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3,117,173

PROCESS OF PREPARING SUBSTANTIALLY ORIENTED FILAMENTS
HAVING CIRCUMFERENTIAL RIDGES ON THE SURFACE

Filed March 19, 1962

2 Sheets-Sheet 1

FIG. 1a



FIG. 1b



FIG. 1c



FIG. 1d

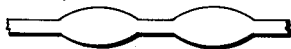


FIG. 2

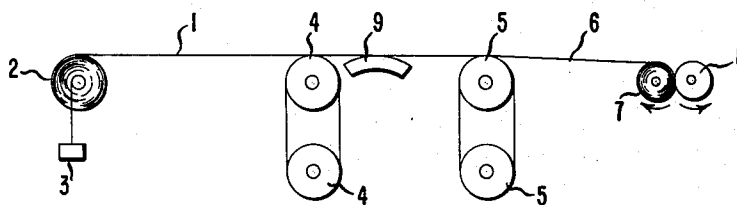
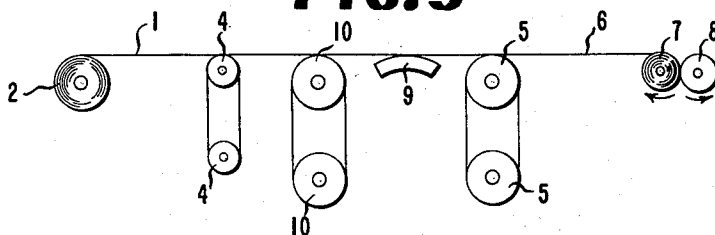


FIG. 3



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2 Sheets-Sheet 2

FIG. 4

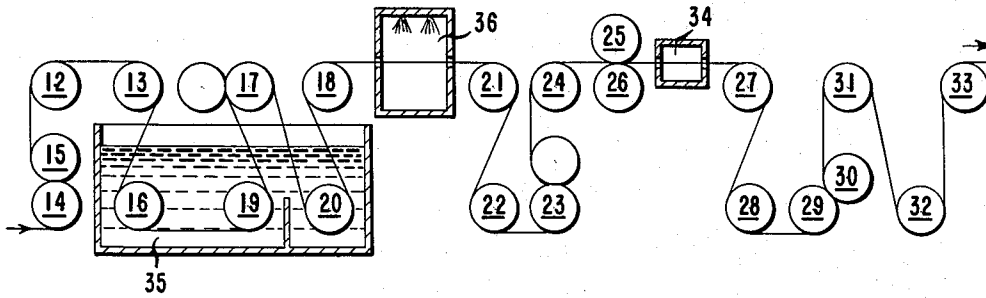


FIG. 5



FIG. 6



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16 Claims. (Cl. 264-210)

This application is a continuation-in-part of my copending application S.N. 828,839, filed July 22, 1959, and now abandoned.

This invention relates to the production of new filaments and fibers and, more specifically, to processes for producing synthetic organic polymer filaments and fibers of fluctuating diameter.

It is well known, in the utilization of synthetic organic polymers for the preparation of fibers and filaments, to introduce non-uniformities of diameter or denier at intervals along the length of a filament. Products prepared in this way can be made into fabrics for textile and other uses with a pleasing hand and with attractive surface variations in appearance. Such fibers duplicate or parallel natural fibers which have a slub content such as, for example, linen and douppioni silk. One process by which nubby yarns have been made is to introduce variations in the feed rate at which the polymeric material is supplied during filament formation. The variation can be regular or random in nature, and for many purposes it is desirable that the variations be random. A great deal of ingenuity has been expressed in the prior art, in the employment of various mechanical or electronic devices giving a truly random or non-uniform distribution of feed variations. Frequently, variations are introduced by altering the speed of operation of a spinning pump of some type.

Another way in which non-uniformities of yarn diameter have been obtained is by taking advantage of the characteristic of synthetic organic polymers known as cold-drawability. Synthetic fibers in general are improved in strength, durability, and dimensional stability by orienting the molecules which constitute the fiber by cold-drawing them; that is, by elongating the fiber after its formation in an irreversible manner, generally to approximately 2 to 6 times its original length. If the drawing process is applied to a fiber or filament in a sporadic or non-uniform fashion, variations in yarn diameter will be achieved because not all of the length of the filament is drawn by the same amount. Thus, it is possible to obtain fibers and filaments of non-uniform diameter in which the sections of greater diameter are substantially undrawn and unoriented or at most partially drawn and partially oriented. There are, in addition, other ways in which it is possible to introduce variation in fiber diameter into a fiber or filament from a synthetic organic polymer. For example, it is known to include at intervals along a filament threadline quantities of an inert filler material, such as sand or the like, which will not decrease in diameter during the drawing process, and, if the grain size of such materials is properly controlled, substantial fluctuations in fiber diameter can be achieved, or to add to a uniform threadline a nonuniform surface coating of some adherent material.

