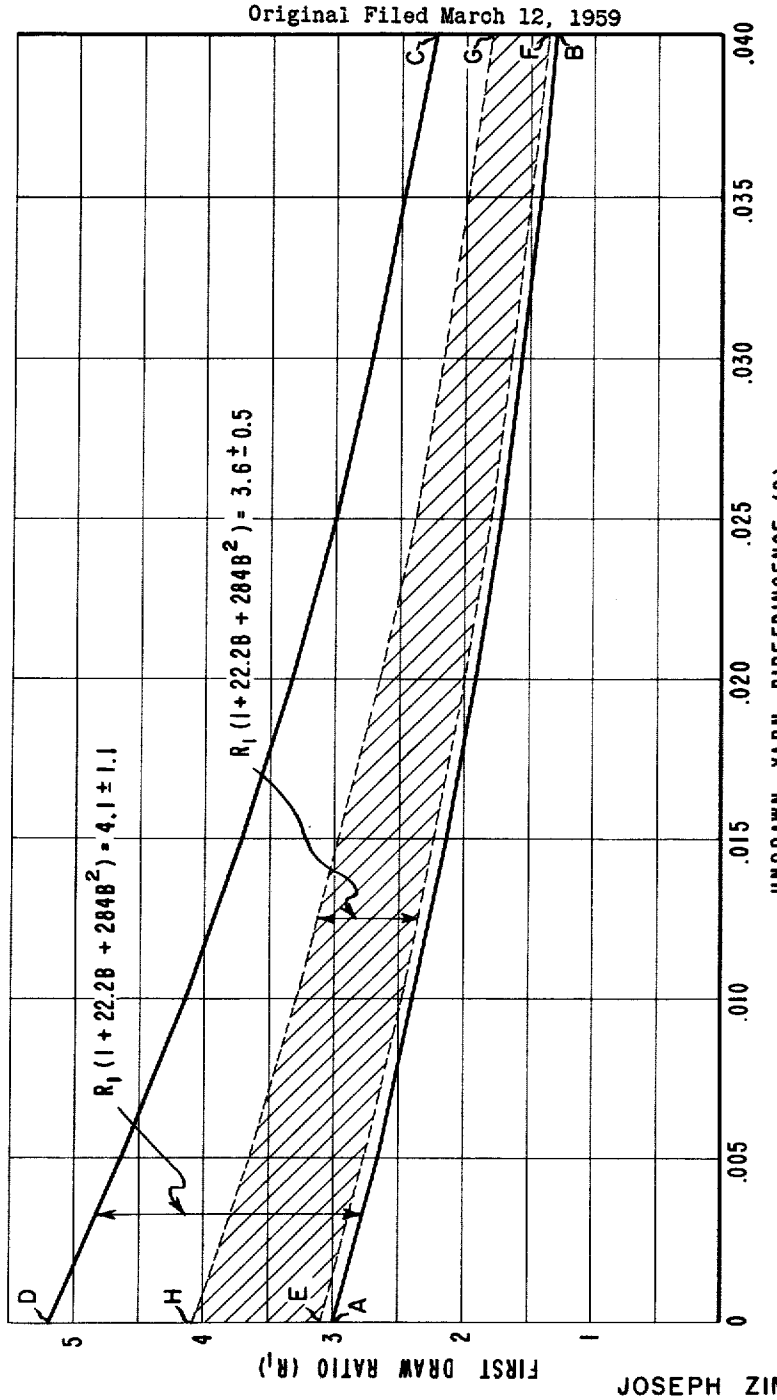
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ORIENTED NYLON FILAMENTS

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# ORIENTED NYLON FILAMENTS

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15 Claims. (Cl. 28—82)

This invention relates to novel polyamide filaments and yarns, the present case being a division of my copending application Serial No. 799,054, filed March 12, 1959, to multistage drawing of nylon filaments to increased length under controlled conditions.

Commercial production of nylon and various other synthetic linear polymeric filaments customarily involves "drawing" the filaments to increased length. Drawing usually produces a more tenacious structure having characteristic X-ray diffraction patterns indicative of internal orientation along the filamentary axis. When carried out below the softening temperature of the filaments, the process often is termed "cold-drawing." Although the desired draw may be imparted in one step or stage or in more than one, any variation in the procedure is likely to give rise to changes and irregularities in properties of the drawn filament. For this reason, multiple-stage drawing, while seeming to afford additional control of product characteristics, is inherently difficult to practice satisfactorily.

An object of the present invention is to provide drawn polyamide filaments and yarns of improved quality. A particular object is to provide filaments of improved quality by a controlled multiple-stage drawing of synthetic linear polyamide filaments. Other objects, together with means and methods for attaining them, will be apparent from the following description.

