

PATENT SPECIFICATION

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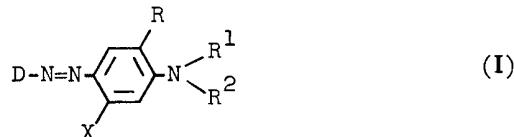
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(54) UNIFORMLY DYED WATER-SWELLABLE CELLULOSIC FIBERS

(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:—

5 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 10 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



in which

D is the radical of a diazo component;
 R is hydrogen, methyl, methoxy or ethoxy;
 15 R¹ is optionally substituted alkyl, cyclohexyl, phenyl, methoxyphenyl or ethoxyphenyl;
 R² is optionally substituted alkyl;
 X is hydrogen, chloro, methyl or acylamino;

provided that at least one group: —CO—R³—Y—Ar is present as a substituent in X, 20 R¹ and/or R², where R³ is C₁ to C₃ alkylene;

Y is oxygen, sulfur or



R⁴ is hydrogen or C₁ to C₄ alkyl; and
 Ar is phenyl or phenyl bearing chloro, bromo, methyl, methoxy, ethoxy, C₁ to C₄ alkoxy carbonyl or cyano as a substituent.

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

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

30 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 C₁ to C₈ alkoxy carbonyl, phenoxy carbonyl, benzyloxy carbonyl, phenoxyethoxy carbonyl and C₁ to C₄ β-alkoxyethoxy carbonyl, optionally

5 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, piperide and morpholide.)

10 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, acetylarnino, propionylarnino and benzoylarnino;

15 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

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

25 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, acetylarnino, benzoylarnino, alkoxy of one to four carbon atoms, alkoxy carbonyl of one to four carbon atoms, alkanoyloxy of one to four carbon atoms or benzoxyloxy as a substituent, cyclohexyl, benzyl, phenylethyl, phenylhydroxyethyl and phenylpropyl.

30 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 -acetylarninoethyl, β -acetylaminopropyl, β -benzoylarninoethyl, β -benzoylaminopropyl, β -methoxyethyl, β -ethoxyethyl, β -butoxyethyl, β -carbo-methoxyethyl, β -carboethoxyethyl, β -acetoxymethyl, β -propionyloxyethyl, β -butyroxyethyl and β -valeroxyloxyethyl.

35 Examples of acylarnino radicals X are acetylarnino, propionylarnino, butyrylarnino, chloroacetylarnino, dichloroacetylarnino, trifluoroacetylarnino, benzoylarnino and $\text{HN}-\text{OC}-\text{R}^3-\text{Y}-\text{Ar}$ and also methylsulfonylarnino, ethylsulfonylarnino and phenylsulfonylarnino.

40 The group $\text{OC}-\text{R}^3-\text{Y}-\text{Ar}$ may also be present in the form of an acyloxy or acylarnino group in the radicals R^1 and/or R^2 .

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

50 Examples of alkoxy carbonyl radicals for Ar are methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl and butoxycarbonyl.

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



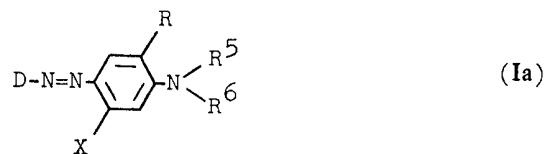
with a coupling component of the formula (III):



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

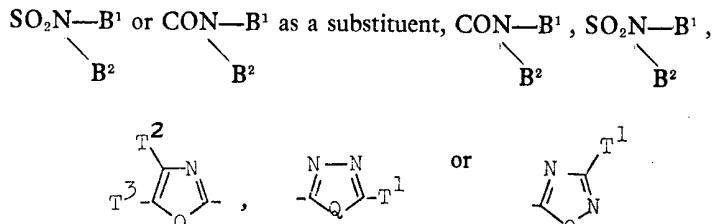
The diazotization of the amines may be carried out by a conventional method. The coupling is also carried out as usual in an aqueous medium with or without the addition of solvents under strongly to weakly acid conditions.

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



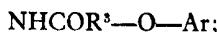
in which

D is phenyl substituted by fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, C₁ to C₈ alkoxy carbonyl, phenoxy carbonyl, benzyloxy carbonyl, phenoxyethoxy carbonyl, C₁ to C₈ alkoxyethoxy carbonyl, methyl, ethyl, methoxy, ethoxy, phenoxy, carboxy, phenylazo, phenylazo bearing fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methyl, ethyl, methoxy, ethoxy,



10 benzothiazolyl bearing nitro, thiocyanato, methylsulfonyl or methoxy as a substituent, 10
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 C₁ to C₄ alkoxy carbonyl ethylmercapto as a substituent;

15 Q is O or S; 15
R is hydrogen, methyl, methoxy or ethoxy;
X is hydrogen, chloro, methyl, C₂ to C₈ alkanoylamino, chloroacetyl amino, trifluoroacetyl amino, benzoyl amino, methylsulfonyl amino, phenylsulfonyl amino or



