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METHOD FOR SPINNING POLYAMIDE YARN OF INCREASED RELATIVE VISCOSITY

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ABSTRACT OF THE DISCLOSURE

Continuous-filament high relative viscosity polyamide yarn is provided by fabricating continuous-filament yarn from polyamide containing from 0.01 to 15% by weight of certain phosphorous compounds, drawing the yarn and subsequently heating the drawn yarn below its melting point.

BACKGROUND OF THE INVENTION

The present invention relates to a process for spinning continuous-filament polyamide yarn having a high relative viscosity and desirable properties.

As used herein the expression relative viscosity refers to the ratio of absolute viscosity in centipoises at 25° C. of a 10% solution of polymer in solvent to the absolute viscosity also in centipoises at 25° C. of the solvent; solvents generally used for this purpose include: aqueous 90% formic acid, aqueous 85% phenol and meta-cresol. Relative viscosity (N_R) of a polymer may be used to determine the intrinsic viscosity ([N]) thereof from which the molecular weight of the polymer can be determined according to the equation:

$$\lim_{c \to 0} \frac{\ln N_R}{c} = [N] = KM^a$$

where M represents molecular weight, and K and *a* are constants and depend on the properties of solvent and polymer molecules and on their interaction. Therefore, relative viscosity values are an indication of polymer chain length and increase as the molecular weight of the polymer increases. Unless otherwise specified relative viscosity values are determined using aqueous 90% formic acid as the solvent according to the above procedure.

Continuous-filament high relative viscosity polyamide yarn is desirable, especially in applications where yarn properties such as tenacity and strength are important, for example in tire yarn. Present melt-spinning technology, however, permits fabrication of continuous-filament yarn from polyamide having a relative viscosity of less than about 90. Higher relative viscosity polyamides have high melt-viscosities which create numerous processing and handling problems in the fabrication and processing of filaments, e.g. in pumping and spinning of the molten polymer and in subsequent drawing of the filaments. More specifically, during melt-spinning operations high relative viscosity polyamide tends to resist filtration through conventional sand packs as well as extrusion through spinneret capillaries which eventually results in cessation of operations. Therefore, continuous-filament nylon 66 yarn, for example, has heretofore been limited to yarn having relative viscosities ranging up to about 90. Nevertheless industry recognizes that in certain applications higher

relative viscosity polyamide yarn would be desirable, since the physical properties of polyamides tend to improve with increases in the molecular weight thereof.

SUMMARY OF THE INVENTION

Continuous-filament high relative viscosity polyamide yarn is provided by the process of the present invention which comprises: fabricating continuous-filament polyamide yarn from polyamide containing from 0.01 to 15% by weight of a phosphorous compound; drawing the yarn up to about six times its length; arranging the drawn yarn in a heating vessel such that all surfaces of the yarn are permeable to gaseous substances; heating the drawn yarn in the vessel under vacuum or in an inert gas sweep to effect solid-state polymerization of the polyamide; removing the resulting yarn from the vessel and, if desired, hot-stretching the yarn to at least 15% of its drawn length.

Solid-state polymerization has been used in the past to increase the relative viscosity or molceular weight of polymer pieces, e.g. chips, flake, pellets, articles, and the like. Three chemical reactions have been observed in solid-state polymerization reactions, which are: (1) condensation resulting in increased relative viscosity and molecular weight of polymer chain, and competing surface reactions involving (2) oxidation and (3) hydrolysis which cause embrittlement of polymer leading to chain scissions and molecular weight reductions. In the case of polymer pieces, reactions (2) and (3), which occur at the surface thereof, are overshadowed by reaction (1) due to the small surface to volume ratios of polymer pieces. On the other hand, polymer filaments have large surface to volume ratios and normally exposure to solid-state polymerization conditions would be expected to actually result in a decrease in yarn relative viscosity. The unexpected increase in relative viscosity attained by the process of the present invention is believed to result from the presence of the phosphorous compound in the yarn.

Fiber-forming polyamides which may be used to fabricate the yarn of the present invention are synthetic linear polycarbonamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two carbon atoms. Polyamides of this type include polymers, generally known in the art as nylons, obtained from diamines and dibasic acids having the recurring unit represented by the general formula:

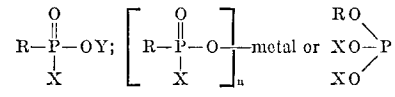
—NHCORCONHR^1—

in which R is an alkylene group of at least two carbon atoms, preferably from 2 to 10; and R^1 is selected from R and phenyl groups. Also, included are copolyamides and terpolyamides obtained by known methods, for example, by condensation of hexamethylene diamine and a mixture of dibasic acids consisting of terephthalic acid and adipic acid. In addition to the above polyamides, the polyamides also include polyamides obtained from amino acids and derivatives thereof.

