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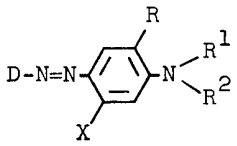
(19)

(54) UNIFORMLY DYED WATER-SWELLABLE CELLULOSIC FIBERS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to uniformly dyed water-swellable cellulosic fibers which are fast to washing, dry-cleaning, sublimation and light and to novel dyes which may be used for dyeing fibers. According to the invention such fibers are produced by contacting water-swellable cellulose fibers with water and an oxy-ethylene smaller-solvent (as hereinafter defined) to swell the fibers and, simultaneously or subsequently while the fibers are still swollen, with an essentially water-insoluble dye of the formula



(I)

in which
D is the radical of a diazo component;
R is hydrogen, methyl, methoxy or ethoxy;
R^1 is optionally substituted alkyl, cyclohexyl, phenyl, methoxyphenyl or ethoxyphenyl;
R^2 is optionally substituted alkyl;
X is hydrogen, chloro, methyl or acylamino;

provided that at least one group: —CO—R^3—Y—Ar is present as a substituent in X, R^1 and/or R^2, where R^3 is C_1 to C_3 alkylene;

Y is oxygen, sulfur or

;

R^4 is hydrogen or C_1 to C_4 alkyl; and
Ar is phenyl or phenyl bearing chloro, bromo, methyl, methoxy, ethoxy, C_1 to C_4 alkoxycarbonyl or cyano as a substituent.

The radicals D are derived particularly from amines of the benzene, naphthalene, benzothiazole, benzoisothiazole, thiazole, thiadiazole, indazole, pyrazole, thiophene, thionaphthene, azobenzene, phthalimide, naphthalimide or anthraquinone series.

Examples of substituents which may be present in the radical D of the diazo component are:

in the case of diazo components from amines of the benzene series: fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, carboxylic ester such as C_1 to C_8 alkoxycarbonyl, phenoxycarbonyl, benzyloxycarbonyl, phenoxyethoxycarbonyl and C_1 to C_4 β-alkoxyethoxycarbonyl, optionally

N-monosubstituted or N,N-disubstituted carbamoyl or sulfamoyl, methyl, ethyl, butyl, octyl, hexyl, methoxy, ethoxy, phenoxy, carboxy, thiazolyl, thiadiazolyl, oxadiazolyl, benzothiazolyl, benzoxazolyl, diphenylphosphinyl and phenylcarbonyl; (N-substituents of carbamoyl or sulfamoyl are for example methyl, ethyl, phenyl, benzyl, phenylethyl, cyclohexyl, norbornyl, propyl, β-hydroxyethyl, γ-hydroxypropyl, β-methoxyethyl, γ-methoxypropyl, γ-ethoxypropyl and also pyrrolidide, piperidide and morpholide.)

in the case of diazo components from amines of the azobenzene series: fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methyl, ethyl, carboxy, methoxy and ethoxy and the carboxylic ester, carbamoyl and sulfamoyl radicals specified for the benzene series, hydroxy, acetylamino, propionylamino and benzoylamino;

in the case of diazo components from amines of the heterocyclic series: chloro, bromo, nitro, cyano, thiocyanato, methyl, ethyl, β-cyanoethyl, phenyl, methoxy, ethoxy, methylmercapto, β-carbomethoxyethylmercapto, β-carboethoxyethylmercapto, β-cyanoethylmercapto, carbomethoxy, carboethoxy, acetyl, methylsulfonyl and ethylsulfonyl; and

in the case of diazo components from amines of the anthraquinone series: chloro, bromo, amino, acetyl, methyl, ethyl, phenylamino, tolylamino, hydroxy, methoxy, ethoxy, cyano and carboxy.

In the benzene and naphthalene series those diazo components are preferred which have at least one substituent which lowers the basicity such as nitro, methylsulfonyl, phenylsulfonyl, ethylsulfonyl, carboxylic ester, optionally N-substituted carbamoyl, chloro, bromo, trifluoromethyl, cyano, thiazolyl, thiadiazolyl, oxadiazolyl, benzothiazolyl and benzoxazolyl. Examples of optionally substituted alkyl R^1 and R^2 are: allyl, alkyl of one to four carbon atoms, alkyl of two to four carbon atoms bearing chloro, hydroxy, cyano, acetylamino, benzoylamino, alkoxy of one to four carbon atoms, alkoxycarbonyl of one to four carbon atoms, alkanoyloxy of one to four carbon atoms or benzoyloxy as a substituent, cyclohexyl, benzyl, phenylethyl, phenylhydroxyethyl and phenylpropyl.

Examples of individual radicals R^1 and R^2 in addition to those already specified are: methyl, ethyl, propyl, butyl, β-hydroxyethyl, β-hydroxypropyl, β-hydroxybutyl, β-chloroethyl, β-cyanoethyl, β-acetylaminoethyl, β-acetylaminopropyl, β-benzoylaminoethyl, β-benzoylaminopropyl, β-methoxyethyl, β-ethoxyethyl, β-butoxyethyl, β-carbomethoxyethyl, β-carboethoxyethyl, β-acetoxyethyl, β-propionyloxyethyl, β-butyroxyethyl and β-valeroyloxyethyl.

Examples of acylamino radicals X are acetylamino, propionylamino, butyrylamino, chloroacetylamino, dichloroacetylamino, trifluoroacetylamino, benzoylamino and HN—OC—R^3—Y—Ar and also methylsulfonylamino, ethylsulfonylamino and phenylsulfonylamino.

The group OC—R^3—Y—Ar may also be present in the form of an acyloxy or acylamino group in the radicals R^1 and/or R^2.

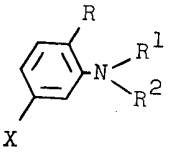
Examples of radicals R^4 are propyl, butyl and particularly methyl and ethyl.

Examples of alkoxycarbonyl radicals for Ar are methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl and butoxycarbonyl.

Dyes of the formula (I) may be prepared by reacting a diazo compound of an amine of the formula (II):

$$D—NH_2 \qquad (II)$$

with a coupling component of the formula (III):

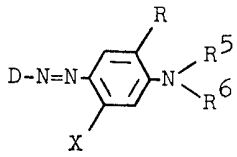


(III)

where D, R, X, R^1 and R^2 have the meanings given above.

The diazotization of the amines may be carried out by a conventional method. The coupling is also carried out as usual in an aqueous medium with or without the addition of solvents under strongly to weakly acid conditions.

Preferred fibers according to the invention are those which have been dyed with a dye of the formula

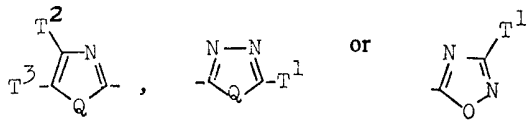


(Ia)

in which

D is phenyl substituted by fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, C_1 to C_8 alkoxycarbonyl, phenoxycarbonyl, benzyloxycarbonyl, phenoxyethoxycarbonyl, C_1 to C_4 alkoxyethoxycarbonyl, methyl, ethyl, methoxy, ethoxy, phenoxy, carboxy, phenylazo, phenylazo bearing fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methyl, ethyl, methoxy, ethoxy,

$SO_2N(B^1)(B^2)$ or $CON(B^1)(B^2)$ as a substituent, $CON(B^1)(B^2)$, $SO_2N(B^1)(B^2)$,



benzothiazolyl bearing nitro, thiocyanato, methylsulfonyl or methoxy as a substituent, benzoisothiazolyl bearing chloro, bromo, nitro or cyano as a substituent, thiazolyl bearing phenyl or nitro as a substituent, or thiadiazolyl bearing phenyl, methylmercapto, ethylmercapto, cyanoethylmercapto or C_1 to C_4 alkoxycarbonylethylmercapto as a substituent;