It is characteristic of the products obtained from any of the processes described above, which depend upon feed variations in the polymer supply, that the fluctuations are substantially rather widely spaced. In general, the repeat distance of such fluctuations may be measured in inches. Any attempts to introduce extremely short-range variations in feed supply during filament formation re-

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sults in a flowing together of the adjacent portions of polymeric material, so that if variations of, for example, $\frac{1}{4}$ " separation are desired, the polymer supply, either in the form of molten polymer or a solution of the polymer, tends to equalize itself and no substantial fluctuations are obtained. Higher frequencies of diameter fluctuation can indeed be achieved by leaving portions of a fiber undrawn at close intervals, but such a fiber or filament has disadvantages because of an inherent tendency of the fiber to draw and thereby lose its dimensional stability at later times. One of the other methods mentioned above, the inclusion of quantities of inert material in particle size large enough to influence the fiber diameter, results in weakening of the fiber structure and breakage of the fiber or filament at the point of increased diameter is apt to occur. Non-uniform surface coatings generally cause a tendency to snag if they are permanent, while otherwise they are apt to rub off during processing. For similar reasons, asymmetrical fluctuations in fiber diameter are undesirable.

An object of the present invention is to provide new filaments and fibers of synthetic organic polymers with improved surface optical and tactile properties. Another object is to provide synthetic fibers and filaments with high frequency symmetrical fluctuations in filament diameter, providing thereby improved optical effects, better mechanical behavior, improved hand, texture, texturizing and breaking characteristics, and other product advantages. It is a further object to provide synthetic fibers and filaments with spaced sections of differential receptivity for dyes, pigments and other modifying additives, while retaining a uniform chemical composition and uniform strength throughout the fiber.

A still further object of this invention is to provide processes by which synthetic fibers and filaments can be prepared with high frequency symmetrical fluctuations in fiber diameter. Another objective is to provide a process by which high frequency fluctuations in fiber denier can be introduced into a fiber or filament during the drawing operation. Another objective is to provide a process by which undrawn filaments of substantially uniform fiber diameter can be drawn so as to provide a drawn fiber of non-uniform diameter with high frequency symmetrical fluctuations of diameter in which the whole filament is substantially oriented. Other objectives will become apparent hereinafter from the description and examples which follow.

In the process of the present invention, an orientable filament of synthetic organic linear polymer is subjected in the presence of a crack-producing agent to tension sufficient to draw the filament to at least 1.01 times its original length and not above about 2.5 times (preferably not above 1.5 times) its original length. This drawing is conveniently carried out at room temperature although higher temperatures can be used up to the temperature at which the agent becomes ineffective to produce cracking, usually at about 80° C. Temperatures below 50° C., and preferably below 30° C., should generally be used. With some agents temperatures of 0° C., or -10° C. or lower are desirable. Drawing under these conditions produces closely-spaced, transverse surface cracks and/or multiple neck drawing, quite unlike the effect of normal or single neck drawing.

Following this predrawing step, the filament is further drawn to at least 1.5 times the length obtained above, under conditions which disassociate the filament from the influence of the cracking agent, so that an oriented filament having good tensile properties is produced as in normal drawing procedures. In this step the influence of the cracking agent can be disassociated by drawing at a temperature at which the cracking agent is no longer

effective, e.g., above 80° C., or by removing the cracking agent from the filament by evaporation, washing or wiping the filament. In order to draw at least 1.5 times in this step, the filament orientation must be sufficiently low prior to the predrawing step. Preferably the initial filament is substantially unoriented, i.e., has a birefringence that is less than 10% of the maximum possible, since this provides for more effective surface modification. Further modification can be achieved by drawing under conditions leading to high shrinkage and thereafter shrinking the filament from 5 to 75% to produce a rough fiber.

There are a variety of suitable cracking agents which will be disclosed subsequently. Preferably it is a liquid which can be applied in aqueous solution and is not a solvent or strong swelling agent for the filament polymer. Certain liquids which have some solvent or swelling tendency can be employed if the contact time is short so that cracking occurs before swelling or plasticizing action has a chance to occur, since the latter prevents formation of surface fissures or cracks. A modification of the process based on the base of a volatile liquid which produces cracking and is imbibed in the filament is to heat the drawn filament to a relatively high temperature at which rapid expansion of the imbibed liquid imparts porosity.

