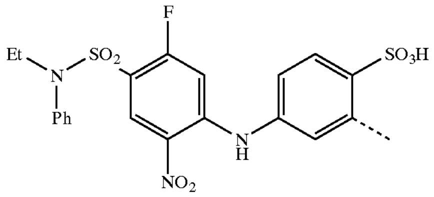
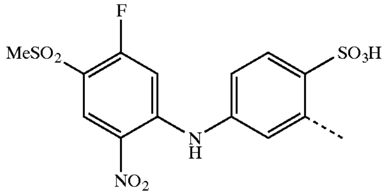
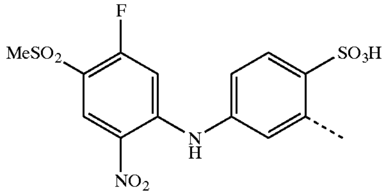
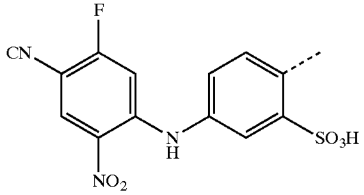
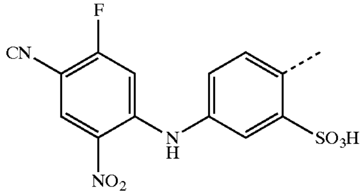
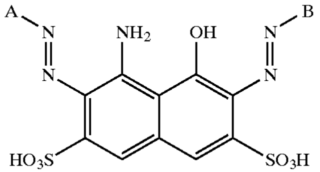
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
6			606 (121) greenish-navy
7			607 (105) greenish-navy
8			623 (121) dark bluish-green

TABLE 1-continued



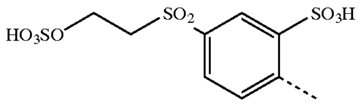
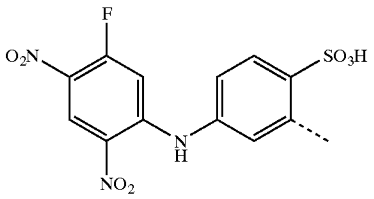
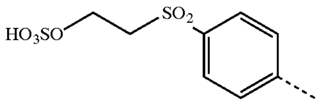
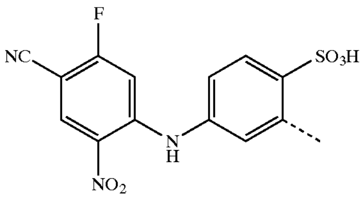
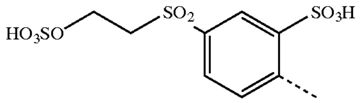
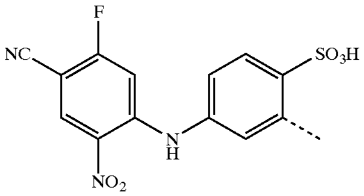
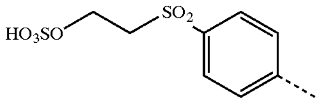
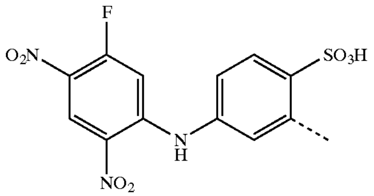
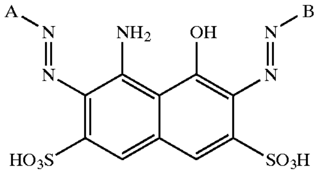
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
9			618 (121) greenish-navy
10			603 (105) greenish-navy
11			618 (130) greenish-navy
12			614 (110) dark bluish-green

TABLE 1-continued



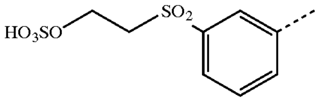
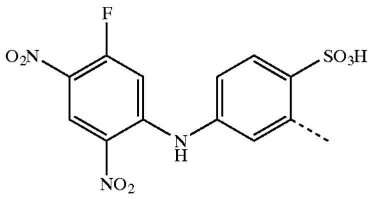
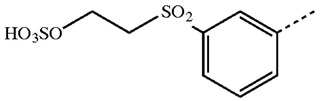
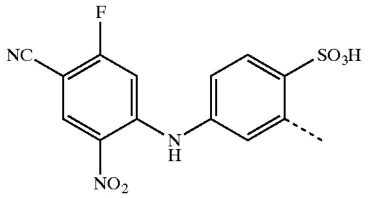
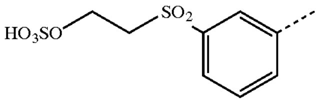
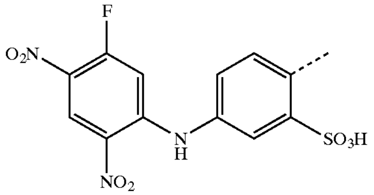
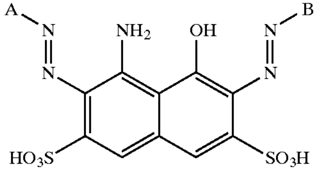
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
13			594 (112) greenish-navy
14			595 (108) greenish-navy
15			604 (110) dark bluish-green

TABLE 1-continued



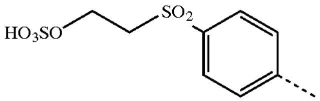
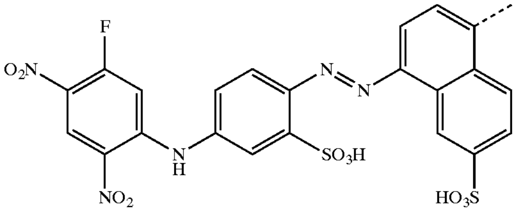
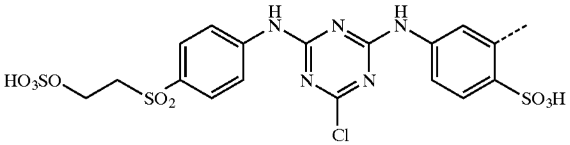
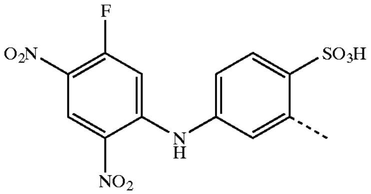
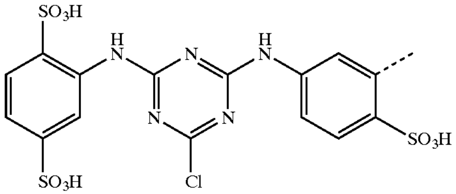
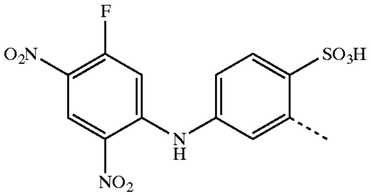
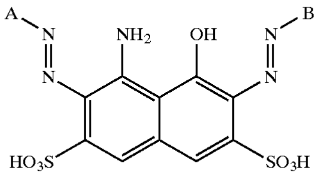
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
16			645 (137) very dull dark green
17			604 (119) greenish-navy
18			603 (127) greenish-navy

TABLE 1-continued



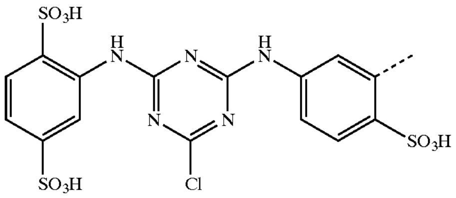
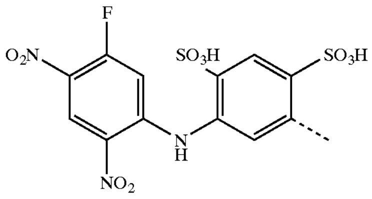
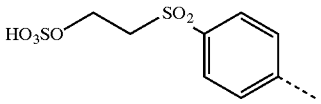
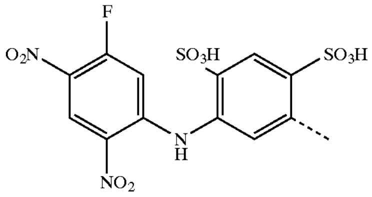
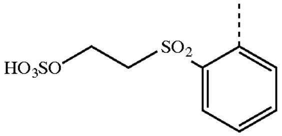
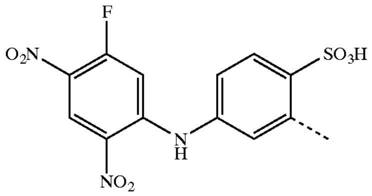
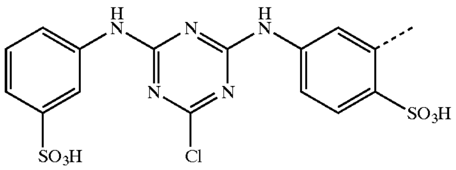
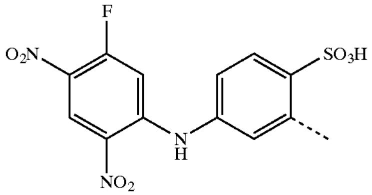
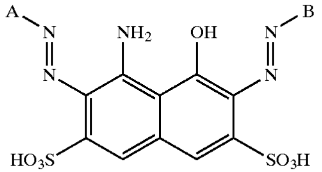
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
19			600 (134) greenish-navy
20			596 120) greenish-navy
21			609 (111) greenish-navy
22			604 (120) greenish-navy

TABLE 1-continued



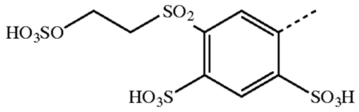
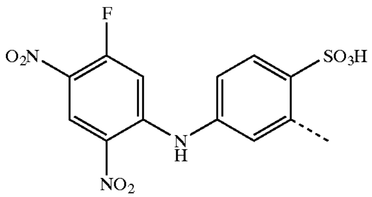
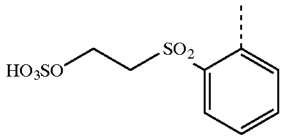
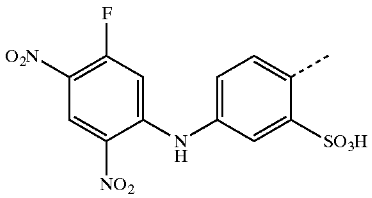
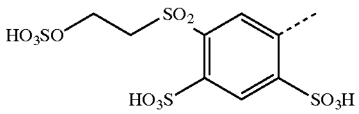
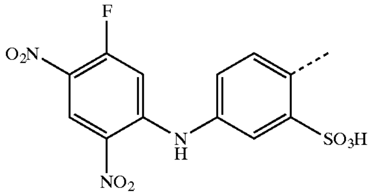
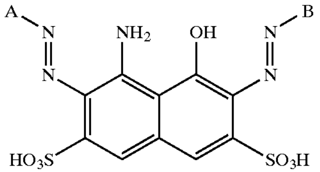
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
23			625 (104) greenish-navy
24			620 (112) dark bluish-green
25			632 (114) dark bluish-green

TABLE 1-continued



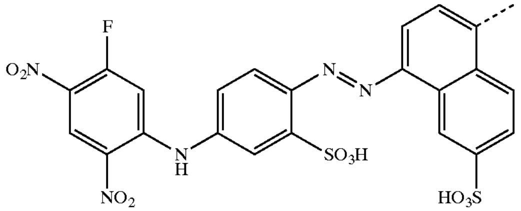
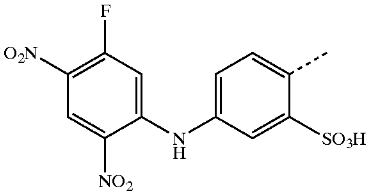
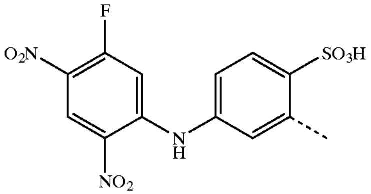
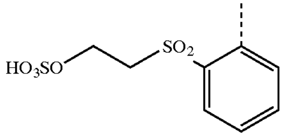
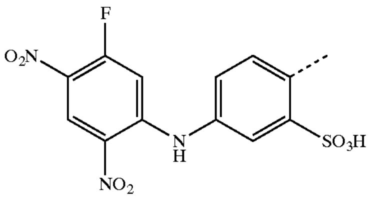
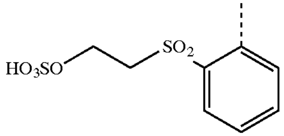
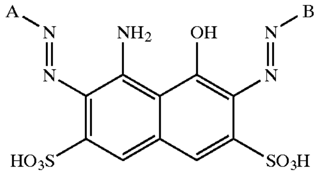
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
26			609 (141) dark bluish-green
27			602 (125) greenish-navy
28			605 (143) dark bluish-green

TABLE 1-continued



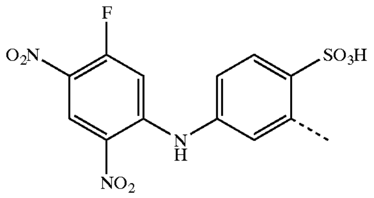
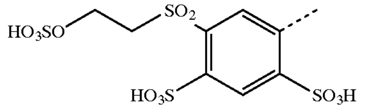
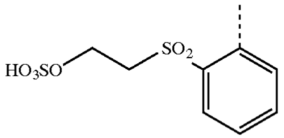
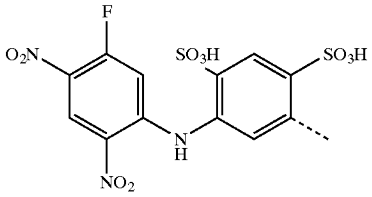
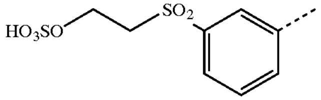
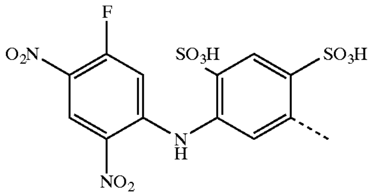
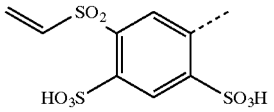
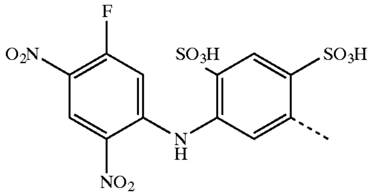
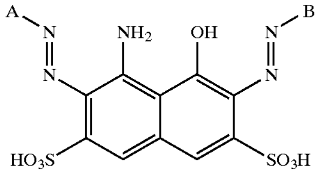
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
29			596 (129) greenish-navy
30			607 (109) greenish-navy
31			595 (107) greenish-navy
32			622 (123) greenish-navy

TABLE 1-continued



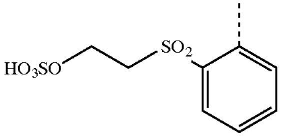
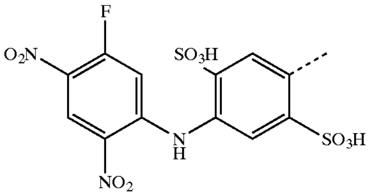
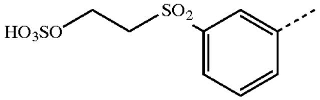
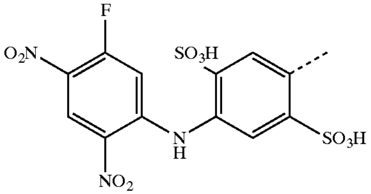
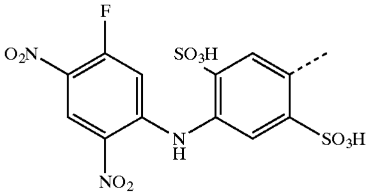
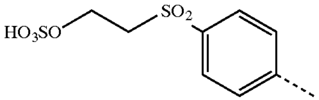
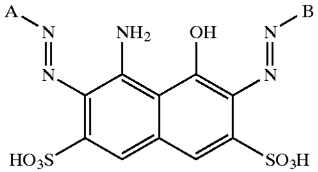
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
33			619 (114) dark bluish-green
34			606 (114) dark bluish-green
35			618 (113) dark bluish-green

