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PROCESS FOR HEAT-TREATING POLYAMIDE FILAMENTS

Koyu Hirono and Ken Kuwano, Mihara-shi, Japan, assignors to Teijin Limited, Umeda, Osaka, Japan, a corporation of Japan

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5 Claims

ABSTRACT OF THE DISCLOSURE

A drawn polyamide filament is subjected to one or more tensions applied in positive increments at a filament temperature of between about 180° C. and about 210° C. so that the initial tension on the filament lies within the range of between about 0.20 gram/denier and about 2.0 grams/denier while the final tension on the filament lies within the range of about 0.50 gram/denier and about 2.0 grams/denier. The filament is heated by means of an inert atmosphere and each tension is applied to the filament for a period of time of between about 1 second and about 10 seconds. Filaments so treated have enhanced dimensional stability, heat resistance, moisture resistance, and fatigue resistance as well as undiminished tensile strength.

This invention relates to the heat treatment of polyamide filaments. More particularly, it relates to the application of heat and tension to nylon-6 filaments to improve the dimensional stability, heat resistance, moisture resistance, and fatigue resistance thereof.

The dimensional stability of presently available polyamide fiber under conditions of stress, particularly at elevated temperatures is generally insufficient to permit optimum use of such fiber in all those applications to which it is potentially suited. Lack of dimensional stability under high stress is manifested, for example, in the phenomenon of "flat-spotting" generally exhibited by automobile tires containing cord made from polyamide filaments which tend to elongate even under normal tire load conditions.

Previous attempts to treat polyamide filaments after drawing to enhance the dimensional stability thereof have been only partially successful; the dimensional stability cannot be significantly enhanced without at the same time sacrificing some of the tensile strength. It is also desirable to improve the properties of fatigue resistance, moisture resistance and heat resistance simultaneously with the improvement in dimensional stability without concomitant loss of tensile strength, which tensile strength is preferably greater than about 9.0-9.5 grams/denier.

Therefore, it is an object of the present invention to provide a process for improving the dimensional stability, fatigue resistance, moisture resistance, and heat resistance of a polyamide fiber without impairing the tensile strength and uniformity thereof.

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

According to the present invention, a spun polyamide filament which has been drawn to the desired denier and tensile strength is exposed to a combination of judiciously

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selected conditions of tension, temperature, and atmosphere for a period of time so as to impart to the filament improved dimensional stability, heat resistance, moisture resistance, fatigue resistance and undiminished tensile strength.

More particularly, according to the present process, a spun polyamide filament, preferably a filament of nylon-6, which has been drawn to the desired denier and tensile strength is heated to a temperature of between about 180° C. and about 210° C., and preferably between about 195° C. and about 210° C. Simultaneously, a series of one or more tensions is applied to the filament, beginning with a tension of between about 0.20 gram/denier and about 0.80 gram/denier and ending with a tension of between about 0.5 gram/denier and about 2.0 grams/denier. Where the process is adapted to consist essentially of a single application of tension, such tension is preferably between about 0.5 gram/denier and about 2.0 gram/denier.

It is an essential feature of the invention that, except for the initially applied tension, each tension which is applied to the filament must be greater than the preceding tension, i.e., all increments in tension must be positive. The duration of application of a given tension ranges from about 1 second to about 10 seconds, and preferably between about 2 seconds and about 6 seconds.

The present process is applicable to the heat treatment of polyamide fiber in any form. Thus, the process can be applied to the heat-treatment of an individual filament or to a plurality thereof, either as zero twist yarn or as yarn which has a twist imparted thereto.

It is a preferred feature of the present invention that the heat treatment of the polyamide filament is performed in such a way that the filament need not come into contact with any solid heating elements during such treatment. The use of solid heating elements to heat the filament via contact therewith can impair the quality and uniformity of the filament, mainly because of the difficulty in securing accurate control of such heating elements at the high temperatures employed in the present process. In the present invention on the other hand, it is preferred that the filament be heated by means of a fluid heat transfer medium which is chemically unreactive toward the filament at the temperatures employed. Those solid objects, e.g., tensioning rollers, which do contact the filament during the heat treatment for the purpose of applying tension thereto are not required to be at a higher temperature than the fluid transfer medium and are preferably maintained in thermal equilibrium with the filament. Consequently, the undersirable effects of contact between the filament and the solid object are minimized.

