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3,226,178

**PROCESS FOR DYEING AND AFTERTREATING
POLYETHYLENE OXIDE MODIFIED NYLON
FIBERS**

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This invention relates generally to the fabrication of textile articles and, more particularly, to the dyeing of nylon fibers which contain an antistatic agent based on polyethylene oxide.

It is known that the tendency of fibers prepared from synthetic linear polyamides to acquire undesirable static charges has been overcome by blending with the polyamide at least 2% of a polyethylene oxide (PEO), prior to forming filaments therefrom. However, the presence of the polyethylene oxide introduces other problems, e.g., polyamide fibers thus modified have relatively poor dye lightfastness. Even when using acid and premetallized acid dyes which are most durable on unmodified nylon, unsatisfactory lightfastness results are obtained. In addition, it has been found that these dyes are thermally unstable when applied to the antistatic polyamide fiber. This deficiency is serious in carpets which must be heated when the latex binder is cured and in fabrics which must be heat set. Even long term use in heated locations may lead to thermal dye fading.

It is an object of this invention to provide antistatic, PEO-modified, polyamide fibers having improved dye lightfastness. It is another object of this invention to provide for improved thermal dye stability in dyed antistatic polyamide fibers.

These objectives are attained in a nylon fiber which contains at least 2% by weight of a polyethylene oxide of at least 600 molecular weight, which fiber is dyed with an acid dyestuff and impregnated with at least 100 p.p.m. (based on weight of polyamide) of copper as a cupric salt.

In one process embodiment, the required amount of cupric ion is added to the dye bath. In a second, preferred embodiment, the cupric ion impregnation is accomplished in a hot water bath after dyeing. In both embodiments, the impregnation bath contains at least about 1% OWY of a substantially neutral ionizable surface active wetting agent.

For dyeing procedures which do not require a pH above about 8.5, it is only necessary to add from 1–5%, based on weight of nylon yarn (OWY), of a water-soluble cupric salt to the dye bath. Otherwise, the salt is not added until the pH has been reduced to less than 8.5 (Example I). When the dye bath pH is relatively high, e.g., in the range of 8–9, to maximize dye exhaust and minimize staining from such components as the jute backing of carpets, it is often desirable to complex the cupric ion with oxalic acid, tartaric acid, ammonium ion complexes and the like. Either such treatment will introduce (via diffusion) from 100 to 3,000 parts per million (p.p.m.) of the cupric ion into the fiber. Of course, the dye bath will also contain the customary additives (including dye) such as leveling salts, buffers, acids, bases, wetting agents and the like.

The preferred method (Example VI) of impregnat-

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ing the PEO-modified polyamide fibers with the cupric ion is to add from 1–5% OWY of a water-soluble cupric salt to a post-dye water bath. This procedure is especially desirable for jute-backed carpets, since mild rinse conditions can be employed, thereby minimizing jute-staining. It is essential that at least about 0.5% OWY of a surface active wetting agent such as the sodium salt of an unsaturated long-chain alcohol sulfate also be present in the water bath.

It should be noted that the process disclosed herein differs from the well-known cuprous ion dyeing of polyacrylonitrile fibers in that use of the cupric ion in the polyacrylonitrile process has the deleterious effect of causing areas of reduced dyeability and poor dye uniformity. Moreover, cupric ions formed in that process, as by oxidation, may be converted to black cupric oxide when heated, thus discoloring the dyed fabric. In contrast, the presence of cuprous ions in the present process improves the dye lightfastness of some shades but actually decreases the dye lightfastness of others. The beneficial effect of the cupric ion in improving dye lightfastness of PEO-modified nylon appears to be unique among metal ions since it consistently improves the dye lightfastness of a wide variety of dyes.

The mechanism by which the cupric ion protects the dye is not known. It is surprising that the manganous ion, which is effective to a lesser degree, is in its lowest valence state, while the copper must be in its highest valence. Many metal ions have no effect, while others act as dye sensitizers, accelerating fading.

Those dyes which are known as neutral dyeing or premetallized acid dyes are especially suitable for use with PEO-modified nylon fibers which are to be treated in accordance with the present invention. Typical examples include the mono-azo dyes which are "half metallized," i.e., two dye molecules are complexed to divalent metal such as chromium or cobalt. The dye is complexible by virtue of hydroxy or carboxy groups in the O or O' positions with respect to the azo group and is water-soluble by virtue of sulfamoyl groups and/or the metal ions of the complex. Examples of such dyes are described in U.S. Patents 2,671,081, 2,885,392, and 3,051,696. In some cases, acid dyestuffs not previously reacted with a metal ion are employed. To be suitable, there can be no change in shade in the event of any reaction between the dyestuff and cupric ion during impregnation. Such acid dyes are used in the exemplified dye mixtures.

