United States Patent [19]

Hoster et al.

[11] **3,884,626**

[45] **May 20, 1975**

[54] **PROCESS FOR THE DYEING OF TEXTILE MATERIAL CONTAINING AMINO OR AMIDE GROUPS**

[75] Inventors: **Hansruedi Hoster**, Dornach; **Branimir Milicevic**, Riehen, both of Switzerland

[73] Assignee: **Ciba-Geigy AG**, Switzerland

[22] Filed: **Apr. 6, 1973**

[21] Appl. No.: **348,657**

Related U.S. Application Data

[63] Continuation of Ser. No. 124,981, March 16, 1971, abandoned.

[52] **U.S. Cl.** ..... **8/54;** 8/1 A; 8/1 E; 8/94; 8/163; 8/171; 8/174

[51] **Int. Cl.** **D06p 3/14**

[58] **Field of Search** ..... 8/1 A, 54, 94, 163, 174, 8/1 E, 86, 171

[56] **References Cited**

UNITED STATES PATENTS

3,510,243	5/1970	Seuret et al.	8/39
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OTHER PUBLICATIONS

Milicevic, Textile Chemists & Col., 3/11/70, Vol. 2, No. 5, pp. 87–90 and 95–98.

WAS White, Amer. Dyestuff Reporter, 7/3/67, pp. 18–23.

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—P. A. Nelson
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

[57] **ABSTRACT**

A process for the dyeing of textile material containing amino or amide groups, especially polyamide such as nylon is disclosed which comprises dyeing said material in a homogeneous solution of one or several water-soluble reactive dyestuffs, in a mixture of a chlorinated aliphatic hydrocarbon, especially trichloroethylene or perchloroethylene, with up to **50** percent of a hydrophilic solvent, especially N,N-dimethylformamide, during about 30 to 50 minutes at a dyeing temperature of about 40° to 130°C. The thus obtained dyeings have excellent fastness properties and the procedure is characterised in shortening the dyeing time compared with the conventional dyeing process.

13 Claims, No Drawings

PROCESS FOR THE DYEING OF TEXTILE MATERIAL CONTAINING AMINO OR AMIDE GROUPS

This is a continuation, of application Ser. No. 124,981, filed Mar. 16, 1971, now abandoned.

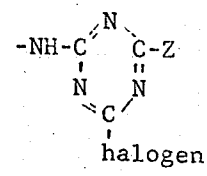
DETAILED DISCLOSURE

With regard to the more stringent regulations applying in many places for the protection of the water against contamination, the dyeing of textile material using conventional methods has the disadvantage that large quantities of water are used and subsequently contaminated during the dyeing process. It has, therefore, already been suggested that textile materials be dyed in dye baths prepared from organic solvents.

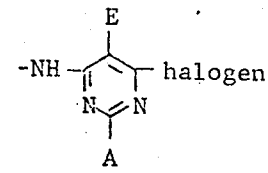
The present invention relates now to this problem. The object of the invention is therefore a process for the dyeing of textile material containing amino or amide groups characterised in that dyeing is performed in a homogeneous solution of one or several dyestuffs containing in each case at least one free sulphonic acid group and at least one fibre-reactive group in a chlorinated aliphatic hydrocarbon, preferably boiling at a temperature of at least 70°C, in a mixture with up to 50 percent of a hydrophilic solvent, preferably at the boiling point of the organic mixture of solvents.

Suitable dyestuffs usable according to the invention are dyestuffs containing not only at least one sulphonic acid group but also at least one fibre-reactive group. The dyestuffs can belong to the most diverse classes of dyestuffs such as to those of the mono-, dis- and polyazo dyestuffs; of the anthraquinone, perinone, quinophthalone, oxazine, nitro, phthalocyanine, stilbene and methine dyestuffs, including the styryl, azamethine, polymethine and azostyryl dyestuffs.