The process of this invention produces ringed or ripple-marked filaments having at least 20 transverse ridges per inch extending in a substantially circumferential direction on the filament surface and of a size, depending upon the conditions of treatment, from sub-microscopic enlargements of less than 0.25 micron in height to clearly visible nodules having diameters up to 2.5 times the base diameter of the filament between enlargements. The term "nodular filaments" will be used hereinafter to refer to filaments having enlargements of diameters in the range of 1.1 to 2.5 times the base diameter, since filaments having smaller enlargements more closely resemble conventional smooth filaments in appearance although having markedly improved frictional properties.

The nodular filaments are characterized by being oriented synthetic organic polymeric filaments of uniform chemical composition having closely spaced intermittent regions of enlarged diameter, preferably 1.2 to 1.6 times the base diameter, the regions of enlarged diameter occurring along the length of the fiber with an average frequency of at least 20 per inch and preferably between 50 and 500 per inch.

These nodular filaments are further characterized by the regions of enlarged diameter being substantially symmetrically disposed around the fiber axis (i.e., the products are not scaly as in Stanton U.S. Patent 2,736,946) and by the absence of sharp edges.

The preferred product is characterized by the random distribution of the enlarged regions both along the length of a filament and across a bundle of filaments in a yarn.

By the expression "of uniform chemical composition" is meant that the filament is composed of one or more components of uniform chemical composition along its length. The regions of increased diameter, referred to hereinafter as "nodules," are of the same polymer as the adjacent regions and contain no large particles of a foreign matter. The filaments may be composed of one polymer only or may be of a composite nature with two or more components of different polymers such as taught in Breen U.S. Patent No. 2,931,091.

The use of the word "diameter" is not intended to restrict the invention to the use of filaments of round cross-section.

By the expression "substantially oriented" is meant that all portions of the filament along its length have a birefringence of at least about 1/3 the maximum obtainable. The absolute value of the maximum birefringence will vary with the polymer concerned. Typical birefringence values (near maximum) on commercial fibers are as follows: polyethylene terephthalate, 0.188; 66 nylon, 0.050;

6 nylon, 0.053; 6-10 nylon, 0.065. (Fibres from Synthetic Polymers, R. Hill, Elsevier Publishing Co. N.Y., 1953.)

The relation between draw ratio, birefringence and tenacity for typical samples of polyethylene terephthalate and polyhexamethylene adipamide filaments are given below.

Draw Ratio	Polyester		Polyamide	
	Birefringence	Tenacity, g.p.d.	Birefringence	Tenacity, g.p.d.
As-spun	0.008	0.8	0.002	1.0
1.5X			.021	1.6
2X	0.054	1.4	0.038	2.1
3.0X	0.096	2.1	0.050	2.4
4.0	0.140	3.2	0.057	3.8
5.0	0.186	4.4	0.058	6.3
6.0	0.187	6.9		

The birefringence values tend to level off as the highest draw ratios (and highest tenacities) are obtained. It will be understood that the exact relationship between the above 3 variables will depend upon the polymer, spinning conditions and drawing conditions.

Fibers that are "substantially oriented" by the above definition are seen to possess a usable tensile strength that is significantly greater than that of the unoriented fibers. For greater utility it is preferred that the fiber have a birefringence that is 75% or more of the maximum possible.

The refractive index was determined, using a Dyson Interferometer Microscope, as described in Fibre Microscopy by J. L. Stoves (D. Van Nostrand Co., Inc., N.Y., 1958).

In the drawing, FIG. 1 shows four diagrammatic sketches of a typical case of the progressive formation of nodular filaments. FIG. 1a shows the filament in which fine cracks have been produced. FIG. 1b shows the same filament which has been partially stretched. FIG. 1c shows the same filament that has been further stretched in the absence of a cracking agent. The portions of smaller diameter in FIG. 1b now become the portions of greater diameter. FIG. 1d represents the appearance of the nodules in the finished yarn. This figure also shows the symmetrical nature of the nodules.

FIGS. 2 and 3 are diagrammatic sketches showing the arrangement of the yarn supply and take up with intermediate draw rolls. In both figures, 1 represents the undrawn yarn soaked with a crack-enhancing liquid. The yarn is supplied by a bobbin or similar package 2 on which a drag weight 3 is mounted. From the supply package the yarn goes to feed rolls 4 and thence over hot plate 9 to draw rolls 5 which operate at a higher speed than feed rolls 4. The drawn yarn 6 is then wound up on package 7 which is driven by drive roll 8. The drag weight 3 exerts sufficient tension on the undrawn yarn as it is pulled by feed rolls 4 so that there is a slight amount of drawing of the filaments soaked with the crack-enhancing liquid. In FIG. 3 an additional set of draw rolls 10 is introduced between the feed rolls 4 and the hot plate 5.