The process of the instant invention is useful in improving dye lightfastness when a single dyestuff is used, to produce a "self shade." The process is also useful when a number of dyestuffs are mixed to provide a compound shade of the desired color. In the latter usage, dye lightfastness requirements are high since it is essential to retard fading of each of the dyes in the mixture in order to avoid a color change on exposure to light. Some improvement in dye lightfastness has also been noted when the cupric salt is used after a dispersed dye treatment.

The substrates particularly operable in the process of this invention are synthetic linear polymers characterized by recurring amide linkages as integral parts of the polymer chain. These polyamides are produced by condensation of monoamino, monocarboxylic acids and their amide-forming derivatives, or of diamine and di-

carboxylic acids or their amide-forming derivatives. Examples of the first group are polycaprolactam and polyaminoundecanoamide. Examples of the second group are poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2-methylhexamethylene adipamide) and the polyamide from bis(p-aminocyclohexyl) methane and sebacic acid. Copolyamides within or among these groups may also be employed. With these polyamides are melt blended at least 2% by weight of a polyethylene oxide. The polyethylene oxide ether glycols having a molecular weight of at least about 1,000 are particularly suitable. Alternatively, the polyethylene oxide may have, as end caps, either one or two radicals of oxyhydrocarbon such as methoxy, ethoxy, phenoxy, dodecyl phenoxy, nonyl phenoxy and the like. The capped polyethylene oxides, especially when capped by aromatic radicals, should have a molecular weight of at least 600. The molecular weight and concentration requirements are imposed by the necessity that enough of the oxide be added to provide a two-phase conductive system, i.e., to render the fiber antistatic. Polyethylene oxide compounds which have ends reactive with the polyamide are excluded since they do not form such a two-phase system.

These PEO-modified polyamides may also contain conventional polyamide additives such as delusterants, pigments, antioxidants, heat stabilizers, plasticizers, adjuvants to increase dyeability, etc. Typical additives are disclosed in U.S. Patents Nos. 2,205,722, 2,510,777, 2,887,462 and 2,345,533.

In addition to polyamide substrates, many other fiber-forming polymers, if melt blended with a suitable polyethylene oxide, are improved with respect to dye lightfastness and acid dye thermal stability when they have been impregnated with the cupric ion. It should be noted that many such fibers are so extremely hydrophobic, e.g., polypropylene, polyethylene terephthalate, and the like, that it is necessary to use a dye carrier or special swelling agent in order to diffuse the cupric ion into the fiber.

As previously indicated, the important factor is to insure diffusion of the required amount of cupric ion into the fiber. This can be accomplished with a water-soluble cupric salt, e.g., cupric chloride, sulfate, nitrate, acetate, or complex tartrates, oxalates and the like.

The process and fibers of the present invention are especially suitable for end uses where repeated aqueous scouring is not required. Such end uses include rugs, upholstery, pile fabrics, dress goods, suitings and the like. The diffused cupric salt is usually retained to a satisfactory degree even under mild washing, e.g., during a rug shampoo. The normal durability can be supplemented by adding a cupric ion salt to the scouring compound, provided alkaline pH is avoided.

EXAMPLE I

Five percent of a polyethylene oxide ether glycol of 20,000 molecular weight is melt blended with polyhexa-

methylene adipamide and extruded to a 68 filament yarn which is subsequently drawn to produce a 1040 denier final product. This yarn is steam bulked, as described by Hallden in U.S. 3,005,251, and tufted into a plain, looped pile, jute-backed carpet, switches of which are used in the dyeing and light exposure tests described hereinafter.

For the various runs reported in Table I, the dye bath to carpet yarn weight ratio is 50-100 to one. The baths contain 1% ammonium hydroxide, 1-2% ethylene oxide/propylene oxide condensation product (leveling salt), and 1% sodium salt of unsaturated long chain alcohol sulfate (all percents based on weight of polyamide yarn, i.e., OWY). A beige shade is achieved, using dye mixture Q of Table III. For each of samples A-D, total dye concentration is 0.124% OWY. The carpet samples are immersed in baths containing the dyes and other dye adjuvants at room temperature. Bath temperature is raised to the boil at the rate of approximately 2° F./min. and held at the boil for one hour at which time the pH is 7-8, as against an initial pH of 10-11. In each instance, cupric sulfate (5% OWY) is added and the bath is maintained at the boil for an additional ½ hour (final pH of 5.7-6.2). Each dyed sample is rinsed thoroughly in cold water.

