United States Patent

Mikula

[15] 3,658,460

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[54] PROCESS FOR DYEING SYNTHETIC POLYAMIDE TEXTILES IN THE PRESENCE OF ORGANIC SULPHONIC ACIDS AND BASIC NITROGEN COMPOUNDS

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[21] Appl. No.: **817,568**

[30] **Foreign Application Priority Data**

Apr. 26, 1968 Switzerland 6293/68

[52] **U.S. Cl.**.....**8/172,** 8/173

[51] **Int. Cl.**.....**D06p 5/06**

[58] **Field of Search**.....8/168, 172, 84, 85, 178

[56] **References Cited**

UNITED STATES PATENTS

3,006,935	10/1961	Albrecht	8/85 X
3,071,427	1/1963	Buehler et al.	8/85 X
3,230,029	1/1966	Cappyccio et al.	8/168
3,391,985	7/1968	Zurbuchen et al.	8/84 X

Primary Examiner—George F. Lesmes

Assistant Examiner—T. J. Herbert, Jr.

Attorney—Wenderoth, Lind & Ponack

[57] **ABSTRACT**

A level dyeing is obtained on fabric of synthetic polyamide fibers having a variable dyestuff affinity by treating the fabric at a temperature of from 70° to 130° C. in a liquor of which the pH value throughout is maintained between 3 and 5, said dye liquor containing an aqueous solution of a surface active compound containing sulphonic acid groups or a surface active sulphuric acid ester, e.g. a sulphated oil constituted by a high molecular weight fatty acid subjected to a high degree or an ester thereof, to which liquor there is then sequentially added, without cooling or going outside the stated pH value range, (i) a basic nitrogen containing compound, or a quaternized derivative thereof, which is an addition product of 20 to 200 mols of ethylene oxide to certain long chain non-cyclic amines defined hereinafter, and (ii), simultaneously or subsequently, an anionic dye which would normally dye said fabric giving a stripy appearance, e.g. a so-called milling acid dye, dyeing being then affected in the usual way.

7 Claims, No Drawings

PROCESS FOR DYEING SYNTHETIC POLYAMIDE TEXTILES IN THE PRESENCE OF ORGANIC SULPHONIC ACIDS AND BASIC NITROGEN COMPOUNDS

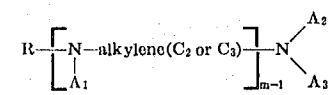
The present invention relates to a process for dyeing textile material of synthetic polyamide fibers having a variable dyestuff affinity, and to the resulting level dyed material.

It is known to dye textile material of synthetic polyamide fibers having variable dyestuff affinity in such a way as to produce dyeings of level appearance by treating said material before dyeing with an aqueous solution at a pH value of from 3 to 4 and temperatures of preferably 70° to 80° C., said solution containing a sulphated high molecular weight fatty acid or a sulphate ester thereof, if desired in admixture with ethoxylated amines having a high molecular weight fatty acid residue. In carrying out the pretreatment in this known dyeing process, the pretreatment bath is cooled to 50° C. and the dye and an acid binding agent are only added after such cooling, whereupon dyeing is effected at the boil. Thus relatively much heat energy and time are required for this known process.

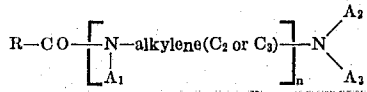
It has now been found that it is possible to dye synthetic polyamide fibers in level shades and having an especially pretty aspect by means of the process of the present invention, described in detail hereinafter, in which process the dyestuff is added to the pretreatment liquor without cooling that liquor.

