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PROCESS OF DYEING SHAPED ARTICLES MADE FROM SYNTHETIC LINEAR CONDENSATION POLYAMIDES AND POLYURETHANES

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The present invention relates to a process of dyeing shaped articles made from synthetic linear condensation polyamides and polyurethanes. The preparation and characteristics of such polyamides are described, for example, in U. S. Patents Nos. 2,071,250; 2,071,253; 2,130,523 and 2,130,948. Linear polyurethanes and their characteristics are described, for example, in French Patent No. 845,917 and in U. S. application Ser. No. 239,456, filed November 11, 1938.

Shaped articles made from linear polyamides, e. g. fibres, filaments, yarns, fabrics, foils, films and the like, may be dyed with dyestuffs usually employed for the dyeing of wool or silk, for example with acid dyestuffs or dyestuffs of the chrome and acid mordant group. It has also been proposed to dye shaped articles made from linear polyamides with dyestuffs of the direct group usually employed for coloring cotton or regenerated cellulose fibres. All these dyestuffs yield powerful and fast shades on linear polyamide fibres; the dyeings, however, are in many cases unlevel.

We have now found that shaped articles of linear polyamides and polyurethanes may be dyed fast and powerful shades which at the same time are satisfactorily level by treating these articles with aqueous solutions or suspensions of complex metal compounds derived from azo dyestuffs or azo methine dyestuffs free from sulfonic acid groups.

An object of this invention is, therefore, the treatment of shaped articles made from linear polyamides and polyurethanes with aqueous dispersions, which expression whenever used in the following specification and claims includes solutions as well as suspensions of metal-containing dyestuffs of the azo and azomethine group, in particular mono azo dyestuffs and mono azomethine dyestuffs, free from sulfonic acid groups.

Suitable metal-containing dyestuffs are in particular those derived from trivalent complex-forming metals, e. g. from chromium, iron, cobalt or aluminum. Dyestuffs containing manganese, nickel or copper may, however, also be used. The metals may be combined by groups capable of binding metals in complex form, for example hydroxy or carboxylic acid groups, which are in ortho-position to the azo or azomethine bridge of the dyestuffs or by groups capable of binding metals in complex form which are located distant from these bridges, for example by a hydroxy group and a carboxylic acid group in ortho-position to each other. Mixtures of different metal-containing dyestuffs may also be employed.

These dyestuffs are applied to the shaped articles to be dyed in the form of aqueous solutions or suspensions, preferably in the presence of dispersing agents. From neutral baths, the dyestuffs are almost completely absorbed by the material to be dyed. Acid dye-baths may also be employed, provided that the metal-containing dyestuff is stable to acid. The dye-baths may contain the usual ingredients, as for example ammonium chloride or sodium sulfate.

The shaped articles may be made from different types of linear polyamides or polyurethanes. Uniform linear polyamides may be used as obtained, for example, by condensing an ω,ω' -dicarboxylic acid with an ω,ω' -diamine or by condensing ω -aminocarboxylic acids or their amide-forming derivatives. Mixtures of linear polyamides of different types may also be used as well as mixtures of linear polyamides with linear polyurethanes. Mixtures of articles from linear polyamides or polyurethanes with other materials, as for example mixed fabrics of polyamide fibres with wool, cotton or rayon, may also be treated according to our invention.

The following examples will further illustrate how our invention may be carried out in practice. The invention, however, is not restricted to these examples.

Example 1

5 grams of a mixture of the chromium compound of the azo dyestuff from diazotized 1-amino-2-hydroxy-4-nitrobenzene and 1-phenyl-3-methyl-5-pyrazolone with 5 grams of the condensation product of naphthalene-2-sulfonic acid with formaldehyde are dissolved in 50 liters of hot water. After having added 100 grams of sodium sulfate, 1000 grams of linear polyamide fibres (prepared from adipic acid and hexamethylene diamine) are introduced and dyed for one hour at boiling temperature. The dyestuff is completely absorbed by the fibres. Powerful bluish-red and level dyeings of excellent fastness are thus obtained.

The dye-bath may also be prepared by first dissolving the chromium compound in an organic solvent, miscible with water, e. g. alcohol or acetone, and then diluting the solution with water.

Example 2

5 grams of the chromium compound of the azo dyestuff from diazotized 1-aminobenzene-2-carboxylic acid and 1-phenyl-3-methyl-5-pyrazolone are dissolved in a small amount of ethyl alcohol and the solution diluted with 50 liters of hot water. 1000 grams of linear polyamide fibres (pre-

pared from ω -amino-caproic acid) are introduced and dyed at boiling temperature for 30 minutes. After having added 50 cubic centimeters of 30 per cent acetic acid, boiling is continued for further 30 minutes. After 15 minutes 20 cubic centimeters of concentrated sulfuric acid are added. The fibres are thus dyed level, fast, powerful and golden-yellow shades.