TABLE 1-continued



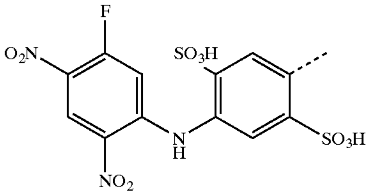
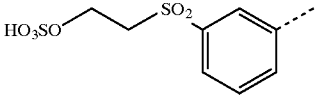
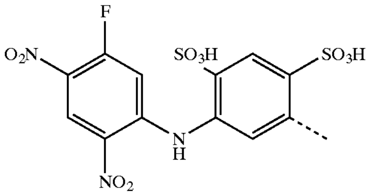
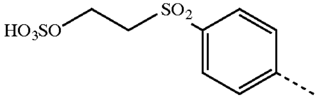
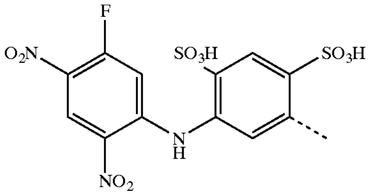
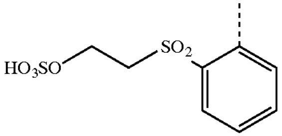
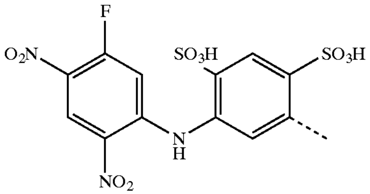
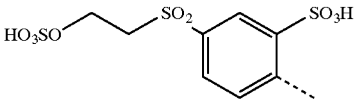
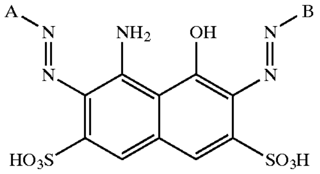
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
36			616 (110) dark bluish-green
37			616 (106) greenish-navy
38			616 (111) dark bluish-green
39			608 (111) greenish-navy

TABLE 1-continued



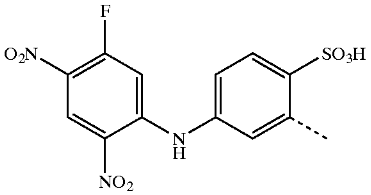
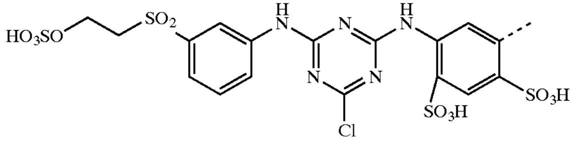
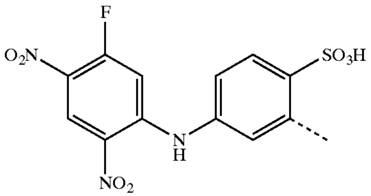
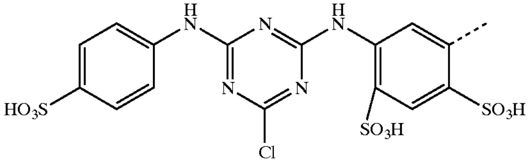
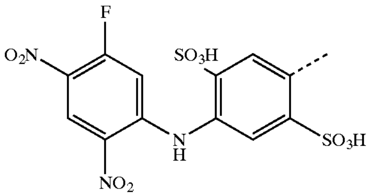
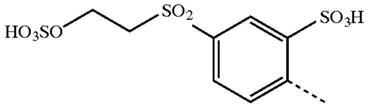
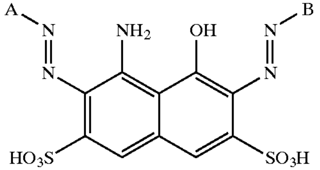
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
40			608 (116) greenish-navy
41			608 (116) greenish-navy
42			616 (111) dark bluish-green

TABLE 1-continued



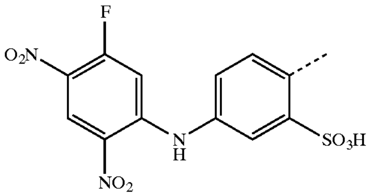
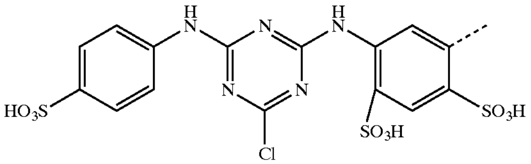
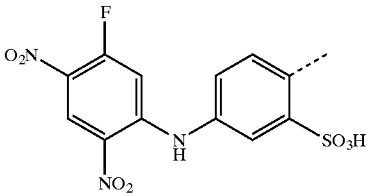
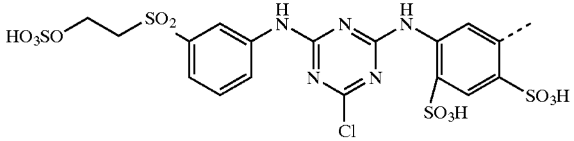
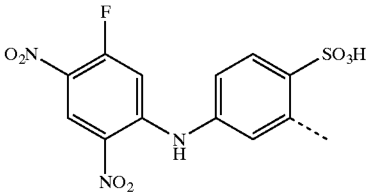
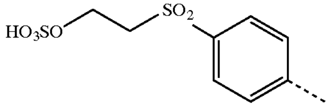
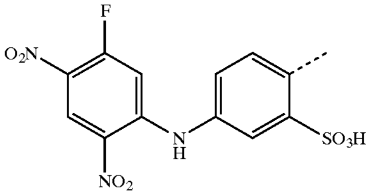
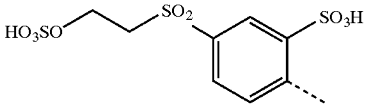
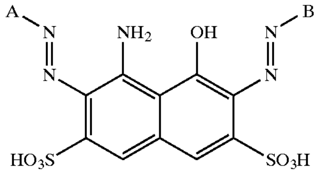
Example	A	B	λ_{max} nm (w$_{1/2}$ nm) Colour on cotton
43			615 (120) dark bluish-green
44			615 (118) dark bluish-green
45			greenish-navy
46			dark bluish-green

TABLE 1-continued



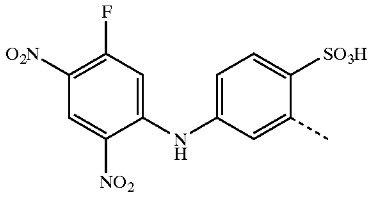
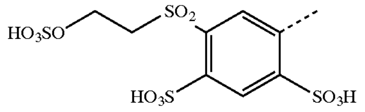
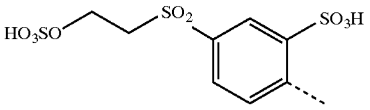
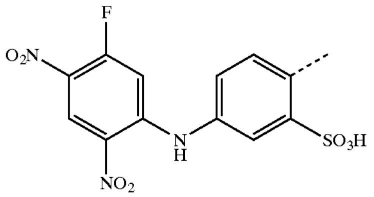
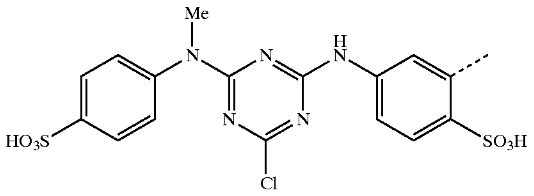
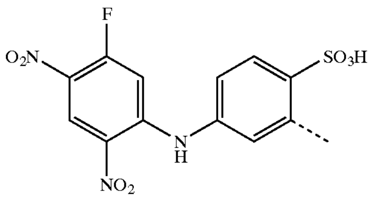
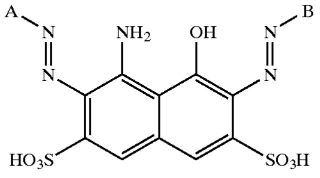
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
47			greenish-navy
48			dark bluish-green
49			greenish-navy

TABLE 1-continued



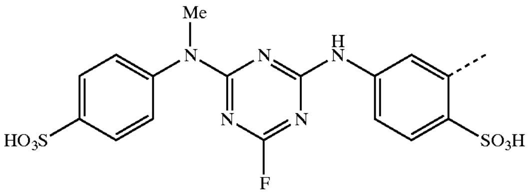
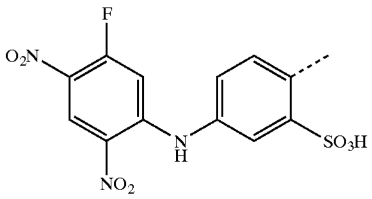
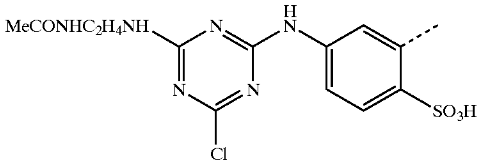
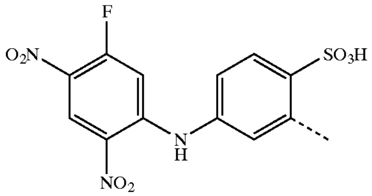
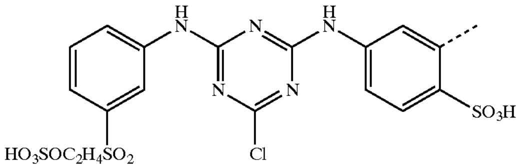
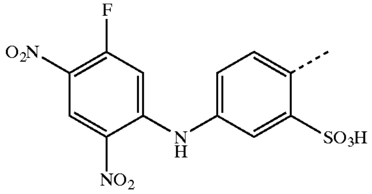
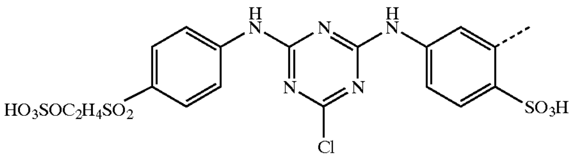
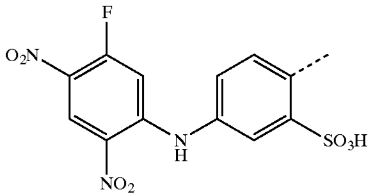
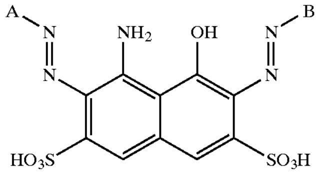
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
50			dark bluish-green
51			greenish-navy
52			dark bluish-green
53			dark bluish-green

TABLE 1-continued



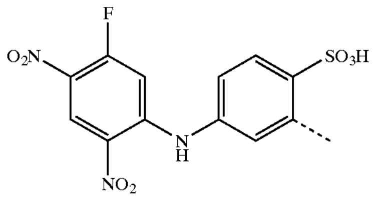
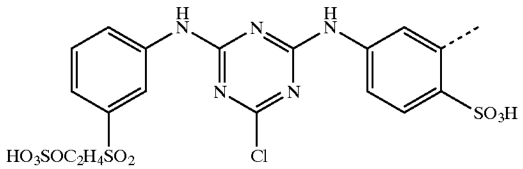
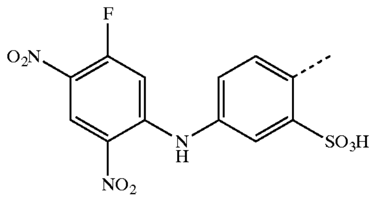
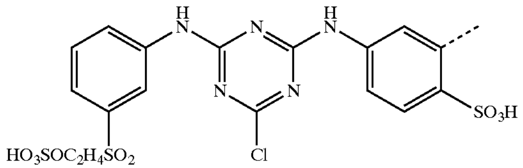
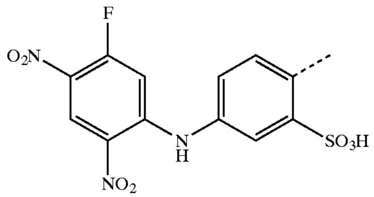
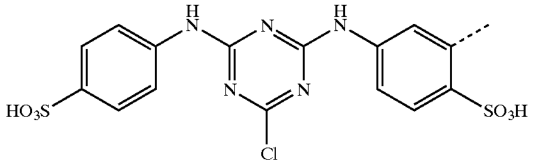
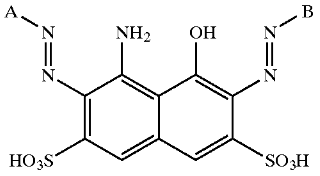
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
54			greenish-navy
55			dark bluish-green
56			dark bluish-green

TABLE 1-continued



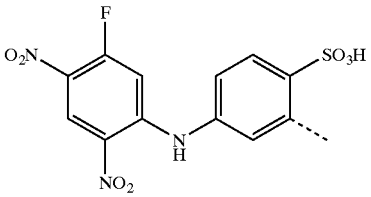
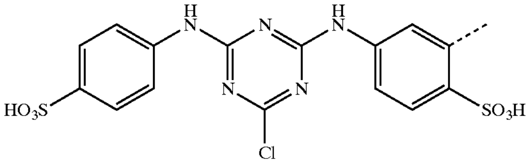
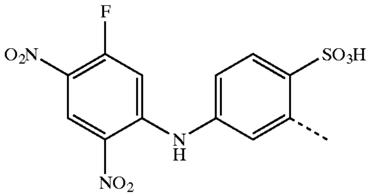
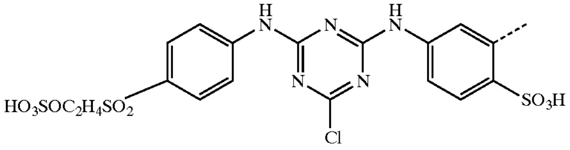
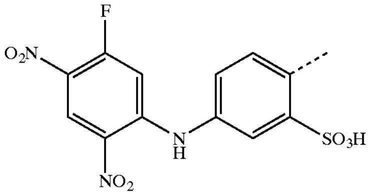
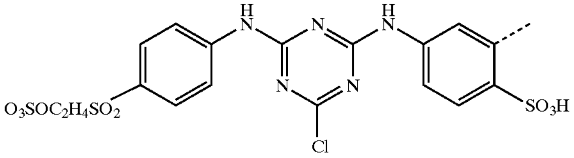
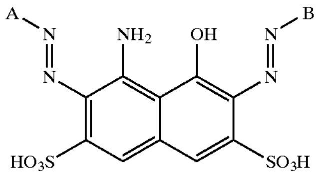
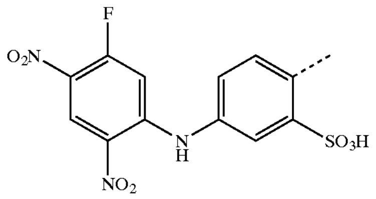
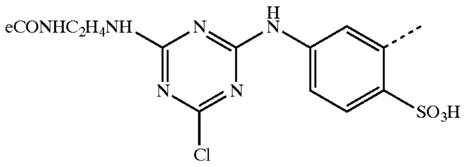
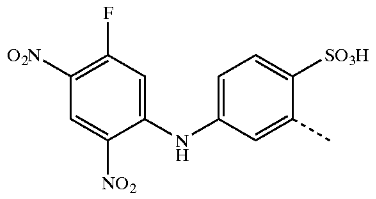
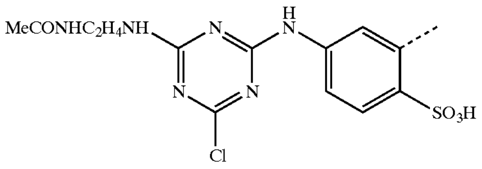
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
57			greenish-navy
58			greenish-navy
59			dark bluish-green

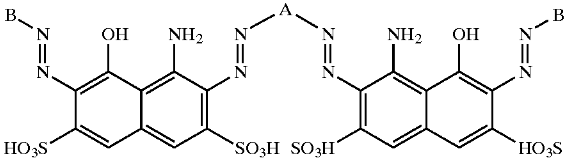
TABLE 1-continued



Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
60			dark bluish-green
61			greenish-navy

[0417]