The carpet switches are then dried, partially covered and exposed to the light of a xenon arc in air, in an Atlas Xenon Weather-Ometer (AXWO). After the indicated exposure time, shade change is estimated visually, based on a scale of 1 to 5, wherein 5 indicates no change, 4 a slight, 3 a moderate and 2 a considerable shade change. These estimates are reported in Table I which gives a comparison of carpets containing nylon with and without the polyether glycol which were dyed with and without the cupric ion treatment.

Table I

Exposure time, hours.....	Shade change	
	80	160
Sample:		
A-PEO-modified nylon, with Cu ⁺⁺	4-	3
B-PEO-modified nylon, no Cu ⁺⁺	3-	2-
C-Unmodified nylon, no Cu ⁺⁺	4-	3
D-Unmodified nylon, with Cu ⁺⁺	4-	3

The tabulated comparisons show that a cupric ion treatment increases the dye lightfastness (DLF) of the PEO-modified nylon to the level of unmodified nylon.

EXAMPLE II

Following the procedures of Example I, several A samples are dyed, using different acid dye mixtures to produce different shades. DLF results and cupric salt contents in parts per million (p.p.m.) are reported in Table II. Dye compositions are specified in Table III.

Table II

Dyes used.....	P	Q	R	S	T
Shade.....	Gray.....	Beige.....	Brown.....	Green.....	Turquoise.....
Percent cupric sulfate in bath (OWY).....	CuSO ₄ , 5%.....	CuSO ₄ , 5%.....	CuSO ₄ , 5%.....	CuSO ₄ , 5%.....	CuSO ₄ , 5%.....
Percent copper in yarn (p.p.m.).....	287.....				379.....
Shade change after 160 AXWO hrs.....	3-.....	3+.....	3.....	4-3.....	4-3.....
Shade change in control yarn (No Cu).....	1.....	1.....	1+.....	1.....	1+.....

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Table III

Mix	Shade	Percent dye concentration in bath (OWY)		
		C. I. Acid Red 182	C. I. Acid Orange 64	C. I. Acid Green 25
P-----	Gray-----	.033	.015	.031
Q-----	Beige-----	.045	.061	.018
R-----	Brown-----	.075	.160	.037
S-----	Green-----	.034	.210	.110
T-----	Turquoise---	.016	.0015	.099

EXAMPLE III

Using the dye mixtures of Table III and the procedures of Example I, several samples of carpet A (PEO-modified nylon) are dyed in baths containing a lesser concentration of cupric sulfate and in baths containing different concentrations of cupric chloride. Comparative results are reported in the following table.

Table IV

Dye mix-----	P	Q	R	S	T
CuSO ₄ , 1% OWY:					
CuSO ₄ in yarn (p.p.m.)-----				215	222
Shade change after 160 AXWO hrs.		3+	4-	3	3
CuCl ₂ , 1% OWY:					
CuCl ₂ in yarn (p.p.m.)-----				305	326
Shade change after 160 AXWO hrs.	4-3	4-	4	4-3	4-3
CuCl ₂ , 5% OWY:					
CuCl ₂ in yarn (p.p.m.)-----		684			638
Shade change after 160 AXWO hrs.	3+	4-	4	4	4-3

When CuCl₂ is replaced by a like amount of cupric acetate, a lesser improvement is noted.

EXAMPLE IV

On trying various dye bath procedures, it is noted that the dye bath pH at the time of cupric salt addition is important. At a pH of 9 or above, it is observed that Cu(OH)₂ precipitates. If the bath pH is below about 8.5 (preferably below 8.0) when the salt is added, no precipitation occurs. The drop in the bath pH is, of course, due to loss of the transient base NH₄OH and is dependent on the time and severity of the boiling process.

When the CuSO₄ of Example II is replaced by an equivalent amount of a copper complex produced by reaction between 1 mole of CuSO₄ and 2 moles of oxalic acid, improved stability is obtained in the pH range of 8.0 to 8.5. The copper concentration in the thus treated PEO-modified carpets is about 200 p.p.m. When tested for DLF, using dye mixtures Q, S and T (Table III), the shade change is one unit less severe than without this copper complex.

EXAMPLE V

This example shows the improved thermal stability of dyes on PEO-modified nylon when impregnated with suitable amounts of the cupric ion.