FIG. 4 is a diagrammatic view of a suitable arrangement of draw rolls, bath and stretch rolls described more fully in Example VI. FIG. 5 is a diagrammatic enlarged view of a filament drawn as described in Example VI. FIG. 6 is a cross sectional view of a composite filament made according to Example VIII.

While it is not intended to limit the scope of this invention by speculation on the means by which these products are obtained, it has been observed, in one preferred modification, that when an undrawn synthetic filament is exposed to a surface cracking agent under tension as described above, transverse cracks are formed as shown in FIG. 1a which give discrete and separated but closely spaced oriented increments in diameter along the filament

and that if the tension applied during contact with the cracking agent is less than sufficient to complete the orientation process, there will remain in the intermediate product substantially undrawn portions of the filament. The partially drawn filament at this point has been observed to have the appearance shown in FIG. 1b. Then, when the filament is removed from the cracking agent and the drawing process is completed, the previously undrawn sections draw by conventional drawing techniques to a highly oriented filament; while the sections of the yarn corresponding to the original cracks, extended while the filament was still within the cracking bath, remain as nodules of substantially greater fiber diameter as shown in FIGS. 1c and 1d which are substantially oriented. Another means of obtaining nodular filaments is illustrated in Example VII where the sections drawn in a non-cracking medium swell to form nodules upon relaxation of the filament. The frequency and size of the nodules and the spacing between them is determined by the condition of the undrawn filaments, the nature of the cracking bath, the time of exposure of the undrawn filament to cracking, the tension during the cracking process and the amount of stretch which is caused to take place while the filament is still in contact with the cracking agent. Thermal or chemical shrinkage of the fiber may be used to accent the nodularity.

Nodular filaments exhibit a delustered effect of an improved kind. Most fibers are delustered, that is, are rendered less transparent, by adding pigments to increase the opacity and scatter either transmitted or reflected light. Such pigments have the undesirable property of leaving the filament to which they are added in the form of a smooth cylindrical surface which has a high sheen due to uniform light reflection. Nodular filaments have a dull luster because they scatter reflected light by virtue of constantly varying surface angles relative to the incident light. Nodular filaments exhibit deeper shades of dyeing, since the quantity of dye present in the fiber is not masked by the presence of pigment and is not diluted by white light uniformly reflected by pigments or from the cylindrical surface. Nodular filaments, in addition, have mechanical properties which provide beneficial physical behavior, such as improved hand and texture, and the like. The symmetrical nature of the nodules is especially desirable in this regard.

The striking difference in optical properties between cylindrical and nodular filaments may be used to create more stable moire effects in fabrics while using only one type yarn. The tension in the cracking zone between rolls 4 and 10 in FIG. 3 is caused to fluctuate above and below that required to produce cracks. Thus sections of nodular fibers will alternate with sections of smooth, cylindrical form in the finished yarn.

In addition, it has been observed that the interior sections of the nodules themselves are susceptible to a much higher degree of dyeing and dye penetration than is possible with conventional polymer in filamentary form. This property can be utilized in several different ways to considerable advantage. In the first place, if the nodules are closely spaced, that is, in the neighborhood of 100-500 nodules per inch, the accumulated effect of the large number of nodules is, as far as dyeability goes, one of increased dyeability with a uniform appearance. If the nodules are farther apart, say 50-100 per inch, visible variations in dyeability can be achieved. At still lower variation levels, it is possible to have non-uniformities of dyeing which are visible to the naked eye. Thus, it is possible to control the optical characteristics of the yarn by means of controlling the concentration of nodules. In addition, because apparent dye depth is an optically integrated, rather than an average, phenomenon, closely spaced sections of deep dyeability appear as a uniform length of highly dyed filament, which means that greater apparent dye depth can be achieved with relatively small concentrations of dye.

The following examples illustrate the preparation and utilization of nodular filaments derived from a number of different polymer compositions, together with some of the advantages of the present invention.