TABLE 2



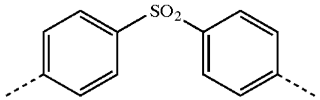
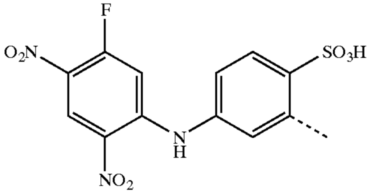
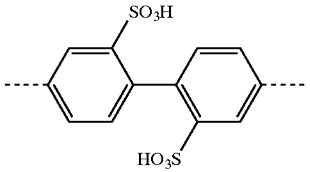
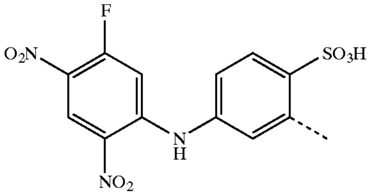
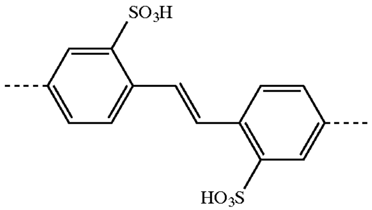
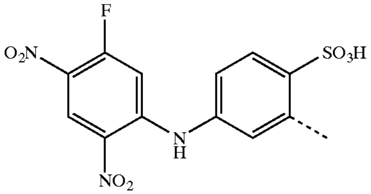
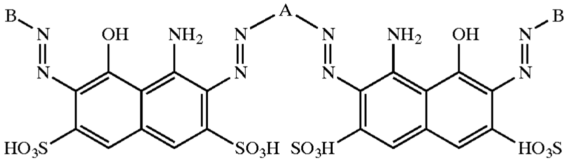
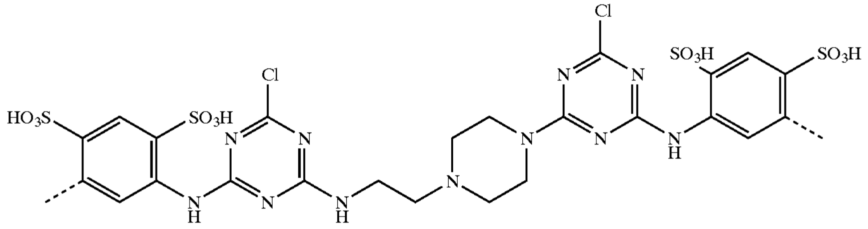
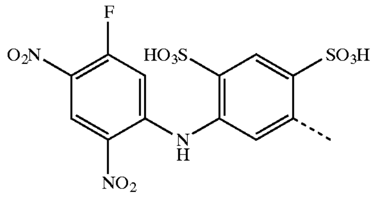
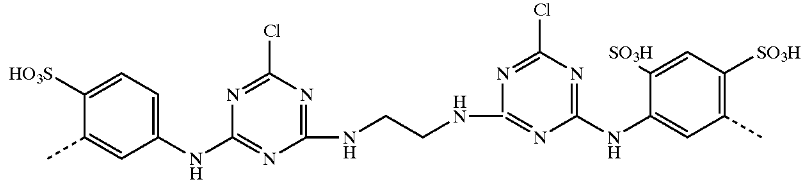
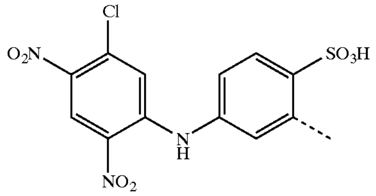
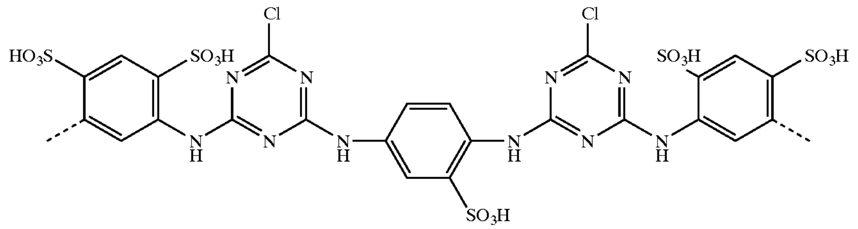
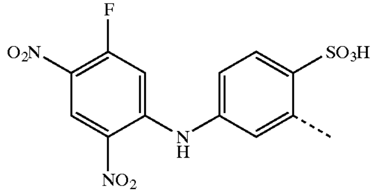
Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
62			609 (118) dull dark green
63			608 (112) dull dark green
64			630 (130) daull dark green

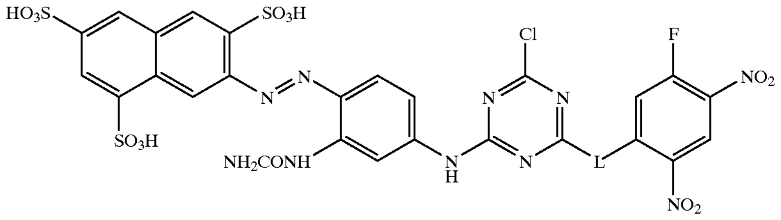
TABLE 2-continued



Example	A	B	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
65			Greenish-navy
66			Greenish-navy
67			Greenish-navy

[0418]

TABLE 3



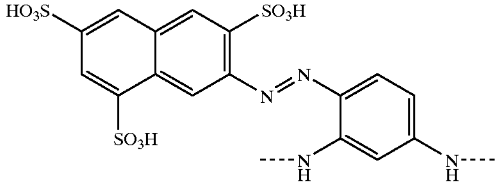
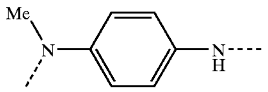
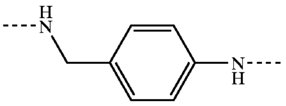
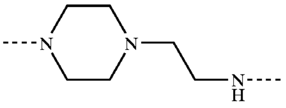
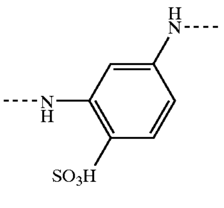
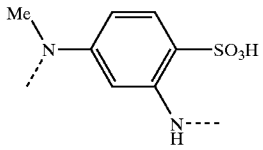
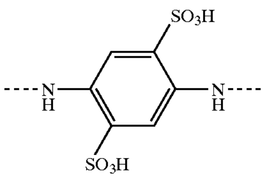
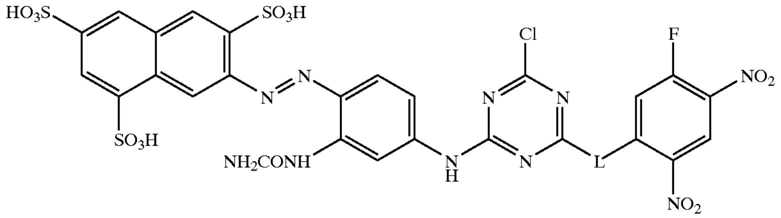
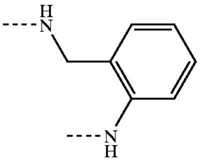
Example	L	λ_{max} nm	$w_{1/2}$ nm	Colour on cotton
69		415	139	Golden yellow
70		367	140	Golden yellow
71		403	200	Golden yellow
72		419	200	Golden yellow
73		366	119	Golden yellow
74	NHC_2H_4NH	410	170	Golden yellow
75		378	155	Golden yellow
76		389	150	Golden yellow

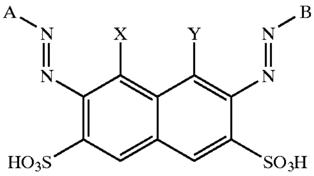
TABLE 3-continued



Example	L	λ_{max} nm	$w_{1/2}$ nm	Colour on cotton
77		360	160	Golden yellow

[0419]

TABLE 4



B

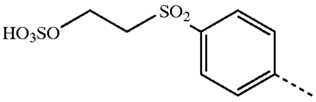
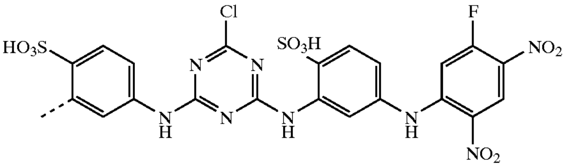
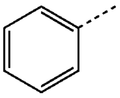
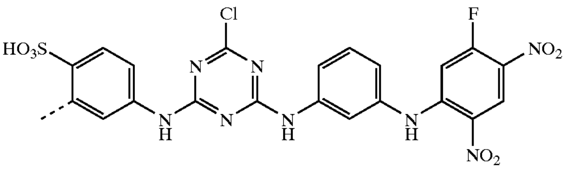
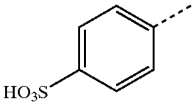
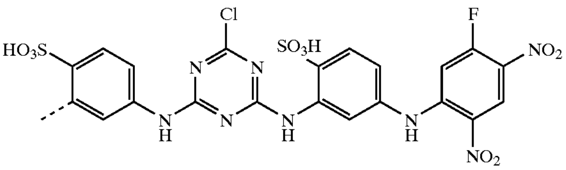
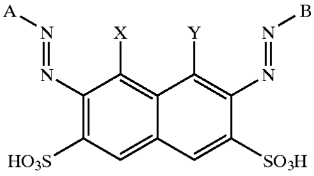
Example	A	B	X	Y	Colour on cotton
78			NH_2	OH	Greenish navy
79			OH	NH_2	Greenish navy
			NH_2	OH	Greenish navy

TABLE 4-continued



B

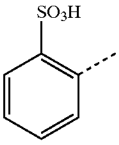
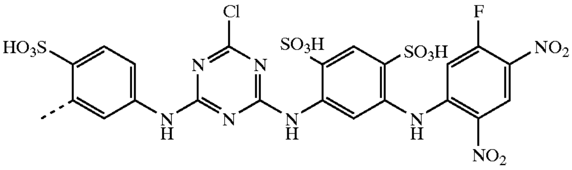
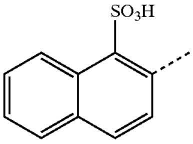
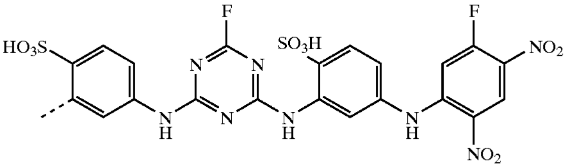
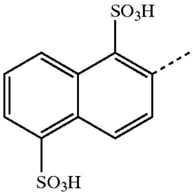
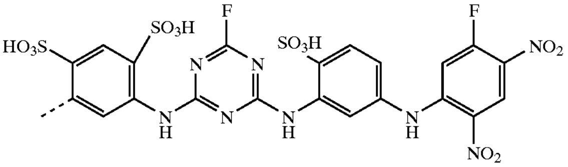
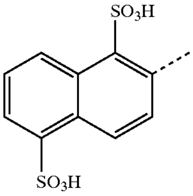
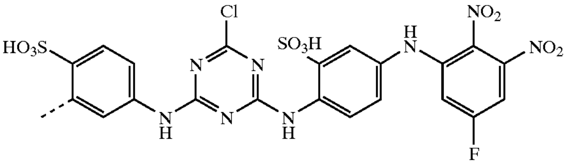
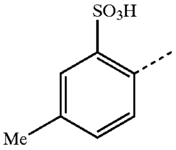
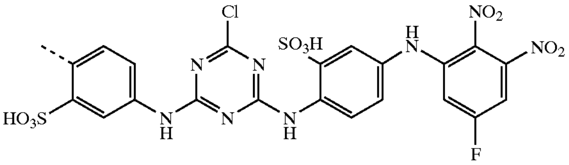
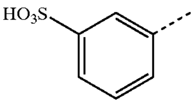
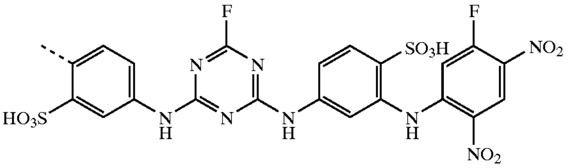
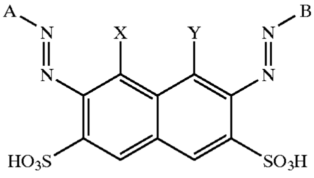
Example	A	B	X	Y	Colour on cotton
81			OH	NH_2	Greenish navy
82			NH_2	OH	Greenish navy
83			OH	NH_2	Greenish navy
84			NH_2	OH	Greenish navy
85			OH	NH_2	Greenish navy
86			NH_2	OH	Greenish navy

TABLE 4-continued



B

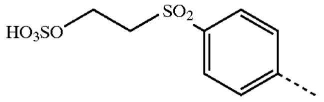
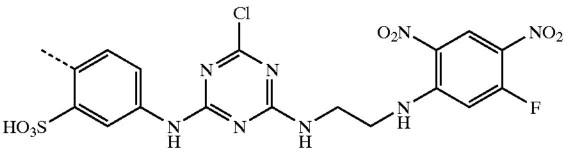
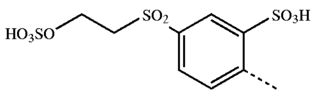
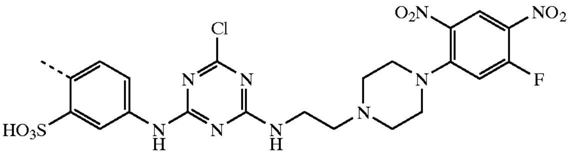
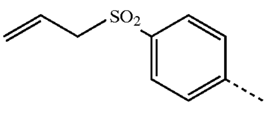
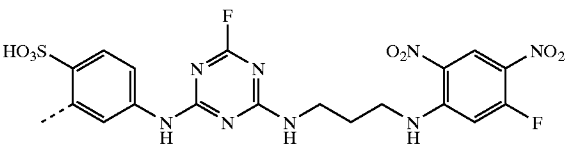
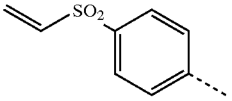
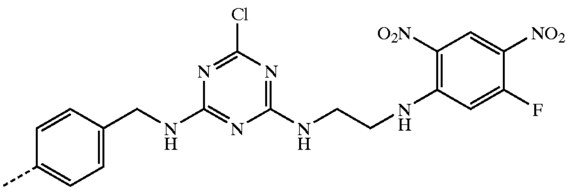
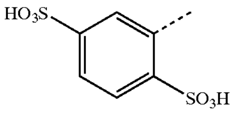
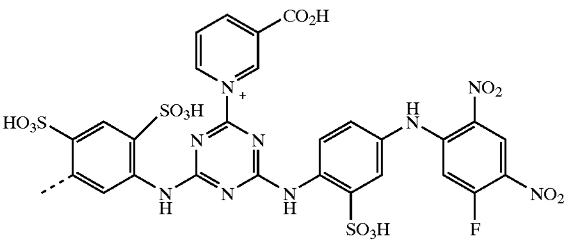
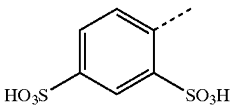
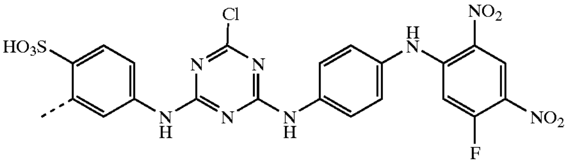
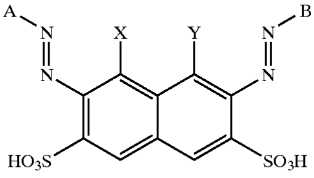
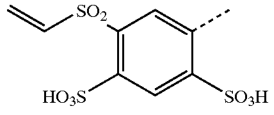
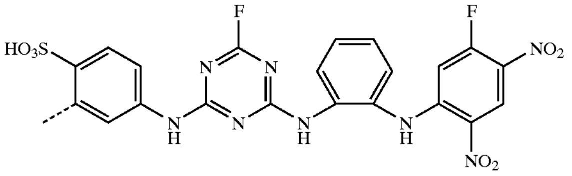
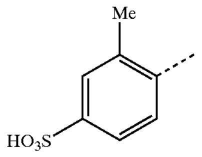
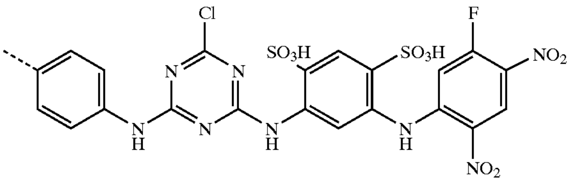
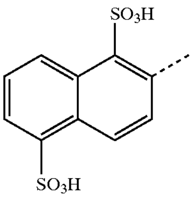
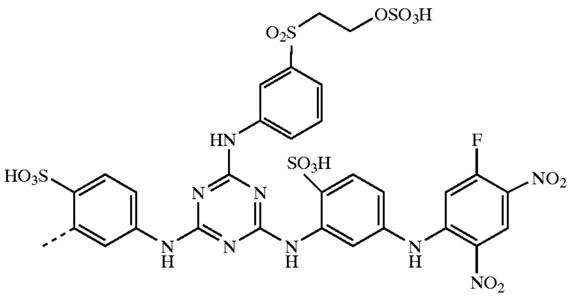
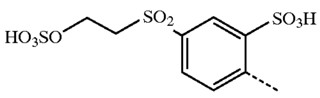
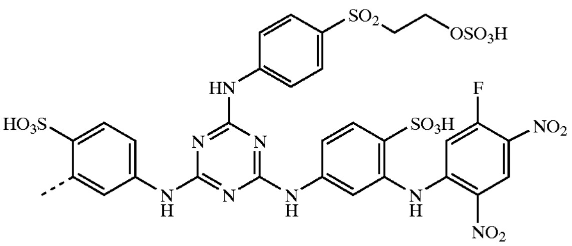
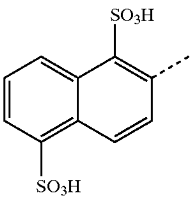
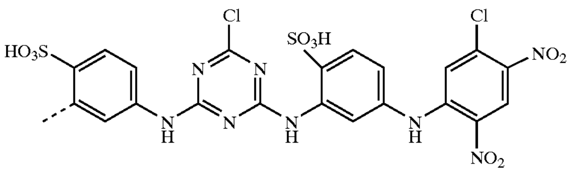
Example	A	B	X	Y	Colour on cotton
87			OH	NH_2	Greenish navy
88			NH_2	OH	Greenish navy
89			OH	NH_2	Navy
90			NH_2	OH	Navy
91			OH	NH_2	Greenish navy
92			NH_2	OH	Greenish navy