Example 3

5 grams of a mixture of equal amounts of the complex chromium compounds of the azo dyestuffs from diazotized 1-amino-2-hydroxy-5-nitrobenzene and 1-phenyl-3-methyl-5-pyrazolone and from diazotized 1-amino-2-hydroxy-4-nitrobenzene and the same coupling component are intimately mixed with 5 grams of the condensation product of naphthalene-2-sulfonic acid with formaldehyde. The mixture is dissolved in 50 liters of hot water, and 1000 grams of polyamide fibre (consisting of a mixture of the condensation product from adipic acid and hexamethylene diamine with the condensation product from ω -amino caproic acid) are dyed for one hour in the bath at boiling temperature. The dyeing is effected for 20 minutes in neutral solution. 50 cubic centimeters of 30 per cent of acetic acid are then added and dyeing is continued for further 40 minutes. Very level yellowish red shades of good fastness are thus obtained.

Example 4

A mixture of 13.5 grams of the complex cobalt compound of the azo dyestuff prepared from diazotized 1-amino-2-hydroxy-4-nitrobenzene and 2-hydroxynaphthalene with 13.5 grams of the condensation product of a cresol-formaldehyde resin with 1- ω -sulfomethyl-2-hydroxynaphthalene-6-sulfonic acid are dissolved in 40 liters of hot water. 1000 grams of linear polyamide fibres of the type described in Example 1 are dyed in this solution in the manner described in Example 1. Very level deep blue-violet shades of excellent fastness are thus obtained.

When using 70 grams of the corresponding chromium compound very level bluish black shades of good fastness are obtained.

Example 5

8 grams of the complex chromium compound of the azomethine dyestuff prepared from 1-amino-2-hydroxy-5-nitrobenzene and 1-aldehyde-2-hydroxybenzene and 10 grams of the condensation product of naphthalene-2-sulfonic acid with formaldehyde are dissolved in 160 cubic centimeters of alcohol. When diluting the solution with 50 liters of hot water a clear solution is obtained. In the manner described in Example 1 there are dyed 1000 grams of linear polyamide fibres in this bath. Very level golden-yellow shades of excellent fastness properties are thus obtained. The dyestuff may also be used in the dispersed form together with a dispersing agent, e. g. evaporated sulphite-cellulose waste liquor. The corresponding dyestuff prepared from 1-aldehyde-2-hydroxy-3,5-dichlorbenzene yields reddish yellow shades.

The following Table shows further metal-containing dyestuffs which may also be dyed in the manner described in the foregoing Examples.

	Dyestuff	Dyed according to—	Shade of dyeing
5	Chromium compound of the azo dyestuff from 1-amino-3-nitrobenzene and salicylic acid.	Example 1.	Yellow.
10	Chromium compound of the azo dyestuff from 1-amino-4-nitrobenzene and salicylic acid.	do.	Yellowish orange.
	Chromium compound of the azo dyestuff from 1-amino-benzene-2-carboxylic acid and resorcinol.	do.	Reddish orange.
15	Cobalt compound of the azo dyestuff from 1-amino-benzene-2-carboxylic acid and resorcinol.	Example 3	Reddish brown.
	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-5-nitrobenzene and resorcinol.	Example 1.	Bluish red
	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-5-methylbenzene and resorcinol.	Example 3	Do.
20	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-3-nitro-5-chlorbenzene and resorcinol.	do.	Red-violet.
	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-5-chlorbenzene and resorcinol.	Example 2	Do.
	Iron compound of the azo dyestuff from 1-amino-2-hydroxy-3,5-dinitrobenzene and resorcinol.	do.	Dark brown
25	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-5-chlorbenzene and β -naphthol.	Example 1	Blue-violet
	Cobalt compound of the azo dyestuff from 1-amino-2-hydroxy-4-nitrobenzene and β -naphthylamine.	Example 3.	Black.
30	Chromium compound of the azo dyestuff from 1-amino-2-hydroxy-3,5-dinitrobenzene and tetrahydro- β -naphthol.	do.	Do.
	Cobalt compound of the azo dyestuff from 1-amino-2-hydroxy-5-nitrobenzene and aceto acetic acid anilide.	Example 1.	Yellow.
35	Mixture of chromium compounds of the azo dyestuffs from 1-amino-benzene-2-carboxylic acid and salicylic acid and from 1-amino-2-hydroxy-5-nitrobenzene and salicylic acid.	do.	Yellow-orange.
	Chromium compound of the azomethine dyestuff from 1-amino-2-hydroxy-4-nitrobenzene and 1-aldehyde-1-hydroxybenzene.	do.	Orange.
40	Chromium compound of the azomethine dyestuff from 1-amino-2-hydroxybenzene and 1-aldehyde-1-hydroxybenzene.	do.	Yellow.
	Chromium compound of the azomethine dyestuff from 1-amino-2-hydroxy-3,5-dinitrobenzene and 1-aldehyde-1-hydroxybenzene.	do.	Do.
45	Chromium compound of the azomethine dyestuff from 1-amino-2-hydroxy-5-chlorbenzene and 1-aldehyde-1-hydroxybenzene.	do.	Do.

Example 6

5 grams of the complex chromium compound of the azo dyestuff prepared from diazotized 1-amino-2-hydroxy-4-nitrobenzene and 1-phenyl-3-methyl-5-pyrazolone with 5 grams of the condensation product from naphthalene-2-sulfonic acid with formaldehyde are dissolved in 50 liters of hot water. After having added 100 grams of sodium sulfate, 1000 grams of polyurethane fibres are dyed in this bath for 1 hour at boiling-temperature. The dyestuff is completely absorbed. Powerful bluish-red dyeings of excellent levelness are thus obtained.

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