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3,558,569

PRODUCTION OF POLYAMIDE FILAMENTS HAVING A HIGH DEGREE OF POLYMERIZATION

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6 Claims

ABSTRACT OF THE DISCLOSURE

Fiber-forming polyamides containing no more than about 0.2% by weight water are melt-spun in the presence of between about 0.01% by weight and about 2.0% by weight of an alkyl ester of phosphorous acid. The dwell time, S, in minutes, of the polyamide at melt-spinning temperature T, in degrees centigrade, is maintained within the limits of the following relationship:

$$S = \frac{980 - 3T}{20} \pm 2$$

The resulting filaments have a molecular weight greater than that of unspun polyamide and exhibit a high degree of tensile strength and resistance to wet-heat.

This invention relates to polyamide filaments of a high degree of polymerization. More particularly it relates to the melt-spinning of polyamide filaments having a substantially higher degree of polymerization than the polyamide prior to melt-spinning.

The tenacity and versatility of polyamide filaments increases with increasing degree of polymerization, i.e., increasing molecular weight of the polyamide chains constituting the filaments. Unfortunately, while it is possible to produce bulk polyamides of very high molecular weight, i.e., molecular weights greater than about 35,000, it has heretofore been difficult to produce filaments therefrom by conventional melt-spinning techniques without incurring a substantial decrease in the molecular weight of the polyamide as it passes through the spinneret. The reason for this is that the viscosities of molten polyamides of molecular weight greater than about 35,000 require melt-spinning temperatures which are generally higher than those customarily employed for polyamides in the melt-spinning art. At such high temperatures, thermal degradation and depolymerization become significant so that the molecular weight of the spun filament is generally less than that of the polyamide prior to melt-spinning. Furthermore, while it is known that the absence of water in a polyamide tends to increase the molecular weight of filaments spun therefrom, such an expedient is generally of no avail when melt-spinning polyamides having molecular weights in excess of about 35,000.

Therefore, it is an object of the present invention to provide a process for melt-spinning polyamides into filaments of very high molecular weight.

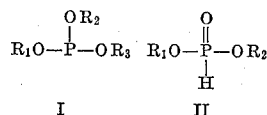
Yet another object is to provide a polyamide spun filament of very high molecular weight.

These and other objects as well as a fuller understanding of the present invention can be had by reference to the following detailed description and claims.

According to the present invention, a fiber-forming polyamide containing no more than about 0.2% by weight water is melt-spun in the presence of between about 0.01% by weight and about 2.0% by weight of a deriva-

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tive of phosphorous acid of either of the two following types:



Formulas I and II represent respectively diesters and triesters of phosphorous acid, in which R₁, R₂ and R₃ each represents an alkyl substituent, preferably a straight-chain alkyl substituent desirably composed of at least about 10 carbon atoms. In further accordance with the present invention, the length of time (hereinafter referred to as "dwell time" or "S"), in minutes, during which the polyamide is maintained at the melt-spinning temperature, T, is determined by the following heretofore unrecognized quantitative relationship:

$$S = \frac{980 - 3T}{20} \pm 2$$

When a fiber-forming polyamide is melt-spun in accordance with the present invention, the resulting filament possesses the remarkable and quite unexpected property of having a molecular weight which is considerably higher than the molecular weight of the polyamide prior to melt-spinning. This unusual behavior is amply demonstrated by the data in Table I, hereinbelow. Prior art knowledge would have predicted a filament molecular weight no greater than, and probably less than, the molecular weight of the unspun bulk polyamide. Thus, the present innovation permits the production of polyamide filaments having molecular weights in excess of about 35,000 from bulk polyamides of substantially lower molecular weight. Such polyamides have melt viscosities which permit the use of melt-spinning temperatures well within the range of temperatures commonly employed in melt-spinning filaments of a much lower degree of polymerization, and which are less thermally destructive of the filaments.

Polyamides suitable for use in the present invention include those heretofore recognized as generally suitable for melt-spinning, e.g., poly-ε-caproamides, polyhexamethylene adipamides, polyhexamethylene sebacamides, and the like, and mixtures thereof. Especially useful for the product and process of the present invention are the fiber-forming poly-ε-caproamides, especially those having molecular weights of between about 15,000 and about 35,000 and melting at temperatures below about 300° C.