In accordance with my new process, a polyamide strand (filament, yarn, etc.) is subjected to a multiple-stage drawing operation with the ratio of drawn length to undrawn length (termed herein "draw ratio," and represented by the symbol $R_1$) in the first stage of the drawing operation being governed by the birefringence of the strand immediately prior to drawing. The functional relation is expressed by the equations

$$R_1(1+22.2B+284B^2)=3.6\pm0.5 \quad (1)$$

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

wherein B refers to the "birefringence" which for the present purpose is the absolute difference in refractive indexes along and perpendicular to the axis of a filament in unswollen condition. The term "birefringence" as applied to multifilament yarns or strands herein refers, of course, to the birefringence of the filaments in those yarns or strands.

Equation 1 (area EFGH in the FIGURE) relates undrawn yarn birefringence to the first stage draw ratio where the undrawn yarn is packaged ("lagged") before drawing. Equation 2 (area ABCD in the figure) applies to drawing operations wherein freshly extruded yarn is drawn, such as yarn supplied immediately from spinning. The wider limits of processability permitted with fresh yarn is presently believed due to the reduced level of crystallinity exhibited by such yarn, which is relatively amorphous compared to yarn which has been lagged. The extent of processability defined by each equation is based on operability of the drawing process, expressed in terms of filament breaks. Substantially no broken filaments are encountered during the first stage of a multistage drawing operation carried out according to Equation 1 or 2, and operation in the following second stage



draw is also markedly improved over known drawing processes.

The basis for the relationships (1) and (2) is the discovery that polyamide yarn of improved properties is produced in a multi-stage drawing process when a critical amount of draw is used in the first stage to provide a predetermined amount of molecular orientation, as illustrated in the examples. Some orientation is produced in the spinning process, and is a function of spinning speed, polymer viscosity, quenching conditions, snubbing produced by yarn guides, etc. Such orientation is measured by determining the birefringence in filaments of the spun yarn. In order to achieve the predetermined level of molecular orientation in the yarn product of the first stage drawing, a change in the orientation produced in spinning will require adjustment to a different machine draw ratio in the first stage. The proper adjustment can be calculated if the equation (curve) relating draw ratio and orientation is first determined experimentally. This relation shows increasing orientation as draw ratio is increased. Since, according to the invention, it is necessary to produce a predetermined level of orientation in the drawn yarn of the first stage, the orientation to be introduced by the first stage machine draw ratio will be the difference between this predetermined level of orientation and the orientation produced in the spinning step. This difference is given mathematically by Equations 1 and 2, and is shown graphically in the FIGURE for the range of birefringence which may be practically achieved in spun yarn.

Although the best yarn will usually be obtained when using the first stage draw ratio calculated from the appropriate Equation 1 or 2 by ignoring the plus or minus limits of $\pm0.5$ and $\pm1.1$, respectively, good quality yarn will be obtained at draw ratios within these limits, i.e., the areas indicated in the drawing. This yarn is structurally distinct from prior art yarns, as explained hereinafter.

In the areas defined by Equations 1 and 2 a novel and highly useful drawn yarn is produced. This product is characterized not only by unusually attractive mechanical properties (high tenacity, high modulus, high work-to-break), but more significantly by its structural uniformity, evidenced by improved birefringence uniformity along the length of the individual filaments of the yarn. Such improvement is several fold over the best prior art yarns. It is this structure uniformity which characterizes the product produced by the process of this invention. The limits of the equations defining the first stage draw ratio for freshly-spun and prepackaged yarn are established so as to enclose those areas of the FIGURE in which the standard deviation of the birefringence of the drawn yarn (as measured below) is equal to or less than the quantity $5/2(T-3)\times10^{-4}$, where T is the yarn tenacity in grams per denier. The birefringence profile of a drawn yarn is determined by measuring the birefringence at 1 millimeter intervals for representative 5 centimeter length samples taken from a plurality of yarn filaments from the same yarn bundle. Birefringence uniformity of the yarn is then expressed as the average of the standard deviations (hereinafter symbolized "$\bar{\sigma}_B$" for each of the individual filament samples, the term "standard deviation" having its usual statistical significance.

By the practice of my new process, i.e., by drawing in accordance with Equations 1 or 2, whichever is applicable, there is produced a novel class of yarns having tenacities of at least 5.5 grams per denier which at any given level of tenacity exhibit substantially improved infrafilament birefringence uniformity, as compared with nylon yarns known heretofore. Such unique yarns are characterized by having values of $\bar{\sigma}_B$ determined as defined above,

