May 28, 1963

TIN-YAM AU

3,090,997

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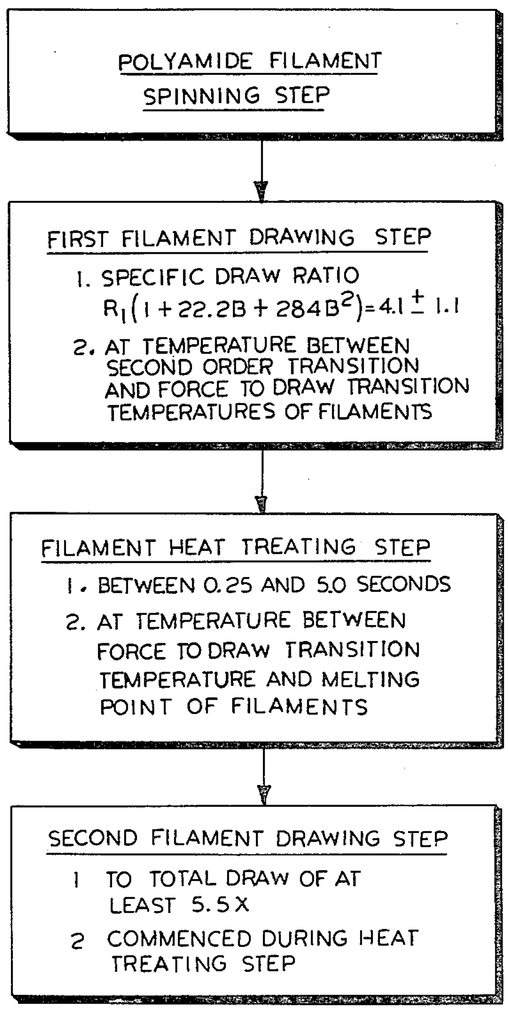
Filed Nov. 26, 1958



INVENTOR

TIN YAM AU

BY Harry C. Braddock

ATTORNEY

3,090,997
Patented May 28, 1963

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METHOD OF CONTINUOUS TREATMENT OF AS-SPUN BIREFRINGENT POLYAMIDE FILAMENTS

Tin-Yam Au, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Filed Nov. 26, 1958, Ser. No. 776,406
3 Claims. (Cl. 18—48)

This invention relates to an improved process for the multistage drawing of polyamide filaments and to the filaments produced thereby.

Tire cords prepared from polyamide filaments have demonstrated a notable degree of utility, owing to their outstanding properties. However, the propensity of such cords to elongate under normal load conditions somewhat limits this utility and has barred widespread commercial acceptance. Added incentive for reducing cord growth stems from the recent finding that growth is the singular cord property which appears to correlate with the "flat-spotting" tendencies of completed tires. Although cord growth can be reduced by hot stretching, the extent of such improvement is very limited, since both the properties of cord elongation and resistance to in-rubber fatigue are diminished during the same operation. Moreover, highly stretched cords exhibit increased shrinkage and shrinkage tension at elevated temperatures which, in turn, may create difficulties during subsequent tire-building operations. Accordingly, the conditions of hot-stretching are carefully compromised on the basis of a balance among cord properties, rather than to achieve the ultimate improvement in any one property.

With nylon tire cords, the permissible extent of hot-stretching depends on and is limited by the fine structure of the individual filaments in the yarn bundles which make up the cord. Desirably, the component filaments exhibit high tenacity and good lengthwise structural uniformity, which depend upon such factors as polymer quality, spinning conditions, drawing conditions, and particularly the thermal and mechanical treatments encountered during drawing. The thermomechanical experience of a filament during "cold drawing" is termed the "drawing profile." A drawing process for preparing a filament having high tenacity and excellent lengthwise birefringence uniformity is described in copending applications to Zimmerman, U.S. Serial Nos. 683,558 (filed September 12, 1957) now abanded and 799,054 (filed March 12, 1959), and comprises a controlled multistage drawing operation wherein the critical first stage draw ratio is determined as a function of the as-spun (undrawn) yarn birefringence. Such controlled multistage drawing permits close control of the drawing profile and enables the preparation of yarns having improved fine structure characteristics.