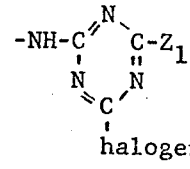
To be mentioned as fibre-reactive groupings, e.g. reactive groupings capable of reacting with the substrate to form a covalent bond, there are mentioned the chloromaleinylamino groups, the propiol groupings, mono- and dichlorocrotonylamino groups, bromo- or chloroacrylamino groups, acrylamino groups, vinyl-sulphone groups and, in particular, the groupings containing a labile substituent, which, with accompaniment of the bonding electron pair, are easily split off, e.g. aliphatically bound sulphuric acid ester groups or thiosulphuric acid ester groups, and aliphatically bound sulphonyl or sulphonyloxy groups, or halogen atoms, particularly an aliphatically bound chlorine atom. These labile substituents are advantageously in α- or β-position of an aliphatic radical which is bound by way of an aminocarbonyl or aminosulphonyl group to the dyestuff molecule; in the case of the dyestuffs under consideration, which contain halogen atoms as labile substituents, these exchangeable halogen atoms can also be, e.g. in an acetyl radical, or in the α- or β-position of a propionyl radical. Examples of such radicals are, e.g. chloro- or α,β-dichloro- or dibromopropionylamino groups, or α-chloroacetylamino groups. Preferably, however, the cleavable halogen atoms are in a heterocyclic radical preferably containing 2 to 3 ring-hetero atoms, especially ring nitrogen atoms, e.g. in a phthalazine, pyridazine, pyridazone, quinoxaline, quinazoline, oxazole, thiazole, in particular, however, in a pyrimidine or especially triazine ring, e.g. in a grouping of the formula



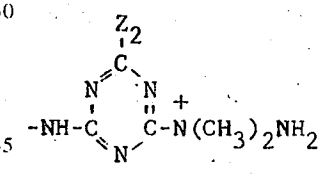
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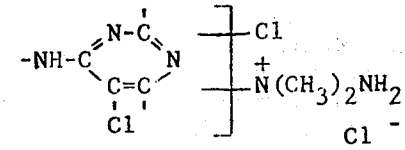
wherein Z represents a hydrogen atom, an optionally substituted amino group, an etherified oxy or mercapto group, or a halogen atom, or an alkyl, aryl or aralkyl group, A represents halogen or alkylsulphonyl and E represents hydrogen or halogen. The halogen atoms are, e.g. fluorine or bromine atoms, preferably however, chlorine atoms. Of particular interest is the use of dyestuffs containing the grouping of formula



wherein Z_1 represents a chlorine atom, an NH_2-group, of the radical of an aliphatic or aromatic amine or alcohol; also such fibre-reactive groups of which the cleavable substituent is a quaternary ammonium or hydrazinium group bound especially to a carbon atom of a heterocyclic radical, i.e. a group of the formula



or



wherein Z_2 represents a hydrogen atom, an optionally substituted amino group, or an etherified oxy or mercapto group.

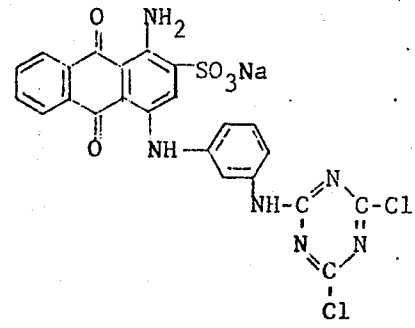
The sulphonic acid groups containing water-soluble, fibre-reactive dyestuffs used according to the present invention can, furthermore, contain the following fibre-reactive groups: 2-methylthio-4-fluoropyrimidine-5-carbonyl, 2,4-bis-(phenylsulphonyl)-triazinyl-6-, 2-(3'-carboxyphenyl)-sulphonyl-4-chlorotriazinyl-6-, 2-(3'-sulphophenyl)-sulphonyl-4-chlorotriazinyl-6-, 2,4-bis-(3'-carboxyphenylsulphonyl-1')-triazinyl-6-, 2-carboxymethylsulphonylpyrimidinyl-4-, 2-methylsulphonyl-6-methyl-pyrimidinyl-4-, 2-phenylsulphonyl-6-ethyl-pyrimidinyl-4-, 2,6-bismethylsulphonyl-pyrimidinyl-6-, 2,6-bis-methylsulphonyl-5-chloropyrimidinyl-4-, 2,4-bis-methylsulphonyl-pyrimidinyl-5-sulphonyl, 2-methylsulphonyl-pyrimidinyl-4-, 2-phenylsulphonyl-pyrimidinyl-4-, 2-trichloromethylsulphonyl-6-methyl-pyrimidinyl-4-, 2-methylsulphonyl-5-chloro-6-methyl-pyrimidinyl-4-, 2-methylsulphonyl-5-bromo-6-methyl-pyrimidinyl-4-, 2-methylsulphonyl-5-chloro-6-ethyl-pyrimidinyl-4-, 2-methylsulphonyl-5-chloro-6-chloromethylpyrimidinyl-4-, 2-methylsulphonyl-4-