20 R⁵ is C₁ to C₄ alkyl, allyl, β -hydroxyethyl, β -cyanoethyl, β -acetoxyethyl, β -methoxyethyl, β -ethoxyethyl, cyclohexyl, benzyl, β -phenylethyl or C₂H₄OCOR³-OAr; 20
R⁶ is C₁ to C₄ alkyl, allyl, acetoxyethyl, β -cyanoethyl, benzyl or C₂H₄OCOR³OAr;
B¹ is hydrogen, C₁ to C₈ alkyl, cyclohexyl, β -hydroxyethyl, benzyl, phenylethyl or phenyl optionally bearing chloro, methyl or methoxy as a substituent, and
B² is hydrogen, C₁ to C₄ alkyl or β -hydroxyethyl, or 25

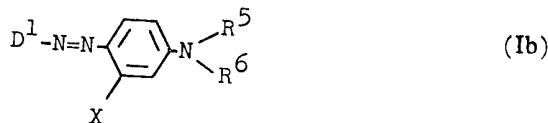
N-B¹ is pyrrolidyl, piperidyl, morpholyl or NH(CH₂)₃OC₂H₄OB³;
 B^2

30 B³ is C₁ to C₄ alkyl, cyclohexyl, phenyl or tolyl;
T¹ is C₁ to C₈ alkyl, methoxymethyl, phenoxy methyl, phenyl or phenyl bearing chloro, bromo, nitro, methoxy or ethoxy as a substituent;
T² is hydrogen or methyl; and

30 T³ is methyl, ethyl, phenyl or phenyl bearing chloro, bromo, or methyl as substituent; or
T² and T³ together are a fused benzene ring optionally bearing methoxy, ethoxy, methyl or chloro as a substituent;

35 R³ is C₁ to C₃ alkylene; and
Ar is phenyl or phenyl bearing chloro, bromo, methyl or methoxy as a substituent and at least one of the radicals R⁵, R⁶ or X contains a group of the formula OCOR³-OAr.

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



in which

D¹ is the radical of a diazo component of the benzene, thiadiazole, benzoisothiazole, phthalimide, naphthalimide, anthraquinone or azobenzene series;
 5 R⁵ is C₁ to C₄ alkyl, allyl, β -hydroxyethyl, β -cyanoethyl, β -acetoxyethyl, β -methoxyethyl, β -ethoxyethyl, cyclohexyl, benzyl, β -phenylethyl or $-\text{C}_2\text{H}_4\text{OCOR}^3-\text{Y}-\text{Ar}$;
 R⁶ is C₁ to C₄ alkyl, β -acetoxyethyl, β -cyanoethyl, benzyl or $-\text{C}_2\text{H}_4\text{OCOR}^3-\text{Y}-\text{Ar}$;
 and X, R⁷, Y and Ar have the meanings given above.

10 The radical D¹ 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-2,6-dichlorobenzene-4-methylsulfone, 2,4-dinitroaniline, 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 morpholidide of 2-aminobenzoic, 3-aminobenzoic or 2-aminobenzoic acid, the diamide or bis- γ -methoxypropylamide of 5-aminoisophthalic acid, the dimethylamide, diethylamide, pyrrolidide, morpholidide or N-methylanilide of 2-aminobenzenesulfonic, 3-aminobenzenesulfonic or 4-aminobenzenesulfonic acid, 4-aminoacetophenone, 4-amino-benzophenone, 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-butyrimide, 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-

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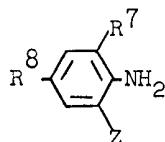
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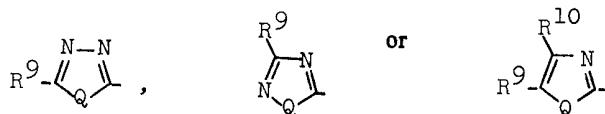
5 nitro - 1,2 - benzoisothiazole, 4 - amino - 5 - chloro - 7 - nitro - 1,2 - benzisothiazole, 4 - amino - 5 - bromo - 7 - nitro - 1,2 - benzisothiazole, 3 - amino - 5 - nitro - 2,1 - benzoisothiazole, 3 - amino - 5 - nitro - 7 - bromo - 2,1 - benzisothiazole, 3 - amino - 2,1 - benzoisothiazole, 2 - phenyl - 5 - amino - 1,3,4 - thiadiazole, 3 - methyl-10 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.

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



15 in which
 R⁷ is hydrogen, chloro, bromo or cyano;
 R⁸ is hydrogen, chloro, bromo or nitro; and
 Z is a radical of the formula

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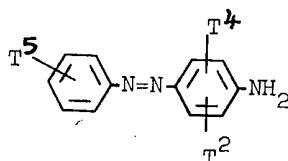
20 where Q is oxygen or sulfur;
 R⁹ is C₁ to C₈ alkyl or C₁ to C₈ alkoxyalkyl, phenyl, methylphenyl, chlorophenyl, methoxyphenyl or dichlorophenyl; and
 R¹⁰ is methyl or C₁ to C₄ alkoxy carbonyl; or
 R⁹ and R¹⁰ together are a fused benzene ring which may bear methoxy, ethoxy, methyl, or chloro as substituents.