Q is O or S;

R is hydrogen, methyl, methoxy or ethoxy;

X is hydrogen, chloro, methyl, C_2 to C_3 alkanoylamino, chloroacetylamino, trifluoroacetylamino, benzoylamino, methylsulfonylamino, phenylsulfonylamino or

$NHCOR^3—O—Ar$;

R^5 is C_1 to C_4 alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or $C_2H_4OCOR^3—OAr$;

R^6 is C_1 to C_4 alkyl, allyl, acetoxyethyl, β-cyanoethyl, benzyl or $C_2H_4OCOR^3OAr$;

B^1 is hydrogen, C_1 to C_8 alkyl, cyclohexyl, β-hydroxyethyl, benzyl, phenylethyl or phenyl optionally bearing chloro, methyl or methoxy as a substituent, and

B^2 is hydrogen, C_1 to C_4 alkyl or β-hydroxyethyl, or

$N(B^1)(B^2)$ is pyrrolidyl, piperidyl, morpholyl or $NH(CH_2)_3OC_2H_4OB^3$;

B^3 is C_1 to C_4 alkyl, cyclohexyl, phenyl or tolyl;

T^1 is C_1 to C_8 alkyl, methoxymethyl, phenoxymethyl, phenyl or phenyl bearing chloro, bromo, nitro, methoxy or ethoxy as a substituent;

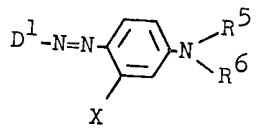
T^2 is hydrogen or methyl; and

T^3 is methyl, ethyl, phenyl or phenyl bearing chloro, bromo, or methyl as substituent; or T^2 and T^3 together are a fused benzene ring optionally bearing methoxy, ethoxy, methyl or chloro as a substituent;

R^3 is C_1 to C_3 alkylene; and

Ar is phenyl or phenyl bearing chloro, bromo, methyl or methoxy as a substituent and at least one of the radicals R^5, R^6 or X contains a group of the formula $OCOR^3—OAr$.

Dyes and dye mixtures which are particularly valuable for producing the dyed fibers of the invention are those of the formula (Ib):—



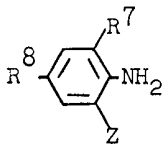
(Ib)

in which
D^1 is the radical of a diazo component of the benzene, thiadiazole, benzoisothiazole, phthalimide, naphthalimide, anthraquinone or azobenzene series;
R^5 is C_1 to C_4 alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or —$C_2H_4OCOR^3$—Y—Ar:
R^6 is C_1 to C_4 alkyl, β-acetoxyethyl, β-cyanoethyl, benzyl or —$C_2H_4OCOR^3$—Y—Ar;
and X, R^3, Y and Ar have the meanings given above.

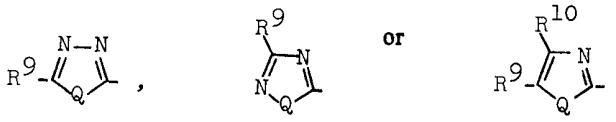
The radical D^1 may be derived in particular from the following amines: o-nitroaniline, m-nitroaniline, p-nitroaniline, o-cyanoaniline, m-cyanoaniline, p-cyanoaniline, 2,4-dicyanoaniline, o-chloroaniline, m-chloroaniline, p-chloroaniline, 2,4-dichloroaniline, 3,4-dichloroaniline, 2,5-dichloroaniline, 2,4,5-trichloroaniline, 2,4,6-trichloroaniline, o-bromoaniline, m-bromoaniline, p-bromoaniline, 2,4,6-tribromoaniline, 2-chloro-4-nitroaniline, 2-bromo-4-nitroaniline, 2-cyano-4-nitroaniline, 2-methylsulfonyl - 4 - nitroaniline, 2 - methoxy - 4 - nitroaniline, 4 - chloro - 2 - nitroaniline, 2,4 - dicyano - 6 - chloroaniline, 2 - cyano - 4,6 - dibromoaniline, 2,4-dicyano - 6 - bromoaniline, 4 - cyano - 2 - chloroaniline, 1 - amino - 2 - trifluoromethyl - 4 - chlorobenzene, 2 - chloro - 5 - aminobenzonitrile, 2 - amino - 5-chlorobenzonitrile, 1 - aminobenzene - 4 - methylsulfone, 1 - amino - 2,6 - dibromobenzene - 4 - methylsulfone, 1 - amino - 2 - chloro - 4 - methylsulfone, 1-amino - 2,6 - dichlorobenzene - 4 - methylsulfone, 2,4 - dinitroaniline, 2,4 - dinitro - 6 - chloroaniline, 2,4 - dinitro - 6 - bromoaniline, 2,4 - dinitro - 6 - cyanoaniline, 1 - amino - 2,4 - dinitrobenzene - 6 - methylsulfone, 2,6 - dichloro - 4-nitroaniline, 2,6 - dibromo - 4 - nitroaniline, 2 - chloro - 6 - bromo - 4 - nitroaniline, 2,6 - dicyano - 4 - nitroaniline, 2 - cyano - 4 - nitro - 6 - chloroaniline, 2 - cyano - 4 - nitro - 6 - bromoaniline, the methyl or β - methoxyethyl ester of 1 - amino - 2,4 - dinitrobenzene - 6 - carboxylic acid, the methyl, ethyl, propyl, butyl, isobutyl, β-ethylhexyl, cyclohexyl, benzyl, phenyl, β-methoxyethyl, β-ethoxyethyl, β-butoxyethyl, methyldiglycol, ethyldiglycol, methyltriglycol, ethyltriglycol or β-acetoxyethyl ester of 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid, the methyl, isobutyl, methyldiglycol, β-methoxyethyl, β-butoxyethyl or β-acetoxyethyl ester of 5-nitroanthranilic acid, the propyl ester of 3,5-dichloroanthranilic acid, the β-methoxyethyl ester of 3,5-dibromoanthranilic, 4-diphenylphosphinylaniline, the dimethyl, diethyl, dipropyl or dibutyl ester of 3-aminophthalic acid, 4-aminophthalic acid, 5-aminoisophthalic acid or aminoterephthalic acid, the amide, methylamide, propylamide, butylamide, isobutylamide, cyclohexylamide, β-ethylhexylamide, γ-methoxypropylamide, γ-ethoxypropylamide, or anilide of 3-aminobenzoic or 4-aminobenzoic acid, the dimethylamide, diethylamide, pyrrolidide or morpholide of 2-aminobenzoic, 3-aminobenzoic or 2-aminobenzoic acid, the diamide or bis-γ-methoxypropylamide of 5-aminoisophthalic acid, the dimethylamide, diethylamide, pyrrolidide, morpholide or N-methylanilide of 2-aminobenzenesulfonic, 3-aminobenzenesulfonic or 4-aminobenzenesulfonic acid, 4-aminoacetophenone, 4-aminobenzophenone, 2-aminobenzophenone, 2-aminodiphenylsulfone, 4-aminodiphenylsulfone, the β-hydroxyethylimide, 3'-methoxypropylimide, phenylimide or p-tolylimide of 3-aminophthalic or 4-aminophthalic acid, 3-amino-6-chlorophthalimide and its N-substitution products, 3-amino-4-cyano-5-methylphthalimide or 3-amino-4-cyano-5-ethylphthalimide and their N-substitution products, 1-amino-2-chloroanthraquinone, 1 - amino - 2 - bromoanthraquinone, 1 - amino - 2,4 - dibromoanthraquinone, 1-amino - 2 - acetyl - 4 - chloroanthraquinone, 1 - aminoanthraquinone - 6 - carboxylic acid, 1 - aminoanthraquinone - 6 - carboxylic acid ethyl ester, 1 - amino - 4-methoxyanthraquinone, 1 - amino - 4 - hydroxyanthraquinone, 1 - amino - 2-chloro - 4 - p - toluidinoanthraquinone, 2 - amino - 1 - chloroanthraquinone, 2-amino - 3 - chloroanthraquinone, 2 - amino - 3 - bromoanthraquinone, 2 - amino-1,3 - dibromoanthraquinone, 2 - amino - 1 - cyano - 3 - bromoanthraquinone, 1-aminobenzanthrone, 6 - aminobenzanthrone, 7 - aminobenzanthrone, 1 - aminoanthraquinone, 2 - aminoanthraquinone, 1 - amino - 4 - chloroanthraquinone, 2,4-dicyano - 3,5 - dimethylaniline, the imide, methylimide, n - butylimide, 2'-hydroxyethylimide, 3' - methoxypropylimide, 2' - ethylhexylimide or phenylimide or 4-aminonaphthalic acid, 4-amino-3-bromonaphthalimide and its N-substitution products, 4 - amino - 7 - nitro - 1,2 - benzoisothiazole, 4 - amino - 5 - cyano - 7-