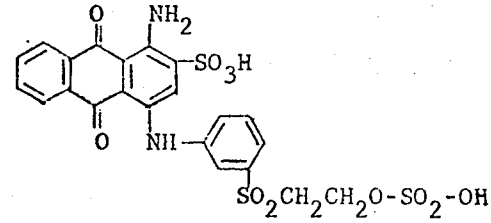
chloro-6-methylpyrimidine-5-sulphonyl-2-methylsulphonyl-5-nitro-6-methylpyrimidinyl-4-, 2,5,-6-tris-methylsulphonyl-pyrimidinyl-4-, 2-methylsulphonyl-5,6-dimethyl-pyrimidinyl-4-, 2-ethylsulphonyl-5-chloro-6-methyl-pyrimidinyl-4-, 2-methyl-sulphonyl-6-chloropyrimidinyl-4-, 2,6-bis-methylsulphonyl-5-chloropyrimidinyl-4-, 2-methylsulphonyl-6-carboxypyrimidinyl-4-, 2-methylsulphonyl-5-sulphopyrimidinyl-4-, 2-methylsulphonyl-6-carbomethoxy-pyrimidinyl-4-, 2-methylsulphonyl-5-carboxy-pyrimidinyl-4-, 2-methylsulphonyl-5-cyano-6-methoxy-pyrimidinyl-4-, 2-methylsulphonyl-5-chloropyrimidinyl-4-, 2-sulphoethylsulphonyl-6-methyl-pyrimidinyl-4-, 2-methylsulphonyl-5-bromopyrimidinyl-4-, 2-phenylsulphonyl-5-chloropyrimidinyl-4-, 2-carboxy-methylsulphonyl-5-chloro-6-methyl-pyrimidinyl-4-, 2-methylsulphonyl-6-chloropyrimidine-4- and -5-carbonyl, 2,6-bis-(methylsulphonyl)-pyrimidine-4- or -5-carbonyl, 2-ethylsulphonyl-6-chloropyrimidine-5-carbonyl, 2,4-bis-(methylsulphonyl)-pyrimidine-5-sulphonyl, 2-methylsulphonyl-4-chloro-6-methyl-pyrimidine-5-sulphonyl or -carbonyl, 2,4-dichloro-5-fluoro-pyrimidine-6-yl, 2-chlorobenzothiazole-5- or -6-carbonyl or -5- or -6-sulphonyl, 2-arylsulphonyl- or 2-alkylsulphonylbenzothiazole-5- or -6-carbonyl or -5- or -6-sulphonyl radical, such as 2-methylsulphonyl- or 2-ethylsulphonylbenzothiazole-5- or -6-sulphonyl, or -carbonyl, 2-phenylsulphonylbenzothiazole-5- or -6-sulphonyl or carbonyl radical, and the corresponding derivatives of 2-sulphonylbenzothiazole-5- or -6-carbonyl or sulphonyl radical, containing on the condensed benzene ring sulpho groups such as 2-chlorobenzothioazole-5- or -6-carbonyl or -sulphonyl, 2-chlorobenzimidazole-5- or -6 -carbonyl or -sulphonyl, 2-chloro-1-methylbenzimidazole-5- or -6-carbonyl or -sulphonyl, 2-chloro-4-methylthiazole-(1,3)-5-carbonyl or -4- or -5-sulphonyl radicals, and the N-oxide of the chloro- or 4-nitroquinoline-5-carbonyl radical. Also mentioned are the 2,2,3,3-tetrafluorocyclobutanecarbonyl-1- or -sulphonyl-1-, 2-fluoro-2-chloro-3,3-difluorocyclobutane-1-carbonyl and β-(2,2,3,3-tetrafluorocyclobutyl-1)-acryloyl, α- or β-bromoacryloyl and α- or β-alkyl- or arylsulphonylacryloyl radicals.

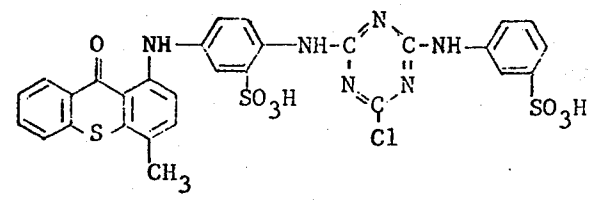
The dyestuffs to be used according to the invention are known in appreciable numbers. The dyestuffs can be prpoduced by the usual methods, e.g. by acylation of dyestuffs containing primary or secondary amino groups, the dyeings being of the most diverse classes as stated, especially, however, of the anthraquinone, phthalocyanine, or azo series, using acylating agents containing one or several reactive groups. Mentioned as such acylating agents are, e.g. the anhydrides or chlorides of the acids corresponding to the above stated aliphatic acylamino radicals, e.g. acrylic acid, propiolic acid, chloromaleic acid, chloroacrylic acid, α,β-dibromopropionic acid, β-chloropropionic acid, etc., particularly, however, the halides corresponding to the heterocyclic reactive radicals.