The present invention thus provides a process for the level dyeing of a textile material of synthetic polyamide fibers having a variable dyestuff affinity with an anionic dye which would normally cause said material to have a stripy appearance, which process comprises first treating the material to be dyed with an aqueous solution of a surface active compound selected from the class consisting of surface active sulphuric acid esters and surface active sulphonic acid group containing substances in a pretreatment bath, then adding to said bath with the textile material still in it, without cooling, a material selected from the class consisting of basic nitrogen containing compounds and quaternized such compounds, said compounds containing at least one non-cyclic radical with 12 to 30 carbon atoms, and at least 20 – 200 ethenoxy groups, and the dyestuff, and finally effecting dyeing, the entire process being effected at a temperature of from 70° to 130° C. and a pH value of from 3 to 5. It will be appreciated that the basic nitrogen containing compound may contain more than one nitrogen atom and the non-cyclic radical may be saturated or unsaturated; the last mentioned radical, which preferably contains 16 – 24 carbon atoms, may (but need not) contain one or more hetero atoms or groups with hetero atoms, e.g. O, S or — CO—NH—.

Examples of said surface active compounds are alkylarylsulphonic acids, alkanesulphonic acids, aminoalkylsulphonic acid amides of high molecular weight fatty acids sulphated high molecular weight fatty acids or their esters, e.g. sulphation products of oleic, elaidic or ricinoleic acid and their esters, especially alkyl ones, for example the methyl, ethyl, propyl or butyl ester, or the glycerine ester of these fatty acids, for example castor oil. Sulphation products having a high degree of sulphation, preferably those with a sulphation degree above 70 percent, are especially suitable. Examples of the basic nitrogen containing compounds are those having the following formulae I—IV:-



(I)



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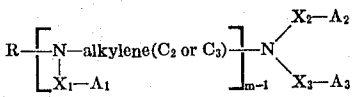

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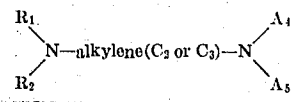


(IV)

wherein each of R and R_1 is independently selected from the class consisting of saturated and unsaturated, non-cyclic radicals with 12 to 30, preferably 16 to 24, carbon atoms,

R_2 is selected from the class consisting of saturated and unsaturated non-cyclic radicals with from one to 30 carbon atoms,

each of A_1, A_2 and A_3 is independently selected from the class consisting of polyethenoxy chains, with the proviso that the sum of the ethenoxy groups in all three chains must be at least 20 and at most 200,

each of A_4 and A_5 is independently selected from the class consisting of polyethylene oxide chains, with the proviso that the sum of the ethenoxy groups for the two chains must be at least 20 and at most 200,

at least one of X_1, X_2 and X_3 is independently selected from the class consisting of monosubstituted ethylene groups substituted with at least one of alkyl and hydroxyalkyl residues having one to 20 carbon atoms and phenyl residues, disubstituted ethylene groups substituted with a polymethylene chain, and disubstituted ethylene groups substituted with 2 non-cyclic, saturated residues each containing from one to 18 carbon atoms (e.g. alkyl radicals),

and any remaining symbol X_1, X_2 and X_3 is independently selected from the class consisting of single bonds, monosubstituted ethylene groups substituted with at least one of alkyl and hydroxyalkyl residues having one to 20 carbon atoms and phenyl residues, disubstituted ethylene groups substituted with a polymethylene chain, and disubstituted ethylene groups substituted with 2 non-cyclic, saturated residues each containing from one to 18 carbon atoms (e.g. alkyl radicals),

n represents an integer selected from 1, 2, 3, 4, 5 and 6,

and *m* represents an integer selected from 1, 2, 3, 4, 5, 6 and 7. It is to be noted that R, R_1 and R_2 may contain hetero atoms or groups of hetero atoms, e.g. O, S or —CO—NH—; these three symbols may, however, be aliphatic radicals.

The above and other suitable compounds are described, for example, in Swiss Pat. Nos. 317,900, 353,013, 363,006, 373,012, 388,903, 401,900 and 409,991.

Especially suitable are the addition products of ethylene oxide or of propylene oxide and ethylene oxide to high molecular weight mono- or polyamines, for example, oleyl-, cetyl-, stearyl- and behenylaminoethylamine or -propylamine and their quaternization products.