nitro - 1,2 - benzoisothiazole, 4 - amino - 5 - chloro - 7 - nitro - 1,2 - benziso-thiazole, 4 - amino - 5 - bromo - 7 - nitro - 1,2 - benzisothiazole, 3 - amino - 5-nitro - 2,1 - benzoisothiazole, 3 - amino - 5 - nitro - 7 - bromo - 2,1 - benzoiso-thiazole, 3 - amino - 5 - chloro - 7 - nitro - 2,1 - benzoisothiazole, 3 - amino-2,1 - benzoisothiazole, 2 - phenyl - 5 - amino - 1,3,4 - thiadiazole, 3 - methyl-mercapto - 5 - amino - 1,2,4 - thiadiazole, 3 - β - carboethoxyethylmercapto - 5-amino - 1,2,4 - thiadiazole, 3 - β - carbomethoxyethylmercapto - 5 - amino - 1,2,4-thiadiazole and 3-β-cyanoethylmercapto-5-amino-1,2,4-thiadiazole.

Examples of suitable diazo components of the benzene series having heterocyclic substituents are compounds of the formula:

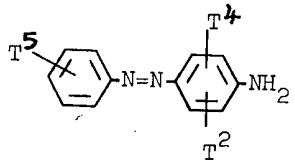


in which
R^7 is hydrogen, chloro, bromo or cyano;
R^8 is hydrogen, chloro, bromo or nitro; and
Z is a radical of the formula



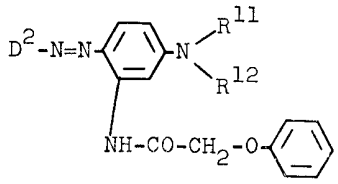
where Q is oxygen or sulfur;
R^9 is C_1 to C_8 alkyl or C_1 to C_8 alkoxyalkyl, phenyl, methylphenyl, chlorophenyl, methoxyphenyl or dichlorophenyl; and
R^{10} is methyl or C_1 to C_4 alkoxycarbonyl; or
R^9 and R^{10} together are a fused benzene ring which may bear methoxy, ethoxy, methyl, or chloro as substituents.

Examples of suitable diazo components of the aminoazobenzene series are: 4-aminoazobenzene, 3 - chloro - 4 - aminoazobenzene, 3 - bromo - 4 - aminoazo-benzene, 2',3 - dimethyl - 4 - aminoazobenzene, 3',2 - dimethyl - 4 - aminoazo-benzene, 2,5 - dimethyl - 4 - aminoazobenzene, 2 - methyl - 5 - methoxy - 4-aminoazobenzene, 2 - methyl - 4',5' - dimethoxy - 4 - aminoazobenzene, 4' - chloro-2 - methyl - 5 - methoxy - 4 - aminoazobenzene, 4' - chloro - 2 - methyl - 4 - amino-aozbenzene, 2,5 - dimethoxy - 4 - aminoazobenzene, 4' - chloro - 2,5 - dimethoxy-4 - aminoazobenzene, 4' - chloro - 2,5 - dimethyl - 4 - aminoazobenzene, 4'-methoxy - 2,5 - dimethyl - 4 - aminoazobenzene, 3,5 - dibromo - 4 - aminoazo-benzene, 2,3' - dichloro - 4 - aminoazobenzene, 3 - methoxy - 4 - aminoazo-benzene, 2',3' - dimethyl - 5 - bromo - 4 - aminoazobenzene, 4' - amino - 2',5'-dimethylazobenzene-4-sulfonic acid amide and 4'-amino-2',5'-dimethylazobenzene-3-sulfonic acid amide and the aminoazobenzenes of the formula:



in which
T^4 is hydrogen, chloro, bromo or methyl;
T^2 is hydrogen or methyl; and
T^5 is a radical of the formula $-A-\underset{\displaystyle R^1}{\underset{|}{N}}-R^2$ or $COOT^6$ in which A is —CO— or $-SO_2-$;
T^6 is an alcohol radical; and R^1 and R^2 have the meanings given above.

Particularly preferred dyes have the formula (Ic):



(Ic)

in which

D^2 is the radical of a diazo component of the benzoisothiazole, thiadiazole, azobenzene or benzene series;

R^{11} is C_1 to C_4 alkyl, β-cyanoethyl, β-hydroxyethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl or phenylethyl; and

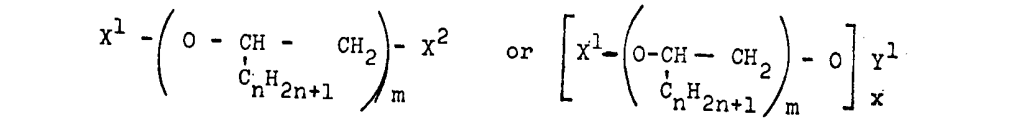
R^{12} is C_1 to C_4 alkyl, β-acetoxyethyl or β-cyanoethyl.

The dyes of the formulae (I), (Ia), (Ib) and (Ic) in which D, D^1 or D^2, as the case may be, is derived from an amine of the benzoisothiazole series or the heterocyclic-substituted benzene series are new. They may be used for dyeing not only cellulosic fibers but also synthetic, e.g. polyester, fibers.

The dyes of the formula (I) may from their constitution be regarded as substantially insoluble disperse dyes whose application for example to cotton is not possible as a rule. U.S. Patent 3,706,525 discloses however a process which enables them to be printed on cellulosic textile material. Statements made therein regarding the process conditions hold good also for dyeing with the dyes of formula (I).

According to the process disclosed in that patent the water-swellable cellulosic material to be dyed is contacted with water in an amount sufficient to swell the cellulosic material, the dye and an amount sufficient to maintain swelling of the cellulose if water is removed of a solvent having the properties given below, referred to in this specification as an oxyethylene sweller-solvent, provided that at some stage during the process the interior of the swollen cellulose is contacted with a solution of the dye in the solvent or aqueous solvent. The oxyethylene sweller-solvent is required to have the following properties:

a) it is at least 2.5 weight percent soluble in water at 25°C;
b) it boils above 150°C at atmospheric pressure;
c) it is a solvent for the dye at some temperature in the range from 0 to 225°C; and
d) it has the formula:



where n is 0 or 1,

m is a positive integer,

X^1 is H, C_{1-8} alkyl, C_{7-15} aralkyl or alkaryl,

$X^3C(=O)-$, X^3SO_2- or $X^3OC(=O)-$,

X^2 is —OH, $-OX^3$, $-SX^3$, NHX^3, $NX^3(C_{1-8}\text{alkyl})$, $NX^3(C_{7-15}$ aralkyl or alkaryl),

$-OCX^3(=O)$, $-OSO_2X^3$, $-OCOX^3(=O)$, —NH(phenyl) or NH(naphthyl),

X^3 is C_{1-8} alkyl, C_{5-10} cycloalkyl, C_{7-15} aralkyl or alkaryl, C_6 aryl, C_{10} aryl or furfuryl,

x is the number of unsatisfied valencies in Y^1,

Y^1 is $X^1OCH_2CHOX^1CH_2$—, —$CH_2CHOX^1CH_2$—, —CH_2CHCH_2—, —$CH_2C(CH_2OX^1)_3$, (—CH_2)$_2$—$C(CH_2OX^1)_2$, (—CH_2)$_3CCH_2OX^1$, (—CH_2)$_4$C, —$CH_2(CHOX^1)_yCH_2OX^1$, —$CH_2(CHOX^1)_yCH_2$— or —$CH_2(CHOX^1)_{y-z}$(—CH_2)$_zCH_2$—,

y is 2, 3 or 4, and

z is 0, 1, 2, 3 or 4 but no greater than y.

