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PROCESS FOR DYEING OR PRINTING OF POLYAMIDE FIBRES

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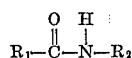
Int. Cl. D06p 1/38, 1/86, 3/24

U.S. Cl. 8—54

11 Claims

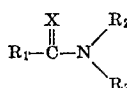
ABSTRACT OF THE DISCLOSURE

In dyeing polyamide fibers with acid dyes, an assistant of the formula



is applied to the fibers before, during, or after contact in the dyebath.

The present invention provides a process for dyeing or printing polyamide fibres, wherein the fibres are treated before or during the dyeing or printing process with a small quantity of a compound of the formula



where:

X represents an oxygen or sulphur atom, or an NH group,

R₁ represents —O—R₄ or



R₄ represents a hydrocarbon radical which may be substituted and may contain hetero-atoms, each of R₅ and R₆ represents hydrogen or a hydrocarbon radical which may be substituted and may contain hetero-atoms,

R₂ represents hydrogen or an aliphatic hydrocarbon radical which may be substituted and may be interrupted by hetero-atoms and has a carbon chain of at least 4 carbon atoms, a cycloaliphatic hydrocarbon radical which may be substituted, a phenyl radical which bears at least one alkyl radical bound directly or through a hetero-atom and is attached to the nitrogen atom either directly or through a polyalkylenoxy chain, or an acyl radical, and

R₃ represents hydrogen or alkyl, at least one of the radicals R₁ and R₂ containing at least 4 carbon atoms bound to each other.

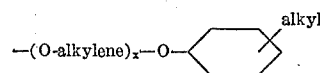
For the purpose of defining what is meant by a small quantity, we may set an upper limit of 4% of the compound in the dyebath. In this specification and claims the expression dyeing, when used in a general sense, is to be taken as including padding and printing and the expression dyebath is intended to include padding liquor or printing paste. The optimum quantity will normally be at least 0.25 part by weight per 1000 parts of dyebath, particularly from 0.5 to 5 parts and especially from 0.5 to 2 parts in exhaustion dyeing and from 5 to 40 parts and especially from 10 to 20 parts in padding and printing.

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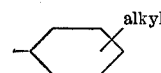
Suitable polyamides are both natural polyamidic fibres such as silk, hairs and especially wool, and synthetic polyamides such as the condensation products of hexamethylenediamine with adipic acid (nylon 66) or sebacic acid (nylon 610), from ε-caprolactam (nylon 6) or from ω-aminoundecanoic acid (nylon 11) or from hexamethylenediamine, adipic acid and ε-caprolactam (nylon 66/6). The polyamide fibres may be used at any stage of their processing, thus, for example, in the form of filaments, yarns, woven or knitted fabrics, and wool, hairs and silk also in the loose form.

The process is also suitable for mixtures of fibres, especially of wool and synthetic polyamide fibres or for the polyamide portion of mixtures of fibres or of mixed fabrics.

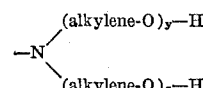
The radical R₁ is e.g. —O-alkyl, alkyl containing preferably 1 to 6 carbon atoms and bearing eventually substituents such as —OH, —O-methyl or —O-ethyl, further —(O-alkylene)_x —OH, —(O-alkylene)_x —O-alkyl, —(O-alkylene)_x —O-alkenyl or



wherein alkylene contains 2 to 3 carbon atoms, alkyl and alkenyl contain 8 to 18 carbon atoms,



contains altogether 14 to 20 carbon atoms and x has a value of from 1 to 10. The radical R₁ can also be —NH-alkyl or —N=(alkyl)₂, alkyl containing preferably 1 to 6 carbon atoms and bearing eventually substituents such as —OH, —O-methyl or —O-ethyl, or also —NH—(alkylene-O)_x—H or



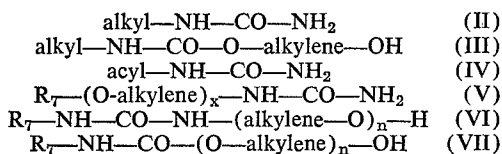
alkylene and x having the aforesaid meanings and y and z together having a value of from 2 to 10.

The radical R₂ is e.g., hydrogen or an alkyl radical with about 4 to 18, preferably 6 to 12, carbon atoms, which may contain hydroxy groups and/or double bonds, an alkoxyalkyl radical with at least 4 carbon atoms in the alkoxy group (alkoxymethyl, alkoxyethyl or alkoxypropyl), an alkyl —(O-alkylene)_x-radical, alkyl containing about 8 to 18 carbon atoms and alkylene and x having the aforesaid meanings, a cycloalkyl radical (cyclohexyl or methylcyclohexyl), an aralkyl radical (benzyl or phenylethyl), an alkylphenyl radical (alkylphenyl with about 4 to 12 carbon atoms in the alkyl group, dialkylphenyl with altogether 4 to 12 carbon atoms in the two alkyl groups which may be different from each other), alkoxyphenyl with 4 to 12 carbon atoms in the alkoxy group, an alkylcarbonyl or alkylsulphonyl residue whose alkyl radical contains about 4 to 18 carbon atoms, or an arylcarbonyl or arylsulphonyl residue.