The ethoxylated amines may be used either as such or in the form of their quaternization products. Suitable quaternization agents are, for example, dimethylsulphate, diethylsulphate, methyl chloride, benzyl chloride, methyl- or ethylbenzene sulphonate, methyl- or ethyl- para-methylbenzene sulphonate etc. Depending on the amount of quaternization agent used, it is possible to quaternize one, several or all of the basic nitrogen atoms.

The pretreatment is effected with a liquor of which the pH value has been adjusted to from 3 to 5 by means of an acid such as, for example, acetic acid, formic acid or sulphuric acid and may last about 10 to 30 minutes.

The amount of the said surface active compound may be, for example, from 0.5 to 5 percent of the weight of the fibers; in general, however, 0.7 to 2 percent are sufficient. The amount of the basic compound which may be used is likewise from 0.5 to 5 percent of the weight of the fibers, preferably however about 0.7 to 1.5 percent thereof. All these quantity data relate to 100 percent of active substance. The dyeing may be effected at the boil or at temperatures above 100° C. at superatmospheric pressure.

Examples of dyestuffs which normally lead to a stripy appearance in the dyeing of synthetic polyamide fiber textile articles having a variable dyestuff affinity are 1:2-chromium or 1:2-cobalt complex dyestuffs, for example the 1:2-chromium or 1:2-cobalt complex compounds of 1-(2'-hydroxy-5'-

methylaminosulphonylphenylazo)-2-hydroxynaphthalene, the so-called milling acid dyes, for example 1,4-bis-[4'-(4''-chlorophenoxy)- 2'-sulphophenylamino]-anthraquinone or 1-hydroxy-2-(2'-phenoxy-5'-chlorophenylazo)-8-(4''-methylphenylsulphonylamino)-naphthalene-3,6-disulphonic acid, and the acid dyes for wool such as 1-amino-2-bromo-4-(4'-methylphenylamino)-anthraquinone-2-sulphonic acid.

These give level dyeings of good light and wash fastness in accordance with the process of the invention.

One preferred basic nitrogen containing compound is an addition product of 90 to 100 mols of ethylene oxide to 1 mol of C_{20-22}-alkyl-3-propylamine.

It is to be noted that the dyestuff may be added simultaneously with or subsequently to said basic nitrogen containing compound or quaternization product thereof.

In the following Examples parts are parts by weight, percentages are percentages by weight and the temperatures are stated in degrees Centigrade.

EXAMPLE 1

100 parts of a fabric of Nylon-66 which would normally dye with a stripy appearance are treated for 30 minutes in 4,000 parts of a boiling aqueous liquor of which the pH valve has been adjusted to 4–5 by means of acetic acid and which contains 3.3 parts of castor oil sulphated to 80 percent containing 30 percent of active substance. Thereafter 1.4 parts of an addition product of 100 mols of ethylene oxide and 1 mol of behenylamino-3-propylamine are added to the liquor without cooling it. 1 part of the acid dye Blue 127 (61135), Color Index II 1956, is then added to the boiling liquor and dyeing is effected for 1 hour. A level blue dyeing is obtained which is level and fast to washing, perspiration and light.

Instead of using the above sulphated castor oil it is possible to use, with a similar success, the same amount of oleic acid which has been sulphated to 95 percent, or 1.8 parts of 75 percent sodium salt of dibutylnaphthalenesulphonic acid or 1.4 parts of 98 percent sodium salt of dodecylbenzenesulphonic acid.