which are no greater than values given by the formula

$$5/2(T-3)\times10^{-4} \quad (3)$$

where T is at least 5.5 and is the tenacity of the yarn bundle, expressed as an absolute number and measured in conventional manner on a gram/denier basis. Formula 3 gives the maximum value of $\bar{\sigma}_B$ for yarn drawn in accordance with the instant invention to a tenacity of 5.5 or greater. Within the family of yarns defined by Formula 3, certain species stand out as especially useful. Yarns having a tenacity T of at least about 5.5 grams per denier and an average standard birefringence deviation $\bar{\sigma}_B$ less than $6\times10^{-4}$ are useful in textile applications. Yarns having a tenacity T of at least about 7 grams per denier and an average standard birefringence deviation $\bar{\sigma}_B$ less than $1.0\times10^{-3}$ are useful in many of the less-demanding industrial applications. Yarns having a tenacity T of at least about 9 grams per denier and an average standard birefringence deviation $\bar{\sigma}_B$ less than $1.5\times10^{-3}$ are useful in industrial applications, such as in power transmission belting. Particularly preferred yarns are those having a tenacity T of at least about 10 grams per denier and an average standard birefringence deviation $\bar{\sigma}_B$ less than $1.0\times10^{-3}$; such yarns are useful in applications demanding the utmost in resistance to fatigue, such as encountered in most industrial applications, and, particularly, in tire cords. The yarns of this invention may be composed of fiber-forming polyamides generally, especially polyhexamethylene adipamide or polycaproamide.

The concept of controlling a first draw ratio in multi-stage drawing of nylon in accordance with the birefringence of the undrawn yarn is clearly expressed in U.S. application Serial No. 519,227 (filed June 30, 1955), and now abandoned; in U.S. application Serial No. 585,742 (filed May 18, 1956), and now abandoned; and in U.S. application Serial No. 683,558 (filed September 12, 1957), and now abandoned, of all of which this application is a continuation-in-part. One equation set forth in the latter applications is

$$\log_{10}\left(\frac{2.1}{R_1-2.0}\right)=50B \quad (4)$$

where $R_1$ and B have the same significance as set forth hereinabove. This relationship is substantially entirely contained in Equations 1 and 2 above.

By the expression "first stage of drawing" is meant generally that drawing which occurs below the so-called force-to-draw transition temperature but above the second order transition temperature, both defined hereinafter. Otherwise, starting with an undrawn yarn, the stages of drawing are differentiated by the rather abrupt increase in slope of the drawing tension versus draw ratio relationship, which change occurs near the end of the first stage of drawing. The quantity $R_1$ refers to the first stage draw ratio and is conveniently measured by determining the relative peripheral speeds of the feed and draw rolls, provided there in substantially no slippage of the yarn thereon. Such slippage is readily prevented by customary means known to the art, such as by means of pinch rolls, multiple wraps, or the like. It should also be recognized that the draw ratio as defined hereinabove refers to the rato of drawn length to undrawn length of yarn in process; if such measurement is made (e.g., by a denier determination) at a later time on yarn samples which have been left free to retract, erroneous results may be obtained. To avoid this error, it is necessary to make correction for the slow retraction known to occur in polyamides which have been stretched beyond their elastic limit.

As is usual in drawing operations, all drawing here should be carried out below the softening temperature of the polymer, it usually being desirable not to employ any drawing temperature higher than about twenty degrees centigrade below the melting temperature, but not



below what is known generally as the "second-order transition" temperature, at which a discontinuity exists in relationship of first-derivative thermodynamic properties versus temperature (v. "Advances in Colloid Science" by Boyer and Spencer, vol. 2, published in 1946 by Interscience). Also, for best results in the practice of the present invention, the following additional temperature precautions will be observed. The temperature at which the critical first-stage drawing is conducted should be below, and that of the subsequent stage or stages above, what is denoted herein as the "force-to-draw transition" temperature, at which a discontinuity exists in the relationship of a logarithmic function of the tension required to draw an undrawn filament to certain extent under certain conditions versus the reciprocal of the drawing temperature expressed in degrees on an absolute temperature scale.

Any suitable apparatus may be used in practicing this invention. Drawing usually is localized at a snubbing surface, such as a pin or plate about or over which the filaments pass, as shown in Patent 2,533,013 by Hume, who also discloses there an arrangement for two-stage drawing that can be used satisfactorily in the practice of this invention, provided there is maintained sufficient control over the extent of drawing which takes place in each stage. Ordinarily, drawing below the force-to-draw transition temperature, i.e., in the first stage of drawing, is effected with snubbing pins (U.S. Patent No. 2,289,232 to Babcock) whereas drawing above the force-to-draw transition temperature, i.e., in the second stage of drawing, is accomplished by using heated pipes, plates, cylinders, etc. Moreover, each stage of drawing usually is separated by draw rolls or the like, in order to maintain control and uniformity in the individual stages of drawing, although in certain applications the need for such means can be obviated. Of course, amount of draw in any stage may be determined readily by comparing the relative rates of movement of filaments leaving and entering the drawing zone.