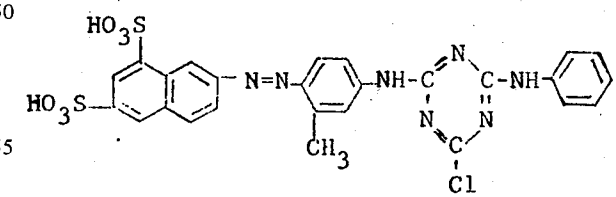
Particularly preferred are such dyestuffs containing reactive heterocyclic groups with at least two hetero atoms such as halogentriazinyl radicals carrying phenoxy, alkoxy, alkoxy-alkoxy or arylamino radicals, those containing heterocyclic radicals having sulphonyl groups splitting off, and those containing fluorine-containing heterocycles, especially fluorine-containing pyrimidyl radicals as well as dyestuffs containing as reactive grouping halogenated C_{1-4} fatty acids.

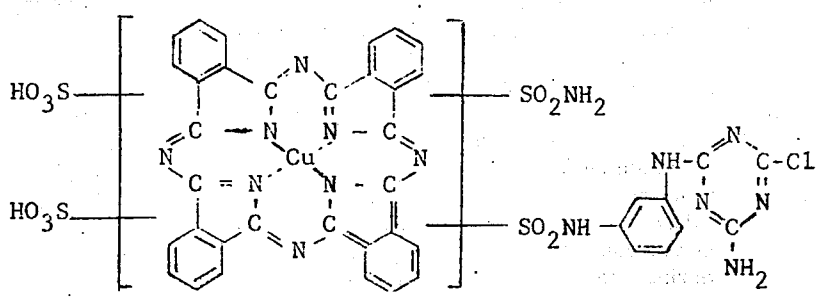
Examples of such dyestuffs which can be used according to the invention are:

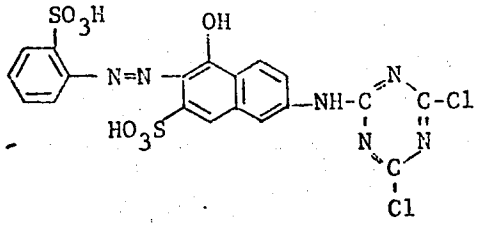




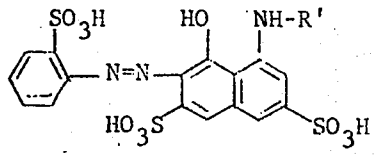




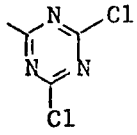


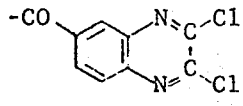


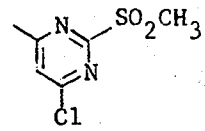
as well as

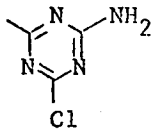


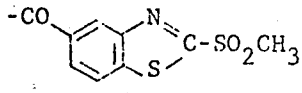
wherein R' is a group of the formulae

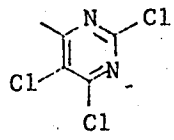




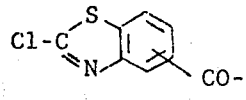








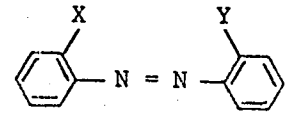
or



It is moreover possible to use fibre-reactive dyestuffs having sulpho groups and which contain heavy metals in a complex bond.

Suitable heavy metals are manganese, iron, and, preferably, chromium, cobalt, nickel and, in particular, copper.

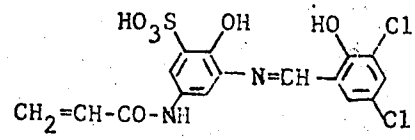
Such dyestuff complexes are derived preferably from such azo dyestuffs which contain a group of the formula



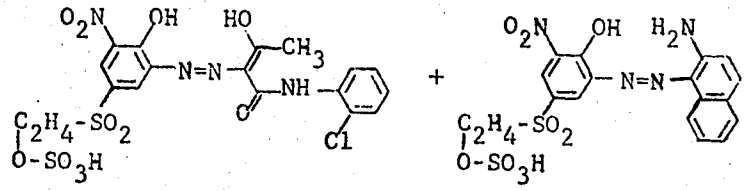
wherein

X and Y are each hydroxyl groups, carboxyl groups, amino groups, or alkylsulphonylamino groups. Also suitable, however, are dyestuffs of the phthalocyanine series.