A fluid heat transfer medium suitable for use in the present process may be liquid or gaseous. Preferably, the fluid heat transfer medium is a gas, e.g., air, superheated steam, nitrogen, carbon dioxide, and the like, or mixtures thereof. In further connection with the heating atmosphere of the present process, the temperature of such an atmosphere required to sustain a filament temperature of between about 180° C. and about 210° C. is between about 200° C. and about 300° C. The filament temperature is preferably determined by non-contact methods conventional to the thermometric arts, e.g., by means of a non-contact-type running filament thermometer.

It is necessary that the temperature of the filament in each stage of the heat treatment process be maintained between about 180° C. and about 210° C. Filament temperatures below about 180° C. are ineffectual; filament

temperatures above about 210° C. cause deterioration of the filament with accompanying loss of tensile strength. The filament temperature of each stage is at least as high as, and preferably equal to the filament temperature of the preceding stage. Furthermore, it is necessary to conduct each stage of application of tension (tensilization) for a period of no less than about 1 second and no more than about 10 seconds. Tensilization for less than about 1 second is ineffectual. Tensilization for more than about 10 seconds results in decreased tensile strength due to thermal deterioration.

According to the present invention, the number of stages of successively increasing tension can be one or any number greater than one, provided that each tension applied to the filament is greater than that preceding. When the present process is conducted using a single application of tension, it is desirable that such tension have a value of between about 0.50 gram/denier and about 2.0 grams/denier. If the tension is less than about 0.5 gram/denier, the tensile strength and Young's modulus are undesirably diminished while the denier of the filament is undesirably increased. If the tension is greater than about 2.0 grams/denier, the tensile strength is diminished and the heat resistance of the filament is not substantially improved. In a particularly preferred mode of conducting the present process using a single application of tension, such tension has a value of between about 0.5 gram/denier and about 0.8 gram/denier.

When a two-stage process is employed, it is preferred that the initial tension have a value between about 0.20 gram/denier and about 0.80 gram/denier; the tension in the final stage is preferably between about 0.50 gram/denier and about 2.0 grams/denier. If the tension applied in the first stage is less than about 0.20 gram/denier, the tensile strength and Young's modulus are undesirably lowered and this result cannot be remedied in the second stage regardless of the tension applied therein. If the tension applied in the second (and final) stage is less than about 0.5 gram/denier, the tensile strength and Young's modulus are undesirably diminished while the denier of the filament is undesirably increased, since the tension applied in the preceding stage must also be less than about 0.5 gram/denier. If the tension applied in the second stage is greater than about 2.0 grams/denier, the tensile strength of the filament is lowered and the heat resistance thereof is not substantially improved. In a particularly preferred two-stage process, a tension of between about 0.20 gram/denier and about 0.30 gram/denier is employed in the first stage, and a tension of between about 0.50 gram/denier and about 1.0 gram/denier is employed in the second stage. In the first stage of the two-stage heat treatment, the dimensional stability of the filament is improved; the second stage is effective in maintaining high tensile strength.

When a three-stage process is employed, it is preferred that the initial tension have a value of between about 0.50 gram/denier and about 0.80 gram/denier. The tension in the second stage is preferably between about 0.8 gram/denier and about 1.3 grams/denier. The tension in the third stage is preferably between about 1.3 grams/denier and about 1.8 grams/denier.

In general, the aforementioned objects of the present invention with regard to dimensional stability, fatigue resistance, heat resistance, moisture resistance, and tensile strength are most satisfactorily achieved by operating at higher temperatures, longer heating times, and lower tensions consistent with the limits of those conditions set forth hereinabove.

Polyamide filaments heat treated according to the process of the present invention have increased density and melt temperature. These, together with analytical measurements to be described hereinafter in connection with Examples I-III, indicate that polyamide filaments so treated have an enhanced crystalline structure compared with untreated filaments. Without wishing to be bound by

theory, it is suggested that the improvement in dimensional stability, heat resistance, moisture resistance and fatigue resistance are consequences of the improved crystalline structure of the polyamide filaments.

The process of the present invention is preferably applied to the heat treatment of Nylon-6 fiber. Spun and drawn filaments of Nylon-6 in condition for heat treatment according to the present process can be prepared, for example, by spinning a polycapromide of formic acid relative viscosity preferably between about 60 and about 140 and having a melt temperature of preferably between about 270° C. and about 290° C. After being cooled, oiled and reeled, the filaments of Nylon-6 are drawn at a draw ratio of preferably between about 4.0 and about 6.0.

The process of the present invention can be conducted using any apparatus which is suitably adapted to effectuate the heat treatment of polyamide fiber in the manner disclosed hereinabove. By way of example, a suitable system of conventional draw rollers can be advantageously used in conjunction with conventional fluid heating means to secure the sequential tensioning at the appropriate temperatures and for the prescribed durations of tensioning in accordance with the present invention.