Diesters and triesters of phosphorous acid (hereinafter "phosphite diesters" and "phosphite triesters", respectively, and "phosphite esters" generically) which are suitable for use in the present invention are derived from aliphatic alcohols, preferably saturated straight-chain aliphatic alcohols desirably composed of at least about 10 carbon atoms per molecule, and preferably between about 10 and about 20 carbon atoms per molecule. The phosphite diesters and phosphite triesters derived therefrom can be mixed esters, although esters in which the R₁, R₂, and R₃ substituents are identical are preferred. Illustrative of the phosphite diesters and phosphite triesters suitable for use in the present invention are the following:

Diesters:

- Di-n-decyl phosphite
- Di-n-undecyl phosphite
- Di-n-dodecyl phosphite ("dilauryl phosphite")
- Di-n-tridecyl phosphite
- Di-n-tetradecyl phosphite ("dimyristyl phosphite")

Di-n-pentadecyl phosphite
 Di-n-hexadecyl phosphite ("dicetyl phosphite")
 Di-n-heptadecyl phosphite
 Di-n-octadecyl phosphite ("distearyl phosphite")

Triesters:

Tri-n-decyl phosphite
 Tri-n-undecyl phosphite
 Tri-n-dodecyl phosphite ("trilauryl phosphite")
 Tri-n-tridecyl phosphite
 Tri-n-tetradecyl phosphite ("trimyristyl phosphite")
 Tri-n-pentadecyl phosphite
 Tri-n-hexadecyl phosphite ("tricetyl phosphite")
 Tri-n-heptadecyl phosphite
 Tri-n-octadecyl phosphite ("tristearyl phosphite")

Generally, phosphite triesters are preferred over phosphite diesters. Especially preferred among the phosphite triesters are tri-n-decyl phosphite, trilauryl phosphite, trimyristyl phosphite, tricetyl phosphite, and tristearyl phosphite.

It is a feature of the present invention that the amount of phosphite diester, triester, or mixture thereof added to the polyamide is such that the polyamide contains between about 0.01% by weight and about 2.0% by weight of the phosphite ester. Preferably, a phosphite ester content in the polyamide of between about 0.1% by weight and about 1.5% by weight is employed, a phosphite ester content of between about 0.3% by weight and about 1.0% by weight being especially preferred. If the phosphite ester content is less than about 0.01% by weight, the effect thereof becomes negligible, whereas if the phosphite ester content exceeds about 2.0% by weight of the polyamide, then hydrolysis of the ester with resultant liberation of phosphorous acid and alcohol, becomes significant, thereby lowering the quality of the spun fiber.

The phosphite ester can be added to the polyamide at any convenient stage of the present process, provided that such addition is made prior to passage of the molten polyamide through the spinneret and results in a uniform distribution of the phosphite ester within the polyamide. Preferably, the phosphite ester is added during the formulation of the polyamide because it has been found that the presence of such phosphite esters during the polymerization step enhances the rate of formation of polyamide.

In the present process, various conventional property-modifying agents can be added to the polyamide without adversely affecting the objects of the present invention. Examples of such additives include fire-retardants, delustrants, pigments, antistatic-agents, adhesion promoters, heat and light stabilizers, transition metal ions, organic amines, fluorescing agents, brighteners, bacteriostats, antioxidants, and the like.

It is another feature of the present invention that polyamides which are melt-spun according to the present process should not contain water in excess of about 0.2% by weight, and preferably less than about 0.1% by weight of the polyamide because an excessive water content of the polyamide exerts a substantial influence on the molecular weight of the polyamide during melt-spinning. The exercise of strict control over the water content of the polyamide, particularly with a view toward maintaining said content at less than about 0.2% by weight, will ensure unimpaired quality of filaments melt-spun in accordance with the present invention.

It has been discovered that in the present process, the dwell time of the polyamide must be carefully controlled in order to fully realize the advantages of the present invention. In particular, it has been discovered that the requisite dwell time is a function of the melt-spinning temperature, to wit, that for a given melt-spinning temperature, T , the dwell time, S , must be maintained within the limits delineated by the following relationship:

$$S = \frac{980 - 3T}{20} \pm 2 \text{ minutes}$$

It has been found that if the dwell time exceeds the value given in the above expression, no substantial increase in the degree of polymerization will occur, and in some instances, an actual decrease therein will result. On the other hand, a dwell time which is less than the minimum prescribed in the above expression will prevent the salutary action of the phosphite ester additive in securing a polyamide spun filament of increased molecular weight compared to the bulk polyamide precursor.

While, generally speaking, melt-spinning temperatures heretofore employed in producing ordinary polyamide filaments are suitable for the process of the present invention, it is preferred to employ such temperatures which are greater than or equal to the melt temperature of the polyamide but less than about 300° C. Especially preferred are melt-spinning temperatures between about 250° C. and about 290° C. Polyamide filaments of the present invention possess all of the advantages and desirable features which characterize filaments having a very high degree of polymerization, e.g., high tensile strength, uniformity, and thermal stability, particularly with regard to the effect of steam ("wet-heat") on the melting point of the spun filament. The resistance to wet-heat of filaments produced in accordance with the present invention is illustrated in connection with Examples 1 and 2 hereinbelow. The filaments of the present invention are generally useful for purposes heretofore recognized for polyamide fibers. The present novel filaments are particularly useful in applications, e.g. tire yarn, which require fiber and textile products possessing the above desirable properties to a high degree.