For each of two of the commercially most important fiber-forming polyamides, polyhexamethylene adipamide and polycaproamide, the second-order transition temperature is about 50° C. and the force-to-draw transition temperature is in the vicinity of 150° C., being about 155° C. for polyhexamethylene adipamide; the melting temperature is about 265° C. for polyhexamethylene adipamide and about 215° C. for polycaproamide. At about the force-to-draw transition temperature, polyhexamethylene adipamide undergoes a reversible transition from hexagonal (above) to triclinic (below) crystallinity. Determination of the force-to-draw transition temperature is accomplished conveniently upon filaments freshly produced at 275 yards per minute and forwarded from the spinning windup package at 2½ yards per minute to and about a hot steel snubbing pin one inch in diameter with chrome-plated matte finish and drawn thereby to 4½ times the original length (i.e., a 4.5× draw).

Of course, this invention is applicable to filaments and similar strands composed of synthetic linear polyamides generally; it is exemplified below in illustrative detail using, unless otherwise indicated, polyhexamethylene adipamide of 55 relative viscosity (e.g., prepared by the method of Spanagel, U.S. 2,163,636) formed in conventional manner (e.g., using the apparatus of Greenewalt, U.S. Patent No. 2,217,743) into a 140-filament yarn of about 4800 total denier. All physical testing is done on yarn which has been stored for at least 48 hours at 55% relative humidity and 75° F.

Tenacity is measured in a constant rate of extension machine (Instron Tensile Tester) in accordance with ASTM specifications (Ref. ASTM standards on Textile Materials, prepared by ASTM Committee D–13 on Textile Materials, pages 42–46, 523–526, November, 1956). Industrial yarns are preconditioned at 55% relative humidity, 25° C. A 10-inch sample is extended at a

rate of 60% per minute. In general, a twist of 1–3 turns per inch is used to obtain clean breaks. Textile yarns are conditioned at 72% relative humidity; otherwise, the procedure is the same. Tenacity is expressed in units of grams/denier.

In all examples, not otherwise indicated, yarn is led directly from the usual spinning feed roll to pass about a heated ½-inch snubbing pin (one 360° wrap), to a set of rolls for controlling the amount of drawing in the first stage; the yarn then went directly to and over a relatively long heated surface (3 wraps at a 60° helix angle about a pipe 1 inch in diameter and 30 inches long), thence to another set of rolls for controlling the amount of drawing in this second stage, and finally to a windup. Birefringence was determined throughout from observation of representative filaments between crossed plane-polarizing elements (e.g., Nicol prisms) using a Soleil Compensator for accuracy; the method is treated in detail by Heyn in Textile Research Journal 22, 513 (1952).

## EXAMPLE I

Freshly formed multifilament nylon having a birefringence of 0.004 is advanced at 380 yards per minute to the first drawing stage. The pin temperature is 75° C., and the draw ratio in the first stage is 3.3. The temperature of the drawing surface in the second stage is 190° C., and the draw ratio is 1.77, giving a total draw of 5.84×. Breakage frequency during drawing is 0.05 per pound, and the drawn yarn has a tenacity of 9.3 grams per denier (g.p.d.), elongation of 17.3%, and initial tensile modulus of 43 g.p.d. Birefringence measurements are given in Example VI.

## EXAMPLE II

Freshly formed nylon yarn having a birefringence of 0.0025 is advanced at 275 yards per minute to the first drawing stage. The pin temperature is 75° C., and the draw ratio in the first stage is 3.6. The yarn is fed then to the second stage, in which temperature is 230° C. and the draw ratio is 1.7, giving a total draw of about 6×. Breakage frequency during drawing is 0.10 per pound, and the drawn yarn has a tenacity of 9.0 g.p.d. elongation of 16.3%, and initial modulus of 42 g.p.d.

By proper selection of processing conditions, including yarn characteristics and drawing speed and temperature, a two-stage drawing process may be conducted satisfactorily without controlling rolls intervening between the stages. The following example illustrates this practice, the apparatus employed being otherwise the same as that of the above examples.

## EXAMPLE III

A freshly formed multifilament nylon having a birefringence of 0.004 is advanced at 380 yards per minute to the first drawing stage. The pin temperature is carefully maintained at 100° C., and the draw ratio in the first stage is 3.4. The temperature of the drawing surface in the second stage is 180° C., and the yarn makes only two helical wraps about the drawing element; the draw ratio is 1.68, giving a total draw of 5.7×. The drawn yarn has a tenacity of 9.3 g.p.d., elongation of 16.0%, and initial modulus of 42 g.p.d.

## EXAMPLE IV

Freshly formed multifilament nylon yarn having a birefringence of 0.006 is advanced at 440 yards per minute to the first drawing stage. The pin temperature is 120° C., and the draw ratio in the first stage is 3.05. The yarn is then fed by draw rolls to the second stage, where the temperature is 175° C., and the draw ratio is 1.85 giving a total draw of 5.65×. Breakage frequency during drawing is 0.7 break per 100 lbs. of yarn, and the drawn yarn has a tenacity of 9.5 g.p.d., elongation of 15.2%, and an initial modulus of 52.3 g.p.d. Birefringence measurements are given in Example VI.