It is a feature of the present process that there is provided thereby a Nylon-6 fiber of high tensile strength (i.e., in excess of 9.0-9.5 grams/denier), and improved dimensional stability under conditions of stress and elevated temperature (manifested by the facts that shrinkage of the yarn in boiling water is decreased by 4-8% and tensilized thermal shrinkage, as described in Example I, is decreased by 1-3%). Fatigue resistance is generally increased by about 20-70% and moisture and heat resistance are generally increased by about 5-15%.

The following examples illustrate the application of the process of the present invention to the heat-treatment of a 204-filament Nylon-6 yarn having a total denier of 1200 and a twist number of 39 x 39 twists/10 cm. (ASTM). The yarn is prepared by spinning and drawing Nylon-6 having a formic acid relative viscosity of 90.

Tensile strengths are determined by means of a conventional Instron-type tension meter.

Filament temperatures are determined by means of a non-contact running filament thermometer.

EXAMPLE I

The 1200 denier/204-filament yarn is subjected to a single-stage heat treatment in an atmosphere of air maintained at a temperature of 240° C. The yarn is exposed to the heated air for 6 seconds while under a tension of 0.70 gram/denier. The yarn reaches a maximum temperature of 210° C., which temperature subsists for 3 seconds. A comparison of some of the physical properties of the heat treated yarn with the corresponding properties of the same yarn prior to treatment is presented in Table I.

TABLE I.—SINGLE-STAGE HEAT TREATMENT

	Untreated yarn	Process of present invention
Yarn strength (grams/denier).....	9.5	9.5
Yarn shrinkage in boiling water (percent)....	11.0	5.0
Young's modulus (kg./mm. ²).....	400	400
Tensilized thermal shrinkage (percent) ^a	13.0	11.0
Fatigue resistance ^b	1.00	1.25
Crystal size (A.): °		
(101) face.....	70	85
(002) face.....	40	50
Long period ^d	110	115
Fiber density (grams/cc. ³).....	1.148	1.151

^a This term refers to the degree of shrinkage, after 30 minutes in air at 175° C., of yarn having an initial length of 50 centimeters and an initial tensile load thereon of 1/200 gram/denier.

^b This property is measured by the tube fatigue testing method of JIS LI017-1963. Values shown are ratios of the fatigue resistance of tested yarn to that of untested yarn.

^c This property is expressed in terms of space indices as determined by Oda et al., in Chem. High. Polymers (Japan), 7, 122 (1950).

^d This property is a measure of the average repeat period of crystalline regions and amorphous regions. Long period is measured by conventional X-ray small angle scattering techniques.

5 EXAMPLE II

The 1200 denier/204-filament yarn is subjected to a two-stage heat treatment in an atmosphere of nitrogen maintained at a temperature of 270° C. in both stages. The first stage of the process is conducted for 4 seconds during which time a tension of 0.23 gram/denier is applied to the yarn; the maximum temperature of the yarn in this stage is 210° C., which temperature subsists for 2 seconds. The second stage of the process is conducted for 4 seconds during which time a tension of 0.52 gram/denier is applied to the yarn; the maximum temperature of the yarn in this stage is 210° C., which temperature subsists for 2 seconds. A comparison of some of the physical properties of the heat treated yarn with the corresponding properties of the same yarn prior to treatment is presented in Table II, wherein the tabulations have the same meaning as in Table I.

TABLE II.—TWO-STAGE HEAT TREATMENT

	Untreated yarn	Process of present invention
Yarn strength (grams/denier).....	9.5	9.5
Yarn shrinkage in boiling water (percent)....	11.0	4.0
Young's modulus (kg./mm. ²).....	400	370
Tensilized thermal shrinkage (percent).....	13.0	10.3
Fatigue resistance.....	1.00	1.45
Crystal size (A.):		
(101) face.....	70	95
(002) face.....	40	55
Long period.....	110	120
Fiber density (grams/cc. ³).....	1.148	1.153

EXAMPLE III

The 1200 denier/204-filament yarn is subjected to a three-stage heat treatment in an atmosphere of air maintained at 250° C. in the first stage, 260° C. in the second stage, and 270° C. in the third stage. The residence time of the yarn in each stage is 4 seconds. In the first stage, a tension of 0.8 gram/denier is applied to the yarn; the maximum temperature of the yarn in the first stage is 195° C., which temperature subsists for 1.4 seconds. In the second stage, a tension of 1.2 grams/denier is applied to the yarn; the maximum temperature of the yarn in the second stage is 203° C., which temperature persists for 1.7 seconds. In the third stage, a tension of 1.6 grams/denier is applied to the yarn; the maximum temperature of the yarn in the third stage is 210° C., which temperature persists for 2.0 seconds. A comparison of the quality of the yarn subjected to this three-stage heat-treatment is compared with the quality of the same yarn in an untreated state. The results of this comparison are summarized in Table III wherein the tabulations have the same meaning as in Table I.