Example I

A sample of undrawn polyethylene terephthalate filament yarn containing 34 filaments was soaked in a purified kerosene which had been distilled to give a narrow boiling range. When the yarn had been thoroughly wet with the kerosene, it was placed in a drawing apparatus represented schematically in FIG. 2. In that figure, 1 represents the undrawn yarn, the bulk of which is contained in a bobbin supply 2. A drag weight 3 is placed on the mounting of the bobbin supply, and the yarn is taken off in an unrolling fashion. From the supply package the yarn goes to feed rolls 4 and thence to draw rolls 5 which are operating at a higher speed than feed rolls 4. The drawn yarn 6 is then wound up on package 7 which is driven by a drive roll 8. The drag weight 3 exerts sufficient tension on the undrawn yarn, and it is pulled by feed rolls 4 so that there is a slight amount of drawing of the kerosene soaked filaments between the package 2 and feed rolls 4 then the yarn is passed over the hot plate held at approximately 95° C. and drawing is completed by draw rolls 5. The tension of the undrawn yarn causes cracking prior to the conventional drawing, and it is observed that low tension is sufficient for this; that is, tension between supply package 2 and feed rolls 4 is about 25% less than the conventional drawing tension. The cracked yarn draws at the hot plate in the conventional manner, because the plasticizing action of the heat furnished by the hot plate lowers the tension required for drawing below that needed for crack-drawing. The filaments are thus disassociated from the influence of the cracking agent by being provided with an easier alternative step. Typical filaments have birefringence values of 0.16 and 0.13 for the thick and thin portions respectively. The resulting yarn is a 34 filament, 70 denier yarn with a high degree of modification of diameter consisting of many nodules, about 120 per inch along the threadline on the average, which have approximately 20% greater diameter than the basic threadline. This yarn has a very dry hand, and, when assembled into a bundle, it gives a remarkable opaque appearance which is due to the diffractive power of the irregular surface.

Example II

A sample of undrawn polyethylene terephthalate yarn, the same as that described in Example I, is soaked on a bobbin in purified kerosene. The yarn is then cracked and drawn in a two-stage drawing apparatus as shown in FIG. 3. In FIG. 3, 2 represents the supply package of undrawn yarn 1, going to a set of feed rolls 4 and thence to a first set of draw rolls 10 which operate to give a 1.1× draw at a speed of 40 yards per minute. This partial drawing operation cracks the yarn and introduces some orientation. The cracked yarn is then fully drawn over hot plate 9 by the action of a second set of draw rolls 5 operating at 148 yards per minute to give a 3.7× total draw. The fully drawn yarn is then wound up on package 7 by drive roll 8. The appearance of this yarn after cracking and drawing was opaque and equivalent to highly pigmented polyester fibers in opacity, although these filaments had a very low pigment content. Photomicrographs of the drawn filaments showed that individual filaments had between 100 and 300 nodules per inch on the average. The diameter in the nodular sections was approximately 25% greater than that in the sections between nodules. The drawn filaments of 3.2 denier per filament have a tenacity of 4.9 grams per denier, an elongation at the break of 52% and an initial modulus of 69 grams per denier.

A sample of undrawn polyethylene terephthalate filament yarn, 30 filaments with a total undrawn denier of 600 was wet as before with purified kerosene. This yarn was then drawn in a two-stage drawing process, the first stage being a cold draw at $1.25\times$ with a step roll. Following this, the yarn was drawn to a total draw ratio of $4.5\times$ at 40 yards per minute over a hot pin held at 118°C . with a pin wrap of 100° . The yarn product was a highly drawn, strong polyethylene terephthalate yarn with nodules, frequency between 120 per inch and 360 per inch, all nodules being highly oriented as shown by examination under crossed polarizers.

Using apparatus identical with that described above and similar operating conditions, similar polyethylene terephthalate yarns have been processed into nodular filaments using different cracking agents, including 100% ethanol, mixtures of ethanol and water containing as little as 20% by weight of ethanol, perchloroethylene, methylene chloride, carbon tetrachloride, and ethyl Cellosolve. Other less satisfactory cracking agents include phenol, 100% formic acid, and 100% acetone.

Example IV

A sample of undrawn poly(hexamethylene adipamide) nylon monofil of an undrawn denier suitable for giving a 15 drawn denier monofil was cracked by immersion in methyl isobutyl ketone at room temperature and was elongated by 10% while in this bath. The cracked monofil was then removed from the bath, wiped carefully, and drawn by hand to high orientation. The product was a nodular filament with about 100 nodules per inch, the individual nodules being greater in diameter than the base filament diameter by a factor of 1.58. This nodular filament was heat set at 140°C . to remove any residual solvent, and no change in diameter ratio resulted as an aftermath of this process. The optical diffracting effect of the nylon filaments was comparable to that obtained with the polyethylene terephthalate yarns described above.