## EXAMPLE V

Freshly formed nylon multifilament yarn having a birefringence of 0.011 is advanced at 700 yards per minute to the first drawing stage. The pin temperature is 130° C., and the draw ratio in the first stage is 2.7. The yarn is then fed to the second stage where it passes in three wraps around the heated tube which has a temperature of about 185° C. The draw ratio in this stage is 1.9, making a total draw of 5.2×. No broken filaments are observed at the first draw surface. The drawn yarn has a tenacity of 9.0 g.p.d., an elongation of 16.0, and an initial modulus of 47.7 g.p.d.

When the first draw ratio is reduced to 2.2, retaining the same total draw of 5.2×, many broken filaments occur in the second drawing stage, forming wraps on the rolls and ultimately breaking down the threadline. The tenacity of the yarn drawn under these conditions is substantially lower than the 9.0 g.p.d. obtained when following the teachings of this invention.

In Examples VI to XI the nylon is poly(hexamethylene adipamide) of 65 relative viscosity.

## EXAMPLE VI

Freshly formed multifilament nylon having a birefringence of 0.0035 is advanced at 340 y.p.m. to the first drawing stage. The pin temperature is 50° C. and the draw ratio in the first stage is 3.4. The temperature of the drawing surface in the second stage is 195° C. and the draw ratio is 1.74, giving a total draw of 5.83×. The break frequency during drawing is negligible, 3 broken filaments per minute being observed on the draw roll. The drawn yarn has a tenacity of 9.3 g.p.d., elongation of 16.4%, and initial tensile modulus of 60 g.p.d.

Samples of this yarn are allowed to relax free for 48 hours at 55% relative humidity at 20° C. A load of 0.85 gram is then applied to each filament in order to maintain it in an extended position. Representative 5 centimeter lengths are sampled, and the birefringence is determined at intervals of 1 millimeter. Independent measurements of filament diameter are made at right angles to the path of light transission in each of the retardation measurements in order to avoid errors due to out-of-round filaments. The 51 readings for each sample are averaged, and the average birefringence of these filaments along with the average standard deviation ($\bar{\sigma}_B$) are reported. The average birefringence of the above-exemplified yarn is 0.0625, and $\bar{\sigma}_B$ is $5.30\times10^{-4}$. The above measurements on the drawn yarn of Example I give an average birefringence of 0.0625, and $\bar{\sigma}_B$ is $5.5\times10^{-4}$. When this technique is applied to the drawn yarn of Example IV, an average birefringence of 0.0612 results, with $\bar{\sigma}_B$ of $5.76\times10^{-4}$.

## EXAMPLE VII

Freshly formed multifilament nylon yarn having a birefringence of 0.0066 is advanced at 440 y.p.m. to the first drawing stage. The pin temperature is 110° C., and the draw ratio in the first stage is 3.2. The yarn is then immediately fed to a second stage where the temperature is 185° C., and the draw ratio is 1.77, giving a total draw of 5.65×. Breakage frequency during drawing is 0.02 break per pound of yarn, and the drawn yarn has a tenacity of 9.2 g.p.d., elongation of 14.6%, and an initial modulus of 64 g.p.d. The average birefringence of this yarn is 0.0612, and $\bar{\sigma}_B$ is $5.76\times10^{-4}$.

## EXAMPLE VIII

Freshly formed multifilament nylon yarn having a birefringence of 0.0035 is advanced at 340 y.p.m. to the first drawing stage. The pin temperature is 55° C., and the draw ratio is 4.1. In the second stage, the yarn is passed (1 wrap) over a 6-inch drum maintained at 162° C., then passes in three 60° wraps over a 3½ inch pipe

maintained at 180–200° C. The draw ratio in this stage is 1.53×, resulting in a total draw of 6.25×. Breakage frequency during drawing is 0.012 break per pound, and the drawing yarn has a tenacity of 10.8 g.p.d., elongation of 14.8%, and initial tensile modulus of 70 g.p.d. The average birefringence of this yarn is 0.0629; $\bar{\sigma}_B$ is $4.28\times10^{-4}$. Substantially the same results are obtained when the first stage draw pin is replaced by tandem pins of the same construction and run at about the same temperature. The yarn takes ½ wrap (ca. 180°) about each pin in this system. When the yarn of this example is processed under conditions similar to the above, with the exception that the first stage draw ratio is increased to 4.5 at the same total draw ratio, operability remains good, and a uniform yarn is produced. This process is repeated except that the first stage draw ratio is 5.1, outside the area defined by Equation 2. In the second stage, a draw ratio of 1.18× is used to give a total draw of 6.05×. There are many broken filaments in this sample, and the tenacity of the yarn is 9.9 g.p.d. with an elongation of 14.8%, and an initial modulus of 64. The average birefringence of this yarn is 0.0631 and the average standard deviation of the birefringence ($\bar{\sigma}_B$) obtained from the birefringence profile measurements is $2.2\times10^{-3}$, which is outside the relationship of Equation 3.