TABLE 4-continued



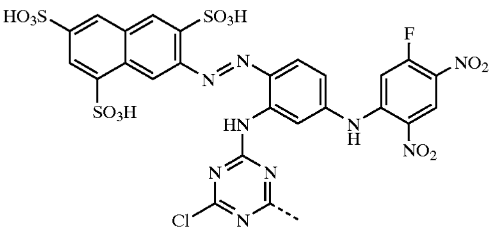
B

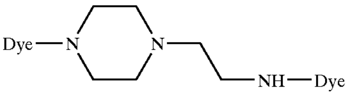
Example	A	B	X	Y	Colour on cotton
93			OH	NH_2	Greenish navy
94			OH	NH_2	Greenish navy
95			NH_2	OH	Greenish navy
96			OH	NH_2	Greenish navy
97			OH	NH_2	Greenish navy

[0420]

TABLE 5

Dye =

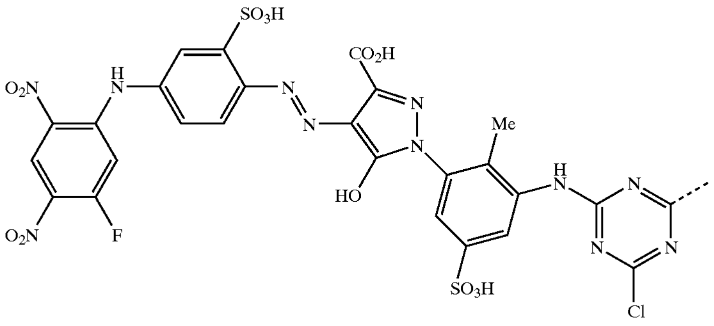


Example	Structure	λ_{max} nm	$w_{1/2}$ nm	Colour on cotton
98	Dye-SC_2H_4OH	407	148	Golden yellow
99	Dye-$N(CH_3)Ph$	403	138	Golden yellow
100	Dye-$NHC_2H_4SO_3H$	407	129	Golden yellow
101	Dye-$NHC_2H_4OC_2H_4OH$	412	134	Golden yellow
102	Dye-NHC_6H_3-m-SO_3H	409	143	Golden yellow
103	Dye-NHC_2H_4NH-Dye			Golden yellow
104		412	130	Golden yellow

[0421]

TABLE 6

Dye =



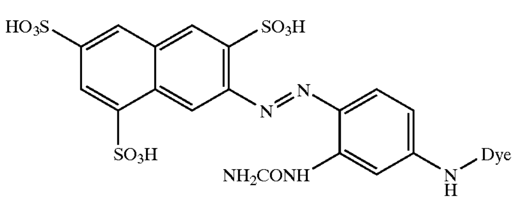
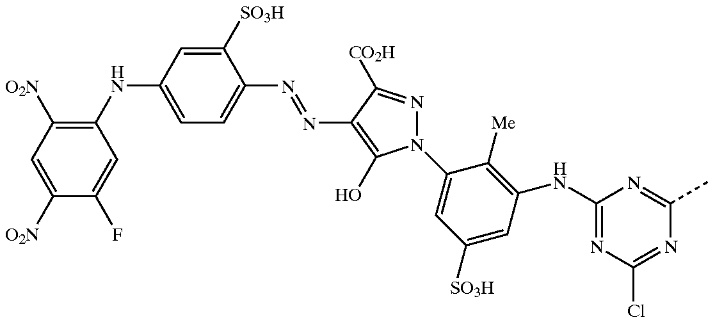
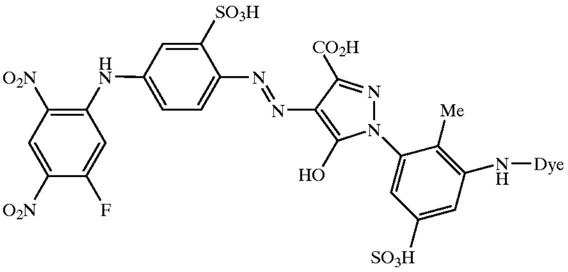
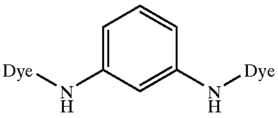
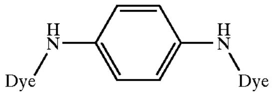
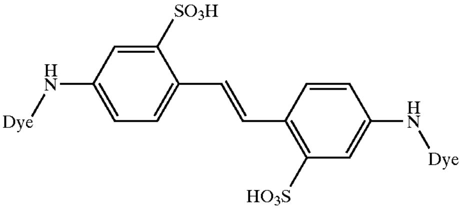
Example	Structure	λ_{max} nm	$w_{1/2}$ nm	Colour on cotton
105	Dye-SC_2H_4OH	437	151	Mid yellow
106		430	135	Mid yellow
107	Dye-$NHC_2H_4OC_2H_4OH$	436	141	Mid yellow

TABLE 6-continued

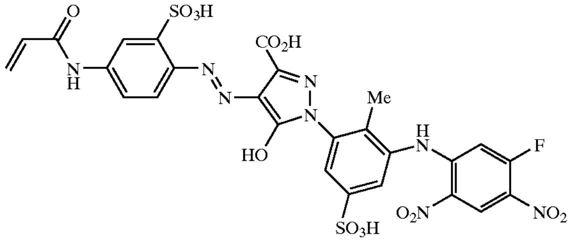
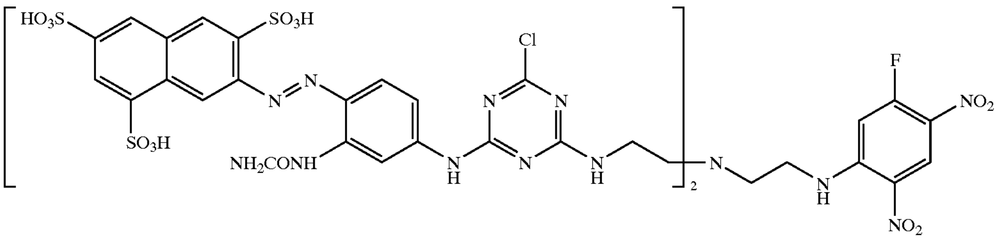
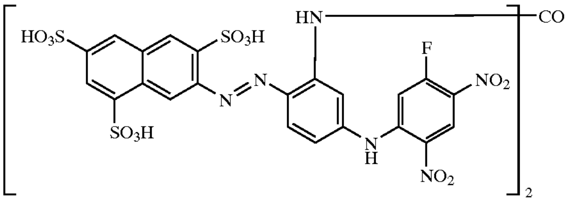
Dye =



Example	Structure	λ_{max} nm	$w_{1/2}$ nm	Colour on cotton
108		435	132	Mid yellow
109		439	143	Mid yellow
110		438	149	Mid yellow
111		437	131	Mid yellow
112	Dye-NHC_2H_4NH-Dye			Mid yellow
113	Dye-NHC_3H_6NH-Dye			Mid yellow

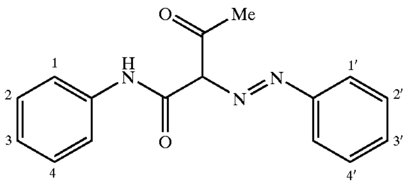
[0422]

TABLE 7

Example	Structure	λ_{max} nm ($w_{1/2}$ nm) Colour on cotton
114		435 (172) mid yellow
115		422 (148) golden yellow
116		406 (124) golden yellow

[0423]

TABLE 8



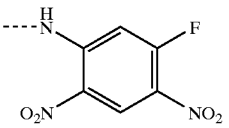
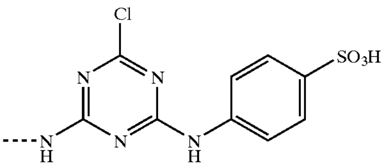
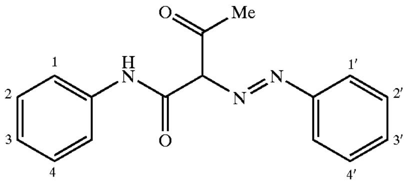
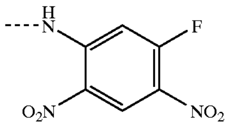
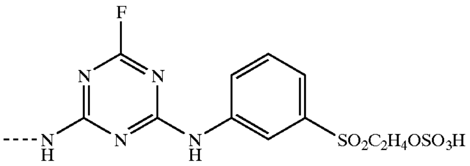
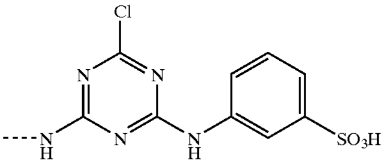
Example			Other substituents	Colour on cotton
117	4-	1,3-$(SO_3H)_2$	3'-$SO_2C_2H_4OSO_3H$	Yellow
118	3-	1,4-$(SO_3H)_2$	2'-$SO_2C_2H_4OSO_3H$	Yellow
119	4-	1,1'-$(SO_3H)_2$	4'- 	Yellow

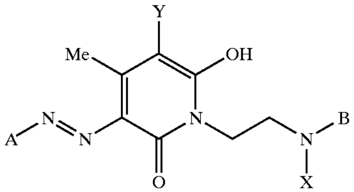
TABLE 8-continued



Example			Other substituents	Colour on cotton
120	4-	1,1'-$(SO_3H)_2$	3'- 	Yellow
121	4'-	1,1',4-$(SO_3H)_3$	3'- 	Yellow

[0424]

TABLE 9



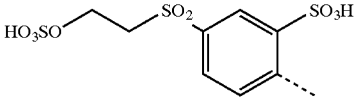
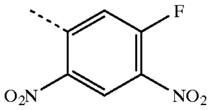
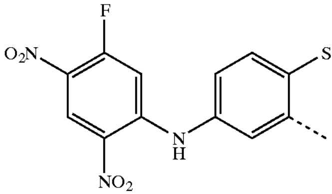
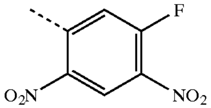
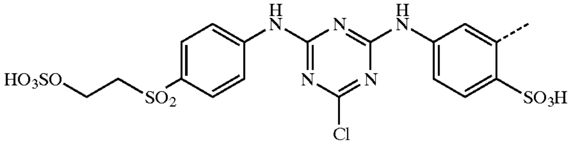
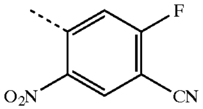
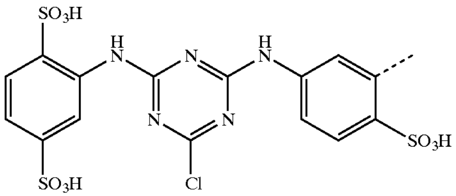
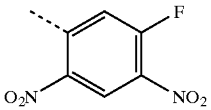
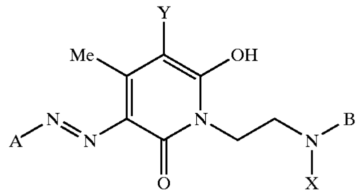
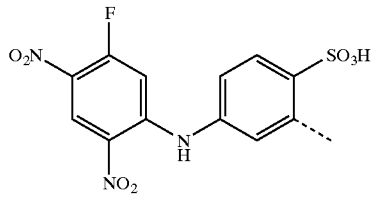
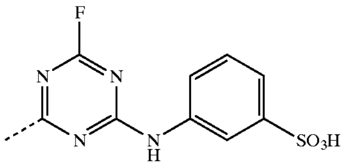
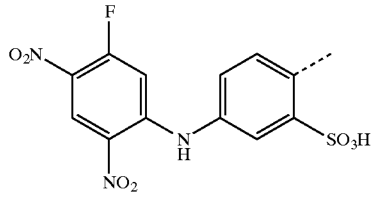
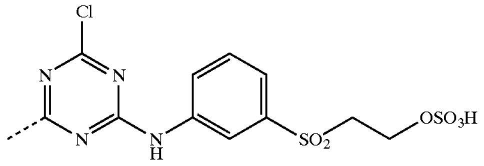
Example	A	B	X	Y	Colour on cotton
122			H	H	Greenish-yellow
123			H	CN	Greenish-yellow
124			H	$CONH_2$	Greenish-yellow
125			C_2H_4OH	H	Greenish-yellow

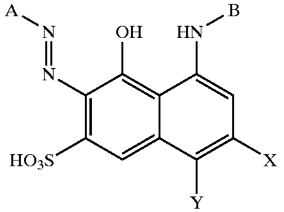
TABLE 9-continued



Example	A	B	X	Y	Colour on cotton
126			C_2H_4OH	$CONH_2$	Greenish-yellow
127			H	H	Greenish-yellow

[0425]

TABLE 10



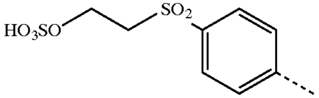
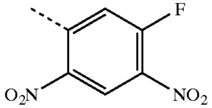
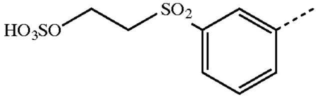
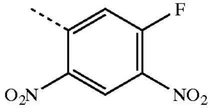
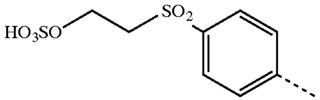
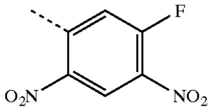
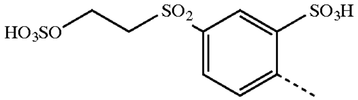
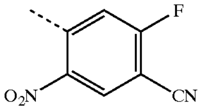
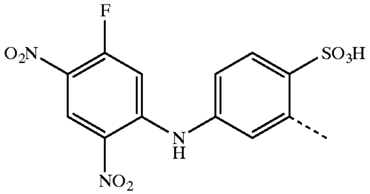
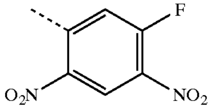
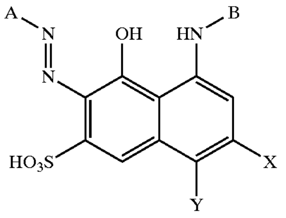
Example	A	B	X	Y	Colour on cotton
128			SO_3H	H	Blueish red
129			SO_3H	H	Blueish red
130			H	SO_3H	Blueish red
131			SO_3H	H	Blueish red
132			SO_3H	H	Blueish red

