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3,377,314

STABILIZED DYE RECEPTIVE POLYAMIDE CONTAINING COPPER ACETATE, POTAS- SIUM IODIDE AND HEXAMETHYLENEDI- AMMONIUM PHENYLPHOSPHINATE

Anthony Anton, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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2 Claims. (Cl. 260—45.75)

ABSTRACT OF THE DISCLOSURE

Polyamide yarns having a high degree of blue-whiteness contain specified amounts of copper acetate, potassium iodide and hexamethylenediammonium phenylphosphinate.

DETAILED DESCRIPTION OF THE INVENTION

This application is a continuation-in-part of Ser. No. 396,354, filed Sept. 14, 1964, and now abandoned.

This invention relates to high tenacity, deep dyeing nylon yarns and to methods for making the same.

Nylon yarns have been employed in automobile seat belts, awnings and other industrial applications requiring high tenacity yarns which have good appearance and high wear qualities in the face of exposure to the elements. The yarns generally employed for this purpose are high denier (greater than 5 d.p.f.) yarns which have been drawn under appropriate conditions to provide the required tenacity. However, these yarns leave something to be desired with respect to the combination of whiteness, dye-absorbability, resistance to degradation when exposed to heat and/or air, resistance to loss of strength when exposed to ultra-violet light or sunlight, and processability.

One object of this invention is to provide a polyamide yarn, which yarn has a superior combination of high strength, whiteness, high dye-absorbability, resistance to loss of strength when exposed to ultra-violet light or sunlight, resistance to thermal degradation, and good processability. A further object of this invention is to provide industrial yarns of these characteristics and to provide a process for making such yarn. Other objects will appear hereinafter.

Textile fibers that are inhibited against yellowing by the presence of certain phosphinates are disclosed in Ben, U.S. Patent 2,981,715. A poly(hexamethylene adipamide) yarn is specifically described therein which contains 0.25% by weight of sodium phenylphosphinate, 0.03% by weight of cupric acetate and 1% by weight of potassium iodide. Such a yarn, while inhibited against yellowing, lacks the whiteness and dye-receptivity desired in the aforementioned industrial applications. It has also been known in Stamatoff, U.S. Patent 2,705,227 to heat-stabilize polyamides by incorporating with the polymer, a composition comprising a copper compound, a halogen compound and certain phosphorus compounds.

It has been noted that the use of sodium phenylphosphinate at or above the levels indicated in the Ben and Stamatoff patents, namely, 0.25% causes processing difficulties. The number of draw-twist breaks and draw-roll wraps that occur are so extensive as to prohibit a commercial operation at the draw-ratio levels required for the production of industrial yarns, namely, at or above 4×.

In accordance with the present invention, the above difficulties are substantially eliminated by preparing a

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polyamide composition containing between about 0.05% and 1.0% by weight of hexamethylene diammonium phenylphosphinate, from about 0.01% to 0.05% by weight of cupric acetate and from about 0.1% to 1.0% by weight of potassium iodide, based on the weight of the polymer and thereafter melt-spinning the polymer to form filaments and drawing the filaments at least 4×.

Drawing is accomplished in an apparatus similar to that disclosed in U.S. Patent 2,289,232. The draw ratio of 4× or greater refers to the length of the filament or yarn after drawing divided by the length of the filament or yarn as it is supplied to the drawing process. Issuance of the polymer from the spinneret pack is adjusted to provide a final, drawn filament of at least 5 denier.

Preferably, polymerization of the polyamide is carried out in the presence of the aforementioned phosphinate, acetate and iodide additives. For use in the invention, hexamethylene diammonium phenylphosphinate may be prepared by neutralizing to a pH of 7.2 an aqueous slurry of phenylphosphinic acid with an aqueous solution of hexamethylene diamine. Then, the hexamethylene diammonium phenylphosphinate can be added to the autoclave as the neutralized aqueous solution, or preferably, as an aqueous solution made from the crystallized salt. The solid hexamethylene diammonium phenylphosphinate can be obtained by evaporating the aqueous solution or the salt can be precipitated by the addition of acetone. Hexamethylene diammonium phenylphosphinate is a white, water-soluble powder melting at 135° C. (275° F.).

The invention will be more readily understood by reference to the following examples which are illustrative and are not intended to limit the invention in any manner.

EXAMPLE I

This example illustrates the improved processability and blue-whiteness of the yarn of the invention as compared with a similar yarn wherein sodium phenylphosphinate replaced hexamethylene diammonium phenylphosphinate.

A polymerization procedure similar to that of Example I of U.S. Patent 2,163,636 is followed.