## EXAMPLE IX

Freshly formed multifilament nylon yarn having a birefringence of 0.0008 is advanced at 80 y.p.m. to the first drawing stage. The pin temperature is 85° C., and the draw ratio in the first stage is 5.1. The temperature of the drawing surface in the second stage is 198° C., and the draw ratio is 1.3, giving a total draw of 6.6×. The break frequency during drawing is practically negligible, and the birefringence uniformity of the yarn is excellent.

## EXAMPLE X

As a comparison with the results in the above examples, the following table gives results obtained in a two-stage drawing operation performed upon the undrawn yarn of Example VI, supplied to the first stage of drawing at a rate of 340 y.p.m. Drawing is carried out using the apparatus described in Example VIII. These results show over-all drawing operability, expressed in terms of broken filaments per minute in the second stage of drawing at constant total draw ratio, for varying first stage draw ratios. These results further reflect the significance of Equation 2 and the improvement in operability resulting from drawing according to the present invention.

*Table*

| First Stage Draw Ratio $R_1$ | Total Draw Ratio | Breaks per minute |
|---|---|---|
| 2.6 | 6.0 | 23.0 |
| 3.4 | 6.0 | 4.7 |
| 4.1 | 6.0 | 0.7 |

The drawing process of this invention need not be carried out in two immediately successive stages; a similar result may be obtained in following the controlled first stage draw at a later time by one or more additional drawing stages. The following example illustrates this practice.

## EXAMPLE XI

Freshly formed multifilament nylon having a birefringence of 0.004 is advanced at 340 y.p.m. to the first drawing stage. The pin temperature is 55° C., and the draw ratio is 4.1×. The yarn is passed one wrap over a 6-inch pin maintained at 163° C. without further drawing. This yarn is packaged. The partially drawn packaged yarn is then fed at 340 y.p.m. over a 6-inch pin maintained at 167° C. to a hot pipe whose temperature is 205° C. for second stage drawing. The draw ratio in the second stage is 1.59×, giving a total draw of 6.5×. Breakage frequency during drawing in the second stage is 0.02 break per pound, and the drawing yarn has a tenacity of 10.0 g.p.d. and an elongation of 13.2% and an initial modulus of 67 g.p.d. The average birefringence of the drawn yarn is 0.0644, and $\bar{\sigma}_B$ is $7.06\times10^{-4}$. The above-illustrated method (Example XI) is general, requiring only that the yarn be heated to a temperature above the force-to-draw transition temperature after drawing in the first stage, prior to interstage packaging. It is most useful with polyhexamethylene adipamide, taking advantage of the reversible crystalline transition which occurs at about the force-to-draw transition temperature. Upon second stage drawing, the yarn is first heated over a hot pin, plate, or the like prior to such drawing to reachieve the desired hexagonal crystalline modification. This method is highly advantageous in that it permits all of the advantages of a coupled spinning and drawing operation without necessitating the high windup speeds sometimes required when both stages of drawing are carried out in immediate sequence.

It is sometimes desirable to carry out the drawing as an operation completely separate from spinning, the yarn having been wound up ("lagged") in the meantime. The following examples illustrate this practice.

## EXAMPLE XII

Polyhexamethylene adipamide of 55 relative viscosity is spun in conventional manner at 400 yards per minute (y.p.m.) to produce an 1180 denier yarn containing 34 filaments and exhibiting a birefringence of 0.004. Upon being withdrawn from the spinning windup package, the yarn is led over an "Alsimag" snubbing pin 3/16 inch in diameter heated to a temperature of 55° C. by contact with the yarn, whereupon the yarn is drawn 3.5×. Then the yarn is passed in one wrap about a ¾-inch polished steel tube 10 inches long heated to a temperature of 160° C., whereupon the yarn is drawn an additional 1.6×. Wound up on a package at 200 y.p.m., the yarn has a tenacity of 8.9 g.p.d., elongation of 14.0%, and an initial modulus of 51 g.p.d. Operability of this process is good, giving only 20 breaks per 100 pounds and draw roll wraps for less than 15% of the total operation.

## EXAMPLE XIII

Polyhexamethylene adipamide is spun in conventional manner at 1200 yards per minute to produce a 230 denier yarn containing thirty-four filaments having a birefringence of 0.018. The package of spun yarn is transferred from the spinning machine to a drawing machine, where the yarn is led over an "Alsimag" snubbing pin 3/16 inch in diameter heated to a temperature of 55° C. by contact with the yarn, whereupon the yarn is drawn to 2.3 times its original length. An intermediate set of tensioning rolls forwards the yarn to a ¾ inch heated steel tube about which it passes in a 180° wrap. The steel tube is heated to a surface temperature of 180° C. The yarn is thus drawn an additional 1.38×, for a total draw of 3.17×. Wound on a package at 440 y.p.m., the yarn has a tenacity of 5.3 g.p.d., elongation of 26%, and an initial modulus of 42 g.p.d. The operability of the process is good, since draw roll wraps occurred for less than 3% of the total operation.