TABLE 10-continued



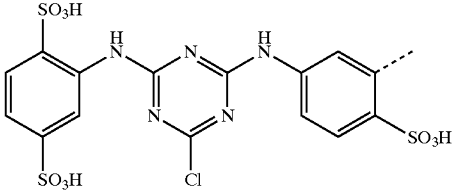
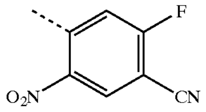
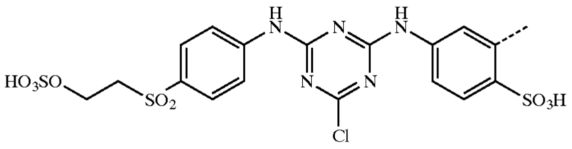
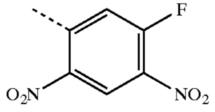
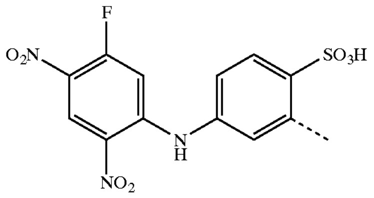
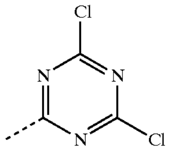
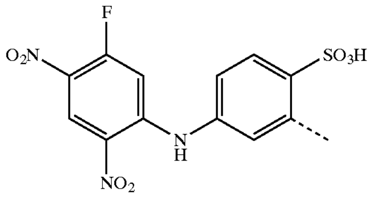
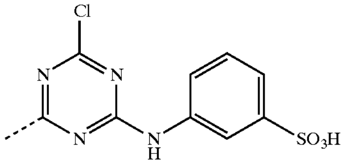
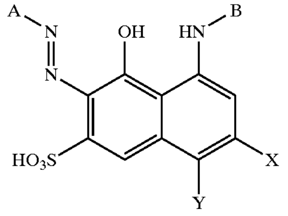
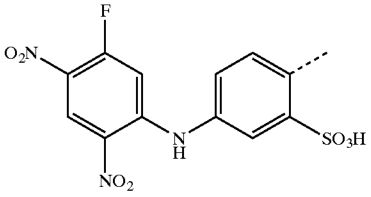
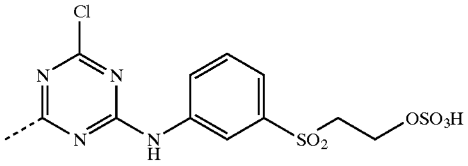
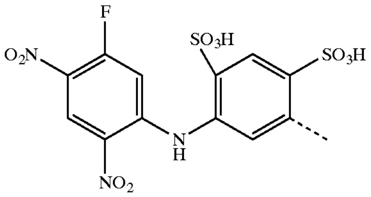
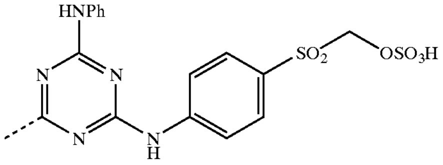
Example	A	B	X	Y	Colour on cotton
133			H	SO_3H	Blueish red
134			SO_3H	H	Blueish red
135			SO_3H	H	Blueish red
136			SO_3H	H	Blueish red

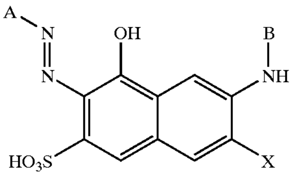
TABLE 10-continued



Example	A	B	X	Y	Colour on cotton
137			H	SO_3H	Blueish red
138			SO_3H	H	Blueish red

[0426]

TABLE 11



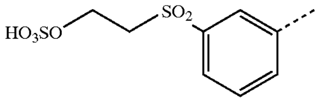
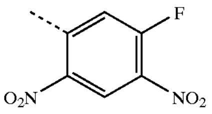
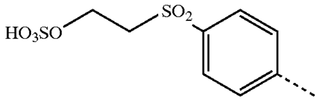
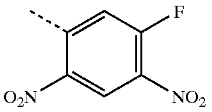
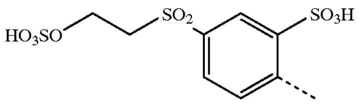
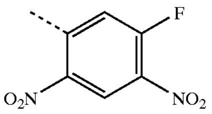
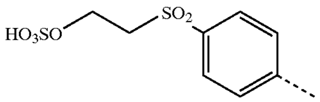
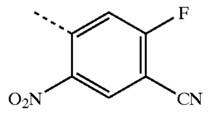
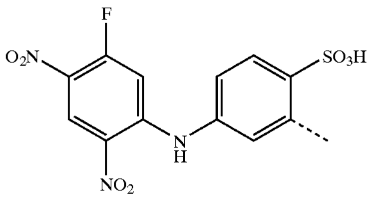
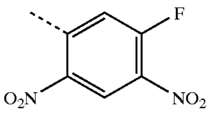
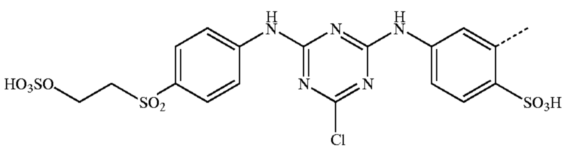
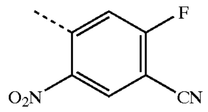
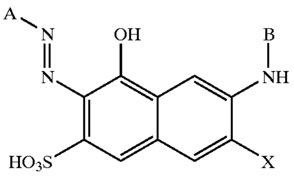
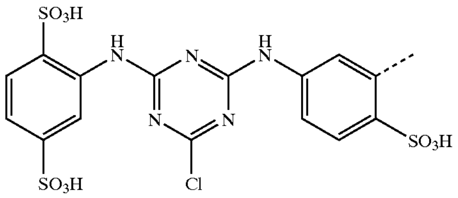
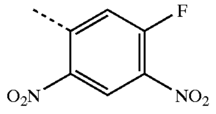
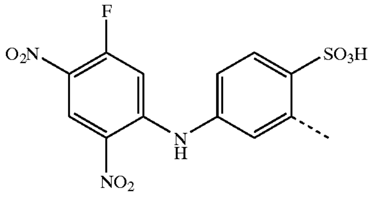
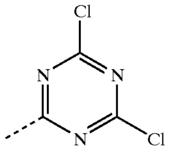
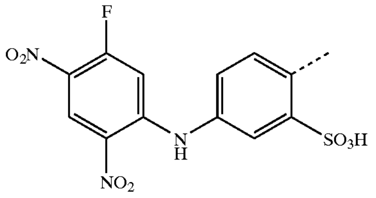
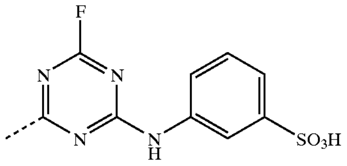
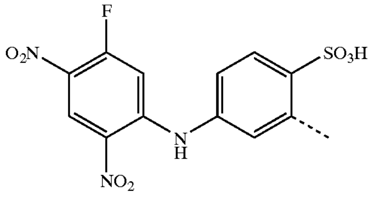
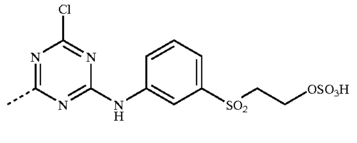
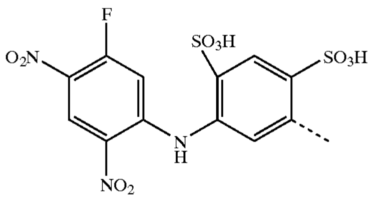
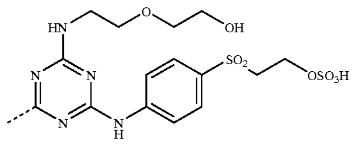
Example	A	B	X	Colour on cotton
139			H	Red
140			SO_3H	Red
141			H	Red
142			SO_3H	Red
143			H	Red
144			SO_3H	Red

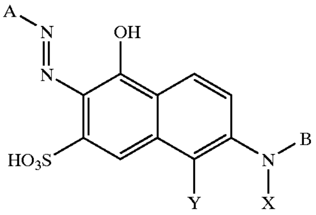
TABLE 11-continued



Example	A	B	X	Colour on cotton
145			SO_3H	Red
146			SO_3H	Red
147			H	Red
148			H	Red
149			SO_3H	Red

[0427]

TABLE 12



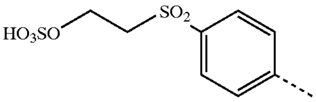
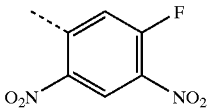
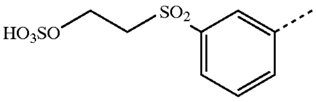
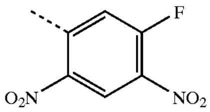
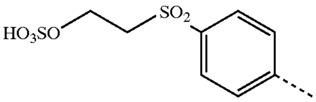
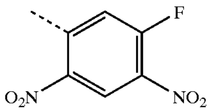
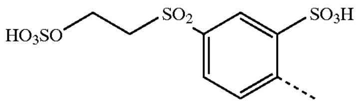
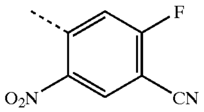
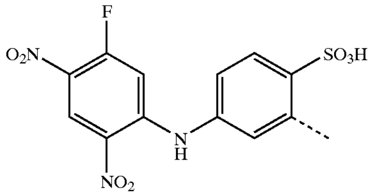
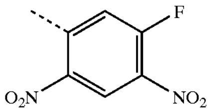
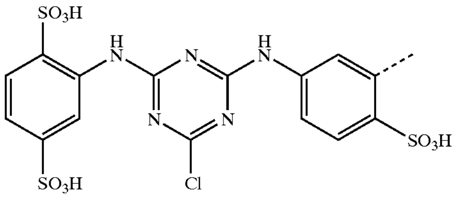
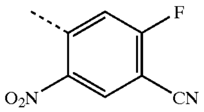
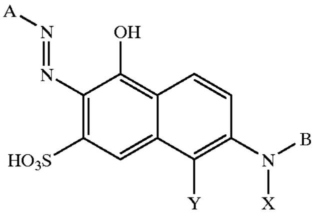
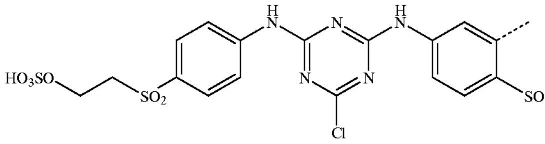
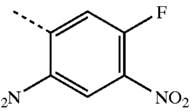
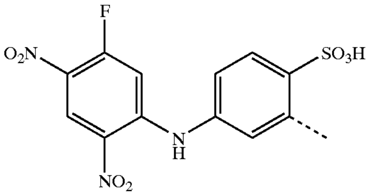
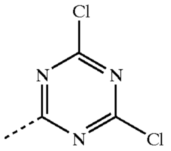
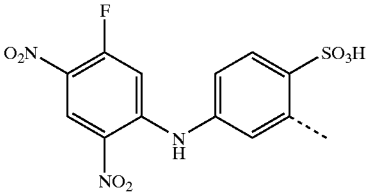
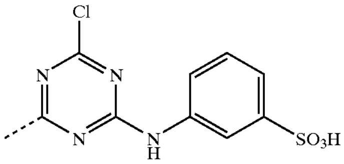
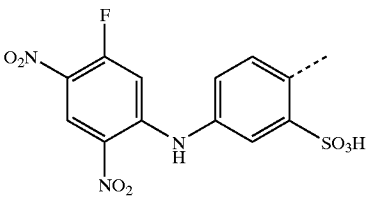
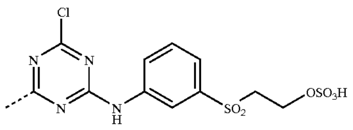
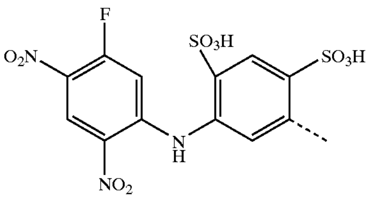
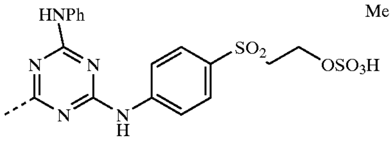
Example	A	B	X	Y	Colour on cotton
150			H	H	Reddish yellow
151			H	SO_3H	Reddish yellow
152			Me	H	Reddish yellow
153			H	H	Reddish yellow
154			H	H	Orange
155			H	SO_3H	Orange

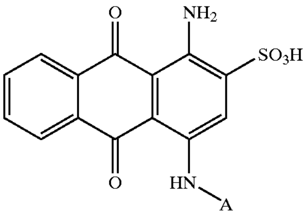
TABLE 12-continued

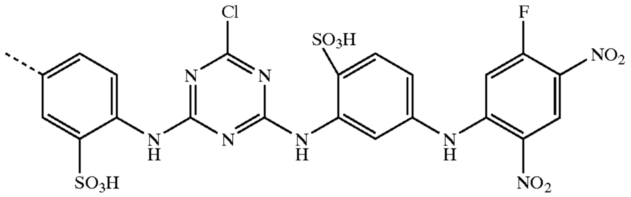
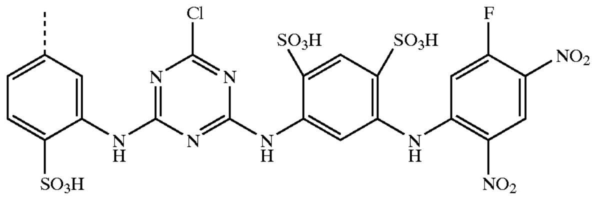
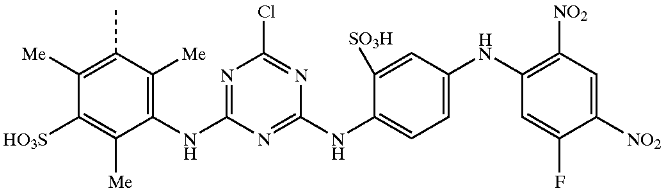
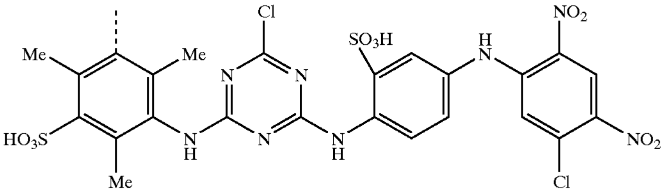


Example	A	B	X	Y	Colour on cotton
156			Me	H	Orange
157			H	H	Orange
158			H	H	Orange
159			H	SO_3H	Orange
160			Me	H	Orange

[0428]

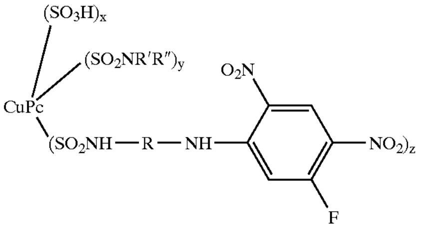
TABLE 13



Example	A	Colour on cotton
161		Greenish blue
162		Greenish blue
163		Greenish blue
164		Greenish blue

[0429]

TABLE 14



x + y + z =< 4

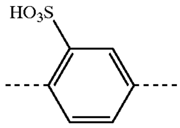
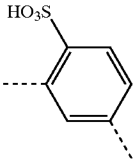
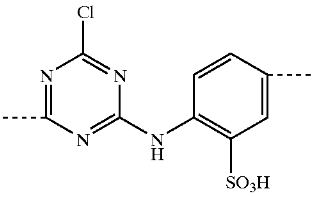
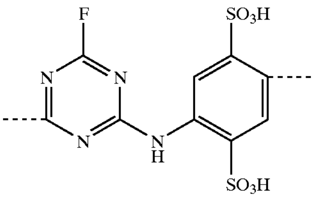
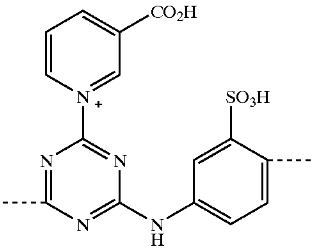
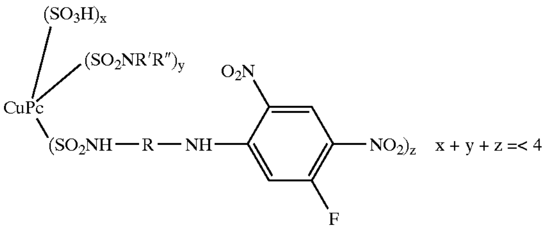
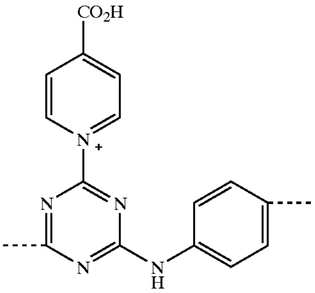
Example	R	R'	RΛ	x	y	z	Colour on cotton
165		H	H	2	0	2	Green
166		H	H	1.5	0.5	2	Green
167	C_2H_4	H	H	2	0	2	Bluish-green
168	C_3H_6	CH_3	CH_3	1.7	0.3	2	Bluish-green
169		H	$C_2H_4OSO_3H$	2.5	0.5	1	Green
170		H	H	1.5	1.5	1	Green
171		H	$C_2H_4SO_3H$	2.5	0	1.5	Green