As shown in Example IV, methyl isobutyl ketone is a satisfactory cracking agent for nylon. In addition, the following other cracking agents have been used successfully in a similar apparatus to that described in the earlier examples: acetone, dimethylformamide, dimethylsulfoxide, methyl ethyl ketone, and methylene chloride. Other materials which have been found to be unsuccessful as cracking agents for polyamides include carbon tetrachloride and kerosene.

Example V

A wholly aromatic polyamide, poly(meta-phenylene isophthalamide) in a form of a continuous filament of 60 filaments and 720 denier before drawing was cracked using methyl isobutyl ketone as a cracking agent by running it rapidly over a hot plate at 200°C . with partial draw. The temperature treatment was necessary to modify the yarn sufficiently to permit cracking. As the yarn cracked, the cracking agent was also volatilized by the hot plate. The fiber was then air dried and seen to be highly cracked by visual observation under the microscope. This yarn was then hot drawn over a plate at 90°C . to give a nodular filament containing approximately 100 nodules per inch and a final denier of 180. In a modification of the above experiment, it was possible to make a continuous operation including sequential cracking and full drawing by controlling the contact time with the hot plate so that the yarn would first crack draw, then dry and then substantially orient over the outer portion of the plate to give a nodular filament.

In a similar experiment, a solution of 10% acetic acid in water was used as a cracking agent and gave a good nodular product.

Polyethylene terephthalate polymer of relative viscosity (N_r) 15.5 is spun into yarn and yarns combined to give a tow containing 5,000 filaments with a total denier of 56,000. The tow is run through the apparatus as depicted in FIG. 4 and into a bath 35 containing 25% aqueous ethanol, then through a spray 36 comprising an aqueous finish at 72°C ., then through the drive rolls and on to a suitable packaging device. Rolls 12, 13, 14, 15, and 16 operate at 38 feet per minute. Rolls 17, 18, 19, and 20 operate at 55 feet per minute thus affording a $1.4\times$ draw in the cracking zone (while the yarn is wet with the cracking agent). Rolls 21, 22, 23, 24, 25, and 26 operate at 100 feet per minute affording a further draw ratio of $1.8\times$ in the hot spray zone. The second drawing is a normal type and does not produce cracking.

The drawn product has an appearance similar to FIG. 5 (approximately $150\times$ magnification). The nodules have a diameter of about 1.7 times greater than the diameter of the thinner segments of the filament and are randomly spaced along the filament at a frequency of about 270 to 450 per inch. Samples of the drawn fiber shrink about 10% in boiling water and have an elongation at the break after such relaxation of 20 to 30% with a tenacity of 1.2 grams per denier. The thick and thin portions have birefringence values of about 0.06 and 0.17 respectively.

Similar results are obtained with use of the polyester from 2,6-naphthalene dicarboxylic acid and ethylene glycol.

In a modification of the above process, the drawn yarn is conducted through an oven such as 34 (FIG. 4) maintained at $130\text{--}160^{\circ}\text{C}$. with rolls 27, 28, 29, 30, 31, 32, and 33 operating at 100 feet per minute so as to permit no relaxation or further draw in the oven. This product after boiling in water has the same appearance under a microscope as the above product but has an improved tenacity of 2.0 g.p.d.

To obtain the best products in the above process, the draw ratio in the cracking zone should be maintained at about 1.2 to $1.6\times$. The second stage draw ratio in which the uncracked portions of the yarn are drawn by virtue of the reduced tension at the elevated temperature should be such so as to afford a yarn of 20 to 40% elongation at the break. The actual draw ratio to use will depend upon the particular polymer used, its composition and molecular weight, and will be apparent to one skilled in the art. The temperature of the hot spray or alternatively hot liquid through which the tow could be run should be between 65 and 90°C . The process can be operated at any convenient feed speed, preferably below about 160 yards per minute.

Example VII

A yarn of 240 total denier of 34 filaments is prepared from polyethylene terephthalate of N_r 25. The yarn is passed from a feed roll at 100 y.p.m. into a bath of 10% aqueous pyridine at room temperature around a $\frac{1}{2}$ " diameter pin in the pyridine bath, out of the bath to two forwarding rolls and then to a first stage draw roll operating at 150 yards per minute. From the first stage draw roll the cracked yarn is then passed over pins and around a $\frac{1}{2}$ " Alsimag pin in a bath of water at 80°C . thence out of the bath to a second stage draw roll operating at 290 yards per minute from whence it is forwarded to a windup. Thus the yarn is drawn $1.5\times$ in the cracking bath (since the pin localizes the drawing at that point) and the cracked yarn is further drawn $1.93\times$ in the warm water bath.