When the process is repeated, the only exception being that the first draw is 3.0, so many broken filaments result so that there are wraps upon the draw roll for 79% of the time.

## EXAMPLE XIV

Polycaproamide of 50 relative viscosity (relative viscosity as defined in U.S. 2,385,890) is spun into 1000 denier 74 filament yarn and is wound up at a speed

of 350 y.p.m. The spun yarn has a birefringence of 0.006. The spinning package of yarn is transferred to a draw machine substantially as in Example XII, where it is drawn over an "Alsimag" snubbing pin heated to 80° C. The draw ratio in this first stage is 3.2. An intermediate set of tensioning rolls forwards the yarn to a ¾-inch heated steel tube about which it passes in a 180° wrap. The steel tube is heated to a surface temperature of 190° C. The yarn is thereby drawn an additional 1.8×, for a total draw of 5.7×, and is wound up at a speed of 83 y.p.m. The drawn yarn has a tenacity of 9.5 g.p.d., an elongation of 15%, and an initial modulus of 40 g.p.d. The operability of the process is good, with a satisfactory freedom from filament wraps upon the yarn forwarding rolls.

## EXAMPLE XV

A copolymer of polyhexamethylene adipamide and polyhexamethylene terephthalamide in the proportions of 70 parts to 30 parts (by weight), respectively, is spun to a yarn containing 140 filaments. The yarn has a relative viscosity of 47.8 and a spun denier of 4300 and a birefringence of 0.015. The yarn is forwarded to a drawing stage as in Example I at a rate of 440 y.p.m., where it is drawn 2.6×. The pin over which it is drawn has a surface temperature of 110° C. The yarn is then forwarded to a second drawing stage where it is given a 1.9× draw while it wraps five times around a 1¼ inch pipe heated to a surface temperature of 170° C. The total draw ratio is 5.05. The drawing process has acceptable operability, and the drawn yarn has a tenacity of 6.8 g.p.d., an elongation of 13.6%, and an initial modulus of 52.5 g.p.d.

## EXAMPLE XVI

Packaged multifilament nylon yarn having a birefringence of 0.0045 is advanced at 242 y.p.m. to the first drawing stage. The pin temperature is 155° C., and the draw ratio in the first stage is 3.3×. The yarn is then fed to the second stage in which the temperature is 205° C., and the draw ratio is 1.59×, giving a total draw of 5.24×. Breakage frequency during drawing is less than 0.02 break per pound, and the drawn yarn has a tenacity of 8.7 g.p.d., an elongation of 17%, and initial modulus of 50 g.p.d. The average birefringence of this yarn is 0.0631 and the average standard deviation of the birefringence ($\bar{\sigma}_B$) obtained from birefringence profile measurements is $7.41\times10^{-4}$. When $R_1$ is 3.0, and the total draw ratio and processing conditions the same as above, the average birefringence of the drawn yarn is 0.0644, and $\bar{\sigma}_B$ is $1.3\times10^{-3}$. In another run, $R_1$ is increased to 4.5, all other conditions remaining the same, the average birefringence of the drawn yarn is 0.0618, $\bar{\sigma}_B$ increasing to $3.6\times10^{-3}$. This latter run is outside the area of Equation 1.

## EXAMPLE XVII

The following example is representative of a typical prior art drawing process which is outside the area (EFGH of FIGURE 1) of Equation 1. In this process, spun yarn with a birefringence of 0.0045 is drawn from a package at 242 y.p.m. over a 160° pin to a draw ratio of 4.9×. The yarn is then fed directly to a hot plate maintained at 185° C. where it is drawn 1.07× for a total draw of 5.24×. There is no mechanical separation of the first and second stages of drawing of this process. This yarn has an average birefringence of 0.0632 to 0.0641, and $\bar{\sigma}_B$ ranging from 2.3 to $2.4\times10^{-3}$.

The advantages of practicing the present invention include not only substantially decreased interruption (due to yarn breakage) in the processing of continuous nylon filaments, but also higher and more uniform quality characteristics in the drawn product; namely, a uniform birefringence profile. The invention has been illustrated by the drawing of unswollen filamentary structures; presence of a swelling agent permits lowering of the optimum temperature for the drawing steps by about 5 to 20 degrees. Suitable swelling agents include not only water, but also phenols and alcohols and like materials, such as those disclosed by Miles in Patent 2,289,377.