A stainless steel autoclave is purged of air, filled with nitrogen and charged with a water solution of the following ingredients.

Ingredient:	Weight (lbs.)
Hexamethylenediammonium adipate	3014
Potassium iodide	5.2
Cupric acetate monohydrate	0.52
Hexamethylenediammonium phenylphosphinate	15.07
Total water (approx.)	3150

The autoclave and contents are heated to approximately 240° C. (464° F.) and 250 pounds per square inch (17.6 kg. per cm.²) pressure where bleeding off of water vapor is begun.

Upon completion of the polymerization reaction, the molten polymer has the relative viscosity of about 43.

The polymer is extruded in the form of a ribbon upon a casting wheel. After quenching, it is cut into chips suitable for remelting at the grid of a spinning assembly. The poly(hexamethylene adipamide) flake is first melted in a steam atmosphere as taught in Waltz, U.S. Patent 2,571,975 and then is spun as yarn (A) at a rate of 370 yards per minute (338 meters per min.) and drawn a total of about 5× into an 840-denier, 68-filament yarn. During drawing, 0.017 draw-twist breaks per pound and 22% draw-roll wraps occur.

Replacement of hexamethylene diammonium phenylphosphinate with sodium phenylphosphinate in the polymer composition produces yarn (B) that gives 0.08 draw-

twist breaks per pound and 26% draw-roll wraps during draw.

Unscoured yarns (A and B) are evaluated for color using the method described by L. G. Glasser and D. J. Troy in Journal of the Optical Society of America, vol. 42, p. 652 (1952). The results are given in Table I.

TABLE I

	L	B
Yarn A.....	36.82	-11.6
Yarn B.....	45.68	-6.5

L=White to black range; 0=black, 100=white.
B=Blue-yellow value; +=yellow, -=blue.

These data shown that yarn A is more blue-white (or less yellow) than yarn B. This very desirable result confirms visual observations that yarns containing hexamethylenediammonium phenylphosphinate, cupric acetate, and potassium iodide have superior whiteness. The consumer demand for whiteness in synthetic fibers is described in Chemical and Engineering News, Apr. 12, 1965, page 37. In dyeing yarns A and B with other than yellow dyes it is found that the yellow of yarn B will interfere with the color effects obtained.

EXAMPLE II

This example illustrates the superior dyeability of yarns containing hexamethylenediammonium phenylphosphinate, potassium iodide, and cupric acetate as compared with yarns containing only potassium iodide and cupric acetate.

Yarns E and C are prepared in a manner similar to those in Example I, with yarn C lacking the hexamethylenediammonium phenylphosphinate. The drawn yarns (E and C) are now scoured, washed, and dyed for 90 minutes at 70° C. ± 1° C. (158° F. ± 1.8° F.) in a neutral 100:1 dye bath comprising 1.0% by weight (based on weight of yarn) C.I. Acid Red 57.

The dye rate (amount of dye absorbed) for the two yarns is shown in Table II. These data show that yarn (E) containing hexamethylenediammonium phenylphosphinate, potassium iodide, and cupric acetate absorbs dye at a rate 3 to 4 times greater than control yarn (C).

TABLE II

Time minutes.....	2	5	10	30	80	90
Percent dye absorbed by yarn E.....	25	42	38	63	73	81
Percent dye absorbed by yarn C.....	8	12	13	15	20	25

¹ Estimate.

EXAMPLE III

This example illustrates the superior dyeability of polyamide yarn containing hexamethylenediammonium phenylphosphinate (0.57%), potassium iodide (0.2%) and cupric acetate (0.02%) (yarn A) over yarn containing sodium phenylphosphinate (0.57%), potassium iodide (0.2%), and cupric acetate (0.02%) (yarn B) as disclosed in Ben, U.S. Patent 2,981,715 and yarn (F) containing only potassium iodide (0.2%) and cupric acetate (0.02%). Yarns (A) and (B) are those prepared in Example I. Yarn F was prepared in a manner similar to Example I. These yarns were compared for dye absorption by suspending for one minute a 5 gram yarn skein in an agitated boiling solution (pH 6.5) containing 0.01 weight percent of C.I. Acid Red 57. The data presented in Table III shows that in this period, yarn A absorbs about 50% more dye than does yarn B, and 150% more dye than does yarn F.

TABLE III

Sample:	Percent dye absorbed
Yarn A	56
Yarn B	38
Yarn F	22

EXAMPLE IV

The drawn yarn of this invention is also provided from molten polymer fed from a continuous polymerization unit to a spinning machine thereby obviating the extrusion, quenching, cutting and remelting steps specified in Example I. Polymerization is carried out as taught in U.S. Patent 2,361,717. Tests of the drawn yarn of this example give results similar to yarn A of Example I.