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25 Examples of suitable diazo components of the aminoazobenzene series are: 4-aminoazobenzene, 3 - chloro - 4 - aminoazobenzene, 3 - bromo - 4 - aminoazobenzene, 2',3 - dimethyl - 4 - aminoazobenzene, 3',2 - dimethyl - 4 - aminoazobenzene, 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 - aminoazobenzene, 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 - aminoazobenzene, 2,3' - dichloro - 4 - aminoazobenzene, 3 - methoxy - 4 - aminoazobenzene, 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:

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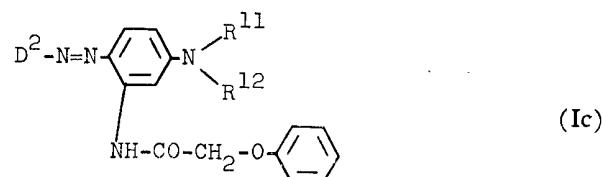


in which
 T⁴ is hydrogen, chloro, bromo or methyl;
 T² is hydrogen or methyl; and

40 T⁵ is a radical of the formula —A—N—R² or COOT⁶ in which A is —CO— or —SO₂—;
 T⁶ is an alcohol radical; and R¹ and R² have the meanings given above.

40

Particularly preferred dyes have the formula (Ic):



in which

D^2 is the radical of a diazo component of the benzoisothiazole, thiadiazole, azo-benzene 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

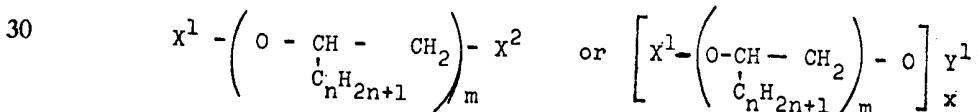
R^{12} is C_1 to C_4 alkyl, β -acetoxyethyl or β -cyanoethyl.

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:

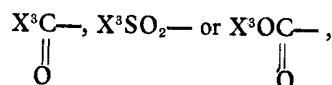
- it is at least 2.5 weight percent soluble in water at 25°C ;
- it boils above 150°C at atmospheric pressure;
- it is a solvent for the dye at some temperature in the range from 0 to 225°C ; and
- it has the formula:



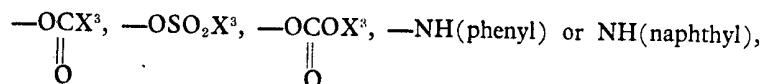
where n is 0 or 1,

m is a positive integer,

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



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



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 ,

Y¹ is X¹OCH₂CHOX¹CH₂—, —CH₂CHOX¹CH₂—, —CH₂CHCH₂—, —CH₂C(CH₂OX¹)₃, (—CH₂)₂—C(CH₂OX¹)₂, (—CH₂)₃CCH₂OX¹, (—CH₂)₄C, —CH₂(CHOX¹)_yCH₂OX¹, —CH₂(CHOX¹)_yCH₂— or —CH₂(CHOX¹)_{y-z}(—CH₂)_zCH₂—, 5
y is 2, 3 or 4, and 5
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 10 300—350 and optionally reacted with boric acid.

Other methods are disclosed in German laid-open Patent Application DOS 15 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 20 25 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 25 30 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 30 35 usually employed for disperse dyes. Specific examples are lignin sulfonates, sulfo-methylation 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 35 40 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.

40 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 N₂O₅). 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-(phenoxyacetoxyethyl)-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.

45 50 55 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 60 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 982

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.

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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.

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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.

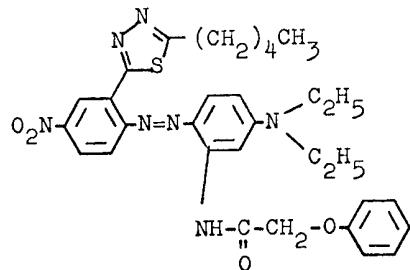
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The dyes set out in Examples 5 to 10 are prepared in the manner described in Examples 1 to 4.

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

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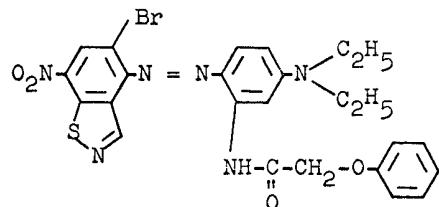


45 or the corresponding amount of a dye formulation containing the dye, 100 parts of polyethylene oxide having a molecular weight of 300 and 790 parts of a 3% aqueous alginate thickening. The print is dried at 100°C, treated for one minute at 200°C with hot air, rinsed cold, soaped at the boil, again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

45

EXAMPLE 6.