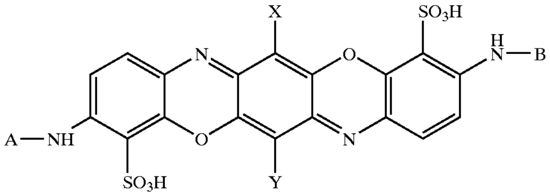
TABLE 14-continued



Example	R	R'	RΔ	x	y	z	Colour on cotton
172		H	H	3	0	1	Green

[0430]

TABLE 15



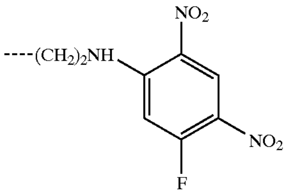
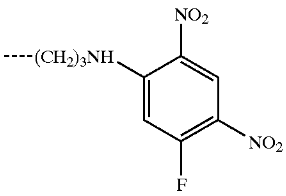
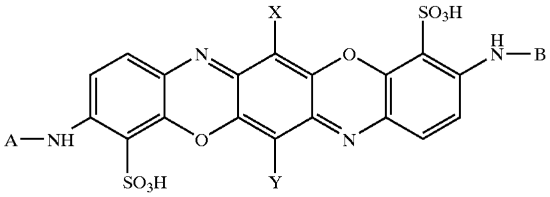
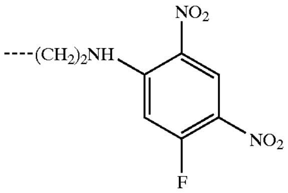
Example	A
173	
174	

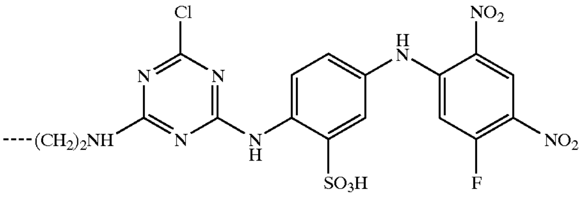
TABLE 15-continued



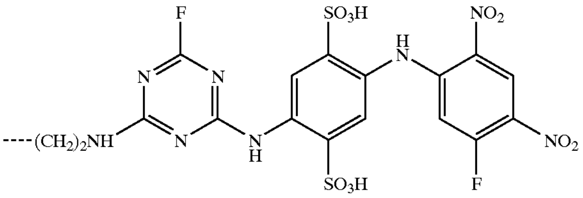
175



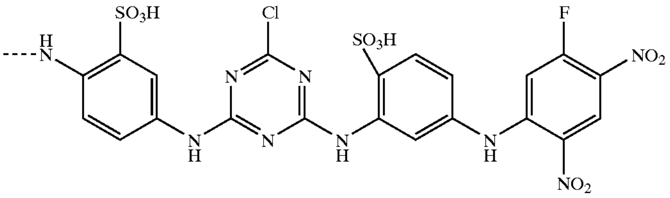
176



177

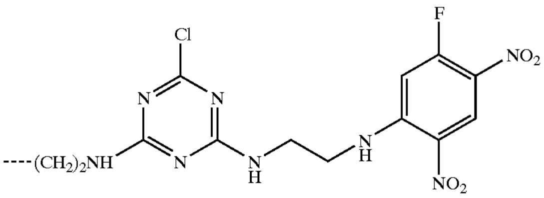


178



179 H

180



181

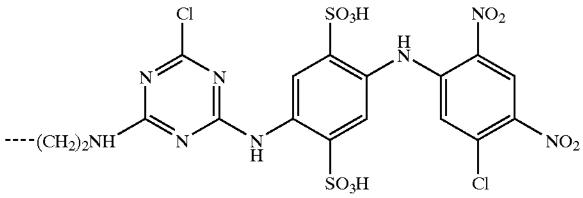
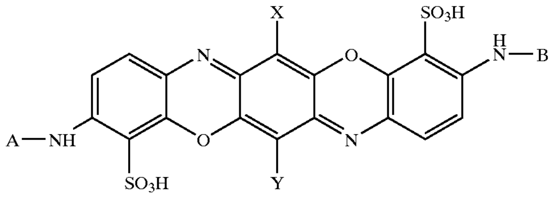


TABLE 15-continued



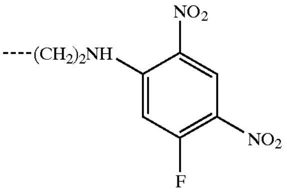
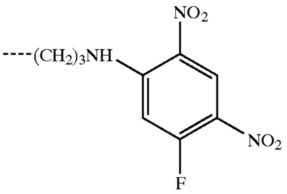
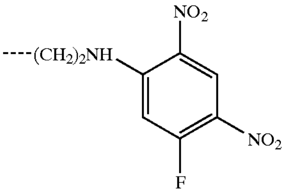
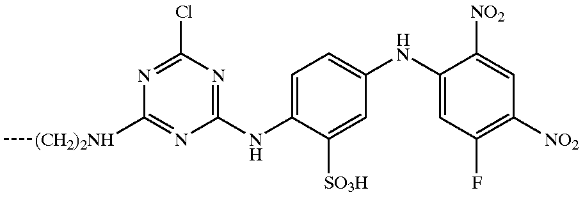
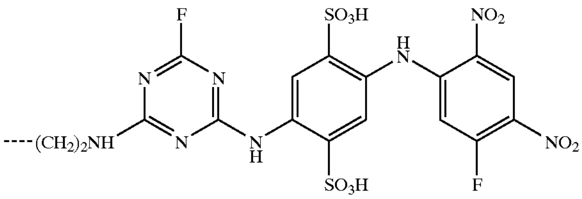
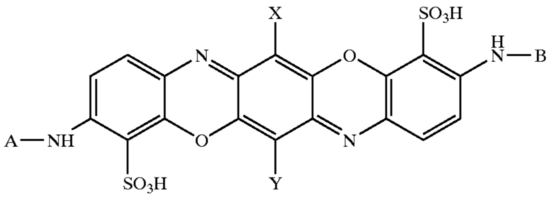
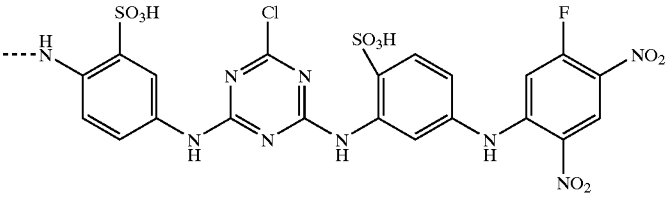
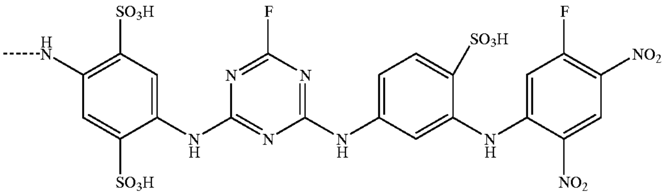
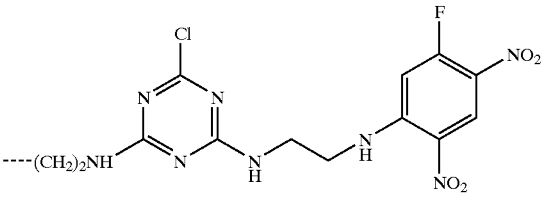
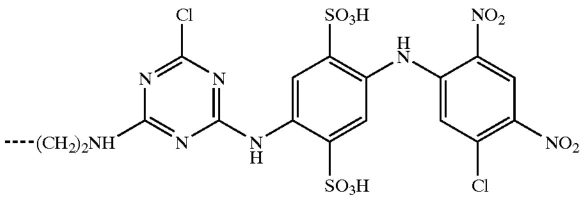
Example	B	X	Y	Colour on cotton
173		Cl	Cl	Blue
174		Cl	Cl	Blue
175		Cl	Et	Blue
176		Cl	Cl	Greenish blue
177		Cl	Et	Greenish blue

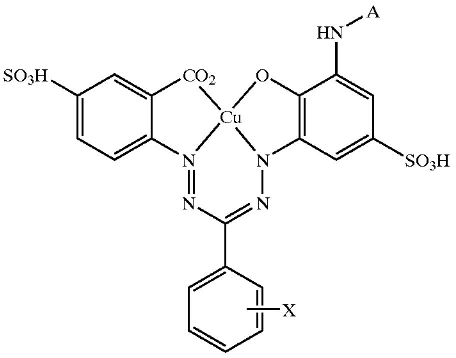
TABLE 15-continued



178		Cl	Cl	Greenish blue
179		Cl	Cl	Greenish blue
180		Cl	Me	Blue
181		Cl	Cl	Greenish blue

[0431]

TABLE 16



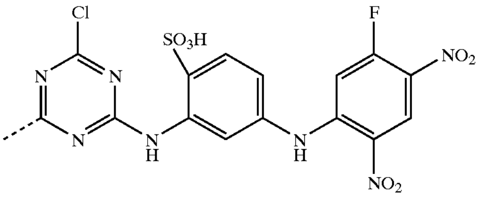
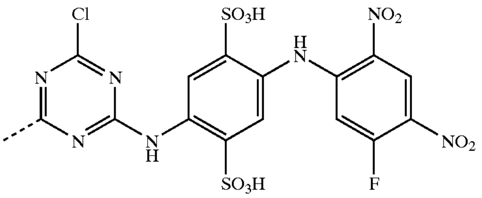
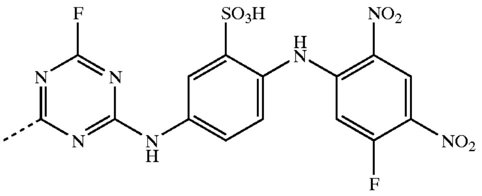
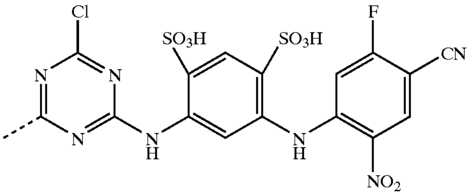
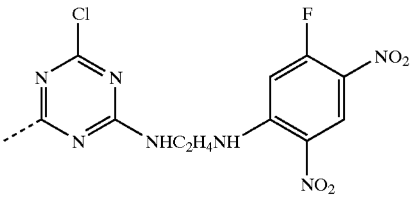
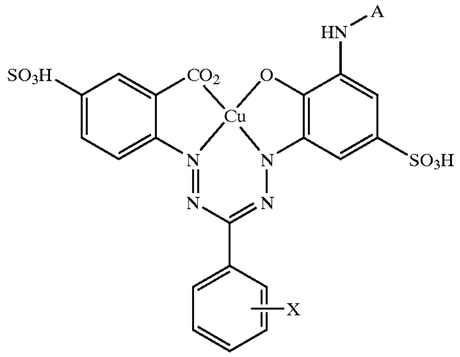
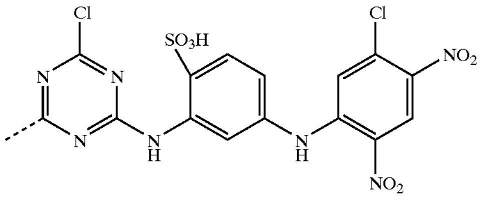
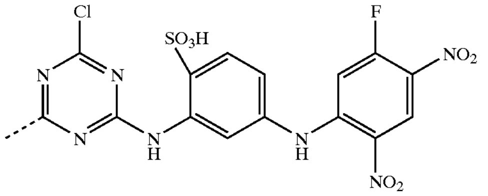
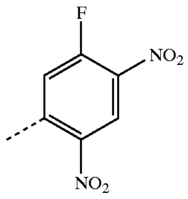
Example	A	X	Colour on cotton
182		H	Dull greenish blue
183		H	Dull greenish blue
184		Dull greenish blue	
185		H	Dull greenish blue
186		H	Dull blue

TABLE 16-continued

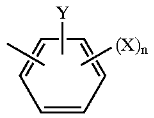


Example	A	X	Colour on cotton
187		H	Dull greenish blue
188		3-SO_3H	Dull greenish blue
189		4-$SO_2C_2H_4OSO_3H$	Dull greenish blue

1. A dye containing

at least one chromophore D;

at least a first, halobenzene, reactive group Z^1, of the formula (I)



(I)

in which:

n is 1 or 2

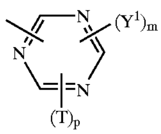
X, or each X independently, is an electron withdrawing group; and

Y is a halogen atom;

at least a second reactive group Z^2 selected from

(1) a group of the formula (I), given and defined above, but selected independently thereof;

(2) a group of the formula (II)



(II)

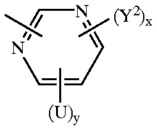
wherein

m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

Y^1, or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

T is C_{1-4}alkoxy, C_{1-4}thioalkoxy or $N(R^1)(R^2)$, in which each of R^1 and R^2 independently is hydrogen, optionally substituted C_{1-4}alkyl or optionally substituted aryl;

(3) a group of the formula (III)



(III)

wherein:

x is 1, 2 or 3; y is zero, 1 or 2; and

$x+y \leqq 3$;

Y^2, or each Y^2 independently, is a halogen atom or an optionally substituted pyridinium group; and

U or each U independently, is C_{1-4}alkyl or C_{1-4}alkylsulphonyl;

(4) a group of the formula (IV)

$$—SO_2CH_2CH_2X^1 \qquad (IV)$$

wherein

X^1 is an eliminatable group;

(5) a group of the formula (V)

$$—SO_2(CH_2)_zCH{=}CH_2 \qquad (V)$$

wherein

z is zero or 1; and

(6) a group of formula (VI)

$$—W—C(R^{10}){=}CH_2 \qquad (VI)$$

wherein:

R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

W is —OC(=O)— or —N(R^{11})C(=O)— in which R^{11} is hydrogen or C_{1-4} alkyl;

at least a first linking group L_1, linking the said first, halobenzene, reactive group Z^1 to one of components (i) the or a chromophore D and (ii) the second reactive group Z^2, which said first linking group L^1 presents an amino nitrogen to the reactive group Z^1 and to the component (i) or (ii) or, when component (i) contains a heterocyclic nitrogen atom, is linked directly to the nitrogen atom and which said first linking group L^1 optionally includes a hydrocarbon bridging group, which hydrocarbon bridging group B has at least two carbon atoms, is optionally substituted, optionally includes at least one hetero atom and is optionally a chromophore; and

when Z^2 is selected from the said groups (I)-(III), at least a second linking group L^2 linking the second reactive group Z^2 to one of (i) the or a chromophore D and (ii) the said first reactive group Z^1, which said linking group L^2 is selected from

(1) a linking group L^1, but selected independently thereof; or

(2) an amide linkage; and

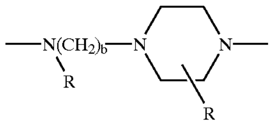
(3) a sulphonamide linkage; and optionally at least one aromatic group Ar which, when Z^2 is selected from the said groups (IV)-(VI), may carry the said reactive group Z^2.

2. A dye according to claim 1, wherein the linking group L^1 has the formula $(VII)^1$

$$N(R) \qquad (VII)^1$$

wherein R is hydrogen or optionally substituted C_{1-4}alkyl, such that the same amino group presents itself to each of the reactive group Z^1 and the component (i) or (ii), as defined in claim 1.

3. A dye according to claim 1, wherein the linking group L^1 is a piperazinoalkylamino group of the formula $(VII)^2$



$(VII)^2$

wherein each R, independently, is as defined in claim 2, such that respective amino nitrogens, one of the piperazine group and the other of the alkylamino group, present themselves respectively, to the reactive group Z^1 and to the component (i) or (ii), as defined in claim 1.

4. A dye according to claim 1, wherein the linking group L^1 has the formula $(VII)^3$

$$—N(R)BN(R)— \qquad (VII)^3$$

wherein B is a hydrocarbon bridging group as defined in claim 1, each R, independently , is as defined in claim 1 and B is optionally linked additionally to at least one additional group —N(R).