Essentially, therefore, the oxyethylene sweller-solvent has an oxyethylene chain (which may be substituted by methyl) present one or more times in the molecule and may thus be regarded as ethylene glycol or a derivative thereof. Examples of solvents which may be used in conjunction with water in producing the fibers of the present invention are polyethylene glycol or polyethylene oxide, e.g. of molecular weight 300—350 and optionally reacted with boric acid.

Other methods are disclosed in German laid-open Patent Application DOS 2,528,743 and may also be used for obtaining the dyed fibers according to this invention. Printing processes are preferred. As well as cellulose fibers it is possible to dye and print mixtures of cellulose fibers and synthetic fibers, particularly mixtures of cotton and polyester.

The fibers according to the invention have excellent fastness to washing, dry cleaning, sublimation and light, the wet fastness and in some cases also the light fastness being particularly worthy of mention. In the case of prints there is no staining of any white ground, for example during washing.

For dyeing and printing, the dyes of formula (I) are advantageously used in the form of dye formulations which, in addition to the dye of formula (I), contain a dispersant, a water retention agent and water and, if so desired, one or more other conventional constituents in dye formulations, for example disinfectants or antifoam agents.

Dispersants which may be used include cation-active compounds, but are preferably nonionic or, particularly, anion-active compounds, i.e. the dispersing agents usually employed for disperse dyes. Specific examples are lignin sulfonates, sulfomethylation products of phenol, condensation products of phenolsulfonic acids, phenol, formaldehyde and urea, condensation products of β-sulfonaphthalene and formaldehyde and also polyaddition products of propylene oxide and ethylene glycol, propylene glycol or ethylene diamine.

Glycols and glycol ethers such as ethylene glycol, propylene glycol, diethylene glycol or ethylene glycol monomethyl ether are particularly suitable as water retention agents for the dye formulations.

In the following Examples, which illustrate the invention, parts and percentages are by weight unless otherwise specified.

EXAMPLE 1.

69 parts of 4 - amino - 5 - bromo - 7 - nitro - 1,2 - benzoisothiazole is dissolved at 10° to 15°C in 500 parts of 96% sulfuric acid. 150 parts of a mixture of acetic acid and propionic acid in the ratio 17:3 is added at 0° to 5°C and diazotization is carried out by dripping in 75 parts of nitrosylsulfuric acid (11.5% of N_2O_3). The whole is stirred for another three to four hours at 0° to 5°C and the diazo solution is then allowed to flow into a suspension of 125 parts of N,N-bis-(phenoxyacetyloxyethyl)-m-toluidine in 500 parts of acetic acid, 200 parts of concentrated hydrochloric acid, 5 parts of sulfamic acid, 1000 parts of ice and 1000 parts of water. The whole is then diluted with about 2000 parts of ice-water and stirred overnight. The crystalline precipitate is suction filtered, washed with water until neutral and dried at 60°C at subatmospheric pressure. The dye obtained as an olive-black powder is printed according to the invention onto cotton or union fabric of cotton and polyester, the cotton fibers having been swollen with water and a polyethylene glycol, and fixed with hot air or superheated steam. Deeply colored violet prints having good fastness properties are obtained.

Commercial formulations of this and following dyes may be obtained for example as follows:

30 parts of dye,
6 parts of dispersant,
10 parts of water retention agent,
1 part of disinfectant and about
53 parts of water are ground in an agitator mill to a particle size of about 0.5 micron. A dispersion of the dye is thus obtained which is stable in storage.

EXAMPLE 2.

55 parts of 2 - (2 - methyl - 1,3,4 - oxadiazolyl) - 4 - nitroaniline is introduced at 0°C to 5°C into a mixture of 500 parts of 85% sulfuric acid and 81 parts of nitrosylsulfuric acid (11.5% of N_2O_3). After stirring for four hours at 0° to 5°C the diazo solution is poured into a solution of 77 parts of N,N-diethyl-N'-phenoxyacetyl-1,3-phenylenediamine in 500 parts of glacial acetic acid, 5 parts of sulfamic acid, 1000 parts of ice and 1000 parts of water. Coupling is completed by the addition of 400 parts of sodium acetate (crystalline) in 2000 parts of water. The crystalline black-violet product is filtered off, washed with water until free from salt and neutral and dried at subatmospheric pressure at 50°C. The dye dissolves in dimethylformamide and polyethylene glycol with a reddish violet color. When cotton or union fabric of polyester and cotton, the cotton fibers of which have been swollen by water and polyethylene glycol, is printed with the dye and then treated with superheated steam or hot air clear reddish violet prints having good fastness properties are obtained.

EXAMPLE 3.

73 parts of 4-diphenylphosphinylaniline is dissolved in 800 parts of 85% sulfuric acid at 40° to 50°C. The whole is cooled to 0° to 5°C, diazotized by the addition of 81 parts of nitrosylsulfuric acid (11.5% of N_2O_3 and stirred for three to four hours at 0° to 5°C. After coupling with 77 parts of N,N-diethyl-N'-phenoxyacetyl-1,3-phenylenediamine in the manner described in Example 2 a red powder is obtained which dissolves in dimethylformamide and polyethylene glycol with a reddish orange color. Clear and deep orange hues having very good fastness properties are obtained on cloth of cotton or polyester/cotton blends in accordance with the invention by the procedure of Example 1 or 2.

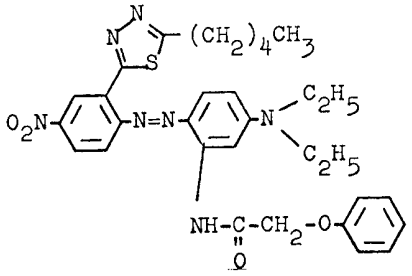
EXAMPLE 4.

66.5 parts of 2',3-dichloro-4-aminoazobenzene and 10 parts of an oxyethylated sperm oil alcohol containing about 23 ethylene oxide radicals are stirred overnight with 500 parts of water and 110 parts of 36% hydrochloric acid. 250 parts of ice is added and diazotization is carried out by adding 55 parts by volume of a 23% sodium nitrite solution. After the whole has been stirred for two hours at 5° to 10°C the excess nitrous acid is removed with sulfamic acid. The diazo compound is coupled with 77 parts of N,N-diethyl-N'-phenoxyacetyl-1,3-phenylenediamine in the manner described in Example 2. The reddish brown powder obtained which dissolves in dimethylformamide and polyethylene glycol with a reddish violet color gives ruby prints having good fastness properties when dyed onto cotton or polyester/cotton union fabric according to the invention by the procedure of Example 1 or 2.

The dyes set out in Examples 5 to 10 are prepared in the manner described in Examples 1 to 4.

EXAMPLE 5.