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



5 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.

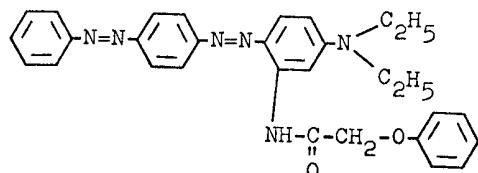
10 A light and wash fast navy blue print on a white ground is obtained.

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EXAMPLE 7.

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



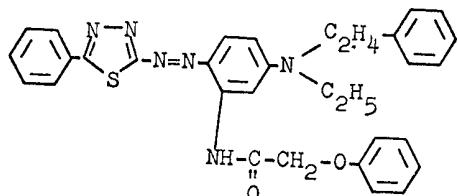
15 or the corresponding amount of a dye formulation containing the dye, 110 parts of polyethylene oxide having a molecular weight of 350, 30 parts of the diethanolamide of oleic acid and 845 parts of a 10% aqueous alginate thickening. The print is dried at 100°C, fixed by a treatment with hot air for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

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

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25 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.

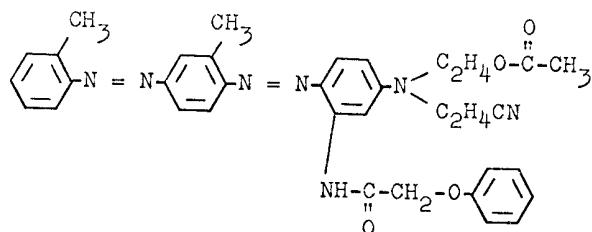
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Cotton cloth is padded with a solution containing 20 parts of the dye of the formula:

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EXAMPLE 9.

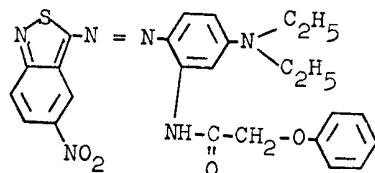


5 or the corresponding amount of a dye formulation containing the dye, 300 parts of a 3% aqueous alginic acid thickening, 550 parts of water and 130 parts of polyethylene oxide of the molecular weight 300. The liquor take-up should be 80%. The cloth is dried at 100°C. It is then treated for five minutes 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.

10 Instead of cotton cloth a union fabric of polyester and cotton (67:33 by weight) 10 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.

15 EXAMPLE 10.

15 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

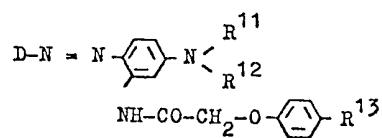


20 on the corresponding amount of a dye formulation containing the dye, and 970 parts of a 10% aqueous alginic acid thickening. After the print has been dried at 105°C it is 20 treated for seven minutes at 185°C with superheated steam and then finished off by rinsing and soaping as described in Example 5.

A fast turquoise print on a white ground is obtained.

25 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-benzothiazole	C ₂ H ₅	C ₂ H ₅	H	bluish green
12	4-amino-5-cyano-7-nitro-1,2-benzothiazole	C ₂ H ₅	C ₂ H ₅	H	blue
13	4-amino-7-nitro-1,2-benzothiazole	C ₂ H ₅	C ₂ H ₅	H	bluish violet
14	4-amino-7-nitro-1,2-benzothiazole	C ₂ H ₄ CN	C ₂ H ₄ CN	CH ₃	ruby
15	2-phenyl-5-amino-1,3,4-thiadiazole	C ₂ H ₅	C ₂ H ₅	H	ruby
16	3-methylmercapto-5-amino-1,2,4-thiadiazole	C ₂ H ₅	C ₂ H ₅	H	red
17	3-β-carbomethoxyethylmercapto-5-amino-1,2,4-thiadiazole	C ₂ H ₄ OCH ₃	C ₂ H ₄ CN	Cl	red
18	3-β-carbomethoxyethylmercapto-5-amino-1,2,4-thiadiazole	C ₂ H ₅	C ₂ H ₅	H	reddish violet
19	3-aminophthalic acid-p-tolylimide	C ₂ H ₅	C ₂ H ₅	H	red
20	4-aminophthalic acid phenylimide	C ₂ H ₄ CN	C ₂ H ₅	H	red
21	4-aminophthalic acid-3'-methoxypropylimide	C ₂ H ₅	C ₂ H ₅	H	red
22	1-aminoanthraquinone	C ₂ H ₅	C ₂ H ₅	H	brown
23	2-aminodiphenylsulfone	C ₂ H ₅	C ₂ H ₅	H	orange
24	2-aminobenzophenone	C ₂ H ₄ CN	C ₂ H ₅	CH ₃	orange
25	1-aminobenzene-4-methylsulfone	C ₂ H ₅	C ₂ H ₅	H	orange
26	4-aminonaphthalic acid-2'-ethylhexylimide	C ₂ H ₅	C ₂ H ₅	H	reddish violet

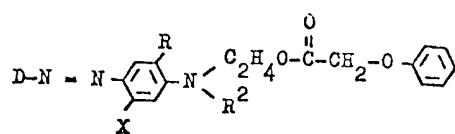
TABLE 1 (cont.)