5. A dye according to claim 4, wherein the hydrocarbon bridging group B is an optionally substituted aryl group.

6. A dye according to any preceding claim, of the formula (VIII)

$$Z^1\text{-}L^1\text{-}D\text{-}(L^2)_a\text{-}Z^2 \qquad (VIII)$$

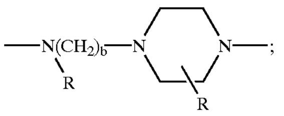
wherein:

D is a chromophore;

each of L^1 and L^2 is an amine or piperazine linkage of the formula

$$—N(R)— \qquad (VII)^1;$$

(VII)^2



or

—N(R)BN(R)— (VII)^3

wherein:

R, or each R independently, is hydrogen or C_{1-4} alkyl;

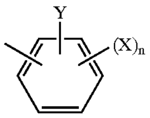
B is a hydrocarbon bridging group which has at least two carbon atoms, is optionally substituted, optionally includes at least one hetero atom and is optionally a chromophore;

a is zero or 1; and

b is from 2 to 6 inclusive;

Z^1 is a group

(I)



in which:

n is 1 or 2;

X, or each X independently, is an electron withdrawing group; and

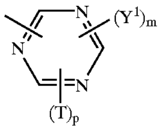
Y is a halogen atom; and

when a is 1, Z^2 is:

a group of the formula (I), given and defined above but selected independently thereof; or

a group of the formula (II)

(II)



wherein:

m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

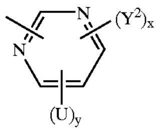
Y^1, or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

T is C_{1-4} alkoxy, thioalkoxy or $N(R^1)(R^2)$ in which R^1 is hydrogen, optionally substituted C_{1-4} alkyl or optionally substituted aryl and

R^2 is hydrogen or optionally substituted C_{1-4} alkyl; or

a group of the formula (III)

(III)



wherein: x is 1, 2 or 3; y is zero, 1 or 2; and $x+y \leqq 3$;

Y^2, or each Y^2 independently, is a halogen atom; and

U, or each U independently, is C_{1-4} alkyl or C_{1-4} alkylsulphonyl; and

when a is zero, Z^2 is:

$—SO_2CH_2CH_2X^1$ (IV)

in which

X^1 is an eliminatable group; or

$—SO_2(CH_2)_zCH{=}CH_2$ (V)

wherein

z is zero or 1; or

a group of formula (VI)

$—W—C(R^{10}){=}CH_2$ (VI)

wherein:

R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

W is $—OC({=}O)—$ or $—N(R^{11})C({=}O)—$ in which R is hydrogen or C_{1-4} alkyl.

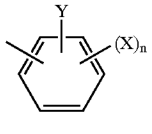
7. A dye according to any preceding claim , wherein, in formula (I), X, or each X independently, is selected from nitro, cyano, alkylsulphonyl, dialkylaminosulphonyl and sulphonic acid or a salt thereof.

8. A dye according to any preceding claim, wherein a group of the formula (II) is present, in which Y^1, or each Y independently, is fluorine, chlorine or optionally substituted pyridinium.

9. A dye according to any one of claims 2 to 8, wherein R, or each R independently, is hydrogen.

10. A dye according to any preceding claim, wherein each of Z^1 and Z^2, independently, is a group:

(I)

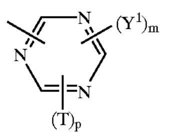


wherein each of X, n and Y is as defined in claim 1.

11. A dye according to claim 10, wherein each of Z^1 and Z^2 is the same as the other.

12. A dye according to any one of claims 1 to 9, wherein a is 1 and Z^2 is

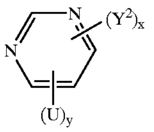
(II)



wherein Y^1, m, T and p are as defined in claim 1.

13. A dye according to any one of claims 1 to 9, wherein a is 1 and Z^2 is

(III)



where Y^2, x, U and y are as defined in claim 1.

14. A dye according to any one of claims 1 to 9, wherein a is zero and Z^2 is

$$—SO_2CH_2CH_2X^1 \quad (IV)$$

where X^1 is as defined in claim 1; or

$$—SO_2(CH_2)_zCH{=}CH_2 \quad (V)$$

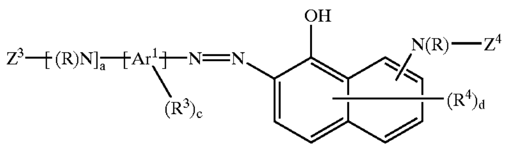
wherein z is as defined in claim 1.

15. A dye according to any preceding claim, wherein D is an azo chromophore.

16. A dye according to claim 15, wherein D is a monoazo chromophore.

17. A dye according to claim 16, which has the formula (XVII)

(XVII)



wherein:

each R independently and a is as defined in claim 1;

one of Z^3 and Z^4 is a group Z^1 and the other is is a group Z^2;

the group Z^4 is selected from the groups of the formulae (I)-(III), given and defined in claim 1;

Ar is a benzene or naphthalene nucleus;

R^3, or each R^3 independently, is C_{1-4} alkyl, nitro, halo or sulphonic acid or salt thereof;

c is zero or 1-4;

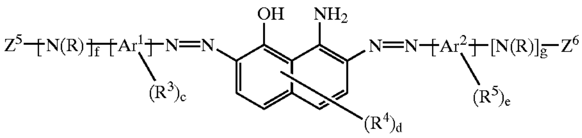
R^4, or each R^4 independently, is a sulphonic acid or a salt thereof; and

d is 1 or 2.

18. A dye according to claim 15, wherein D is a disazo chromophore.

19. A dye according to claim 18, which has the formula (XVIII)

(XVIII)



wherein: one of Z^5 and Z^6 is a group Z^1 and the other is a group Z^2;

each of f and g independently is zero or 1;

when Z^5 or Z^6 is any of the groups of the formulae (I)-(III), given and defined in claim 1, f or g respectively is 1 and when Z^5 or Z^6 is any of the groups of the formulae (IV)-(VI), given and defined in claim 1, f or g respectively is zero;

each of c and e, independently, is zero or 1-4;

d is 1 or 2;

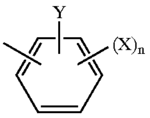
each R independently is as defined in claim 1;

each of Ar^1 and Ar^2 is an optionally substituted aryl group; and

each of R^3 and R^4 is as defined in claim 17.

20. A dye according to claim 19, wherein each of Z^5 and Z^6 is the same group

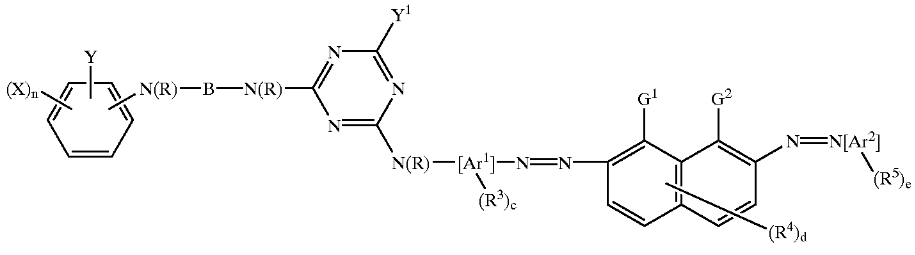
(I)



wherein X, Y and n are as defined in claim 1.

21. A dye according to claim 19, wherein one of Z^5 and Z^6 is a group of the formula (I), given and defined in claim 1, and the other of Z^5 and ^{6} Z is selected from groups of the formulae (II) and (III), given and defined in claim 1.

22. A dye according to claim 18, which dye has the formula



wherein:

B is a hydrocarbon bridging group as defined in claim 1;

one of G^1 and G^2 is ODH and the other is NH_2;

each of X, Y, Y^1 and n is as defined in claim 1;

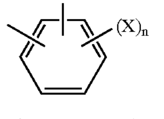
each of Ar^1, Ar^2, R3, R^4, c and d is as defined in claim 19; and

each of R^5 and e is as defined in claim 19.

23. A dye according to claim 22, wherein B is an optionally substituted aryl group.

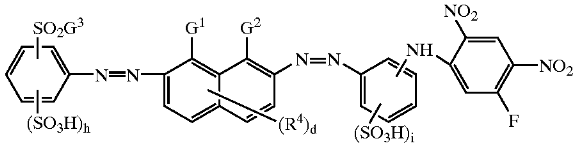
24. A dye according to claim 19, wherein one of Z^5 and Z^6 is a group

(I)



wherein: X, Y and n are as defined in claim 1 and the other of Z^5 and Z^6 is the group —$SO_2CH_2CH_2OSO_3H$ or —$SO_2CH{=}CH_2$.

25. A dye according to claim 24, which has the formula



wherein

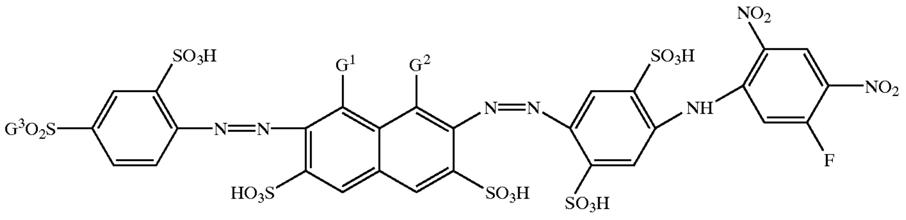
G^3 is $C_2H_4OSO_3H$ or a salt thereof or —$CH{=}CH_2$;

G^1 and G^2 are as defined in claim 22;

R^4 and d are as defined in claim 17; and

each of n and 1, independently, is zero, 1 or 2.

26. A dye according to claim 25, which has the formula



where each of G^1 and G^2 is as defined in claim 22 and G^3 is as defined in claim 25.

27. A dye according to claim 1, of the formula

$$Z^1\text{-}L^1\text{-}D\ [L^3]_q\text{-}[Z^3\text{-}L^4{}_r[J^1]_s[L^2]_a Z^2[L^5\text{-}J^2]_t$$

wherein:

Z^3 is a third reactive group selected from the groups of the formulae (I)-(III), given and defined in claim 1;

each of J^1 and J^2, independently, is an optionally substituted aryl group or a chromophore;

L^3 is a linking group linking Z^3 and D;

L^4 is a linking group linking Z^3 and J^1;

L^5 is a linking group linking Z^2 and J^2;

each of q, r, s and t independently, is zero or 1;

each of Z^1, Z^2, L^1, L^2 and a is as defined in claim 1; and

when at least one of a and t is 1, Z^2 is selected from the groups of the formulae (I)-(III), given and defined in claim 1.

28. A dye according to claim 27, wherein q is 1, r is 1, s is 1, each of a and t is zero and Z^2 is selected from the groups of the formulae (IV)-(VI), given and defined in claim 1.

29. A dye according to claim 27, wherein q is 1, r is 1, s is zero, a is zero and t is 1.

30. A dye according to any one of claims 27 to 29, wherein each of L^3 and L^4, independently, is selected from one of the groups of the formulae $(VII)^1$, $(VII)^2$ and $(VII)^3$, given and defined in claim 6.

31. A dye according to claim 30, wherein each of L^3 and L^4 is a group of the formulae $(VII)^1$, given and defined in claim 6.

32. A dye according to claim 27, wherein q is 1, r is zero, s is 1, a is zero and t is zero.

33. A dye according to claim 32, wherein L^3 is a group of the formula $(VII)^3$

$$\text{—N(R)BN(R)—} \qquad (VII)^3$$

wherein B is a triazine group substituted by a non-reactive group.

34. A dye according to any one of claims 27 to 33, wherein the chromophore D is an azo chromophore derived from 1-hydroxy-8-aminonaphthalene substituted by at least one sulphonic acid group.

35. A dye according to claim 1 of the formula

$$Z^1\text{-}L^1\text{-}D^1[L^3\text{-}Z^3(L^4\text{-}Z^4)_1L^5\text{-}D^2]_k[L^2]_aZ^2$$

wherein:

D^1 is a first chromophore;

D^2 is a second chromophore;

Z^3, when present, is a third reactive group selected from the groups of the formulae (I)-(III), given and defined in claim 1;

Z^4, when present, is a fourth reactive group selected from the groups of the formulae (I)-(III), given and defined in claim 1;

L^3 is a linking group linking Z^3 to D^1;

L^4 is a linking group linking Z^3 to Z^4;

L^5 is a linking group linking D^2 to one of Z^3 and Z^4;

each of k and l, independently, is zero or 1; and

each of Z^1, Z^2, L^1, L^2 and a is as defined in claim 1.

36. A dye according to claim 35 wherein a is 1, Z^2 is a group of the formula (I), given and defined in claim 1, k is zero and D^1 is a tetrakisazo chromophore containing two residues of H-acid linked together by a group forming part of the chromophore.

37. A dye according to claim 35, wherein a is 1, each of Z^1 and Z^2 is a group of the formula (I), given and defined in claim 1, each of k and l is 1;

each of D^1 and D^2 is a disazo chromophore containing a respective residue of H-acid,

each of Z^3 and Z^4 is a group of the formula (II), given and defined in claim 1, and

L^4 is a linking group of the formula $(VII)^2$ or $(VII)^3$, given and defined in claim 6.

38. A dye according to claim 35, wherein a is 1, Z^2 is a group of the formula (I), given and defined in claim 1, k is 1 and l is 1.

39. A dye according to claim 35, wherein a is 1, Z^2 is a group of the formula (I), given and defined in claim 1, k is 1 and l is zero.

40. A dye according to claim 1, of the formula

$$Z^1\text{-}L^1\text{-}Z^3\text{-}L^3\text{-}D\text{-}Z^2$$

wherein:

Z^3 is a third reactive group selected from the groups (I)-(III), given and defined in claim 1; and

L^3 is a third linking group selected from the groups $(VII)^1$, $(VII)^2$ and $(VII)^3$, given and defined in claim 6;

Z^2 is a second reactive group selected from the groups (IV)-(VI), given and defined in claim 1; and

each of Z^1 and L^1 is as defined in claim 1.

41. A dye according to claim 40, wherein L^1 is a linking group of the formula $(VII)^2$ or $(VII)^3$, given and defined in claim 6.

42. A dye according to claim 40 or claim 41, wherein Z^3 is a group of the formula (II), given and defined in claim 1.

43. A dye according to claim 1, of the formula

$$D\text{-}L^2\text{-}Z^2\text{-}L^1\text{-}Z^1$$

wherein:

Z^2 is selected from groups of the formulae I-(III), given and defined in claim 1; and

each of D, Z^1, L^1 and L^2 is as defined in claim 1.

44. A dye according to claim 43, wherein Z^4 is a group of the formula (II), given and defined in claim 1.

45. A dye according to claim 43 or claim 44, wherein L^2 is a linking group selected from the groups $(VII)^1$, $(VII)^2$ and $(VII)^3{}_1$, given and defined in claim 6.

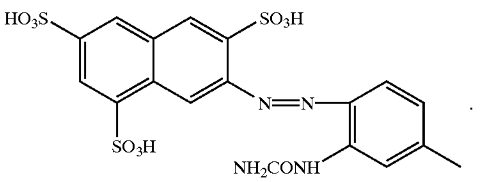
46. A dye according to claim 43, wherein L^2 is a linking group of the formula $(VII)^2$ or $(VII)^3$, given and defined in claim 6.

47. A dye according to any one of claims 43 to 46, wherein L^1 is a group of the formula (VII^3), given and defined in claim 6, in which B is an optionally substituted aryl group.

48. A dye according to any one of claims 43 to 46, wherein L^1 is a group of the formula (VII^3), given and defined in claim 6, in which B is a chromophoric bridging group.

49. A dye according to any one of claims 40 to 48, wherein the chromophore D is a disazo dye containing a residue derived from H-acid and having azo groups at the 2- and 7-positions.

50. A dye according to any one of claims 43 to 48, wherein D is a group of the formula



51. A dye according to claim 1, of the formula

$$D^2\text{-}L^2\text{-}Z^2\text{-}L^3\text{-}D^1\text{-}L^1\text{-}Z^1$$

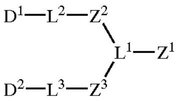
wherein:

each of D^1 and D^2, independently, is a chromophore;

L^3 is a linking group selected from groups of the formula (I)-(III), given and defined in claim 1; and

each of Z^1, Z^2, L^1 and L^2 is as defined in claim 1.