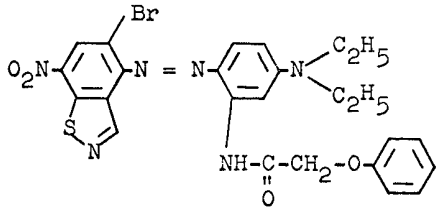
Cotton cloth is printed by rotary screen printing with a paste comprising 10 parts of the dye of the formula:



or the corresponding amount of a dye ofrmulation containing the dye, 100 parts of polyethylene oxide having a molecular weight of 300 and 790 parts of a 3% aqueous alginate thickening. The print is dried at 100°C, treated for one minute at 200°C with hot air, rinsed cold, soaped at the boil, again rinsed cold and dried. A reddish violet print on a white ground is obtained; it is fast to light and washing.

EXAMPLE 6.

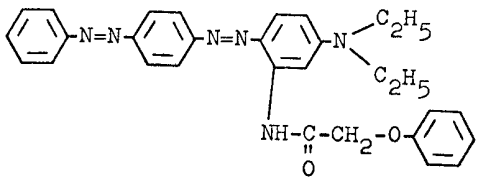
Polyester/cotton (67:33) fabric is printed with a paste consisting of 20 parts of the dye of the formula:



or the corresponding amount of a dye formulation containing the dye, 120 parts of the reaction product of polyethylene oxide having a molecular weight of 300 with boric acid in a molar ratio of 3:1 and 860 parts of a 10% aqueous alginate thickening. The print is dried at 105°C, treated for six minutes at 180°C with superheated steam, rinsed with cold water, soaped at 80°C, again rinsed cold and dried. A light and wash fast navy blue print on a white ground is obtained.

EXAMPLE 7.

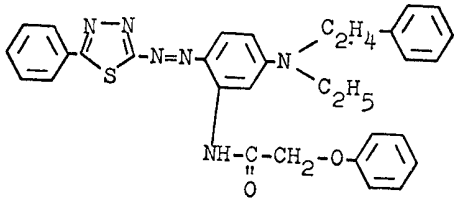
A cotton cloth is roller printed with a paste consisting of 15 parts of the dye of the formula:



or the corresponding amount of a dye formulation containing the dye, 110 parts of polyethylene oxide having a molecular weight of 350, 30 parts of the diethanolamide of oleic acid and 845 parts of a 10% aqueous alginate thickening. The print is dried at 100°C, fixed by a treatment with hot air for one minute at 195°C and finished off as described in Example 5. A fast red print is obtained on a white ground.

EXAMPLE 8.

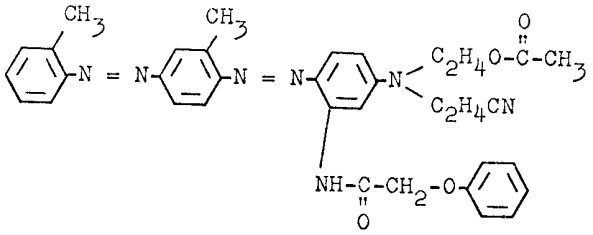
Polyester/cellulose (67:33) fabric is screen printed with a color consisting of 30 parts of the dye of the formula:



or the corresponding amount of a dye formulation containing the dye, 100 parts of the reaction product of polyethylene oxide having a molecular weight of 300 with boric acid in a molar ratio of 3:1, 30 parts of the diethanolamide of oleic acid and 840 parts of a 3% aqueous alginate thickening. The print is dried at 110°C, treated for five minutes at 185°C with superheated steam and finished off as described in Example 6. A fast reddish violet print on a white ground is obtained.

EXAMPLE 9.

Cotton cloth is padded with a solution containing 20 parts of the dye of the formula:

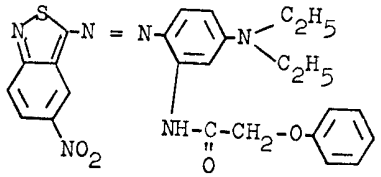


or the corresponding amount of a dye formulation containing the dye, 300 parts of a 3% aqueous alginate thickening, 550 parts of water and 130 parts of polyethylene oxide of the molecular weight 300. The liquor take-up should be 80%. The cloth is dried at 100°C. It is then treated for five minutes with superheated steam at 190°C to fix the dye, rinsed cold and washed at 90°C in a liquor which contains 3 parts of the condensation product of a long-chain alcohol with ethylene oxide and 997 parts of water. A red dyeing is obtained.

Instead of cotton cloth a union fabric of polyester and cotton (67:33 by weight) may be padded with the solution described. A red dyeing is obtained in which the two phases are equal in shade.Fixation with hot air at 195°C for two minutes may be used instead of treatment with superheated steam.

EXAMPLE 10.

Cotton cloth is padded with a solution of 150 parts of polyethylene oxide in 850 parts of water so that the liquor take-up is 80% and the padded cloth is dried at 100°C. The cloth pretreated in this way is printed by rotary screen printing with a paste consisting of 30 parts of the dye of the formula

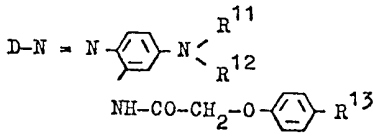


or the corresponding amount of a dye formulation containing the dye, and 970 parts of a 10% aqueous alginate thickening. After the print has been dried at 105°C it is treated for seven minutes at 185°C with superheated steam and then finished off by rinsing and soaping as described in Example 5.

A fast torquoise print on a white ground is obtained.

The dyes set out in the following Tables are obtained analogously to Examples 1 to 4. On polyester or cotton fibers and also on union fabric of the two types of fibers they exhibit similar tinctorial properties to the dyes set out in Examples 1 to 10.

TABLE 1



No.	D–NH_2	R^{11}	R^{12}	R^{13}	Hue on polyester/cotton
11	3-amino-5-nitro-7-bromo-2,1-benzo-isothiazole	C_2H_5	C_2H_5	H	bluish green
12	4-amino-5-cyano-7-nitro-1,2-benzo-isothiazole	C_2H_5	C_2H_5	H	blue
13	4-amino-7-nitro-1,2-benzoisothiazole	C_2H_5	C_2H_5	H	bluish violet
14	4-amino-7-nitro-1,2-benzoisothiazole	C_2H_4CN	C_2H_4CN	CH_3	ruby
15	2-phenyl-5-amino-1,3,4-thiadiazole	C_2H_5	C_2H_5	H	ruby
16	3-methylmercapto-5-amino-1,2,4-thiadiazole	C_2H_5	C_2H_5	H	red
17	3-β-carbomethoxy-ethylmercapto-5-amino-1,2,4-thiadiazole	$C_2H_4OCH_3$	C_2H_4CN	Cl	red
18	3-β-carbomethoxy-ethylmercapto-5-amino-1,2,4-thiadiazole	C_2H_5	C_2H_5	H	reddish violet
19	3-aminophthalic acid-p-tolylimide	C_2H_5	C_2H_5	H	red
20	4-aminophthalic acid phenylimide	C_2H_4CN	C_2H_5	H	red
21	4-aminophthalic acid-3′-methoxy-propylimide	C_2H_5	C_2H_5	H	red
22	1-aminoanthraquinone	C_2H_5	C_2H_5	H	brown
23	2-aminodiphenylsulfone	C_2H_5	C_2H_5	H	orange
24	2-aminobenzophenone	C_2H_4CN	C_2H_5	CH_3	orange
25	1-aminobenzene-4-methylsulfone	C_2H_5	C_2H_5	H	orange
26	4-aminonaphthalic acid-2′-ethylhexyl-imide	C_2H_5	C_2H_5	H	reddish violet

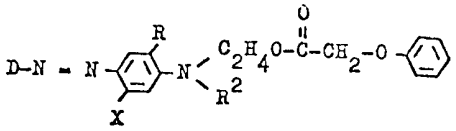
TABLE 1 (cont.)