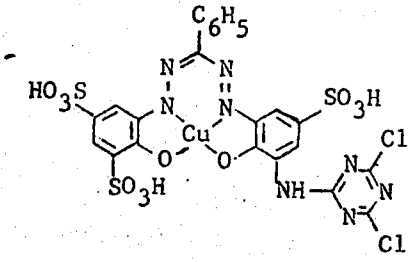
Mentioned as examples of suitable fibre-reactive metal complexes containing sulphonic acid groups are complexes such as, e.g.:

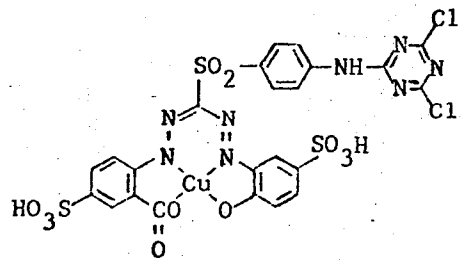


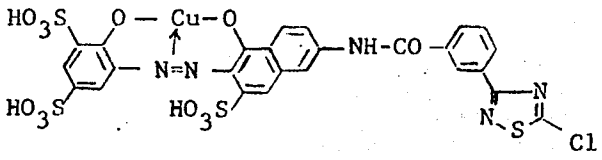
1:2-chromium complex

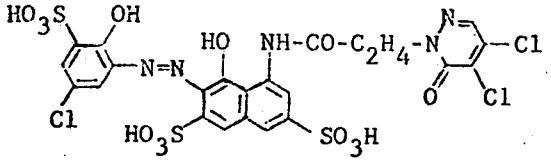


1:2-cobalt mixed complex

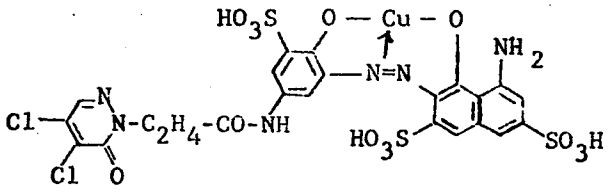


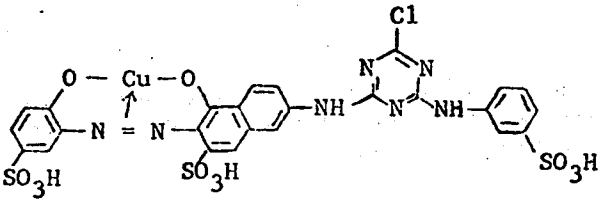


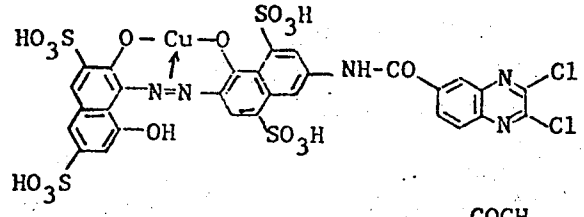


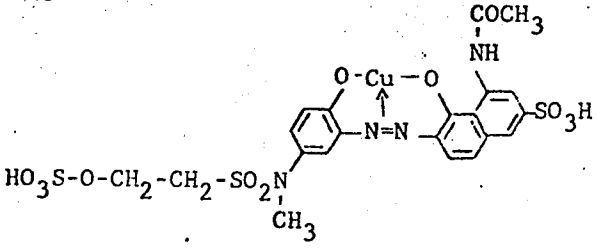


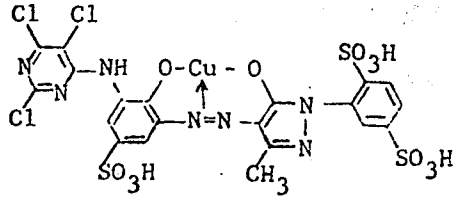
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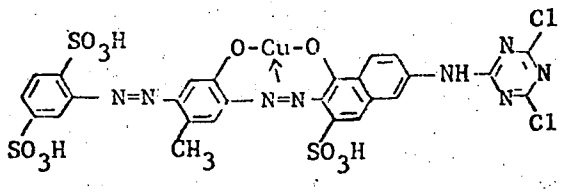