A primary object of this invention is to provide nylon filaments which, in the form of hot-stretched cord, exhibit practically insignificant cold growth at acceptable levels of fatigue resistance and break elongation. A further object is to provide such filaments which are resistant to extreme conditions of temperature and/or tension. A particular object is an improved process for controlled multistage drawing of synthetic linear polyamide filaments. Yet another object is the substantial elimination of flat-spotting in tires reinforced with nylon cords. Other objects will appear hereinafter.

In accordance with this invention there are provided nylon filaments which, in the form of tire cords, exhibit a tenacity in excess of 9.0 grams per denier (g.p.d.), break elongation greater than about 12%, relaxed cold growth less than about 4%, and a fatigue resistance of less than about 15% tenacity loss after 24 hours of disc-fatigue endurance. Such tire cords can be prepared from the instant filaments by customary hot-stretching techniques.

FIGURE 1 is a block diagram, or flow sheet, illustrating the process of this invention.

Certain of the important objects of this invention are accomplished by the provision of a process for treating as-spun birefringent polyamide filaments comprising the steps of drawing as-spun polyamide filaments, having a birefringence B, so that the ratio R_1 of drawn length to undrawn length is determined by the equation

$$R_1(1+22.2B+284B^2)=4.1\pm1.1$$

while maintaining the filaments at an elevated temperature lying between the second-order transition temperature and the force-to-draw transition temperature of the polyamide filaments, followed by the step of heating the filaments to an elevated temperature lying between the force-to-draw transition temperature and a temperature at least 20° C. below the melting point of the polyamide filaments for a period of time of at least 0.25 second and then during said period additionally drawing said filaments an amount sufficient to achieve the desired property levels of tenacity, break elongation and resistance to fatigue.

The "force-to-draw" transition temperature of the polyamide is that temperature at which there is observed an abrupt decrease in the tension required to draw an undrawn length of filament, and is in the vicinity of 150° C. for both poly(hexamethylene adipamide) and polycaproamide, being about 155° C. for poly(hexamethylene adipamide). At about this same temperature, poly(hexamethylene adipamide) undergoes a reversible transition from triclinic to hexagonal crystallinity, hence the temperature of the partially oriented yarn prior to second-stage drawing can be indirectly confirmed by dynamic X-ray diffraction measurements of structure, or may be determined directly by infra-red measurements. The structural changes which occur above the "force-to-draw" transition temperature are believed essential to the practice of the instant invention.

According to a preferred embodiment of this invention, nylon filaments, immediately after spinning, are converged into a yarn bundle and drawn (i.e., with no intervening packaging step), the first stage of drawing being carried out in accordance with the following relationship (as discussed in the copending applications to Zimmerman referred to above):

$$R_1(1+22.2B+284B^2)=4.1\pm1.1 \quad (1)$$

where B is the birefringence of the undrawn yarn, and R_1 is the first-stage draw ratio, i.e., the ratio of a certain length of filament after drawing to the length of the same mass of material immediately prior to drawing, normally expressed, for example, as 2× or 3× where the ratio is respectively 2 or 3. The second-stage draw rolls are heated to about the same temperature as that of the yarn as it emerges from the second stage of drawing, i.e., as it leaves the second-stage drawing element.

In practicing this invention, all drawing is carried out at temperatures sufficiently below the softening point of the polymer, but not below the "second-order transition" temperature of the polymer, i.e., the point at which there is observed a discontinuity in the relationship between first-derivative thermodynamic properties versus temperature (v. "Advances in Colloid Science" by Boyer and Spencer, vol. 2 Interscience, 1946). More particularly, the temperature at which first-stage drawing is conducted should be below, and that of the subsequent drawing stage or stages above the "force-to-draw" transition temperature, as hereinabove described.