Similar effects are likewise obtained when, instead of the ethoxylated behenylaminopropylamine, there is used the same amount of an addition product of 30 mols ethylene oxide to 1 mol of monocetyl- or monstearyl aminoethylaminoethylamine or to 1 mol of a mixture of fatty amines with 18–22 carbon atoms in the alkyl radical, or the same amount of an addition product of 20 mols ethylene oxide to 1 mol coconut amine, or the same amount of 25–80 mols of ethylene oxide to 1 mol of oleyl-, cetyl-, or stearylamine, or the same amount of 90–120 mols ethylene oxide to 1 mol of eicosyl-, docosyl- or tetracosylamine, or the same amount of 80–200 mols ethylene oxide to 1 mol of hexadecyl-, octadecyl-, eicosyl-, docosyl- or tetracosyl-3-aminopropylamine.

Using the same method of dyeing, very good dyeings are likewise obtained with a 1:2-cobalt complex compound of 1-(2'-hydroxy-3'-acetylamino-5'-methylphenylazo)-2-hydroxy-5-nitrobenzene or of 1-(2'-hydroxy-5'-methylaminosulphonylphenylazo)-2-hydroxynaphthalene, or with a 1:2-chromium complex compound of 1-(3'-chlorophenyl)-3-methyl-4-(2'-carboxy-4'-aminosulphonylphenylazo)-5-pyrazolone, of α-(2'-hydroxy-5'-amino-sulphonylphenylazo)-aceto-acetylamino-octane, of 1-(4'-cyanophenyl)-3-methyl-4-(2'-hydroxy-4'-methylaminosulphonylphenylazo)-5-pyrazolone or of 1-(2'-hydroxy-5'-methylsulphonylphenylazo)-2-hydroxy-8-acetylaminonaphthalene, or with any one of the following dyes: 1-amino-4-(2',4',6'-trimethylphenylamino)-anthraquinone-2-sulphonic acid, 1-amino-4-phenylamino-anthraquinone-2-sulphonic acid, 1,4-bis-(2',4',6'-trimethyl-3'-sulphophenylamino)-anthraquinone, 1-(4'-(4''-cyclohexylphenoxy)-phenylazo)-2-(2''',4''',6'''-trimethylphenylamino)-8-hydroxy-naphthalene-6,2'-disulphonic acid, 1-amino-2-(4'-amylphenoxy)-4-(2'',4'',6''-trimethylphenylamino)-anthraquinone-2',3''-disulphonic acid or 1-acetyl-2-hydroxy-4-methyl-6-(4'-chlorophenyl-amino)-3-azobenzanthrone-2'-sulphonic acid.

Similar effects are obtained by using 1.4 parts of 85 percent sodium salt of the methyltauride of oleic acid instead of the sulphated castor oil.

EXAMPLE 2

100 parts of a Nylon-6 fabric which would normally dye with a stripy appearance are treated for 30 minutes in 3,000 parts of a boiling aqueous liquor of which the pH value has been adjusted to 4–5 by means of acetic acid and which contains 4 parts of castor oil which has been to 80 percent and has an active substance content of 30 percent.

Without cooling the liquor, 1.4 parts of an addition product of 90 mols ethylene oxide to 1 mol arachinyl-3-aminopropylamine are then added and the nylon fabric is agitated in the liquor for about 5 minutes. Again without cooling, 1 part of the dyestuff Acid Blue 113 (26360), Color Index II 1956, is then added and dyeing is effected at the boil for 1 hour. In this way a level, blue dyeing is obtained which is free of stripes and has a good fastness to light and washing.

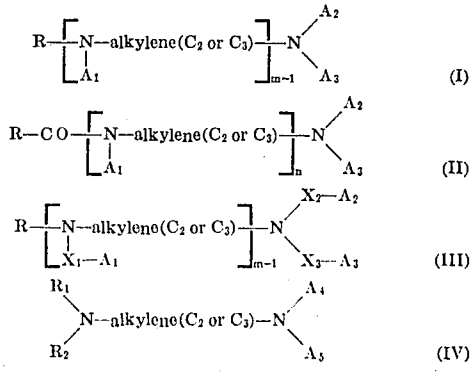
Instead of the ethoxylated arachinylaminopropylamine it is also possible to use with similar success the same amount of a quaternized addition product (which can be obtained according to Example VI of Swiss Pat. No. 388,903) of 85 mols of ethylene oxide to 1 mol of the addition product of 2 mols of propylene oxide to 1 mol of the alkylaminopropylamine there described.