No.	D-NH ₂	R ¹¹	R ¹²	R ¹³	Hue on polyester/cotton
27	4-aminonaphthalic acid-n-butylimide	C ₂ H ₄ OCH ₃	C ₂ H ₅	Cl	reddish violet
28	4-amino-3-bromo-naphthalic acid n-butylimide	C ₂ H ₅	C ₂ H ₅	H	reddish violet
29	2,4,5-trichloroaniline	C ₂ H ₄ CN	C ₂ H ₄ OCOCH ₃	H	golden yellow
30	2,4,5-trichloroaniline	C ₂ H ₅	C ₂ H ₅	H	orange
31	2-amino-5-nitrothiazole	C ₂ H ₅	C ₂ H ₅	H	violet
32	2-bromo-6-cyano-4-nitroaniline	C ₂ H ₅	C ₂ H ₅	H	bluish violet
33	2,4-dinitro-6-bromoaniline	C ₂ H ₅	C ₂ H ₅	H	violet
34	2-(2-methyl-1,3,4-thiadiazolyl)-4-nitro-6-bromoaniline	C ₂ H ₄ CN	C ₂ H ₅	H	reddish violet
35	2-(2-methyl-1,3,4-thiadiazolyl)-4-nitroaniline	C ₂ H ₅	C ₂ H ₅	H	reddish violet
36	3-chloro-4-aminoazobenzene	C ₂ H ₅	C ₂ H ₅	H	reddish violet
37	3-bromo-4-aminoazobenzene	C ₂ H ₄ CN	C ₂ H ₄ OCOCH ₃	H	red
38	2-methyl-4',5-dimethoxy-4-aminoazobenzene	C ₂ H ₅	C ₂ H ₅	H	red
39	3',2-dimethyl-4-aminoazobenzene	C ₂ H ₅	C ₂ H ₅	H	ruby
40	2-(benzothiazolyl-2)-aniline	C ₂ H ₅	C ₂ H ₅	H	orange
41	2-(benzoxazolyl-2)-4-nitroaniline	C ₂ H ₅	C ₂ H ₅	H	ruby
42	2-(2-phenyl-1,3,4-oxadiazolyl)-4,6-dichloroaniline	C ₂ H ₅	C ₂ H ₅	H	red
43	4-aminobenzene-sulfonic acid-N-methylanilide	C ₂ H ₅	C ₂ H 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 ₂ H ₅	C ₂ H ₅	H	golden yellow
45	2-bromo-4-nitro-6- (3-o-tolyl-1,2,4- oxadiazolyl)aniline	O C ₂ H ₄ OC-CH ₃	C ₂ H ₅	H	violet
46	2,6-dichloro-4- nitroaniline	C ₂ H ₅	C ₂ H 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 ₂ H ₄ CN	H	golden yellow
48	4-aminobenzoic acid phenyl ester	H	C ₂ H ₅	NHCOCH ₃	orange
49	2,6-dibromo-4-nitroaniline	H	C ₂ H ₄ CN	H	brown
50	3-β-cyanoethyl-mercapto-5-amino-1,2,4-thiadiazole	OCH ₃	C ₂ H ₄ CN	NHCOCH ₃	red
51	2-phenyl-5-amino-1,3,4-thiadiazole	H	C ₂ H ₅	H	red
52	4-amino-7-nitro-1,2-benzoisothiazole	H	C ₂ H ₄ CN	CH ₃	ruby
53	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	H	-O ₂ CCH ₂ OC ₆ H ₅	NHCOCH ₃	violet
54	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	H	C ₂ H ₅	H	violet
55	3-amino-5-nitro-2,1-benzoisothiazole	H	C ₂ H ₄ CN	NHCOCH ₃	bluish violet
56	4-aminophthalic acid phenylimide	H	C ₂ H ₅	CH ₃	red
57	4-aminonaphthalic acid n-butyrimide	H	C ₂ H ₄ CN	H	ruby
58	4-amino-3-bromo-naphthalic acid methylimide	H	-O ₂ CCH ₂ OC ₆ H ₅	NHCOC ₂ H ₅	violet
59	2-aminodiphenylsulfone	H	C ₂ H ₄ CN	NHCOCH ₃	orange
60	4-diphenylphosphinyl-aniline	OCH ₃	-O ₂ CCH ₂ OC ₆ H ₅	NHCOCH ₃	scarlet
61	4-aminoazobenzene	H	C ₂ H ₄ CN	H	scarlet
62	3,5-dibromo-4-aminoazobenzene	H	C ₂ H 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 ₂ H ₄ OH	NHCOCH ₃	ruby
64	2-(2-phenyl-1,3,4-oxadiazolyl)-4-nitroaniline	H	C ₂ H ₄ CN	H	red
65	2-(4-methyl-1,3-thiazolyl-2)-4-nitroaniline	H	C ₂ H ₅	CH ₃	ruby
66	2-(2-n-pentyl-1,3,4-thiadiazolyl)-4-nitroaniline	H	C ₂ H ₄ CN	H	red
67	1-amino-4-chloroanthraquinone	H	C ₂ H ₄ OH	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 ₂ H ₅	C ₂ H ₅	H	1	blue
70	,	OC ₂ H ₅	,	,	H	1	blue
71	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	H	C ₂ H ₅	C ₂ H 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 ₂ H ₄ CN	CH ₂ -CH=CH ₂	H	1	reddish violet
77	2-(benzooxazoly-1-2')-aniline	H	CH ₂ -CH=CH ₂	CH ₂ -CH=CH ₂	H	1	orange
78	2-(benzothiazoly-1-2')-aniline	H	,	,	H	1	orange
79	2-amino-6-nitro-benzothiazole	H	C ₂ H ₅	C ₂ H ₅	H	1	reddish violet