EXAMPLE V

This example illustrates preparation of the yarn of this invention from nylon copolymers, namely, polyhexamethylene adipamide and polycaproatamide.

A stainless steel autoclave is purged of air, filled with nitrogen, and charged with a water solution of the following ingredients.

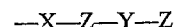
TABLE IV

Ingredient:	Weight (lbs.)
Hexamethylenediammonium adipate	2400
Caprolactam	240
Hexamethylenediammonium phenylphosphinate	12
Potassium iodide	4.75
Cupric acetate monohydrate	0.47
Total water (approx.)	2800

Polymerization is carried out as in Example I. The 66/6 random copolymer (90/10) is extruded, quenched, cut into chips, remelted, and spun into filaments as is yarn A of Example I. The yarn of this example is drawn about 5X, and when tested as is yarn A of Example I, results essentially equivalent to yarn A are observed.

The benefits of this invention are obtained with a variety of polyamides including polyhexamethylene adipamide, polycaproatamide, etc., melt-blended polyamides and copolyamides all wherein the carbonamide linkage is an integral part of the main polymer chain. Typically useful copolyamides are those comprising hexamethylene adipamide copolymerized with one or more members of the group consisting of caproatamide, hexamethylene dodecanamide, hexamethylene sebacamide and hexamethylene suberamide.

Typical of such polyamides are those formed from an aliphatic diamine and an aliphatic diacid containing the repeating unit

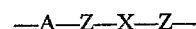


wherein X and Y represent divalent aliphatic, cycloaliphatic, or mixed aliphatic-cycloaliphatic groups, and —Z— represents the



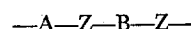
linkage. Especially useful polyamides are those in which —X— and —Y— are (CH₂)_{n-1}, where n is a positive integer of from 1 to 12 inclusive. —X— and —Y— may be the same or different. Polyhexamethylene adipamide and polycaproatamide (i.e., "66" and "6" nylon) are typical. Useful polyamides are also those in which —X— and/or —Y— is cycloaliphatic or aliphatic-cycloaliphatic, such as those derived from hexahydroterephthalic acid, bis(4-amino cyclohexyl)methane and bis(4-aminocyclohexyl)propane-2.

Other suitable polyamides are those having the repeating structure

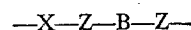


wherein —A— is a divalent aromatic radical and —X— and —Z— are as previously defined. Polyhexamethylene isophthalamide and poly(dimethyl hexamethylene terephthalamide) are illustrative of such polymers.

Additional polyamides having repeating units such as



and



where —B— is a divalent alkaryl (such as xylylene) may be used provided that only the melt-spinnable polymers and copolymers are intended. Poly(m-xylylene adipamide) and poly(p-xylylene sebacamide) are typical.

Another class of suitable polyamides containing other than aromatic intracarbonamide repeating units are those prepared from piperazine, such as those from piperazine and adipic acid and the like, including methyl substituted derivatives of piperazine.

The stabilized polymeric compositions of this invention may also contain small amounts of such additives as antistatic agents, delusterants, dyeing and coloring aids, and ultraviolet screens.

Polymers and copolymers modified according to this invention are useful for spinning continuous filaments, of round, lobed, and odd-cross section, and either of substantially uniform or of mixed deniers. These stabilized polymeric filaments may comprise core and sheath, side-by-side bicomponent, may be irradiation-grafted and may be of a hollow structure. These stabilized polymeric filaments may be processed into tow and staple, and also may be bulked, crimped, textured, etc.

The delusterant for the filamentary structures of this invention may be any of the conventional delusterants such as titanium dioxide, barium sulfate, aluminum trioxide, and the like. These delusterants are disclosed in U.S. 2,205,722.

Many other equivalent modifications will be apparent to those skilled in the art from a reading of the above without a departure from the inventor's concept.

What is claimed is:

1. Polyamide yarn containing from about 0.01% to 0.05% by weight of cupric acetate, from about 0.1% to 1.0% by weight of potassium iodide and from about 0.05% to 1.0% by weight of hexamethylene diammonium phenylphosphinate.

2. Polyamide yarn of at least 5 denier per filament containing from about 0.01% to 0.05% by weight of cupric acetate, from about 0.1% to 1.0% by weight of potassium iodide and from about 0.05% to 1.0% by weight of hexamethylene diammonium phenylphosphinate.

References Cited

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DONALD E. CZAJA, *Primary Examiner.*

JAMES A. SEIDLECK, SAMUEL H. BLECH,
Examiners.

V. P. HOKE, *Assistant Examiner.*