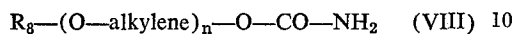
If R₃ represents an alkyl radical, it may contain 1 to 5 carbon atoms (methyl to amyl).

The compound of the Formula I used should advantageously melt below 100° C., preferably below about 70° C. Preferred use is made of compounds of the Formula I that melt at room temperature or little above it, for example up to about 30° C.; they should be only moderately soluble in water. Of readily soluble compounds it would be necessary to use too large amounts, and completely insoluble compounds would likewise prove of little value.

The preferred compounds of the Formula I correspond to the formulae:



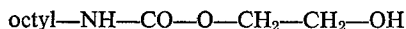
and



wherein:

alkyl contains 6 to 12 carbon atoms,
alkylene contains 2 to 3 carbon atoms,
acyl contains 6 to 12 carbon atoms,
R₇ represents an alkyl or alkenyl radical with from 8 to 18 carbon atoms or an alkylphenyl radical with from 8 to 12 carbon atoms in the alkyl group,
R₈ represents an alkyl or alkenyl radical with from 8 to 18 carbon atoms or an alkylphenyl radical with from 8 to 12 carbon atoms in the alkyl group,
n has a value of from 3 to 10, and
x has a value of from 1 to 10.

Especially suitable products of the above Formulae II to VIII are octyl-urea,



and 3-(2'-ethylhexyloxy)-propyl-urea.

The addition of the aforementioned compounds to the dyebath, to the padding liquor or to the printing paste offers the great advantage that the polyamides, especially wool, can be dyed at temperatures below 100° C. and in some cases more quickly, or that the prints or pad-dyeings may be developed at temperatures below 100° C., or for example the development time when steaming can be shortened.

In this manner the handle of the wool fibre is distinctly improved and, on the other hand, energy is saved. Moreover, this is a particularly economical dyeing method because the known pad-steam process requires long steaming.

It is possible, for example, to dye wool within one hour at 60° to 80° C. deeper tints than was possible by the conventional methods or by dyeing in the presence of, for example, benzyl alcohol; or wool dyeings can be developed at room temperature by the pad batch process within 4 to 6 hours; or the steaming periods for prints and pad dyeings may be reduced, which is of special importance since in all conventional wool dyeing methods the steaming period constitutes the bottleneck.

Apart from the compounds of the Formula I there may be further added—especially to padding liquors—a co-acervating agent. Such assistants are, for example, the condensation products of fatty acids with diethanolamine or the adducts of ethylene oxide with hydrophobic organic residues, preferably adducts whose turbidity point in the padding liquor does not exceed about 20° to 25° C. Such products have been described, for example, in French specification No. 1,312,787.

The dyebath, padding liquors and printing pastes can contain further ingredients, e.g. levelling agents such as alkyl-, alkenyl- or alkylphenylpolyglycol ethers, in which the hydrophobic residue contains preferably from 8 to 18, in the case of alkylphenyl 14 to 18, carbon atoms, or also mixtures of carboxymethylated polyglycol ethers with a hydrophobic residue of from 8 to 24 carbon atoms and high molecular eventually quaternated polyamines (see French Patent No. 1,166,513).

The dyeings, pad dyeings and prints obtained by the present process have considerably tinctorial strength and are level. The penetration of the dyestuff in the interior of the fibre is better, as are the wet fastness properties compared with the conventional dyeing processes. Furthermore, the new process is important for the dyeing of natural or synthetic polyamide fibres in continuous dyeing ranges in which the boiling point of the dyebath cannot

always be attained during the time which is at the dyer's disposal and for the dyeing of wool with reactive dyestuffs at pH values above 6 and at temperatures below 90° C., whereby a damaging of the wool is avoided.

Parts and percentages in the following examples are by weight, and temperatures are shown in degrees centigrade.

EXAMPLE 1

2 parts of the dyestuff No. 23905, Colour Index, II (1956) Acid Red 145, 1 part of acetic acid of 100% strength and 6 parts of octylurea are added at 20° to 25° to 4000 parts of water. 100 parts of wool are immersed in this dyebath, heated within 30 minutes to 70° and then dyed for one hour at 70°. The dyed wool is taken out of the dyebath, rinsed in water and dried. The tinctorial strength of the resulting brilliant scarlet shade is considerably more than that of a comparable dyeing obtained with a similar dyebath that does not contain octylurea or with a similar dyebath that contains up to 50 parts of benzyl alcohol in place of the octylurea.