In Examples 1 and 2 the dyestuff can be added at the same time as each of the ethylene oxide addition products with similar effect as regards the dyeing obtained.

Although the present invention is described herein with particular reference to specific details, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

I claim:

1. A process for the level dyeing of a textile material of synthetic polyamide fibers having a variable dyestuff affinity with an anionic dye which would normally cause said material to have a stripy appearance, which process comprises first treating the material to be dyed with an aqueous solution of a surface active compound selected from the class consisting of alkylarylsulphonic acids, alkanesulphonic acids, aminoalkylsulphonic acid amides of high molecular weight fatty acids, sulphated high molecular weight fatty acids and esters thereof, to the pretreatment bath, then adding to said bath with the textile material still in it, without cooling, a material selected from the class consisting of basic nitrogen containing compounds, said compounds selected from the following formulae I to IV:



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wherein each of R and R_1 is independently selected from the class consisting of saturated and unsaturated, non-cyclic radicals with 12 to 30, preferably 16 to 24, carbon atoms,

R_2 is selected from the class consisting of saturated and unsaturated non-cyclic radicals with from one to 30 carbon atoms,

each of A_1, A_2 and A_3 is independently selected from the class consisting of polyethenoxy chains, with the proviso that the sum of the ethenoxy groups in all three chains must be at least 20 and at most 200,

each of A_4 and A_5 is independently selected from the class consisting of polyethylene oxide chains, with the proviso that the sum of the ethenoxy groups for the two chains must be at least 20 and at most 200,

at least one of X_1, X_2 and X_3 is independently selected from the class consisting of monosubstituted ethylene groups substituted with at least one of alkyl and hydroxyalkyl residues having one to 20 carbon atoms and phenyl residues, disubstituted ethylene groups substituted with a polymethylene chain, and disubstituted ethylene groups substituted with 2 non-cyclic, saturated residues each containing from one to 18 carbon atoms,

and any remaining symbol X_1, X_2 and X_3 is independently selected from the class consisting of single bonds, monosubstituted ethylene groups substituted with at least one of alkyl and hydroxyalkyl residues having one to 20 carbon atoms and phenyl residues, disubstituted ethylene groups substituted with a polymethylene chain, and disubstituted ethylene groups substituted with 2 non-cyclic, saturated residues each containing from one to 18 carbon atoms,

n represents an integer selected from 1, 2, 3, 4, 5 and 6,

and *m* represents an integer selected from 1, 2, 3, 4, 5, 6 and 7,

and quaternized such compounds and the dyestuff, and finally effecting dyeing, the entire process being effected at a temperature of from 70° to 130° C. and a pH value of from 3 to 5.

2. A process according to claim 1, in which the pretreatment is effected with a solution of a sulphated castor oil of which the sulphation degree amounts to at least 70 percent.

3. A process according to claim 1, in which the pretreatment is effected with a solution of a sulphated oleic acid of which the sulphation amounts to at least 95 percent.

4. A process according to claim 1, in which said basic nitrogen containing compound is an addition product of 90 to 100 mols of ethylene oxide to 1 mol of C_{20-22}-alkyl-3propylamine.

5. A process according to claim 1, in which the pretreatment and the adding of the dye are effected at the boiling temperature of the liquor.

6. A process according to claim 1, in which the pretreatment is effected at a pH value of 4.5 to 5.

7. A process according to claim 1, in which dyeing is effected with at least one milling acid dye.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,658,460 Dated April 25, 1972

Inventor(s) Adam Mikula

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The name of the assignee in Item [73] on page 1 of the subject patent should read "Sandoz Ltd."

Signed and sealed this 17th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334