The drawn yarn has a substantially smooth surface when viewed under the microscope (intermediate between FIGS. 1b and 1c where the uncracked portions have been drawn down to substantially the same diameter as the original cracked portions). When this yarn is boiled in

water for three minutes it undergoes a total shrinkage of 21% and the warm wet drawn portions swell to produce a product similar in appearance to FIG. 1c. It has nodules randomly located along its length at the rate of about 500 per inch and the nodules have a diameter approximately $1.43\times$ times that of the thinner portion of the filament. The filaments have a tenacity of 2.8 g.p.d. and an elongation at the break of 74% after boiling in water. The thin and thick (nodules) portions of a filament show birefringence values of 0.135 and 0.09 respectively.

In the preparation of this type of filament the final drawing step is performed under conditions that are termed "amorphous retaining," i.e., they tend to induce a minimum of crystallinity and retain a shrinkage of 30 to 50% or more. The use of unheated pins or rolls with dry or wet yarn or more preferably drawing in a water bath of 60 to 80° C. affords such conditions.

Similar results are obtained when the polyethylene terephthalate in the above example is replaced with filaments made of any of the following polymers:

Poly(ethylene terephthalate/isophthalate) (90/10 mol ratio), poly(ethylene terephthalate/hexahydroterephthalate) (90/10 and 80/20), poly[ethylene terephthalate/5-(sodium sulfo)isophthalate] (98/2 and 96.5/3.5), poly(ethylene 2,6 naphthalene dicarboxylate), poly[ethylene 2,6 naphthalene dicarboxylate/5-(sodium sulfo)isophthalate] (97/3).

The aqueous pyridine can be replaced in the above examples with any of the polymers by the following cracking baths:

100% tertiary butyl alcohol, 20% aqueous dimethoxyethane, 30% aqueous dioxane, 20% aqueous cyclohexanone and a solution of toluene (5%) in kerosene.

The following example teaches the preparation of a nodular two component filament.

Example VIII

Molten streams of polyethylene terephthalate of N_f 31.0 and a copolymer of polyethylene terephthalate containing 3.5 mol percent of the sodium salt of sulfonated isophthalic acid, the copolymer having a N_f of 19.7, are separately fed to a spinneret similar to that shown in Breen U. S. 2,931,091 to form separate components in composite filaments having a cross section similar to that shown in FIG. 6. The composite filaments are wound up at 1200 yards per minute. The 34 filament yarn has a total denier of 204.

Seventy ends of the above yarn are plied to a total denier of about 14,000 and the yarn is drawn in an apparatus similar to that shown in FIG. 4 where the cracking bath 35 contains 100% of denatured (2B) alcohol and the aqueous spray 36 has a temperature of 50° C. The yarn is drawn a total of $2.4\times$ in the spray zone with all forwarding rollers prior to the spray zone operating at 14 yards per minute and those rolls following it operating at 33.7 yards per minute. There is sufficient tension on the yarn in the first zone to crack the filaments and draw them at least $1.01\times$ prior to the spray zone drawing. The drawn tow has a shrinkage of 27% in boiling water and crimps to an extent of 18 helical crimps per inch upon relaxation. The fiber has nodules with a thickness of about 1.6 times the smaller portion of the filament to an extent of about 300-400 per inch.

The drawn unrelaxed tow is mechanically crimped to an extent of 15 crimps per inch. The crimped tow is cut to $3\frac{1}{2}$ " staple length and relaxed at 100 to 140° C. for 20 minutes. The fiber is blended with wool (45 to 55 parts), yarn spun and twill fabrics woven. A fabric of similar construction is made from a yarn that has been processed without the formation of the nodules. It is observed that the fabric from the filaments of this invention has a higher bulk (2.81 cc. per gram at 0.6 p.s.i. pressure) as compared with the control with a bulk of 2.34 cc./gram. The fabric from the fibers of this

invention has a significant improved resistance to cover wear-off and has an improved retention of bottom cover on wearing as opposed to the other control item.

Example IX

The following example teaches the preparation of a filament with low density nodules.

A sample of 70 denier undrawn yarn containing 34 filaments of polyethylene terephthalate containing 0.7% of TiO_2 is conducted over feed rolls and then run in contact with a finish roll wet with 2B denatured alcohol as a crack promoting agent and then around two snubbing pins so that the yarn undergoes a change of direction of 270° in contact with the pins and then over draw rolls so that the yarn is cracked and drawn a total of $3.5\times$. The fully drawn yarn is passed four times over the top and bottom of a hot plate at 220° C. by means of rolls thence to a forwarding set of rolls and a windup.