EXAMPLE 2

2 parts of the dyestuff Acid Red 111 (Colour Index, II (1956), No. 23,265), 2 parts of acetic acid of 100% strength and 8 parts of octylcarbamic acid-(β-hydroxyethyl) ester are added to 4000 parts of water. 100 parts of wool are immersed in this dyebath, the liquor is heated within 30 minutes to 60° and the wool is dyed for one hour at 60°, then taken out of the bath, rinsed in water and dried. A deep scarlet dyeing is obtained. Similar results are obtained when 3-(2'-ethylhexyloxy)-propyl urea is used in place of octylcarbamic acid β-hydroxyethyl ester.

EXAMPLE 3

The procedure of Example 2 is adopted, using as the dyestuff 2 parts of sodium copper phthalocyanine-3,3'-disulphonate. In this case too a full turquoise shade is obtained even at 60°.

EXAMPLE 4

2 parts of the dyestuff Acid Red 111, 2 parts of acetic acid of 100% strength and 8 parts of N,N'-dibutylthiourea are added to 4000 parts of water. 100 parts of wool are immersed in this dyebath, the liquor is heated within 30 minutes to 80° and the wool is dyed for one hour at 80°, then taken out of the bath, rinsed in water and dried. The tinctorial strength of the resulting brilliant scarlet shade is considerably more than that of a comparable dyeing obtained with a similar dyebath that does not contain N,N'-dibutylthiourea or with a similar dyebath that contains up to 50 parts of benzyl alcohol in place of the N,N'-dibutylthiourea.

EXAMPLE 5

The procedure of Example 2 is followed, using 2 parts of the dyestuff Acid Blue 127, dyeing being carried out at 70° for one hour. The tinctorial strength of the resultant blue shade is considerably more than that of a comparable dyeing obtained with a similar dyebath that does not contain octyl carbamic acid β-hydroxyethyl ester or with a similar dyebath that contains up to 50 parts of benzyl alcohol in place of octyl carbamic acid β-hydroxyethyl ester. Acid Blue 127 has the Serial No. 61,135 in Colour Index, II (1956).

EXAMPLE 6

The procedure of Example 5 is followed using 2 parts of the dyestuff Acid Green 60. The tinctorial strength of the resulting olive green shade is enhanced as before. Acid Green 60 is a 1:2 metal complex dyestuff.

EXAMPLE 7

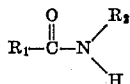
100 parts of nylon 66 fabric are entered into a bath made up from 1 part of acetic acid of 100% strength and 8 parts of octylcarbamic acid β-hydroxyethyl ester in 3000 parts of water. The bath is heated from 40° to

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100°, boiled for 15 minutes and cooled to 30°. 0.5 part of the dyestuff Acid Red 262 is dispersed in the bath which is raised to the boil over 45 minutes and held at the boil for 15 minutes. The dyed nylon is taken out of the dye bath, rinsed and dried. The resultant dyeing is free from barness; under normal conditions or under the same conditions in the absence of octyl carbamic acid β -hydroxyethyl ester the dyeing shows considerable barness. Acid Red 262 is a 1:2 metal complex dyestuff.

Having thus disclosed the invention what I claim is:

1. In an exhaustion dyeing process with an acid dye for polyamide fibers, the improvement which comprises contacting the polyamide fibers in a bath at a temperature from 40° to 100° C. with acetic acid and with from 0.5 to 5 parts by weight per 1000 parts of the bath of a compound of the formula

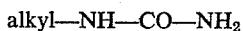


wherein:

R₁ is a member selected from the group consisting of —NH₂ and —O—alkylene—OH; and

R₂ is a member selected from the group consisting of an alkyl radical with 6 to 12 carbon atoms and an alkoxypropyl radical with at least 4 carbon atoms in the alkoxy group.

2. A process according to claim 1 wherein the compound is of the formula



wherein the alkyl contains from 6 to 12 carbon atoms.

3. A process according to claim 1 wherein the compound is of the formula



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wherein the alkyl contains from 6 to 12 carbon atoms and the alkylene contains from 2 to 3 carbon atoms.

4. A process according to claim 1 wherein the compound is of the formula



wherein the alkoxypropyl contains from 6 to 12 carbon atoms.

5. A process according to claim 2 wherein the compound is octyl-urea.

6. A process according to claim 3 wherein the compound is octyl—NH—CO—O—CH₂—CH₂—OH.

7. A process according to claim 4 wherein the compound is 3-(2'-ethylhexyloxy)-propyl-urea.

8. A process according to claim 1 wherein the polyamide fibers are wool fibers.

9. A process according to claim 1 wherein the polyamide fibers are synthetic polyamide fibers.

10. A process according to claim 1 wherein the bath is a pretreatment bath.

11. A process according to claim 1 wherein the bath is the dye bath.

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