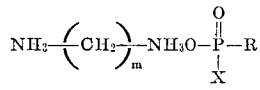
Polyamides of the above description are well-known in the art and include, for example, the copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6), polyhexamethylene sebacamide, and polyhexamethylene adipamide-containing polymers, such as polymers containing

polyhexamethylene adipamide and polyhexamethylene isophthalamide, or polyhexamethylene terephthalamide or polycaproamide, or combinations thereof.

To attain high relative viscosity polyamide yarn via the process of the present invention the polyamide must contain 0.01 to 15% by weight of at least one phosphorous compound selected from compounds represented by the formulas:



wherein R is a C_1 to C_{16} hydrocarbon radical selected from alkyl, cycloalkyl, aryl or arylalkyl groups; X is hydrogen or R; Y is X, an ammonium cation, or



cation; where *m* is an integer from 2 to 10; and *n* is an integer corresponding to the valance of the metal. Generally, the alkyl groups have from 1 to 5 carbons and the cycloalkyl groups from 5 to 10 carbon atoms. Suitable metals include sodium, potassium, lithium, calcium, cesium, tin, rubidium, and the like, i.e. metals listed in Groups I–IV of the Periodic Table of Elements. Exemplary phosphorus compounds which may be used in carrying out the present invention include phenylphosphinic acid, diphenylphosphinic acid, sodium phenylphosphinate, dimethylphosphinic acid, phenylphosphonic acid, triphenylphosphite, ethylphosphonic acid, ethylphenylphosphonic acid, alkylene diammonium arylphosphinates, such as hexamethylene diammonium phenphosphinate, and the like. The phosphorus compound may be incorporated into a polyamide by adding the compound to the monomeric polyamide-forming materials before polycondensation or by adding it to and mixing it with molten polyamide.

The manner in which the yarn is fabricated from polyamide materials containing the above-specified phosphorous compounds and subsequently drawn are not critical to the invention and may be done according to conventional techniques. Thus, yarn may be fabricated by melt-spinning, i.e. extruding molten polyamide containing said phosphorous compound through capillaries of a spinneret into molten streams of polyamide which are solidified into filaments. The filaments are gathered and subsequently drawn by stretching them about 400%.

The drawn yarn, when heated in the heating vessel to effect solid-state polymerization, must be arranged so that gaseous by-products formed as a result of oxidation and hydrolysis surface reactions can diffuse therefrom. These by-products, if trapped within the yarn, offset the effects of the polycondensation reaction and result in an overall decrease in yarn relative viscosity. Yarn arrangements which are satisfactory for use in the process of the present invention are arrangements wherein interstices exist between adjacent yarn strands during processing whereby by-products can permeate the yarn.

However, in conventional drawing operations, after the yarn is drawn and wound onto bobbins, it partially retracts or recovers from the drawing imparting tension and compressive forces to the yarn. With this yarn arrangement, referred to as high tension bobbins, no interstices exist between yarn strands and as a result gaseous by-products cannot permeate the inner yarn, i.e. portions of the yarn would not be exposed to an atmosphere suitable for solid-state polymerization. Therefore, yarn wound onto bobbins in this manner must be rearranged before it is suitable for use in the present invention.

Conveniently, yarn may be unwound from high tension bobbins and wound onto bobbins in a crisscross fashion whereby a plurality of congruent, evenly spaced, diamond-shaped patterns are formed; the center of the diamond is void of yarn and is defined by the yarn windings.

The diamond size may be varied, as desired. The tension applied to the yarn in winding it onto bobbins to form the diamond pattern is, preferably, only sufficient to maintain the yarn on the bobbins. Other arrangements of yarn suitable for use in the invention are: strands, skeins, hanks, or any arrangement which permits gaseous by-products to permeate the yarn during the heating thereof.

The yarn, arranged as described above, may be heated in any suitable vessel, such as a vacuum oven or vented oven, which may be heated by any suitable means, e.g. electricity, gas, steam, etc. During heating, by-products are formed which should be removed from yarn surfaces and, preferably, from the vessel. Removal of the by-products may be accomplished by means of vacuum or inert gas sweep, e.g. a nitrogen sweep. The ultimate relative viscosity attained by the process of the invention is a function of oven time and temperature. Oven temperatures may range from 125° C. to 5–10° C. below the melting point of the polyamide. Oven times may vary from one hour or less to several days or more depending on relative viscosity desired and also on oven temperatures employed. Generally, oven times of 1 to 24 hours are adequate.