TABLE 3 (cont.)

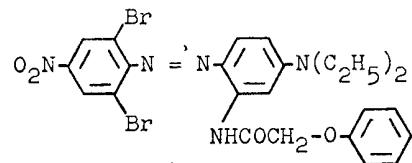
No.	D-NH ₂	R	R ¹¹	R ¹²	R ¹³	Hue on	
						C ₂ H ₅	n
80	1-amino-2-(3-phenyl-1,2,4-oxadiazolyl-5)-benzene	H	,	,	H	1	orange
81	1-amino-2-bromo-4-nitro-6-(4-methyl-5-butoxy carbonyl-thiazolyl-2)-benzene	H	,	,	H	1	bluish violet
82	1-amino-2-(4-methyl-thiazolyl-2)-benzene	H	,	,	H	1	orange
83	1-amino-4-methyl-3-(N-ethyl-N-phenyl-sulfonamido)benzene	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	$ \begin{array}{c} \text{D}-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{R}_2)-\text{C}_2\text{H}_4-\overset{\text{O}}{\text{C}}-\text{C}(\text{CH}_2)_n-\text{o}-\text{C}_6\text{H}_4-\text{R}^{13} \end{array} $		X	n	R ¹³	Hue on polyester/ cotton
		R ²	X				
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 ₂ H ₄ CN	Cl		1	H	orange
90	4-amino-7-nitro-1,2-benzoisothiazole	C ₂ H ₄ CN		NHCOC ₄ H ₉	1	H	violet
91	“	“		NHCOCH ₂ Cl	1	H	violet
92	“	“		NHCOC ₆ H ₅	1	CH ₃	violet
93	4-amino-5-bromo-7-nitro-1,2-benzoisothiazole	CH ₂ -CH=CH ₂		NHSO ₂ C ₆ H ₅	1	H	bluish violet
94	“	“		NHSO ₂ CH ₃	1	H	bluish violet
95	“	C ₂ H ₄ CN		NHCOCH ₃	2	H	violet
96	1-amino-4-(phenoxy-propylamino-sulfonyl)-benzene	C ₂ H ₄ OOCCH ₂ OC ₆ H ₅	CH ₃		1	H	orange
97	3-(benzooxazolyl-2)-aniline	“	H		1	H	orange

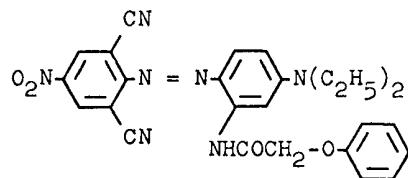
EXAMPLE 98.

60.5 parts of the dye of the formula:



5 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:

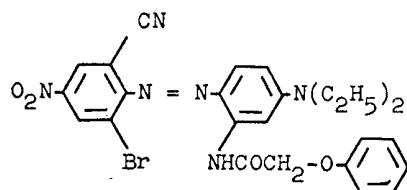
5



10 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.

10

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



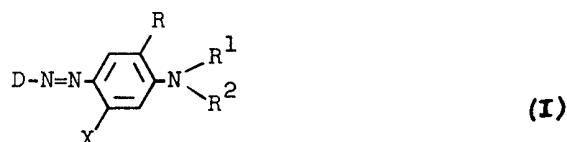
15 with an agent forming cuprous cyanide or by diazotization of 2,6-dicyano-4-nitroaniline and coupling with N,N-dimethyl-N'-phenoxyacetyl-1,3-phenylenediamine as described in Example 2.