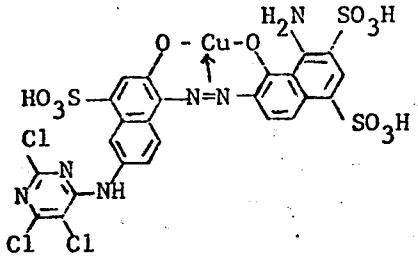


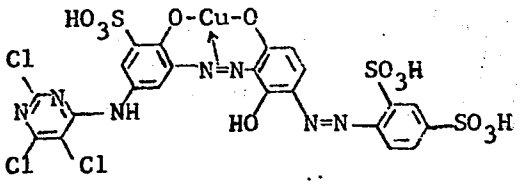


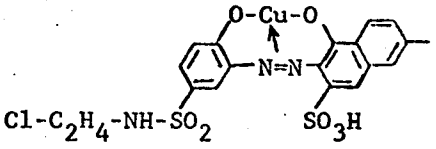


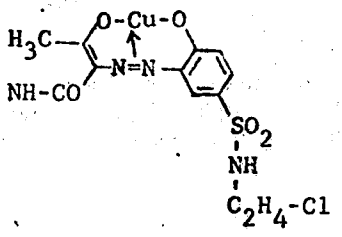












The mixture of organic solvent used according to the invention consists of a chlorinated aliphatic hydrocarbon and a hydrophilic solvent.

As chlorinated aliphatic hydrocarbons are used carbon tetrachloride, chloroform, methylene chloride, trichloroethane, tetrachloroethane, dibromoethylene and, in particular, trichloroethylene and perchloroethylene.

As hydrophilic solvents which are miscible with water are used, e.g. aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, ketones such as acetone, methyl ethyl ketone, cyclohexanone, ether and acetals such as diisopropyl ether, diphenylene oxide, dioxane, tetrahydrofuran glycerinformal and glycolformal, as well as acetonitrile and pyridine, diacetone alcohol, also higher-boiling glycol derivatives such as ethylene glycol monomethyl, -ethyl and -butyl ether and diethylene glycol monomethyl or -ethyl ether and diethylene glycol monomethyl or -ethyl ether, thiodiglycol, ethylene carbonate, γ-butyrolacton, and particularly the group of the water-miscible aprotic hydrophilic solvents boiling above 120°C such as N,N-dimethylformamide, N,N-dimethylacetamide, N-hexamethylphosphoric acid triamide, N-methylpyrrolidone,

1,5-dimethylpyrrolidone, N,N-dimethylmethoxyacetamide, N,N,N',N'-tetramethylurea, tetramethyleneurea, tetramethylenesulphone (sulpholane), 3-methylsulpholane and dimethylsulphoxide.

Preferred mixtures of these solvents contain 98 to 60, preferably 97 to 70, per cent by weight of halogenated aliphatic hydrocarbon, and 2 to 40, preferably 3 to 30, per cent by weight of hydrophilic components.

In especially preferred mixtures of solvents are used as chlorinated aliphatic hydrocarbons trichloroethylene or perchloroethylene in admixture with a hydrophilic solvent or the amide or lactam of a lower fatty acid, especially N,N-dimethylacetamide or N,N-dimethylformamide or phosphorous containing solvents such as N-hexamethylphosphoric acid triamide in admixture with a chlorinated aliphatic hydrocarbon. Efficient mixtures of solvents consist of perchloroethylene-/N,N-dimethylformamide; trichloroethylene/N,N-dimethylformamide, perchloroethylene/N,N-dimethylacetamide and perchloroethylene/N-hexamethylphosphoric acid triamide.

The present dyeing process is suitable for dyeing of textile material containing amino and amide groups, e.g. certain modacrylic fibres, such as polypropylenes modified with amines, modified polyester fibres containing amino groups, and, preferably, synthetic polyamides, especially poly(hexamethylene-adipic acid amide) or Nylon 6.6, (poly-(ω-caprolactam) or Nylon 6, poly(hexamethylenesebacic acid amide) or Nylon 6.10 or poly(11-aminoundecanoic acid) or Nylon 11 as well as natural polyamides such as wool.

In exhaust dyeing, the textile material to be dyed can be in the form of loose material, fleece, yarn, or as knitted goods or fabrics. It is dyed, in loose form or in a form achieved by mechanical means, in a stationary bath, especially in suitable dye-jigs, winch-vats, cheese-dyeing machines, or similar dyeing-machines, depending on the nature of the material to be dyed.