52. A dye according to claim 1, of the formula



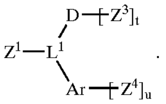
wherein:

each of D^1 and D^2, independently, is a chromophore;

L^3 is a linking group selected from the groups of the formulae (I)-(III), given and defined in claim 1; and

each of Z^1, Z^2, L^1 and L^2 is as defined in claim 1.

53. A dye according to claim 1, of the formula.



wherein:

one of Z^3 and Z^4 is a reactive group Z^2;

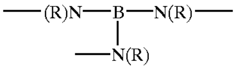
each of Z^3 and Z^4, independently, is a reactive group selected from the formulae (IV)-(VI), given and defined in claim 1;

each of t and u, independently, is zero or 1 and at least one of t and u is 1;

D is a chromophore;

Ar is an optionally substituted aryl group;

L^1 is a group of the formula



$$—(R)N—\underset{\substack{|\\ —N(R)}}{B}—N(R)—$$

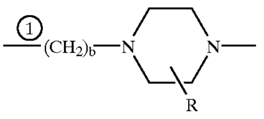
wherein each R, independently, is as defined in claim; and

Z^1 is as defined in claim 1.

54. A dye according to claim 53, wherein D is a disazo dye containing a residue derived from H-acid.

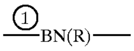
55. A dye according to claim 1, wherein the or a chromophore D contains a heterocyclic nitrogen atom and the linking group has the formula

(VII)^4



or

(VII)^5



$$\overset{①}{—}BN(R)—$$

wherein each of B,R and b is as defined in claim 6 and the bond ① is linked to the heterocyclic nitrogen atom of the chromophore.

56. A dye according to claim 55, of the formula

Z^1-L^1-$D^N$$[L^2]_a$$Z^2$$[L^5—Ar]_t$

wherein:

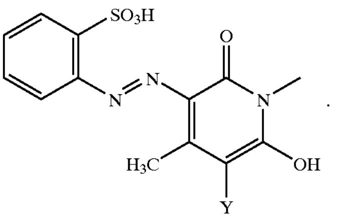
D^N is a chromophore containing a heterocyclic group including a nitrogen atom;

L^1 is a group of the formula (VII)^4 or (VII)^5, given and defined in claim 55, directly attached via the bond ①, to the nitrogen atom of the said chromophore D^N;

Ar is an optionally substituted aryl group;

and each of Z^1, Z^2, L^2, L^5, a and t is as defined in claim 27.

57. A dye according to claim 56, wherein the chromophore D has the formula



58. A dye according to any one of claims 27 to 56, which is an azo dye having at least two azo groups therein.

59. A dye according to claim 15, wherein D is a trisazo or tetrakisazo chromophore.

60. A dye according to claim 1, wherein the chromophore D is an anthraquinone.

61. A dye according to claim 60, which is of the formula

D^A-L^3-Ar-L^2-Z^2-L^1-Z^1

wherein:

D^A is an anthraquinone chromophore;

L^3 is a linking of the formula (VII)^1, given and defined in claim 6;

Ar is an optionally substituted aryl group; and

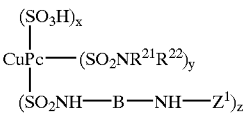
each of Z^1, Z^2, L^1 and L^2 is as defined in claim 1.

62. A dye according to claim 61, wherein each of L^1 and L^2, independently, is a linking group of the formula (VII)^1, (VII)^2 or (VII)^3, given and defined in claim 6.

63. A dye according to claim 62, wherein each of L^1 and L^2, independently is a group of the formula (VII)^3, given and defined in claim 6, in which B is an optionally substituted aryl group.

64. A dye according to claim 1, wherein the chromophore D is a metal phthalocyanine.

65. A dye according to claim 64, of the formula



$$\underset{\substack{|\\ (SO_2NH—B—NH—Z^1)_z}}{\overset{\substack{(SO_3H)_x\\ |}}{CuPc}}—(SO_2NR^{21}R^{22})_y$$

wherein:

Cu PC is a copper phthalocyanine chromophore;

$X+Y+Z \leqq 4$;

each of R^{21} and R^{22}, independently, is hydrogen or optionally substituted C_{1-4}alkyl;

B is a hydrocarbon bridging group; and

Z^1 is as defined in claim 1.

66. A dye according to claim 1, wherein the chromophore D is a triphendioxazine chromophore.

67. A dye according to claim 66, which is of the formula

Z^1-L^1-[Z^3-L^3]$_q$-D^T-[Z^4]$_r$-L^2-Z^2

wherein:

D^T is a triphendioxazine chromophore;

each of L^2, L^3 and L^4, independently, is a linking group of the formula (VII)^1, (VII)^2 or (VII)^3, given and defined in claim 6;

each of Z^2, Z^3 and Z^4 is a reactive group selected from groups of the formulae (I)-(III), given and defined in claim 1;

each of q and r is zero or 1; and

each of Z^1 and L^1 is as defined in claim 1.

68. A dye according to claim 67, wherein Z^2 is a group of the formula (I), given and defined in claim 1 and each of Z^3 and Z^4 is a group of the formula (II), given and defined in claim 1.

69. A dye according to claim 67 or claim 68, wherein each of L^1, L^2, L^3 and L^4 is a group of the formula (VII)^3, given and defined in claim 6.

70. A dye according to claim 1, wherein the chromophore D is a formazan chromophore.

71. A dye according to claim 70, of the formula

[Z^A]$_a$-D^F-L-Z^B-L^1-Z^1

wherein:

D^F is a formazan chromophore;

one of Z^A and Z^B is a group Z^2, given and defined in claim 1;

L is a linking group of the formula (VII)^1, (VII)^2 or (VII)^3, given and defined in claim 6;

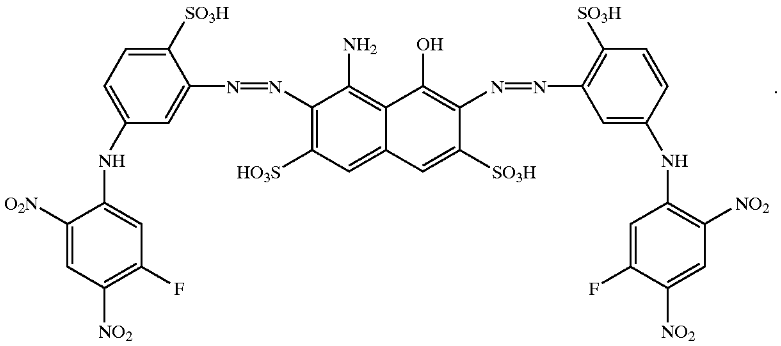
each of Z^1 and L^1 is as defined in claim 1,

a is zero or 1;

Z^A is selected from groups of the formulae (IV)-(VI), given and defined in claim 1; and

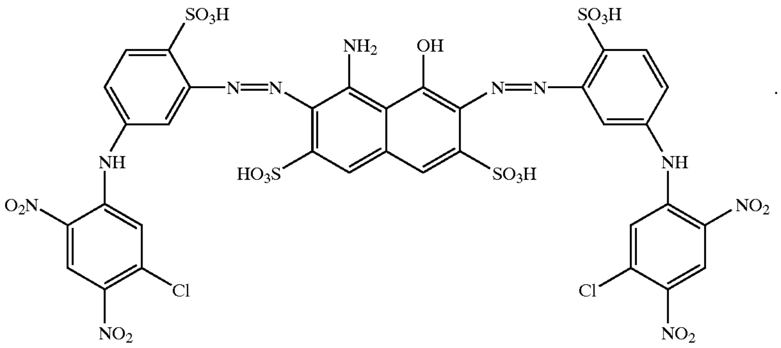
Z^B is selected from groups of the formulae (I)-(III),given and defined in claim 1.

72. A dye of the formula



(1)

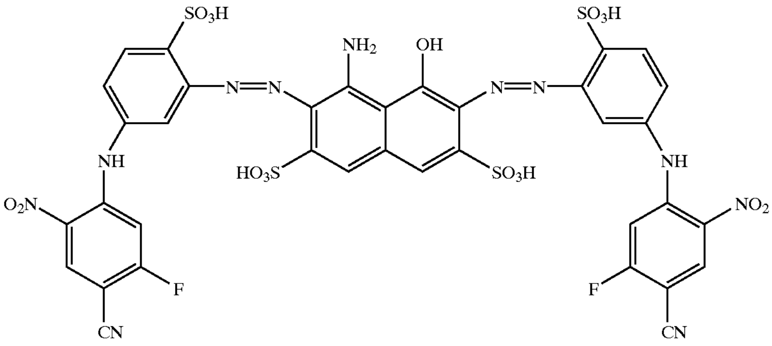
73. A dye of the formula



(2)

74. A dye of the formula

(3)



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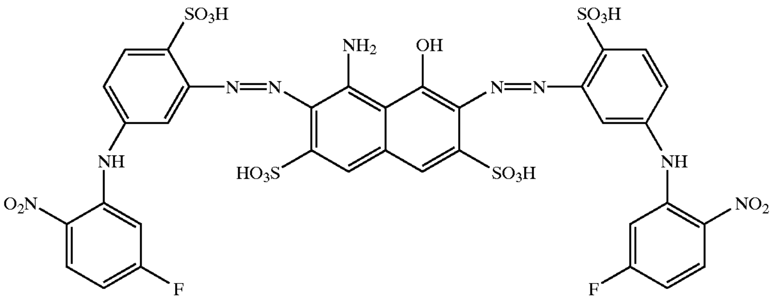
75. A dye of the formula

(4)



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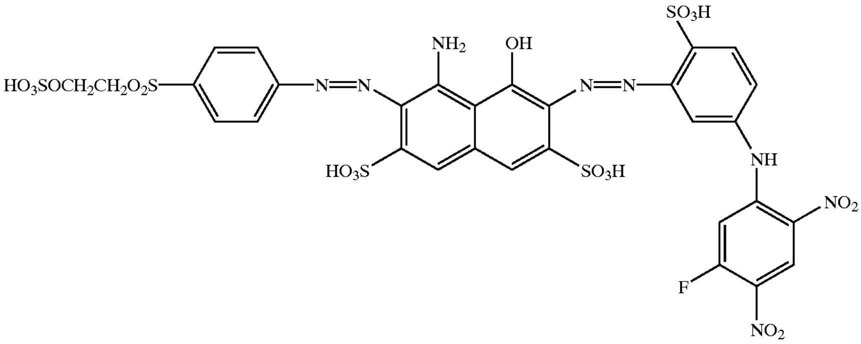
76. A dye of the formula

(5)



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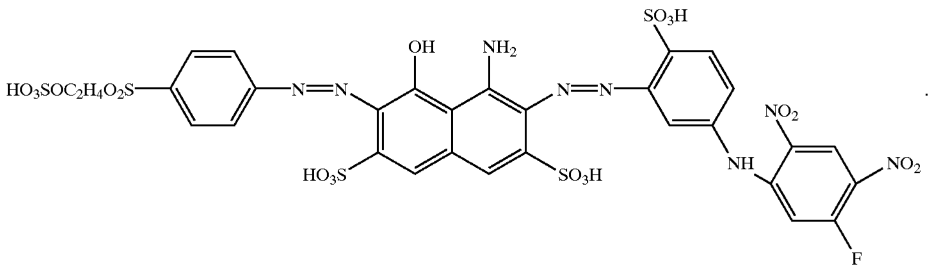
77. A dye of the formula



78. A process for preparing a dye of the formula $(VIII)^1$

$Z^1\text{-}L^1\text{-}D\text{-}L^2\text{-}Z^2$ $(VIII)^1$

wherein:

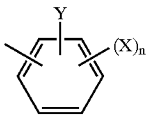
D is a chromophore;

each of L^1 and L^2 independently, is N(R);

each R, independently, is hydrogen or C_{1-4}alkyl;

each of Z^1 and Z^2 is a group

(I)



in which:

n is 1 or 2

X, or each X independently, is an electron withdrawing group; and

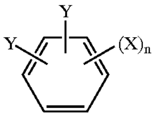
Y is a halogen atom,

which process comprises reacting a chromophoric compound of the formula (XX)

H(R)N-D-N(R)H (XX)

wherein each of D and R is as defined above, with at least two moles, per mole of the chromophoric compound of the formula (XX) , of a dihalobenzene component comprising at least one dihalobenzene compound of the formula (XXI)

(XXI)



wherein each of X, Y and n is as defined above, to obtain the dye of the formula $(VIII)^1$.

79. A process for preparing a dye of the formula $(VIII)^1$

$Z^1\text{-}L^1\text{-}D\text{-}L^2\text{-}Z^2$ $(VIII)^2$

wherein:

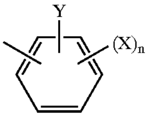
D is a chromophore;

each of L^1 and L^2 independently, is N(R);

each R, independently, is hydrogen or C_{1-4}alkyl;

Z^1 is a group

(I)



in which:

n is 1 or 2

X, or each X independently, is an electron withdrawing group; and

Y is a halogen atom; and

Z^2 is selected from the groups (II) and (III) given and defined in claim 1;

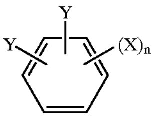
which process comprises reacting a chromophoric compound of the formula (XX)

H(R)N—D—N(R)H (XX)

wherein each of D and R is as defined above, with one mole, per mole of the chromophoric compound of the formula (XX), of each of

(a) a dihalobenzene compound of the formula (XXI)

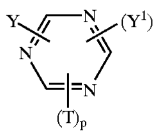
(XXI)



wherein each of Z, X, Y and n is as defined above; and

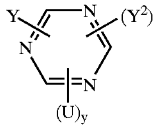
(b) a compound selected from

(XXII)



and

(XXIII)



wherein:

m is 1 or 2; p is 0 or 1; when m is 1, p is 1; and when m is 2, p is 0;

Y^1, or each Y^1 independently, is a halogen atom or an optionally substituted pyridinium group; and

T is C_{1-4}alkoxy, C_{1-4}thioalkoxy or $N(R^1)$ (R^2), in which each of R^1 and R^2 independently is hydrogen, optionally substituted C_{1-4}alkyl or optionally substituted aryl;

x is 1, 2 or 3; y is zero, 1 or 2; and $x+y\leqq 3$;

Y^2, or each Y^2 independently, is a halogen atom or an optionally substituted pyridinium group;

U or each U independently, is C_{1-4}alkyl or C_{1-4}alkylsulphonyl; and

Y is as defined above;

the said reactions of the compound of the formula (XX) with each of the respective compounds of the formulae (XII) and (XIII) being carried out simultaneously or one before the other, in either order, to obtain a dye of the formula $(VIII)^2$.

80. A process for preparing a dye of the formula $(VIII)^3$

$$Z^1\text{-}L^1\text{-}D\text{-}Z^2 \qquad (VIII)^3$$

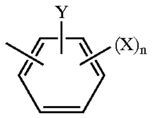
wherein:

D is a chromophore

L^1 is N(R), in which R is hydrogen or C_{1-4}alkyl;

Z^1 is a group

(I)



in which n is 1 or 2; X, or each X independently, is an electron withdrawing group; and Y is a hydrogen atom; and Z^2 is a group of the formula (IV)

$$\text{—}SO_2CH_2CH_2X^1 \qquad (IV)$$

wherein X^1 is an eliminatable group;

a group of the formula (V)

$$\text{—}SO_2(CH_2)_zCH{=}CH_2 \qquad (V)$$

wherein z is zero or 1; and

a group of formula (VI)

$$\text{—}W\text{—}C(R^{10}){=}CH_2 \qquad (VI)$$

wherein:

R^{10} is hydrogen, C_{1-4}alkyl or halogen; and

W is —OC(=O)— or —$N(R^{11})C(=O)$—

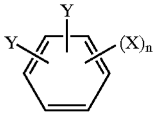
in which R^{11} is hydrogen or C_{1-4}alkyl;

which process comprises reacting a chromophoric compound of the formula (XXIV)

$$H(R)N\text{-}D\text{-}Z^2 \qquad (XXIV)$$

wherein D and Z^2 are as defined above, with a dihalobenzene compound of the formula (XXI)

(XXI)



wherein each of X, Y and n is as defined above, to obtain the dye of the formula $(VIII)^3$.

81. A process for the colouration of a substrate, which process comprises applying to the substrate a dye according to any one of claims 1 to 77.

82. A process according to claim 81, wherein the dye is applied to the substrate by exhaust dyeing, padding or printing.

83. A process according to claim 82, wherein the dye is applied by ink jet printing.

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