In the normal practice of this invention, the optimum first stage drawing temperature will vary with the rate at which the yarn enters the drawing zone. In general, the lower the feeding speed, the closer the drawing temperature should be to the second-order transition temperature. In particular, it is preferable to select a first stage drawing temperature exceeding the transition temperature by from about 2 to 10 degrees for each hundred yards per minute of yarn feeding speed into the drawing zone. Of course, the shape of the drawing element may also affect the optimum drawing temperature, and a gradient of temperature may exist on the drawing element, in which case the temperature maximum at the region of maximum tension in the yarn will be the selected first stage drawing temperature. When drawing above the force-to-draw transition temperature, i.e., during the second stage of drawing, the drawing element should be such that snubbing is delocalized, as is accomplished when a heated pipe or plate is employed. When the two or more stages of drawing are not mechanically separated (e.g., Example III), careful control must be imposed on the system in order to establish and maintain the desired draw ratio in each stage of drawing. Important factors which control drawing in such systems include the rate of drawing, the relative temperatures of each drawing element, the geometry and surface friction characteristics of the drawing elements, their separation distance along the yarn path, the degree of snubbing and yarn contact time on each element, and the like. Often it is advantageous to effect either or both stages of drawing in a stepwise fashion. This can be accomplished in the first stage by using tandem pins (e.g., Example VIII) and, in the second stage (e.g. Example VIII), by using a combination of the larger drawing elements. When using tandem pins, the relative pin temperatures determine the extent of drawing which occurs on each element, all other factors being the same. Further, the closer are the drawing elements along the yarn path, the lower the temperature needed at the downstream element to accomplish desired results. For a given drawing surface, e.g., Alsimag, matte chrome, etc., there exists a minimum friction in the temperature vs. coefficient-of-friction plot, at about which point drawing operability on that element is optimum. The many other relationships concerning drawing elements are deducible through routine experimentation. Many variations may be made in the drawing conditions in conformity with the above discussion without sacrificing the benefits of the present invention.

Extension of the useful range of this invention may be achieved by increasing the as-spun yarn uniformity, both dimensionally and structurally. Such uniformity is accomplished using high quality polymer, higher spinning pack temperature, in order that the temperature gradient which usually exists across the spinneret face is minimized, and by optimizing polymer flow in the distribution space, quenching, and finish application to the individual yarn filaments. Uniform as-spun yarn is characterized by denier and cross section uniformity, low and uniform spherulite content, interfilament birefringence uniformity, and the like.

The process of this invention pemits the production of drawn nylon yarns having properties not heretofore attainable. The nylon yarn products of this invention having a tensile strength of greater than 7 grams per denier and a birefringence average standard deviation of less than $1.0\times10^{-3}$ is particularly useful in all nylon yarn applications calling for high fatigue resistance, in which respect known nylon yarns have been found wanting. The nylon yarn products having a tenacity of at

least 10 and a birefringence average standard deviation of less than $1.0\times10^{-3}$ exhibit at least a two-fold improvement over known nylon yarns in fatigue resistance as measured by a conventional disc fatigue test. Those nylon yarn products having a birefringence average standard deviation of less than $6\times10^{-4}$ are very exceptional in this respect, and in addition, are characterized by particularly uniform dyeing characteristics. The latter yarns are substantially superior to known nylon yarns even at low tensile strengths.

Exemplary polyamides useful for preparing the novel yarns of this invention include those linear polyamides disclosed in U.S. 2,071,251; U.S. 2,071,253; and U.S. 2,130,948.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. A polyamide strand having a tenacity of at least 5.5 grams per denier and a birefringence average standard deviation of less than $5/2(T-3)\times10^{-4}$ where T is the tenacity of the strand in grams per denier.

2. The product of claim 1 in which the polyamide is polyhexamethylene adipamide.

3. The product of claim 1 in which the polyamide is polycaproamide.

4. A polyamide strand having a tenacity of at least 5.5 grams per denier and a birefringence average standand deviation of less than $6\times10^{-4}$.

5. The product of claim 4 in which the polyamide is polyhexamethylene adipamide.

6. The product of claim 4 in which the polyamide is polycaproamide.

7. A polyamide strand having a tenacity of at least 7 grams per denier and a birefringence average standard deviation of less than about $1.0\times10^{-3}$.

8. The product of claim 7 in which the polyamide is polyhexamethylene adipamide.

9. The product of claim 7 in which the polyamide is polycaproamide.

10. A polyamide strand having a tenacity of at least 9 grams per denier and a birefringence average standard deviation less than about $1.5\times10^{-3}$.

11. The product of claim 10 in which the polyamide is polyhexamethylene adipamide.

12. The product of claim 10 in which the polyamide is polycaproamide.

13. A polyamide strand having a tenacity of at least 10 grams per denier and a birefringence average standard deviation less than about $1.0\times10^{-3}$.

14. The product of claim 13 in which the polyamide is polyhexamethylene adipamide.

15. The product of claim 13 in which the polyamide is polycaproamide.

**References Cited** in the file of this patent

UNITED STATES PATENTS

2,533,013 Hume ---------- Dec. 5, 1950