The dyeing may be performed in dyeing apparatus or dyeing vessels which are linked with the outside atmosphere (if necessary via a reflux condenser), or in closed vessels, such as pressure vessels, with or without pressure.

Dyeing is performed at a temperature of about 40° to 130°C, preferably at a temperature where the textile material is not injured, for example polyamide at about 105°C, during 30 to 50 minutes.

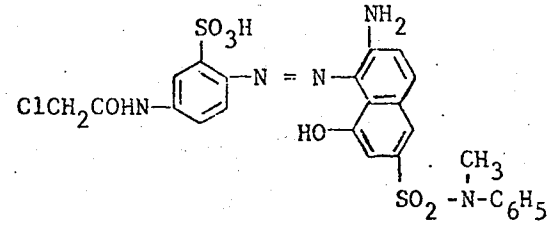
After attainment of the desired depth of colour, the dyed material is removed from the dye-bath and then preferably aftertreated with a commercial cleansing-intensifier dissolved in, e.g. perchloroethylene. For the removal of the solvent still adhering, the textile material is treated either with steam or with hot air stream.

A further advantage of the dyeing process according to the invention is the shortening of the dyeing time compared with the conventional dyeing processes.

In the following non-limitative examples, if not otherwise stated, the term 'parts' denotes parts by weight, percentages are percentages by weight, and temperatures are given in degrees Centigrade.

EXAMPLE 1

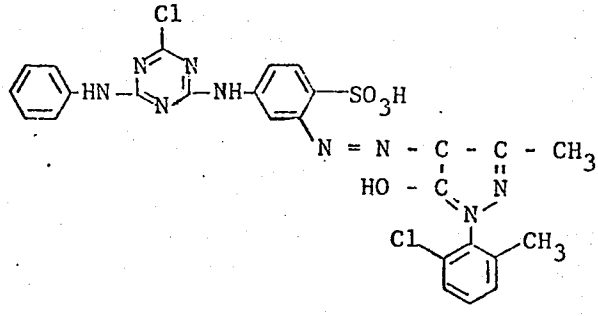
0.3 Parts of the dyestuff of the formula



are dissolved in 16 parts of N,N-dimethylformamide, and diluted with 145 parts of perchloroethylene. In this dye liquor, 5 parts of polyamide knitted fabric are dyed for 40 minutes at 105° and then removed from the dye bath. Of a commercial cleansing-intensifier, such as is used in chemical cleaning, 1 to 2 parts are dissolved in 160 parts of perchloroethylene, and the dyed knitted fabric is aftertreated for 10 minutes at 50° in this bath. The material is subsequently dried in a warm air stream. By this means is obtained an even red dyeing having excellent fastness properties.

EXAMPLE 2

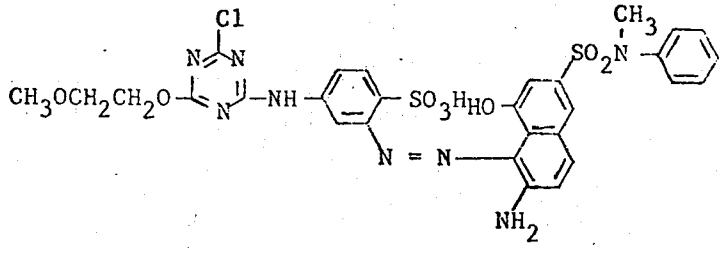
0.8 Parts of the dyestuff of the formula



are dissolved in 19 parts of N,N-dimethylformamide, and diluted with 288 parts of trichloroethylene. In this dye liquor, 10 parts of polyamide 66 knitted fabric are dyed for 45 minutes at about 85° and then removed from the dye bath. 1 to 2 parts of a commercial cleansing-intensifier, such as is used in dry cleaning, are dissolved in 320 parts of perchloroethylene, and the dyed knitted fabric is aftertreated for 10 minutes at 50° in this bath. The material is subsequently dried in a warm air stream. A level yellow dyeing having good fastness properties is obtained.

EXAMPLE 3

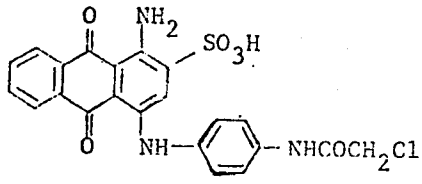
0.2 Parts of the dyestuff of the formula



are dissolved in 19 parts of N,N-dimethylacetamide, and diluted with 288 parts of perchloroethylene. In this dye liquor, 10 parts of polyamide 66 knitted fabric are dyed for 45 minutes at 105° and then removed from the dye bath. 1 to 2 parts of a commercial cleansing-intensifier, such as is used in dry cleaning, are dissolved in 320 parts of perchloroethylene, and the dyed knitted fabric is aftertreated for 10 minutes at 50° in this bath. The material is subsequently dried in a warm air stream. A level scarlet red dyeing having good fastness properties is obtained.