In the following examples, which illustrate the product and process of the present invention, parts and percentages are by weight unless otherwise indicated.

Molecular weights are reported as viscosity average molecular weights, M , determined by the following expression:

$$M = 16,300 (\eta)^{1.65}$$

wherein η is the intrinsic viscosity of a 0.5% by weight solution of the polyamide in metacresol at 35° C.

EXAMPLE 1

A molten mixture of 750 parts epsilon-caprolactam, 9.6 parts water, 0.3 part cupric chloride (heat and light stabilizers), and 2.25 parts (0.3%) tristearyl phosphite is placed in an autoclave. The autoclave is purged thoroughly with nitrogen, sealed, and heated for 3 hours at 265° C. under autogenous pressure. Heating is then continued for an additional 3 hours at 265° C. while passing dry nitrogen over the surface of the reaction mixture at atmospheric pressure. The crude product is removed from the autoclave, quenched in water at ambient temperature, and formed into chips. The chips are extracted with hot water and dried to a water content of 0.08%. This product has a molecular weight of 28,000 and a hot-water extractables content of 1.5%. The chips are melt-spun at 270° C. with a dwell time of 7.5 minutes. The stabilized spinneret pressure during the spinning operation is 240 kg./cm.². The spinneret pressure increases at the rate of 0.38 kg./cm.²/hr. The filaments thus obtained are drawn 4.7× to afford a 1260-denier filament having a tensile strength of 9.59 grams/denier and an elongation of 18.8%. The molecular weight of the fiber is 41,000 and the birefringence thereof is 55×10^{-3} . These results are summarized in Table I.

When two ends of this yarn are plied and the resulting cord heated in air for 10 hours at 180° C., the tensile strength retention is 94%. When the filament is coated with resorcinol-formalin latex and subjected to adhesion heat treatment followed by heating in air for 4 hours at 180° C., the tensile strength retention of the filament is 92%. The temperature at which the cord melts in saturated steam prior to the adhesion treatment is 162° C.

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EXAMPLE 2

A molten mixture of 750 parts epsilon-caprolactam, 9.6 parts water, 0.3 part cupric chloride, 3.75 parts (0.5%) trisearyl phosphite, and 0.45 part N,N'-diphenylparaphenylenediamine (an antioxidant) is placed in an autoclave. Polymerization is conducted in the manner provided by Example 1, except that the polymerization time under dry nitrogen at atmospheric pressure is extended to 6 hours. Subsequent quenching, washing, and drying are performed as in Example 1. The water content of the polyamide chips is 0.02%. The molecular weight thereof is 33,000 and the hot-water extractables content is 1.5%. When these chips are melt-spun at 280° C. with a dwell time of 6.0 minutes, the stabilized spinneret pressure during melt-spinning is 295 kg./cm.² and the rate of spinneret pressure increase is 0.33 kg./cm.²/hr. The filaments thus obtained are drawn 7.4× to afford a 840-denier filament having a tensile strength of 9.13 grams/denier and an elongation of 7.8%. The molecular weight of the fiber is about 50,000 and the birefringence thereof is 56×10⁻³. These data are summarized in Table I.

When two ends of this yarn are plied and the resulting cord heated in air for 10 hours at 180° C., the tensile strength retention is 94%. The temperature at which the cord melts in saturated steam is 168° C.

EXAMPLES 3-6

The procedure and materials used in Example 1 are repeated with several modifications within the scope of

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than straight-chain alkyl substituents. In Example 10, triphenyl phosphite is the additive. In Example 11, trinonylphenyl phosphite is the additive used.

The procedures employed in Examples 10 and 11 are substantially the same as in Example 1. The results are summarized in Table I. It can be seen that, whereas the molecular weight of the spun filament is much greater than that of the unspun polyamide, the spinneret pressure increases to such a degree as to make continued melt-spinning impossible.

The foregoing examples are presented for the purpose of illustrating the novel product and process of the present invention. It is of course understood that variations in the procedures described in those examples as well as changes in the materials used therein can be made without departing from the scope of the invention. Other advantages over the prior art, not disclosed herein may also exist for this invention which is defined in the following claims.

It is apparent from the following table that tri- and di-alkyl phosphite esters when used in the method of this invention increase the molecular weight of the polyamides by a minimum of at least 26% in Examples 1-6. Example 6 shows the lowest increase, i.e., 26%. The table also shows, by comparing Examples 1-6 with the Examples 7-10, which are examples outside the invention, that only by the method of this invention can molecular weight be increased by as much as 52% (Example 5) while still holding the incremental spinnerette pressure below 1 kg./cm.².