The yarn in addition to the phosphorous compound may contain other additives which are commonly incorporated into monomeric mixes prior to polycondensation or the fabricated yarn may be coated with additives which are applied as a finish. Thus, monomeric mixes may contain small amounts 0.01 to 10% on weight of monomer, for example, of acetic acid (viscosity stabilizer); copper acetate and potassium iodide (heat stabilizers); p,p'-dioctyldiphenylamine, other amines, or manganous hypophosphite and/or hindered phenols (oxidation stalizers); titanium dioxide (delustrant); etc., oils, waxes and the like or any combination of these. Since in processing yarn according the present invention the yarn is heated for substantial periods of time, heat stabilizers are preferably incorporated into the yarn, although the presence of these stabilizers have no influence on RV.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The following examples are given for purposes of illustrating the invention. However, the scope of the invention is not intended to be limited to the particular compounds, ranges or conditions recited therein.

Examples 1 and 2 illustrate the affect oven time and temperature during processing have on the ultimate relative viscosity of the yarn. Example 3 shows that the process of the present invention results in solid-state polymerization, rather than cross-linking. Example 4 demonstrates that improved yarn properties are obtained by processing yarn according to the invention process. Example 5 shows that tenacity losses resulting from processing yarn according to the invention may be regained and even improved by hot-stretching the processed yarn.

In the examples RV_f refers to relative viscosity determined using aqueous 90% formic acid and RV_p refers to relative viscosity determined using aqueous 85% phenol.

EXAMPLE 1

Hexamethylene diammonium adipate (nylon salt) and a mixture of 70% nylon salt and 30% hexamethylene diammonium terephthalate, each containing 88 p.p.m. copper as copper acetate, 510 p.p.m. potassium as potassium iodide and 154 p.p.m. phenylphosphonic acid, were each polymerized, spun and drawn into 70 RV_f–840 denier–140 filament yarn (designated as Yarn A) and 20 RV_p–840 denier–140 filament yarn (designated as Yarn B), respectively. The drawn yarns were unwound from standard drawtwist bobbins and wound in a crisscross fashion onto bobbins with low tension being applied to the yarn. Bobbins of each yarn were placed in a vacuum oven and processed 15 hours at specified tem-

peratures ranging from 140° to 220° C. and 30 inches Hg vacuum. The RV_f and RV_p of the yarn on each bobbin was determined; no gel was observed when the yarn was dissolved in its respective solvent, indicating that cross-linking had not occurred. The results are given in Table I.

TABLE I

Oven treatment temprature, ° C.	Yarn A, RV_f	Yarn B, RV_p
None	70	20
140	78	23
195	145	33
205	225	49
220	365	57

EXAMPLE 2

Yarn A arranged on bobbins in a crisscross fashion as described in Example 1 were processed in a vacuum oven at 195° C. and 30 inches Hg vacuum for specified periods of time ranging from 5 hours to 20 hours. The RV of the yarn was determined after various time periods. No evidence of cross-linking was observed. The yarn RV's are given in Table II.

TABLE II

Hours:	Yarn A, RV_f
5	118
10	138
15	158
20	178
25	198

The data in Tables I and II show that relative viscosity increases with increases in oven temperature and time.

EXAMPLE 3

To demonstrate that the process of the invention results in an increase in relative viscosity via solid-state polymerization of the polyamide with substantially no cross-linking, the following experiment was conducted: Three samples having the composition of Yarn B were fabricated, drawn and treated in an electric oven at 160° C. with a nitrogen purge (100 cc. per minute). Each sample was placed into an aluminum cup. Before treatment and at the end of 4 hours of treatment the RV_p and available end groups (NH_2 and COOH) were determined. The end group analysis was carried out by dissolving 2 gram samples of the yarn in aqueous 85% phenol and titrating with 0.1 N HCl to find the inflection point; a second yarn sample was prepared in the same manner and titrated this time with 0.1 N NaOH to find the inflection point; the solvent per se is also titrated with each agent to find the respective inflection points. Then the inflection point of the solvent when titrated with 0.1 N HCl is subtracted from the inflection point of solvent plus sample when titrated with 0.1 N HCl to find mil-equivalents per gram of NH_2 end group. The same procedure is repeated only with the inflection points determined when titrating with 0.1 N NaOH to find mil-equivalents per gram of COOH end group. The results are tabulated in Table III.