EXAMPLE 4

0.2 Parts of the dyestuff of the formula

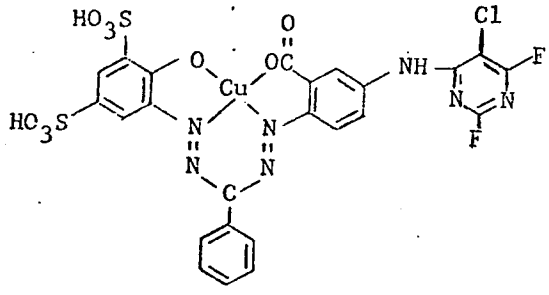


are dissolved in 19 parts of N,N-dimethylformamide, and diluted with 288 parts of perchloroethylene. In this dye liquor, 10 parts of woollen fabric are dyed for 45 minutes at 90° and then removed from the dye bath. 1 to 2 parts of a commercial cleansing-intensifier, such as is used in dry cleaning, are dissolved in 320 parts of perchloroethylene, and the dyed fabric is aftertreated for 10 minutes at 50° in this bath. The material is subsequently dried in a warm air stream. A level blue dyeing having good fastness properties is obtained.

If the 19 parts of N,N-dimethylformamide are replaced by 15 parts of N-hexamethyl-phosphoric acid triamide, and otherwise the procedure of Example 4 is follwed, dyed material is obtained with similarly good properties.

EXAMPLE 5

0.2 Parts of the dyestuff of the formula



are dissolved in 19 parts of N,N-dimethylformamide, and diluted with 288 parts of perchloroethylene. In this dye liquor, 10 parts of polyamide 66 or woollen knitting yarn are dyed for 45 minutes at 121° and then rinsed in a new bath in pure perchloroethylene for 10 minutes at 50°. The dyed material is then dried in a warm air stream. A level blue dyeing having excellent fastness properties is obtained.

What we claim is:

1. A process for the dyeing of a textile material containing amino or amide groups, which consists essentially of performing the dyeing by exhaust dyeing in a homogeneous solution of one or several dyestuffs, each of said dyestuffs containing at least one free sulphonic acid group and at least one fiber-reactive group in a solvent mixture consisting essentially of 98 to 60 percent by weight chlorinated aliphatic hydrocarbon, admixed with 2 to 50 percent by weight of a hydrophilic solvent.

2. A process according to claim **1** wherein the dyeing is performed at the boiling point of the organic solvent mixture.

3. A process according to claim **1** wherein the mixture of organic solvents contains 98 to 60 percent by weight of chlorinated aliphatic hydrocarbon and 2 to 40 percent by weight of a hydrophilic solvent.

4. A process according to claim **1** wherein perchloroethylene is used in admixture with a hydrophilic solvent.

5. A process according to claim **1** wherein the solvent mixture employed is the amide or lactam of a lower fatty acid, especially N,N-dimethylacetamide or N,N-dimethylformamide in admixture with a chlorinated aliphatic hydrocarbon.

6. A process according to claim **1** wherein the mixture of solvents used is: perchloroethylene/N,N-dimethylformamide, trichloroethylene/N,N-dimethylformamide, perchloroethylene/N,N-dimethylacetamide or perchloroethylene/N-hexamethylphosphoric acid triamide.

7. A process according to claim **1** wherein natural or synthetic polyamide materials are dyed.

8. A process according to claim **7** wherein wool is dyed.

9. A process according to claim **7** wherein synthetic polyamide material is dyed.

10. The dyed textile material obtained by the process of claim **1.**

11. A process according to claim **3** wherein the mixture of organic solvents contains 97 to 70 percent by weight of chlorinated aliphatic hydrocarbon and 3 to 30 percent by weight of a hydrophilic component.

12. A process according to claim **1** wherein the sulphonic acid groups containing dyestuffs contain as the fiber-reactive radical a radical of a halogenated C_{1-4} fatty acid.

13. A process according to claim **12** wherein the chlorinated aliphatic hydrocarbon is perchloroethylene and the hydrophilic solvent is N,N-dimethylformamide.

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