Samples corresponding to A of Example I are prepared and dyed according to the procedure therein described. Dye mixtures Q, S and T of Table III are used. The dye bath contains CuCl₂ (5% OWY). After dyeing, the fibers contain 600-700 p.p.m. of the copper salt.

The dyed carpet samples are heated for 30 min. in a circulating air oven. The shade changes produced are estimated and listed in Table V, along with similar estimates for a control carpet dyed without use of the copper ion.

Table V

Dye mix-----	Q	S	T
Shade-----	Beige	Green	Turquoise
With cupric ion, after heating-----	4-3	4+	4-
Without cupric ion, after heating-----	2	2-1	2

6 EXAMPLE VI

The essential feature of the invention in improving dye lightfastness of nylon containing PEO is to impregnate the fibers with at least 100 p.p.m. cupric ion. This can be effectively accomplished by boiling the dyed fibers in a water bath containing the cupric salt and at least about 1% of the sodium salt of an unsaturated long chain alcohol sulfate. This procedure avoids the risk of copper precipitation in alkaline dye baths and minimizes jute staining which may occur in an acidic dye bath.

Carpets prepared from nylon fibers containing 5% by weight of PEO are prepared as in Example I, mock-dyed by subjecting them to the dye procedure without adding dye to the bath, then treated as shown in Table VI and rinsed. In each instance, CuSO₄ (5% OWY) was added to the room temperature water bath which was then heated to the boil in forty minutes. After rinsing and drying, the fibers were analyzed for copper content.

Table VI

Yarn to bath ratio	Percent alcohol sulfate	Time at boil, min.	Copper absorbed (p.p.m.)
1/100	None	30	<80
1/100	>2	30	1,000
1/40	1	(1)	393
1/40	1	30	420

¹ Removed at boil.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A process comprising the steps of: immersing a textile article comprised of PEO-modified nylon fibers in a dye bath containing an acid dyestuff; boiling said bath to dye the article; and boiling the dyed article in an aqueous bath containing at least about 1% OWY of the sodium salt of an unsaturated long chain alcohol sulfate and at least about 1% OWY of a water-soluble cupric salt, said aqueous bath having a pH of less than about 8.5.

2. The process of claim 1 wherein said cupric salt is present in the range of from 1-5% OWY and is selected from the group consisting of cupric chloride, cupric sulfate and the complex produced by reaction between cupric sulfate and oxalic acid.

3. A process comprising the steps of: immersing a textile article comprised of PEO-modified nylon fibers in a dye bath containing an acid dyestuff; boiling said bath to dye the article; transferring the dyed article to an aqueous bath containing at least about 1% OWY of the sodium salt of an unsaturated long chain alcohol sulfate and at least about 1% OWY of a water-soluble cupric salt, said aqueous bath having a pH of less than about 8.5.

4. The process of claim 3 wherein said cupric salt is present in the range of from 1-5% OWY and is selected from the group consisting of cupric chloride, cupric sulfate and the complex produced by reaction between cupric sulfate and oxalic acid.

5. A process comprising the steps of: immersing a textile article comprised of PEO-modified nylon fibers in a dye bath containing both an acid dyestuff and at least about 1% OWY of the sodium salt of an unsaturated long chain alcohol sulfate; boiling said dye bath until the pH is less than about 8.5; adding at least about 1% OWY of a water-soluble cupric salt to said dye bath; and maintaining said bath at the boil to impregnate the fibers with cupric ions.

6. The process of claim 5 wherein from 1-5% OWY of said cupric salt is added and wherein the salt is selected from the group consisting of cupric chloride, cupric sulfate and the complex produced by reaction between cupric sulfate and oxalic acid.

References Cited by the Examiner

UNITED STATES PATENTS

2,205,722	6/1940	Graves.	
2,345,533	3/1944	Graves.	5
2,510,777	6/1950	Gray	260—45.7
2,671,081	3/1954	Billings et al.	260—151
2,673,200	3/1954	Ruckstuhl et al.	8—74 X
2,885,392	5/1959	Csendes et al.	260—145
2,887,462	5/1959	Van Oot.	10
2,922,692	1/1960	Messer	8—74
3,005,251	10/1961	Hallden et al.	28—1

3,051,696	8/1962	Dettwyler	260—147
3,057,845	10/1962	Liechti et al.	260—147 X

FOREIGN PATENTS

839,456	6/1960	Great Britain.
861,354	2/1961	Great Britain.
862,577	3/1961	Great Britain.

OTHER REFERENCES

Colour Index, 2nd ed., 1956, vol. 1, pp. 1081, 1169 and 1318.

NORMAN G. TORCHIN, *Primary Examiner.*