TABLE III

	Sample No.					
	Before oven processing			After oven processing		
	1	2	3	1	2	3
RV_p	17.89	17.89	17.47	18.82	18.82	18.20
M-eq. COOH	44	44	45	46	42	42
M-eq. NH_2	56	62	59	44	41	44

The data show that an increase in yarn relative viscosity is accompanied by a decrease in reactive end groups, indicating polymerization. Moreover, no gel was observed when the samples were placed in solvent which is further indicative that no cross-linking occurred.

EXAMPLE 4

Yarn B was processed in a vacuum oven at 30 inches Hg vacuum for 16 hours at 125° C. (Run 1) and at 135° C. (Run 2); and the RV_p, dry retraction, boil shrinkage and impact strength of the processed yarn were determined and compared with Yarn B not processed according to the present invention and designated as control yarn in Table IV.

TABLE IV

Yarn B	RV_p	Dry retraction, percent	Boil-off shrinkage, percent	Impact strength, grams/denier
Control	19	2.6	10.8	9.4
Run 1	28	0.01	0.3	12.3
Run 2	36	0.03	0.0	11.4

The data of Table IV show that the impact strength, and particularly the boil-off shrinkage, and dry retraction properties of nylon yarn are enhanced by the process of the invention.

EXAMPLE 5

Processing yarn according to the procedure of Example 1 results in a slight decrease in the tenacity of the yarn. However, this loss can be regained and the tenacity even increased beyond that of unprocessed yarn by hot-stretching the yarn at least 15% of its length, according to conventional techniques. To demonstrate this effect, Yarn B, designated in Table V as Yarn B having a RV_p of 27, after being processed according to the invention in a vacuum oven at 30 inches Hg for 15 hours at 195° C. was hot-stretched 15 and 25%. For purposes of comparison the tenacity of Yarn B (not processed) having a RV_p of 20 was also determined. Additionally, the tenacity of unprocessed Yarn B hot-stretched 14% (corresponding to conventional hot-stretched tire yarn) is also given.

TABLE V

Yarn B, RV_p	Oven processing, ° C.	Hot-sretching, percent	Tenacity, gms./den.
20	None	None	6.3
20	None	14	6.6
27	195	None	6.2
27	195	17	6.8
27	195	25	6.9

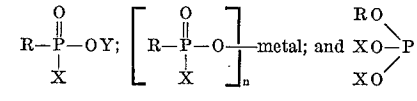
From the foregoing examples, it is apparent that the relative viscosity of polyamide yarn can be increased and the properties thereof enhanced, particularly the boil-off shrinkage characteristics thereof, by the process of the present.

Thus far the invention has been used primarily to increase the relative viscosity and enhance the properties of continuous-filament yarn fabricated from nylon 66 and nylon-containing polymers, e.g. the copolymer formed from hexamethylene diammonium adipate and hexamethylene diammonium terephthalate. However, the process can effectively be carried out with any continuous-filament polyamide yarn so long as the yarn contains from 0.01 to 15% p.p.m. of at least a one-phosphorus compound of the type described herein.

What is claimed is:

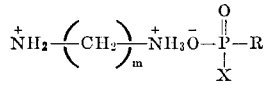
1. A process of increasing the relative viscosity of continuous-filament, drawn polyamide yarn which comprises:

(a) fabricating said yarn from a polyamide containing from 0.01 to 15% by weight of yarn of at least one phosphorous compound selected from the group consisting of:



wherein R is a C_1 to C_5 alkyl group, a C_5 to C_{10} cycloalkyl group, phenyl group or an alkyl-substituted

phenyl group having from 6 to 10 carbon atoms; X is R or hydrogen; Y is X, an ammonium cation or



cation where m is an integer from 2 to 10; and n is an integer corresponding to the valence of the metal, said metal being a Group I to IV metal of the Periodical Table;

(b) arranging said polyamide yarn in a heating vessel such that all surfaces thereof are permeable to gaseous substances;

(c) heating said arranged polyamide yarn at temperatures ranging from about 125° C. to about 5° C. below the melting range thereof; and

(d) removing from said vessel gaseous substance formed during heating of said arranged polyamide yarn.

2. The process as defined in claim **1** wherein the phosphorous compound is phenylphosphinic acid.

3. The process as defined in claim **1** wherein the polyamide is polyhexamethylene adipamide.

4. The process as defined in claim **1** wherein the polyamide is a copolymer of (1) hexamethylene diammonium adipate and (2) hexamethylene diammonium terephthalate.

5. The process of claim **4** wherein the copolymer consists of 70% (1) and 30% (2).

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