The process of this invention can be effected with suitable modification of conventional drawing apparatus to provide the necessary interstage heating means. Such conventional drawing apparatus includes in serial relationship means for advancing the filaments from a spinning position or a package to the first stage of drawing, which means may be a conventional feed roll with an associated canted separator roll, a first-stage drawing element which is usually an externally heated, non-rotable snubbing pin (Babcock, U.S. 2,289,232), and first-stage drawing means, e.g., draw rolls. The first-stage draw rolls are run at a higher peripheral speed than that of the feed roll, hence the yarn is attenuated intermediate the two, the draw point being localized at the snubbing pin. The ratio of the peripheral speeds of the draw roll to that of the feed roll is a measure of the first-stage draw ratio, provided that slippage on the former element is avoided. Similarly, the ratio of filament speeds before and after the snubbing pin also is a measure of the draw ratio in that stage of drawing. The filaments may be packaged after the first stage of drawing or immediately forwarded to the second stage of drawing. In the latter case, which is a preferred mode of operation, the first-stage drawing means serve as forwarding (feed) means for the second stage of drawing. The second-stage drawing element may be a large diameter heated pin, a curved plate (Hume, U.S. 2,533,013) or a pipe, the last-mentioned device being preferred, with the filaments being drawn thereon by the urging of the second-stage drawing means, usually draw rolls. As earlier indicated, the ratio of peripheral speeds of the second-stage drawing and feeding means determines the draw ratio in that stage. Subsequent to second-stage drawing, the filaments are usually packaged but may be advanced through additional stages of drawing by means similar to those already described.

Total draw can be calculated by multiplying together the draw ratio of the individual stages or by comparing a final yarn length immediately after the final draw to its length before the initial draw step.

In accordance with this invention, the filaments are heated to a temperature above the "force-to-draw" transition temperature of the polymer prior to drawing in the second stage. The filaments are conveniently brought to temperature by heating the first-stage draw rolls, either internal or by enclosing the same in an oven. The filaments also may be heated by utilizing auxiliary means, such as a heated drum, positioned intermediate the first-stage draw rolls and the second-stage drawing element. Alternatively, the filaments may pass through a hot-liquid bath, provided the liquid is inert to the polymer; mineral oil, molten metal, or the like may be used in such baths. Radiant heaters or flat plates positioned along the filament path are likewise satisfactory, as are combinations of several of the above means. In the preferred case of heated draw rolls or auxiliary drums, the amount of heat transferred from the element to the yarn can be readily adjusted, e.g., in the case of a change in filament speed, by increasing or decreasing, as required, the number of filaments wraps about the element(s). Otherwise a straightforward change in the temperature of the elements(s) is sufficient to compensate for changes in drawing conditions, such as changes in filament speed, denier, or polymer composition. At extremely high filament speeds, the temperature of the interstage heating element necessarily may even exceed the melting point of the polymer; however, this is compensated by reduced contact time on the element, the time-temperature relationship being adjusted so as to impart a sufficient amount of heat to the filament. If the filament has been packaged subsequent to drawing in the first stage, substantially more heat is required prior to second-stage drawing. It is important that the filament achieve a temperature of at least the "force-to-draw" transition temperature prior to drawing in the second stage. It has been observed that during such interstage heating, a slight amount of drawing is unavoidable; nevertheless, the extent of such

interstage drawing ordinarily should be minimized. After achieving the necessary temperature prior to second-stage drawing, the filaments are maintained at at least that temperature for at least 0.01 second, preferably at least 0.1 second, prior to second-stage drawing and throughout any subsequent stages of drawing. The filaments may be maintained at the necessary temperature for the indicated time by employing heated second-stage draw rolls, or by any other of the means mentioned hereinabove, the similar compensations for changes in filament speed, etc., applying. It is presently believed beneficial to have the time spent above the "force-to-draw" transition temperature distributed about equally, before and after the actual second-stage drawing. In the case of filaments composed of poly(hexamethylene adipamide), it is preferred that such filaments attain a peak temperature of at least about 200° C. after the second-stage drawing and prior to packaging; optimum properties result from such treatment.