TABLE I.-MELT-SPINNING OF POLY-EPSILON-CAPROLACTAM

Example No.	Additive	Amount added (percent)	Polyamide water content (percent)	Molecular weight of polyamide before spinning	Melt-spinning temperature (° C.)	Dwell time (min.)	Rate of spinneret pressure increase (kg./cm. ² /hr.)	Molecular weight of polyamide after spinning
1	Trisearyl phosphite	0.3	0.08	28,000	270	7.5	0.38	41,000
2	do.	0.5	0.02	33,000	280	6.0	0.33	50,000
3	do.	0.3	0.03	30,000	280	6.0	0.4-0.9	41,000
4	do.	0.5	0.08	28,000	275	7.0	0.4-0.9	41,000
5	do.	0.3	0.05	25,000	260	8.5	0.4-0.9	38,000
6	Distearyl phosphite	0.3	0.08	31,000	280	7.0	5-1.0	39,000
7	Trisearyl phosphite	0.3	0.09	29,000	275	11.0	0.4-0.7	31,000
8	None	0.0	0.08	28,000	265	7.0	0.4-0.5	29,000
9	Phosphoric acid	0.5	0.08	28,000	270	7.0	22	42,000
10	Triphenyl phosphite	0.5	0.08	30,000	270	7.0	10-25	40,000
11	Trinonylphenyl phosphite	0.5	0.08	30,000	280	7.0	15-30	48,000

the invention. The materials and procedure used in these examples as well as the results thereof are summarized in Table I.

EXAMPLE 7

The procedure and materials used are substantially the same as in Example 1 except that a dwell time of 11 minutes is employed at a melt-spinning temperature of 275° C., which is outside the scope of the present invention. The fiber obtained has a molecular weight of only 31,000.

EXAMPLE 8

The procedure and materials used are substantially the same as in Example 1 except no phosphite ester is employed. The fiber obtained has a molecular weight of only 29,000.

EXAMPLE 9

A molten mixture of 750 parts epsilon-caprolactam, 9.6 parts water, 0.3 part cupric chloride, and 0.075 part phosphoric acid is treated in the manner provided by Example 1. The washed and dried chips have a molecular weight of 28,000 and a water content of 0.08%. Upon melt-spinning of the chips at 270° C. with a dwell time of 7 minutes, the spinneret pressure increased at the rate of 22 kg./cm.²/hr., and after 7 hours the spinning could not be continued due to yarn breakage. The results are summarized in Table I.

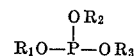
EXAMPLES 10-11

These examples illustrate the diminished efficacy of phosphite esters in which the alcohol moieties are other

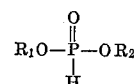
We claim:

1. A process for producing poly-epsilon-caproamide filaments comprising:

- melt-spinning a fiber-forming poly-epsilon-caproamide having a molecular weight between about 15,000 and about 35,000 and a melt temperature less than about 300° C. said poly-epsilon-caproamide containing no more than about 0.1% by weight water;
- conducting said melt-spinning of the fiber-forming polyamide in the presence of between about 0.3% by weight and about 1.0% by weight of a phosphorous acid derivative selected from the group consisting of phosphite esters having the formula:



and phosphite esters having the formula:



wherein R₁, R₂, and R₃ each represents a straight-chain alkyl substituent containing between about 10 and about 20 carbon atoms; and

- maintaining a dwell time, S, at a value given by the following relationship.

$$S = \frac{980 - 3T}{20} \pm 2 \text{ minutes}$$

wherein T is the melt-spinning temperature of be-

tween about 250° and 290° C., to produce a polyamide filament of an increased degree of polymerization relative to the polyamide prior to melt-spinning by at least a 26% increase in molecular weight expressed as a viscosity average molecular weight M_v , where M_v equals $16,300 (\eta)^{1.65}$, wherein η is the intrinsic value of a 0.5 percent by weight solution of the polyamide in metacresol at 35° C., said melt-spinning taking place at a rate of spinnerette pressure increase of 1 or less kg./cm.²/hr.

2. The process according to claim 1 wherein R_1 , R_2 , and R_3 each represents n-decyl.

3. The process according to claim 1 wherein R_1 , R_2 , and R_3 each represents lauryl.

4. The process according to claim 1 wherein R_1 , R_2 , and R_3 each represents myristyl.

5. The process according to claim 1 wherein R_1 , R_2 , and R_3 each represents cetyl.

6. The process according to claim 1 wherein R_1 , R_2 , and R_3 each represents stearyl.

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HAROLD D. ANDERSON, Primary Examiner

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