No.	D–NH_2	R^{11}	R^{12}	R^{13}	Hue on polyester/ cotton
27	4-aminonaphthalic acid-n-butylimide	$C_2H_4OCH_3$	C_2H_5	Cl	reddish violet
28	4-amino-3-bromo-naphthalic acid n-butylimide	C_2H_5	C_2H_5	H	reddish violet
29	2,4,5-trichloroaniline	C_2H_4CN	$C_2H_4OCOCH_3$	H	golden yellow
30	2,4,5-trichloroaniline	C_2H_5	C_2H_5	H	orange
31	2-amino-5-nitrothiazole	C_2H_5	C_2H_5	H	violet
32	2-bromo-6-cyano-4-nitroaniline	C_2H_5	C_2H_5	H	bluish violet
33	2,4-dinitro-6-bromoaniline	C_2H_5	C_2H_5	H	violet
34	2-(2-methyl-1,3,4-thiadiazolyl)-4-nitro-6-bromoaniline	C_2H_4CN	C_2H_5	H	reddish violet
35	2-(2-methyl-1,3,4-thiadiazolyl)-4-nitroaniline	C_2H_5	C_2H_5	H	reddish violet
36	3-chloro-4-amino-azobenzene	C_2H_5	C_2H_5	H	reddish violet
37	3-bromo-4-amino-azobenzene	C_2H_4CN	$C_2H_4OCOCH_3$	H	red
38	2-methyl-4′,5-dimethoxy-4-amino-azobenzene	C_2H_5	C_2H_5	H	red
39	3′,2-dimethyl-4-aminoazobenzene	C_2H_5	C_2H_5	H	ruby
40	2-(benzothiazolyl-2)-aniline	C_2H_5	C_2H_5	H	orange
41	2-(benzoxazolyl-2)-4-nitroaniline	C_2H_5	C_2H_5	H	ruby
42	2-(2-phenyl-1,3,4-oxadiazolyl)-4,6-dichloroaniline	C_2H_5	C_2H_5	H	red
43	4-aminobenzene-sulfonic acid-N-methylanilide	C_2H_5	C_2H_5	H	golden yellow

TABLE 1 (cont.)

No.	D–NH_2	R^{11}	R^{12}	R^{13}	Hue on polyester/ cotton
44	4-aminobenzoic acid benzyl ester	C_2H_5	C_2H_5	H	golden yellow
45	2-bromo-4-nitro-6-(3-o-tolyl-1,2,4-oxadiazolyl)aniline	$C_2H_4OC(=O)-CH_3$	C_2H_5	H	violet
46	2,6-dichloro-4-nitroaniline	C_2H_5	C_2H_5	H	reddish brown

TABLE 2

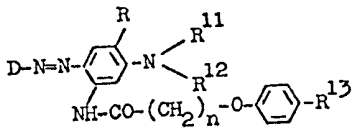


No.	D–NH_2	R	R^2	X	Hue on polyester/ cotton
47	4-aminobenzene-sulfonic acid anilide	H	C_2H_4CN	H	golden yellow
48	4-aminobenzoic acid phenyl ester	H	C_2H_5	$NHCOCH_3$	orange
49	2,6-dibromo-4-nitroaniline	H	C_2H_4CN	H	brown
50	3-β-cyanoethyl-mercapto-5-amino-1,2,4-thiadiazole	OCH_3	C_2H_4CN	$NHCOCH_3$	red
51	2-phenyl-5-amino-1,3,4-thiadiazole	H	C_2H_5	H	red
52	4-amino-7-nitro-1,2-benzoisothiazole	H	C_2H_4CN	CH_3	ruby
53	4-amino-5-bromo-7-nitro-1,2-benzo-isothiazole	H	$-O_2CCH_2OC_6H_5$	$NHCOCH_3$	violet
54	4-amino-5-bromo-7-nitro-1,2-benzo-isothiazole	H	C_2H_5	H	violet
55	3-amino-5-nitro-2,1-benzoisothiazole	H	C_2H_4CN	$NHCOCH_3$	bluish violet
56	4-aminophthalic acid phenylimide	H	C_2H_5	CH_3	red
57	4-aminonaphthalic acid n-butylimide	H	C_2H_4CN	H	ruby
58	4-amino-3-bromo-naphthalic acid methylimide	H	$-O_2CCH_2OC_6H_5$	$NHCOC_2H_5$	violet
59	2-aminodiphenyl-sulfone	H	C_2H_4CN	$NHCOCH_3$	orange
60	4-diphenylphosphinyl-aniline	OCH_3	$-O_2CCH_2OC_6H_5$	$NHCOCH_3$	scarlet
61	4-aminoazobenzene	H	C_2H_4CN	H	scarlet
62	3,5-dibromo-4-aminoazobenzene	H	C_2H_5	CH_3	reddish brown

TABLE 2 (cont.)

No.	D–NH_2	R	R^2	X	Hue on Polyester/ cotton
63	2′,3-chloro-4-aminoazobenzene	H	C_2H_4OH	$NHCOCH_3$	ruby
64	2-(2-phenyl-1,3,4-oxadiazolyl)-4-nitroaniline	H	C_2H_4CN	H	red
65	2-(4-methyl-1,3-thiazolyl-2)-4-nitroaniline	H	C_2H_5	CH_3	ruby
66	2-(2-n-pentyl-1,3,4-thiadiazolyl)-4-nitroaniline	H	C_2H_4CN	H	red
67	1-amino-4-chloro-anthraquinone	H	C_2H_4OH	$NHCOCH_3$	brownish violet

TABLE 3

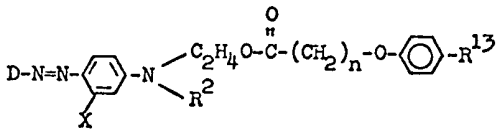


No.	D–NH_2	R	R^{11}	R^{12}	R^{13}	n	Hue on polyester/ cotton
68	4-amino-7-nitro-1,2-benzoisothiazole	H	CH_2–CH=CH_2	CH_2–CH=CH_2	H	1	bluish violet
69	,,	OCH_3	C_2H_5	C_2H_5	H	1	blue
70	,,	OC_2H_5	,,	,,	H	1	blue
71	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	H	C_2H_5	C_2H_5	H	2	navy blue
72	,,	H	,,	,,	H	3	navy blue
73	,,	H	,,	,,	OCH_3	1	navy blue
74	,,	H	,,	,,	Br	1	navy blue
75	3-chloro-4-aminoazobenzene	H	CH_2–CH=CH_2	CH_2–CH=CH_2	H	1	reddish violet
76	,,	OCH_3	C_2H_4CN	CH_2–CH=CH_2	H	1	reddish violet
77	2-(benzooxazolyl-2′)-aniline	H	CH_2–CH=CH_2	CH_2–CH=CH_2	H	1	orange
78	2-(benzothiazolyl-2′)-aniline	H	,,	,,	H	1	orange
79	2-amino-6-nitro-benzothiazole	H	C_2H_5	C_2H_5	H	1	reddish violet

TABLE 3 (cont.)