15

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

WHAT WE CLAIM IS:—

1. Uniformly dyed water-swellable cellulosic fibers produced by contacting water-swellable cellulosic fibers with water and an oxyethylene swellable-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)



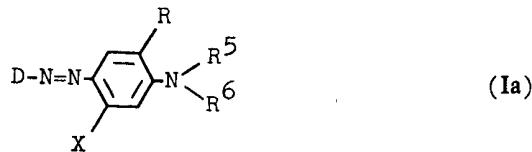
10 in which D is the radical of a diazo component; R is hydrogen, methyl, methoxy, or ethoxy; R¹ is optionally substituted alkyl, cyclohexyl, phenyl, methoxyphenyl or ethoxyphenyl;

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;
 15 Y is oxygen, sulfur or

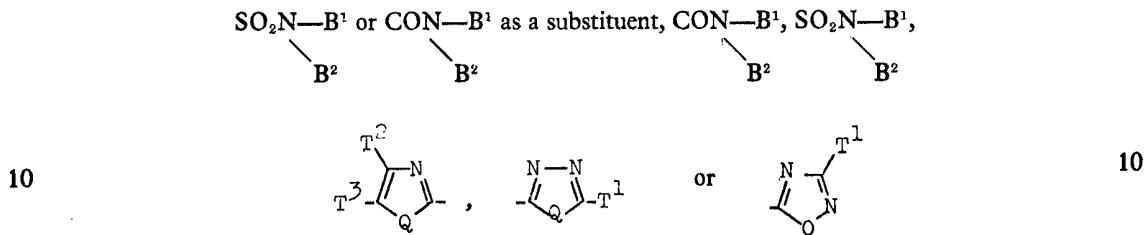


R^4 is hydrogen or C_1 to C_4 alkyl; and
 Ar is phenyl or phenyl bearing chloro, bromo, methyl, methoxy, ethoxy, C_1 to C_4 alkoxy carbonyl or cyano as a substituent.

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



5 in which D is phenyl substituted by fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, C₁ to C₈ alkoxy carbonyl, phenoxy carbonyl, benzoyloxy carbonyl, phenoxyethoxy carbonyl, C₁ to C₄ alkoxyethoxy carbonyl, methyl, ethyl, methoxy, ethoxy, phenoxy, carboxy, phenylazo, phenylazo bearing fluoro, chloro, bromo, nitro, cyano, trifluoromethyl, methyl, ethyl, methoxy, ethoxy,



15 benzothiazolyl bearing nitro, thiocyanato, methylsulfonyl or methoxy as a substituent, benzoisothiazolyl bearing chloro, bromo, nitro or cyano as a substituent, thiadiazolyl bearing phenyl or nitro as a substituent, or thiadiazolyl bearing phenyl, methylmercapto, ethylmercapto, cyanoethylmercapto or C₁ to C₄ alkoxy carbonyl ethylmercapto as a substituent;

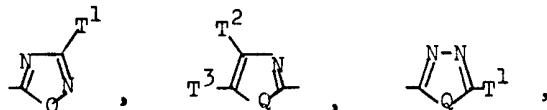
15 Q is O or S;
 R is hydrogen, methyl, methoxy or ethoxy;
 X is hydrogen, chloro, methyl, C₂ to C₄ alkanoylamino, chloroacetyl amino, trifluoroacetyl amino, benzoyl amino, methylsulfonyl amino, phenylsulfonyl amino or NHCOR³—O—Ar;
 20 R⁵ is C₁ to C₄ alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or C₂H₄OCOR³—OAr;
 R⁶ is C₁ to C₄ alkyl, allyl, acetoxyethyl, β-cyanoethyl, benzyl or C₂H₄OCOR³—OAr;
 B¹ is hydrogen, C₁ to C₈ alkyl, cyclohexyl, β-hydroxyethyl, benzyl, phenylethyl or phenyl optionally bearing chloro, methyl or methoxy as a substituent, and
 25 B² is hydrogen, C₁ to C₄ alkyl or β-hydroxyethyl, or

N—B¹ is pyrrolidyl, piperidyl, morpholyl or NH(CH₂)₃OC₂H₄OB³;

$$\begin{array}{c} \diagdown \\ \text{B}^2 \end{array}$$

30 B³ is C₁ to C₄ alkyl, cyclohexyl, phenyl or tolyl,
 T¹ is C₁ to C₈ alkyl, methoxymethyl, phenoxy methyl, phenyl, or phenyl bearing chloro, bromo, nitro, methoxy or ethoxy as a substituent,
 T² is hydrogen or methyl, and
 T³ is methyl, ethyl, phenyl or phenyl bearing chloro, bromo, or methyl as a substituent, or
 35 T² and T³ together are a fused benzene ring optionally bearing methoxy, ethoxy, methyl or chloro as a substituent,
 R³ is C₁ to C₃ alkylene, and
 Ar is phenyl or phenyl bearing chloro, bromo, methyl or methoxy as a substituent, and at least one of the radicals R⁵, R⁶ and X contains a group of the formula COOR³—OAr.

40 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 B¹, B², Q, T¹, T² and T³ have the meanings given in claim 2.

5 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

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

10 6. Fibers according to any of claims 1 to 5, wherein R in the formula (I) or (Ia) is hydrogen. 10

7. Fibers according to any of claims 1 to 6, wherein X in the formula (I) or (Ia) is NHCOR³OC₂H₄OB³, where R³ 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 NHCOCH₂OC₆H₅.