The filaments prepared by this invention characteristically exhibit high tenacity, improved lengthwise uniformity of mechanical and structural properties, and perfected fine structure, e.g., as regards crystallinity. Under ultraviolet spectrophotometric examination, solutions of these filaments (1.6% by weight in formic acid) exhibit absorbence (optical density) values of at least 0.5 and, with preferred filaments, at least 1.0 in the range from 274 to 296 millimicrons. The instant filaments have their greatest utility in tire cords, and are characterized in that form after hot-stretching under optimum conditions, i.e., those conditions which produce cords of highest tenacity and least growth at acceptable levels of break elongation and resistance to fatigue. Since the operations dealing with cord preparation from filaments, cord dipping, and hot-stretching are routine, the observed improvements in cord properties are a direct and useful measure of filament properties and are, therefore, employed herein for that purpose.

"Cold growth" is a particularly important property, being a measure of the increase in tire size on inflation and a measure of "flat-spotting" tendencies of the tire. This quantity is measured as the percent elongation of a known length of cord on which a load of 1.0 g.p.d. has been suspended for a period of 30 minutes. "Cold growth" thus includes not only the instantaneous elongation at the given load, but also the creep which has occurred during the 30-minute interval. Prior to testing, the cord is stored in skein form for 48 hours at 55% relative humidity and 75° F., hence the above-measured growth is properly termed "relaxed cold growth."

Since hot-stretching conditions which are excessive with respect to time, temperature, and/or tension may produce cord with inferior properties, it is customary to measure the resistance of the cord to in-rubber fatigue. The cord fatigue may be conveniently measured using the apparatus shown in U.S. Patent 2,595,069 to Fritz, the so-called "disc fatigue" tester. This device can accurately simulate the stresses imposed on the cords in running tires. The results reported herein are obtained after 24 hours of testing (conditions: 11.7% compression and 7.2% extension per cycle, 2670 cycles per minute), and are expressed as the percent of original tenacity lost during the test. Preparatory to testing, each cord is conditioned then embedded longitudinally in a block of rubber at 0.05 g.p.d. tension, each block being then vulcanized in a hot press. After testing, the cord is cut from the block and its tenacity determined in the usual manner. It is important that the cord show no more than 20% disc fatigue tenacity loss, preferably less than 15%, in 24 hours of testing. The measured resistance to fatigue depends in part on the level of twist in the cord. Accordingly, when several cord samples are compared, the twist level in each sample should be considered.

The following examples illustrate the preparation of yarn in accordance with this invention, and, for purposes of comparison, yarn prepared by a prior art method. Table I shows the properties of the cords prepared from these yarns. All yarns are prepared from poly(hexamethylene adipamide) with a relative viscosity of 57, containing 0.1% potassium iodide and 0.01% cupric acetate (on a weight basis) added as an antioxidant. All yarns, after drawing, are about 840 denier, 140 filaments. All cords are prepared from such yarn in conventional manner by first twisting the single yarn 11.3 turns per inch (t.p.i.) in the "Z" direction, then the singles are combined in pairs at 13.0 t.p.i. S twist to form 1800 denier two-ply cord. The greige cords are treated with a standard adhesive dip prior to hot-stretching. The dip is prepared as follows:

Solution I:

Water	cc	477
Resorcinol	g	22
Formaldehyde (37%)	g	32.4
NaOH (100%)	g	0.6
(Allowed to stand 6 hrs.)		

Solution II:

Water	cc	122
"Gen-Tac"[1] resin	g	488
(pH, adjusted after 16 hrs. with NaOH 9.5)		

[1] Trademark, General Tire and Rubber Company.