No.	D–NH_2	R	R^{11}	R^{12}	R^{13}	n	Hue on polyester/ cotton
80	1-amino-2-(3-phenyl-1,2,4-oxadiazolyl-5)-benzene	H	C_2H_5	C_2H_5	H	1	orange
81	1-amino-2-bromo-4-nitro-6-(4-methyl-5-butoxycarbonyl-thiazolyl-2)-benzene	H	,,	,,	H	1	bluish violet
82	1-amino-2-(4-methyl-thiazolyl-2)-benzene	H	,,	,,	H	1	orange
83	1-amino-4-methyl-3-(N-ethyl-N-phenyl-sulfonamido)benzene	H	,,	,,	H	1	orange
84	1-amino-4-chloro-2-trifluoromethylbenzene	H	,,	,,	H	1	orange
85	1-amino-2-chloro-benzene-4-methylsulfone	H	,,	,,	H	1	scarlet
86	1-amino-4-(phenoxy-ethoxypropylamino-carbonyl)-benzene	H	,,	,,	H	1	orange
87	1-amino-4-(phenoxy-ethoxy-propylamino-sulfonyl)-benzene	H	CH_2–CH=CH_2	CH_2–CH=CH_2	H	1	orange

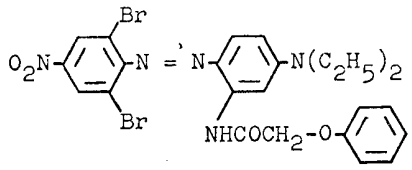
TABLE 4



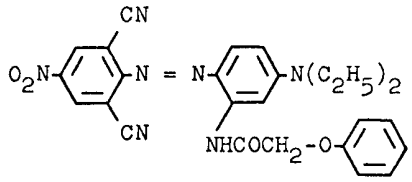
No.	D	R^2	X	n	R^{13}	Hue on polyester/ cotton
88	2-phenyl-5-amino-1,3,4-thiadiazole	CH_2–CH=CH_2	H	1	H	red
89	1-amino-2-(3-phenyl-1,2,4-oxadiazolyl-5) benzene	C_2H_4CN	Cl	1	H	orange
90	4-amino-7-nitro-1,2-benzoisothiazole	C_2H_4CN	$NHCOC_4H_9$	1	H	violet
91	,,	,,	$NHCOCH_2Cl$	1	H	violet
92	,,	,,	$NHCOC_6H_5$	1	CH_3	violet
93	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	CH_2–CH=CH_2	$NHSO_2C_6H_5$	1	H	bluish violet
94	,,	,,	$NHSO_2CH_3$	1	H	bluish violet
95	,,	C_2H_4CN	$NHCOCH_3$	2	H	violet
96	1-amino-4-(phenoxy-propylamino-sulfonyl)-benzene	$C_2H_4OCOCH_2OC_6H_5$	CH_3	1	H	orange
97	3-(benzooxazolyl-2)-aniline	,,	H	1	H	orange

EXAMPLE 98.

60.5 parts of the dye of the formula:

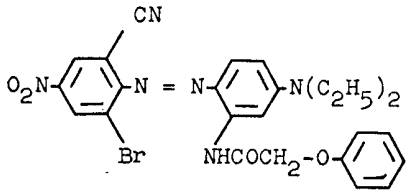


is stirred in 500 parts of N,N-dimethylformamide with 28 parts of cuprous cyanide (70%) for eight hours at 65°C. 400 parts of methanol is added at ambient temperature and the dye is then filtered off, washed with methanol, 10% aqueous ammonia solution and water and dried at 50°C at subatmospheric pressure. The dye of the formula:



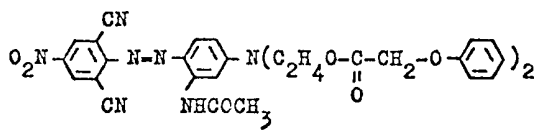
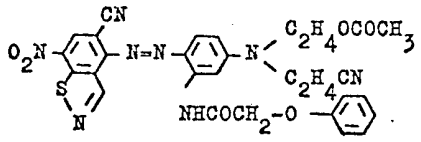
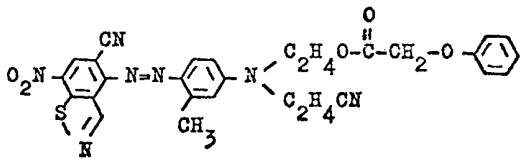
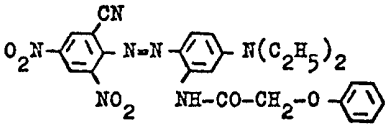
is obtained as a bluish black powder. When the dye is applied to cotton cloth or cotton/polyester union fabric analogously to Examples 5 to 10, bluish violet prints or dyeings are obtained having good fastness properties.

The same dye is obtained by the reaction of a dye of the formula:



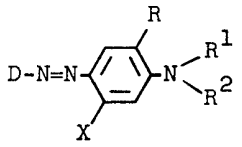
with an agent forming cuprous cyanide or by diazotization of 2,6-dicyano-4-nitroaniline and coupling with N,N-dimethyl-N'-phenoxyacetyl-1,3-phenylenediamine as described in Example 2.

The following dyes having similar tinctorial properties are prepared in the same manner:

Example No.		Hue on polyester/ cotton
99		violet
100		bluish violet
101		violet
102		reddish blue

WHAT WE CLAIM IS:—

1. Uniformly dyed water-swellable cellulosic fibers produced by contacting water-swellable cellulose fibers with water and an oxyethylene sweller-solvent (as hereinbefore defined) to swell the fibers and, simultaneously or subsequently while the fibers are still swollen, with an essentially water-insoluble dye of the formula (I)



(I)

in which D is the radical of a diazo component; R is hydrogen, methyl, methoxy, or ethoxy; R^1 is optionally substituted alkyl, cyclohexyl, phenyl, methoxyphenyl or ethoxyphenyl;

R^2 is optionally substituted alkyl;

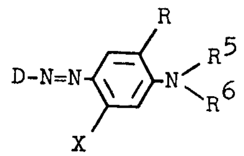
X is hydrogen, chloro, methyl or acylamino; provided that at least one —CO—R^3—Y—Ar group is present as a substituent in X, R and/or R^2, where R^3 is C_1 to C_3 alkylene;

Y is oxygen, sulfur or

R^4 is hydrogen or C_1 to C_4 alkyl; and

Ar is phenyl or phenyl bearing chloro, bromo, methyl, methoxy, ethoxy, C_1 to C_4 alkoxycarbonyl or cyano as a substituent.

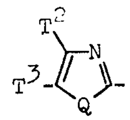
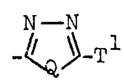
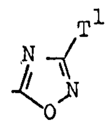
2. Fibers according to claim 1 wherein there is used an essentially water-insoluble dye of the formula (Ia)



(Ia)

in which D is phenyl substituted by fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, C_1 to C_8 alkoxycarbonyl, phenoxycarbonyl, benzyloxycarbonyl, phenoxyethoxycarbonyl, C_1 to C_4 alkoxyethoxycarbonyl, methyl, ethyl, methoxy, ethoxy, phenoxy, carboxy, phenylazo, phenylazo bearing fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methyl, ethyl, methoxy, ethoxy,

$SO_2N(B^2)$—B^1 or $CON(B^2)$—B^1 as a substituent, $CON(B^2)$—B^1, $SO_2N(B^2)$—B^1,

 ,  or 

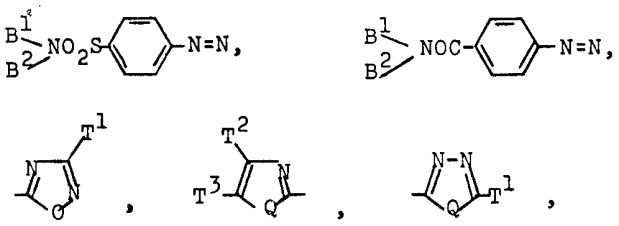
benzothiazolyl bearing nitro, thiocyanato, methylsulfonyl or methoxy as a substituent, benzoisothiazolyl bearing chloro, bromo, nitro or cyano as a substituent, thiazolyl bearing phenyl or nitro as a substituent, or thiadiazolyl bearing phenyl, methylmercapto, ethylmercapto, cyanoethylmercapto or C_1 to C_4 alkoxycarbonylethylmercapto as a substituent;