15 9. Fibers according to any of claims 2 to 8, wherein in the formula (Ia) R⁵ and R⁶ are C₁ to C₄ alkyl, β-cyanoethyl or C₂H₄OCOR³OC₂H₄OB³, where R³ and Ar have the meanings given in claim 2. 15

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



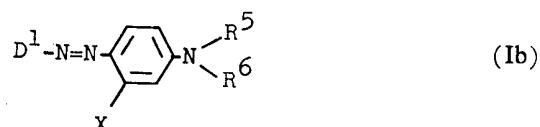
20

is NH(CH₂)₃OC₂H₄OB³, where B³ 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 T¹ and T¹ is C₁ to C₈ alkyl or phenyl.

25 12. Fibers according to any of claims 1 to 11, wherein R³ in the formula (I) or (Ia) is —CH₂—. 25

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



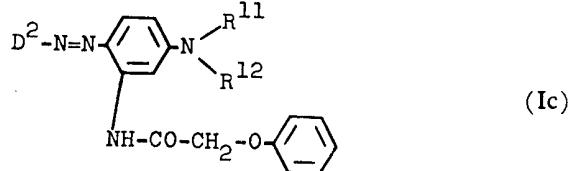
30 in which 30

D¹ is the radical of a diazo component of the benzene, thiadiazole, benzoisothiazole, phthalimide, naphthalimide, anthraquinone or azobenzene series;

R⁵ is C₁ to C₄ alkyl, allyl, β-hydroxyethyl, β-cyanoethyl, β-acetoxyethyl, β-methoxyethyl, β-ethoxyethyl, cyclohexyl, benzyl, β-phenylethyl or —C₂H₄OCOR³—Y—Ar;

35 R⁶ is C₁ to C₄ alkyl, β-acetoxyethyl, β-cyanoethyl, benzyl or —C₂H₄OCOR³—Y—Ar; and X, R³, Y and Ar have the meanings given in claim 1. 35

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



in which

D² is the radical of a diazo component of the benzoisothiazole, thiadiazole, azo-benzene or benzene series;
 5 R¹¹ is C₁ to C₄ alkyl, β -cyanoethyl, β -hydroxyethyl, β -acetoxyethyl, β -methoxyethyl, β -ethoxyethyl, cyclohexyl, benzyl or phenylethyl; and
 R¹² is C₁ to C₄ alkyl, β -acetoxyethyl or β -cyanoethyl.

5

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

10 R is hydrogen,
 X is NHCOCH₂OC₆H₅,
 R⁵ is C₁ to C₄ alkyl, β -cyanoethyl or C₂H₄OCOC₆H₅ and
 R⁶ is C₁ to C₄ alkyl.

10

15. 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.

15

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

20. Fibers according to any of claims 1 to 19, wherein the oxyethylene swell-

25 solvent is a polyethylene oxide.

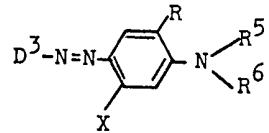
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21. Fibres according to any of claims 1 to 20, wherein the dye is used in the form of a dye formulation also containing water, a dispersant and, as water-retention agent, a glycol or glycol ether.

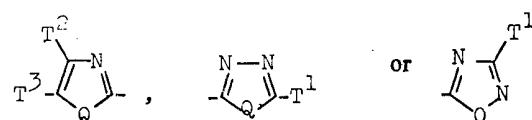
22. A dye as specified in any of the claims 1 to 15, wherein D, D¹ or D² as the case may be is the radical of a diazo component of the benzoisothiazole series or of the benzene series bearing a heterocyclic substituent.

25

23. A compound of the formula:



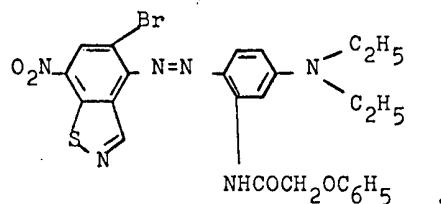
30 in which
 30 D⁸ is phenyl substituted once by



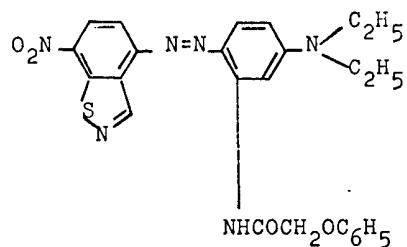
35 and optionally further substituted by chloro, bromo, nitro or cyano, or is benzoisothiazolyl substituted by chloro, bromo, nitro or cyano, and R, R⁵, R⁶, Q, T¹, T², T³ and X have the meanings given in claim 2, at least one of R⁵, R⁶ and X containing the group OCO—R³—O—Ar, where R³ and Ar have the meanings given in claim 2.

35

24. The dye of the formula:



25. The dye of the formula:



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