The Solutions I and II are mixed to form the dip, the final pH being about 11. The yarn is dipped in the solution mixture and then hot-stretched in conventional manner to optimum properties in a Steele Model C–300 oven (sold by W. M. Steele Company, Worcester, Mass.). The severity of hot-stretching conditions employed with each yarn depends upon the properties of that yarn, providing, therefore, a highly useful measure of yarn quality and utility.

EXAMPLE I

Freshly spun yarn having a filament birefringence of 0.0035 is forwarded at 350 yards per minute (y.p.m.) from a spinning position, after applying finish, to a feed roll and thence to a ¾-inch diameter draw pin maintained at 50° C., and to a pair of 6-inch diameter unheated draw rolls, and is thereby drawn at a draw ratio of 4.1 (4.1×). The yarn is immediately advanced to a 3½-inch diameter pipe (matte-chrome surface) maintained at about 180–200° C., making several helical (60°) wraps thereon, is drawn thereon 1.52× (total, 6.25×) by a second pair of 6-inch diameter draw rolls, and then packaged. The yarn remains above the "force-to-draw" transition temperature for only about 0.11 second, achieving that temperature on the hot pipe. The yarn has a tenacity of 10.7 g.p.d., elongation of 14.6%, and an initial modulus of 72 g.p.d. Cord from this yarn is hot-stretched for 60 seconds at 220° C. oven temperature, 11½ lb. cord tension, thereby receiving a net stretch of 18%. This yarn and cord serve as a control, being representative of the best yarn producible by known procedures.

EXAMPLE II

Yarn with filament birefringence of 0.00085 is forwarded from a spinning position at 80 y.p.m. and drawn as in Example I, with the addition of a 6-inch hot drum intermediate the first-stage draw rolls and the hot pipe, the yarn making ½ wrap thereon. The draw pin is at 35° C., the hot drum at 163° C., and the hot pipe at about 190–200° C., the yarn making three helical (60°) wraps thereon. The yarn is drawn 4.1× in the first stage, 1.63× in the second (total draw, 6.7×). The as-drawn yarn has a tenacity of 10.4 g.p.d., elongation of 14.9%, and initial modulus of 51 g.p.d. The yarn is above the "force-to-draw" transistion temperature for about 0.37 second, achieving that temperature prior to encountering the hot pipe. Cord from this yarn is hot-stretched at 240° C. for 60 seconds at 11½ lb. tension, being stretched 23%.

EXAMPLE III

Yarn is spun at 80 y.p.m. and drawn according to Example II. The first-stage draw rolls are heated to 160° C. The first-stage draw ratio is 4.1×, the second 1.71×, a total draw of 7.0×. The yarn remains above the "force-to-draw" transition temperature for about 1.56 seconds; its as-drawn properties are 11.1 g.p.d. tenacity, 12.9% elongation, and 58.5 g.p.d. initial modulus. Cord is hot-stretched at 260° C. for 60 seconds at 9 lb. tension, a net stretch of 31.0%.

EXAMPLE IV

Yarn spun at 80 y.p.m. is drawn according to Example III, excepting that the second-stage draw rolls are maintained at 200° C. Thus, the yarn remains above the "force-to-draw" transition temperature for about 3.84 seconds. This yarn has a tenacity of 10.7 g.p.d., 16.9% elongation, and an initial modulus of 50 g.p.d. Cord is hot-stretched at 250° C. for 60 seconds at 11 lb. tension, a net stretch of 28%.

EXAMPLE V

Yarn spun at 80 y.p.m. is drawn as in Example IV, the first-stage draw rolls being heated to 185° C., the second-stage draw rolls heated to 215° C. This yarn remains above the "force-to-draw" transition temperature for about 3.84 seconds. Yarn properties are 10.5 g.p.d. tenacity, 17.1% elongation, and 48 g.p.d. initial modulus. The cord is hot-stretched at 250° C. for 60 seconds at 11 lb. tension, resulting in a net stretch of 29%.

The properties of the cords from each of the above examples are reported in Table I. In each of Examples II through V the yarn was above the "force-to-draw" temperature for at least 0.01 second in the interval between the first and second stages of drawing and was maintained above that temperature during all subsequent stages of drawing.