Q is O or S;
R is hydrogen, methyl, methoxy or ethoxy;
X is hydrogen, chloro, methyl, C_2 to C_4 alkanoylamino, chloroacetylamino, trifluoroacetylamino, benzoylamino, methylsulfonylamino, phenylsulfonylamino or $NHCOR^3$—O—Ar;
R^5 is C_1 to C_4 alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or $C_2H_4OCOR^3$—OAr;
R^6 is C_1 to C_4 alkyl, allyl, acetoxyethyl, β-cyanoethyl, benzyl or $C_2H_4OCOR^3OAr$;
B^1 is hydrogen, C_1 to C_8 alkyl, cyclohexyl, β-hydroxyethyl, benzyl, phenylethyl or phenyl optionally bearing chloro, methyl or methoxy as a substituent, and
B^2 is hydrogen, C_1 to C_4 alkyl or β-hydroxyethyl, or

$N(B^2)$—B^1 is pyrrolidyl, piperidyl, morpholyl or $NH(CH_2)_3OC_2H_4OB^3$;

B^3 is C_1 to C_4 alkyl, cyclohexyl, phenyl or tolyl,
T^1 is C_1 to C_8 alkyl, methoxymethyl, phenoxymethyl, phenyl, or phenyl bearing chloro, bromo, nitro, methoxy or ethoxy as a substituent,
T^2 is hydrogen or methyl, and
T^3 is methyl, ethyl, phenyl or phenyl bearing chloro, bromo, or methyl as a substituent, or
T^2 and T^3 together are a fused benzene ring optionally bearing methoxy, ethoxy, methyl or chloro as a substituent,
R^3 is C_1 to C_3 alkylene, and
Ar is phenyl or phenyl bearing chloro, bromo, methyl or methoxy as a substituent, and at least one of the radicals R^5, R^6 and X contains a group of the formula $COOR^3$—OAr.

3. Fibers according to claim 1 or 2, wherein in the formula (I) or (Ia) D is phenyl substituted by phenylazo, chlorophenylazo, methylphenylazo,



chloro or bromo; or benzoisothiazolyl substituted by chloro, bromo, nitro or cyano and B^1, B^2, Q, T^1, T^2 and T^3 have the meanings given in claim 2.

4. Fibers according to claim 1 or 2, wherein D in the formula (I) or (Ia) is benzoisothiazolyl substituted by chloro, bromo, nitro or cyano.

5. Fibers according to claim 2 or 3, wherein D includes the symbol Q and Q is oxygen.

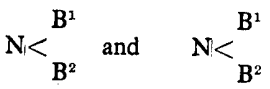
6. Fibers according to any of claims 1 to 5, wherein R in the formula (I) or (Ia) is hydrogen.

7. Fibers according to any of claims 1 to 6, wherein X in the formula (I) or (Ia) is $NHCOR^3OAr$, where R^3 and Ar have the meanings given in claim 1.

8. Fibers according to any of claims 1 to 6, wherein X in the formula (I) or (Ia) is $NHCOCH_2OC_6H_5$.

9. Fibers according to any of claims 2 to 8, wherein in the formula (Ia) R^5 and R^6 are C_1 to C_4 alkyl, β-cyanoethyl or $C_2H_4OCOR^3OAr$, where R^3 and Ar have the meanings given in claim 2.

10. Fibers according to any of claims 2, 3 or 6 to 9, wherein D in the formula (Ia) comprises

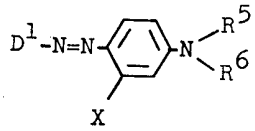


is $NH(CH_2)_3OC_2H_4OB^3$, where B^3 has the meaning given in claim 2.

11. Fibers according to any of claims 2, 3 or 5 to 9, wherein in the formula (Ia) D includes T^1 and T^1 is C_1 to C_8 alkyl or phenyl.

12. Fibers according to any of claims 1 to 11, wherein R^3 in the formula (I) or (Ia) is $—CH_2—$.

13. Fibers according to claim 1, wherein there is used an essentially water-insoluble dye of the formula (Ib):



(Ib)

in which

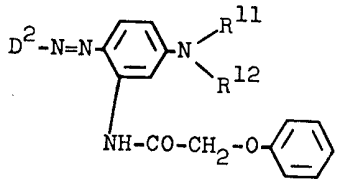
D^1 is the radical of a diazo component of the benzene, thiadiazole, benzoisothiazole, phthalimide, naphthalimide, anthraquinone or azobenzene series;

R^5 is C_1 to C_4 alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or $—C_2H_4OCOR^3—Y—Ar$;

R^6 is C_1 to C_4 alkyl, β-acetoxyethyl, β-cyanoethyl, benzyl or $—C_2H_4OCOR^3—Y—Ar$;

and X, R^3, Y and Ar have the meanings given in claim 1.

14. Fibers according to claim 1, wherein there is used an essentially water-insoluble dye of the formula (Ic):



(Ic)

in which
D^2 is the radical of a diazo component of the benzoisothiazole, thiadiazole, azobenzene or benzene series;
R^{11} is C_1 to C_4 alkyl, β-cyanoethyl, β-hydroxyethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl or phenylethyl; and
R^{12} is C_1 to C_4 alkyl, β-acetoxyethyl or β-cyanoethyl.

15. Fibers according to claim 2, wherein in the formula (Ia) D is benzoisothiazolyl substituted by chloro, bromo, nitro or cyano,

R is hydrogen,
X is $NHCOCH_2OC_6H_5$,
R^5 is C_1 to C_4 alkyl, β-cyanoethyl or $C_2H_4OCOC_6H_5$ and
R^6 is C_1 to C_4 alkyl.

16. Fibers according to claim 1, wherein there is used a dye identified in any of the foregoing Examples 1 to 102.

17. Fibers according to any of claims 1 to 15, wherein the fibers are cotton fibers.

18. Fibers according to any of claims 1 to 17, wherein the cellulosic fibers are admixed or blended with synthetic fibers.

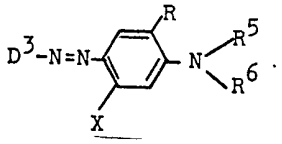
19. Fibers according to claim 18, wherein the synthetic fibers are polyester fibers.

20. Fibers according to any of claims 1 to 19, wherein the oxyethylene sweller-solvent is a polyethylene oxide.

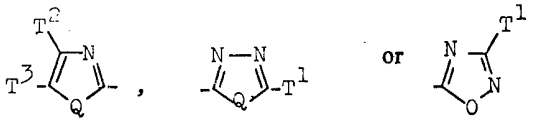
21. Fibres according to any of claims 1 to 20, wherein the dye is used in the form of a dye formulation also containing water, a dispersant and, as water-retention agent, a glycol or glycol ether.

22. A dye as specified in any of the claims 1 to 15, wherein D, D^1 or D^2 as the case may be is the radical of a diazo component of the benzoisothiazole series or of the benzene series bearing a heterocyclic substituent.

23. A compound of the formula:

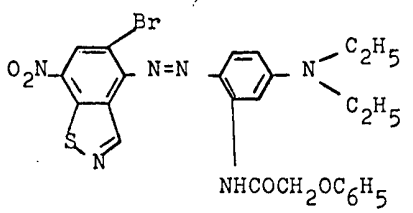


in which
D^5 is phenyl substituted once by

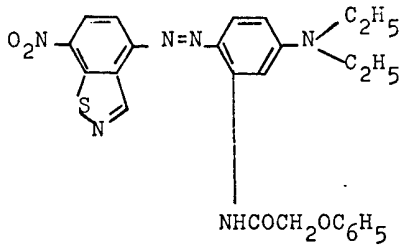


and optionally further substituted by chloro, bromo, nitro or cyano, or is benzoisothiazolyl substituted by chloro, bromo, nitro or cyano, and R, R^5, R^6, Q, T^1, T^2, T^3 and X have the meanings given in claim 2, at least one of R^5, R^6 and X containing the group OCO—R^3—O—Ar, where R^3 and Ar have the meanings given in claim 2.

24. The dye of the formula:



25. The dye of the formula:



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