TABLE III.—THREE-STAGE HEAT TREATMENT

	Untreated yarn	Yarn treated according to Example III
Yarn strength (grams/denier).....	9.5	9.5
Yarn shrinkage in boiling water (percent)....	11.0	6.0
Young's modulus (kg./mm. ²).....	400	450
Tensilized thermal shrinkage (percent).....	13.0	11.3
Fatigue resistance.....	100	125
Moisture and heat resistance *	0.60	0.68

* This term refers to the decrease in tensile strength of yarn having an initial length of 30 centimeters and an initial load thereon of 1/20 gram per denier after subjecting the yarn to a saturated water vapor pressure of 5.5 kg./cm.² at 150° C. in an autoclave for 10 minutes. Values shown are ratios of the tensile strength of tested yarn to that of untested yarn.

The foregoing examples are presented for the purpose of illustrating the process of the present invention and are not intended to limit the scope thereof. It is understood that variations and modifications in the present process not inconsistent with the limits set forth in the specification can be made without departing from the scope of the invention as defined in the following claims.

We claim:

1. A process for treating a drawn polyamide filament comprising:

- 6 (a) heating the filament at a temperature of between about 180° C. and about 210° C.;
- (b) applying a tension to the filament of between about 0.20 gram/denier and about 0.80 gram/denier.
- (c) conducting step (b) for a period of time of between about 1 second and about 10 seconds;
- (d) applying a positive increment of tension to the filament obtained in step (c) at the temperature of step (a) or higher but below 210° C. to give a resulting tension on the filament of between about 0.5 gram/denier and about 2.0 grams/denier; and
- (e) applying each resulting tension in step (d) for a period of time of between about 1 second and about 10 seconds.
2. A process according to claim 1 wherein the polyamide filament is a filament of polycapraamide; the heating step (a) is conducted at a temperature of between about 195° C. and about 210° C. in an inert, fluid heat-transferring medium; the tensioning step (b) is conducted at a tension of between about 0.2 gram/denier and about 0.3 gram/denier; step (b) is conducted for a period of time of between about 2 seconds and about 10 seconds; the increment of tension applied in step (d) is between about 0.20 gram/denier and about 0.8 gram/denier to give a resulting tension on the filament of between about 0.5 gram/denier and about 1.0 gram/denier; and the resulting tension in step (d) is applied for a period of time of between about 2 seconds and about 10 seconds.
3. A process according to claim 2 wherein the polycapraamide is characterized by having a formic acid relative viscosity of between about 60 and about 140 and a melt-temperature of between about 270° C. and about 290° C.; the polycapraamide filament, prior to treatment, is characterized in having been drawn to a draw ratio of between about 4.0 and about 6.0 and having a tensile strength of at least about 9.0 grams/denier; and the fluid heat-transferring medium is selected from the group consisting of air, super-heated steam, nitrogen, and carbon dioxide.
4. A process according to claim 1 wherein the polyamide filament is a filament of polycapraamide; the heating step (a) is conducted at a temperature of between about 195° C. and about 210° C. in an inert, fluid heat-transferring medium; the tension applied to the filament in step (b) is between about 0.5 gram/denier and about 0.8 gram/denier; step (b) is conducted for a period of time of between about 2 seconds and about 10 seconds; step (d) comprises:
 - (A) applying a positive increment of tension to the filament obtained in step (c) to give a tension on the filament of between about 0.8 gram/denier and about 1.3 grams/denier; and
 - (B) applying a positive increment of tension to the filament obtained in step (A) to give a tension on the filament of between about 1.3 grams/denier and about 1.8 grams/denier; and
 each tension in step (d) is applied for a period of time of between about 2 seconds and about 6 seconds.
5. A process according to claim 4 wherein: the polycapraamide is characterized by having a formic acid relative viscosity of between about 60 and about 140 and a melt-temperature of between about 270° C. and about 290° C.; the polycapraamide filament, prior to treatment, is characterized in having been drawn to a draw ratio of between about 4.0 and about 6.0 and having a tensile strength of at least about 9.0 grams/denier; and the fluid heat-transferring medium is selected from the

group consisting of air, super-heated steam, nitrogen, and carbon dioxide.

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JULIUS FROME, Primary Examiner

5 J. H. WOO, Assistant Examiner

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