Table I

CORD

Example	Tenacity, g.p.d.	Elongation, percent	Relaxed Cold Growth, Percent	24-Hour Disc Fatigue, Percent Tenacity loss
I	10.1	15.2	4.2	13
II	9.9	13.7	3.5	----
III	10.2	12.7	3.2	12
IV	10.0	12.5	3.1	13
V	10.2	12.7	3.0	10

When Example II is repeated, excepting that the yarn remains above the "force-to-draw" transition temperature for only about 0.11 second, the properties of the cord are substantially the same as the cord prepared in Example I, even though the yarn achieved that temperature prior to drawing in the second stage. Similarly, when Example IV or V is repeated, excepting that the yarn remains above the "force-to-draw" transition temperature for 1.76 seconds, achieving that temperature on the hot-pipe (draw rolls run "cold," hot drum omitted), the properties of the stretched cord are somewhat inferior to the Example II cord. These results demonstrate the advantages of both elements of the instant process, namely, that the yarn achieve the "force-to-draw" transition temperature prior to drawing in the second stage, and that it remain above that temperature for at least about 0.25 second.

The results in Table I show that the cords have been stretched to comparable "optimum" properties, especially fatigue resistance, and that the "growth" properties of cords prepared from yarns of this invention (Examples II to V) are substantially improved. Surprisingly, such improvement in growth characteristics is a function of the time above the "force-to-draw" transition temperatures. The cord growth improvement also is striking in view of the concomitant improvement in resistance to "flat spotting" in tires prepared therefrom, and when compared to ordinary commercial nylon tire cords. Present-day commercial nylon cords having "relaxed cold growths" of 5% and 4% produce "flat spots" in tires of 170 mils (measured as departures from strict circularity) and 140 mils, respectively; hence the use of cords from Examples III to V results in the substantial elimination of this defect in nylon tire cords, "flat spots" of less than about 115 mils being found unobjectionable. The over-all balance of properties in these cords is likewise impressive compared to the average properties of cords prepared from commercial nylon yarns which have the following characteristics: tenacity, 8.5 g.p.d.; break elongation, 15.8%; "relaxed cold growth," 4.5%; and 24-hour "disc fatigue," 18% tenacity loss. The yarns of this invention also are exceptional as regards other measures of dimensional stability; for example, the yarn of Example V exhibits a 30% reduction in shrinkage tension at 160° C. and a twenty-fold reduction of shrinkage tension at room temperature on the bobbin as compared to the control yarn of Example I. Finally, each of the yarns prepared hereinabove exhibits the excellent lengthwise birefringence uniformity characteristic of yarns drawn in accordance with Equation 1, the average standard deviation of birefringence uniformity, "$\overline{\sigma_B}$," being less than 1.0×10^{-3} in all cases at the indicated tenacities.

The process of this invention has been illustrated by its application to cords, yarns, or filaments of poly(hexamethylene adipamide) because of the great commercial interest in that polyamide. The process is also applicable to cords, yarns, or filaments of polycaproamide. In fact, the process has utility for linear fiber-forming polyamides generally, such as those polyamides disclosed by Carothers in U.S. Patents 2,071,250; 2,071,253; and 2,130,948. It is preferred to add an antioxidant to the polyamide, such as those disclosed by Stamatoff in U.S. Patents 2,705,227; 2,640,044; and 2,630,421. Other useful additives are disclosed by Gray in U.S. Patent 2,510,777 and Dreyfus in U.S. Patent 2,345,700. It is also within the purview of this invention that the polyamide cord may contain conventional delusterants, pigments, and other additives as required. The "force-to-draw" transition temperature for these polyamides is determined as that temperature at which a discontinuity exists in the relationship of a logarithmic function of the tension required to draw an undrawn filament (as defined hereinafter) versus the reciprocal of the drawing temperature in degrees absolute. While this invention has been illustrated by the drawing of unswollen filaments, the presence of a swelling agent is often beneficial. Suitable swelling agents include water, phenols, alcohols, and the like materials, such as those disclosed in U.S. Patent 2,289,377 to Miles. The application of steam during spinning and/or drawing may likewise be beneficial.

If the yarn is packaged after the first stage of drawing, it is necessary that it be heated above the "force-to-draw" transition temperature prior to packaging, as well as prior to drawing in the second stage from the package, as in accordance with this invention.

Yarns prepared according to this invention are eminently suited for use in tire cords, as already demonstrated, and are similarly useful in ropes, cables, and the like; rubberized, non-rubberized, and V belting used for power transmission or materials handling; tarpaulins, nets, and the like; and in many other applications equally demanding of filament or aggregate strength, especially those applications wherein strength on minimum weight basis is a prerequisite. The filaments of this invention satisfy the requirements for such applications at improved levels of over-all dimensional stability, an area in which known nylon filaments have been found deficient. Their inherent ability to withstand more stringent hot-stretching conditions and especially their greater net stretchability results in substantial savings for the consumer, since each pound of yarn prepared in accordance with the instant invention can be converted into more yarn on a length basis, the yarn having, in addition, such superior properties. The process of this invention makes possible the use of higher draw ratios in the second stage of drawing, without incurring a decrease in operability. Other advantages inherent in the practice of this invention will occur to those undertaking their preparation.

The claimed invention:

1. An improved method of continuous treatment of as-spun birefringent polyamide filaments to develop therein desired levels of tenacity, break elongation, resistance to fatigue combined with low relaxed cold growth, said method comprising a first step of drawing as-spun polyamide filaments, having a birefringence B, so that the ratio R_1 of drawn length to undrawn length is determined by the equation

$$R_1(1+22.2B+284B^2)=4.1\pm1.1$$

while maintaining the filaments at an elevated temperature lying between the second-order transition temperature and the force-to-draw transition temperature of the polyamide filaments, followed by a second step of heating the filaments to an elevated temperature lying between the force-to-draw transition temperature and a temperature at least 20° C. below the melting point of the polyamide filaments for a period of time of at least 1.0 second and then during said period of time, additionally drawing said polyamide filaments an amount sufficient to achieve the property levels of tenacity, break elongation and resistance to fatigue desired.

2. A method of continuous treatment of as-spun birefringent polyamide filaments to produce improved tire cords having desired levels of tenacity, break elongation, resistance to fatigue and great resistance to relaxed cold growth, said method comprising, in combination, the steps of drawing as-spun polyamide filaments having a birefringence value B, to a degree such that the ratio, R_1, of drawn length to undrawn length is determined by the equation

$$R_1(1+22.2B+284B^2)=4.1\pm1.1$$

while maintaining the filaments at a temperature between the second-order transition temperature and the force-to-draw transition temperature of the polyamide filaments, heating the filaments to a temperature between the force-to-draw transition temperature and the melting point of the polyamide filaments for a time interval of at least 0.25 second, and during said time interval initiating a continuous additional drawing step to draw the filaments an amount so that the total drawing of the filaments is at least 5.5×.

3. An improved method for treating as-spun birefringent polyamide filaments to increase the relaxed cold growth characteristics of said filaments and concurrently achieve level of properties suitable for use as tire cords, said method comprising in combination the steps of drawing as-spun polyamide filaments having a birefringence value B, to a degree such that the ratio, R_1, of drawn length to undrawn length is determined by the equation

$$R_1(1+22.2B+284B^2)=4.1\pm1.1$$

while maintaining the filaments at a temperature between the second-order transition temperature and the force-to-draw transition temperature of the filaments, then heating the filaments to a temperature between the force-to-draw transition temperature and the melting point of the filaments for a time interval between 0.25 second and 5.0 seconds, and during said interval additionally drawing the filaments to achieve a total draw of at least 5.5 times the initial undrawn length of the filaments.

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