Samples of the drawn yarn taken before the hot plate contain about 125 nodules per inch. The nodules contain the alcohol imbibed during the crack-drawing. The rapid heating of this yarn by the hot plate causes extremely rapid volatilization of the alcohol leading to a porous nodule of reduced density connected by smaller diameter lengths of oriented compact polymer. The rapidly heated yarn has a greatly increased opacity as compared to the unheated product. The final product has a tenacity of 3.76 g.p.d. and an elongation of 26.1%.

Similar results are obtained with the use of methanol, aqueous methanol, a 20% solution of NH_4OH in ethanol, solutions of formaldehyde in methyl ethyl ketone as the liquid on the finish roll.

In general, a heat treatment at about 200° C. or higher is required to make the porous nodule product from the aforementioned polyester and the named liquids.

By choice of imbibed agent and control of tension during the heating operation, one may vary the morphology of the void containing segments. For example, if the nodules contain a solution of formaldehyde, single, large voids will occupy the core section of the nodule. If ethanol in water is contained in the nodules and the fibers are not allowed to shrink while traversing the hot zone many small voids will be formed but, if the tension of the fibers in the hot zone be reduced so that the fibers shrink, the voids will become larger and fewer until single large voids are produced. If even higher shrinkage is permitted, the single, large voids will become several fiber diameters in size, and eventually will burst through where the wall is weakest.

The process illustrated can be modified to obtain a product in which sections of nodular character are alternated with sections of conventional nature. This product can be achieved by causing the undrawn filaments to be contacted with the cracking agent only at intervals along the threadline.

Fabrics prepared from nodular filaments are highly dimensionally stable, because there are no undrawn sections in the filaments. This may be contrasted to nubby yarns or speck yarns which are prepared from synthetic fibers by leaving certain portions of the yarn undrawn. Fabrics from yarns of this latter type are highly desirable for certain end uses, but they do not have the dimensional stability of the fabrics prepared from the fibers of the present invention.

In contrast to prior art products of varying denier, the nodular filaments of this invention have a much higher frequency of fluctuation of filament diameter, and this is what confers upon them the attractive optical refractive behavior. Filaments containing alternating thin and thick sections spaced inches apart do not reflect or transmit light in this diffused way and therefore do not have the high opacity and covering power of the present yarns.

As has been indicated above, the nodular product of the present invention is a yarn with a high degree of opacity and a remarkably high light scattering surface.

Preferred products are those with at least 50 nodules per inch, since these give the most satisfactory degree of light scattering. When the frequency of nodules is increased above about 500 per inch, the nodules are so closely spaced that they tend to overlap, and the amount of random light scattering again decreases. Excellent results are observed in the range of 50 to 500 nodules per inch.

In addition to the optical properties, the nodular sections of the filament confer highly desirable and attractive improvements in handle and texture of a fabric prepared from such filaments. The slight surface roughening avoids the waxy or slick feeling which has under some circumstances been found undesirable in fabrics prepared from synthetic filament yarns. This also tends to decrease filament migration in a fabric and render even the sheerest fabrics prepared from continuous filament synthetic fibers much less sleazy or mobile. However, since these nodules are not sharp, but are rather gently rounded and symmetrical in their profile, there is no pickiness or harshness in such a fabric. In addition, nodular filaments are found to have low friction during processing.

This last mentioned improvement also applies when the process is used to give products which do not have visible nodules. This is particularly surprising when the ridges are sub-microscopic and can only be seen with an electron microscope. Such products have the appearance of conventional filaments and yarns but have sufficient surface roughening to reduce the high level of dynamic friction against surfaces, which is of particular importance in maintaining low running tension on surfaces in contact with moving yarns. These products are preferably produced by applying a high molecular weight cracking agent and allowing the filaments to age for a while before drawing in a separate operation from the spinning. The cracking agent can be applied as part of the spinning operation and the yarn or tow then stored until convenient for drawing. Since the cracking agent is of high molecular weight, hence does not evaporate, the yarn can be stored for long periods of time before drawing if desired. The following examples illustrate this process:

Example X

Polyethylene terephthalate containing 0.3% titanium dioxide delusterant is melt spun to give a 34 filament yarn having a total denier of 210. Prior to windup the filaments are coated with an aqueous solution containing 400 molecular weight polyethylene oxide. The filaments are aged for about 3 hours in contact with the polyethylene oxide cracking agent and then drawn in a two-stage process. In the first stage the filaments are drawn at a draw ratio of 1.05 times at room temperature with a cold snubbing pin in the draw zone. In the second stage the filaments are passed around a draw pin heated to 95° C. and drawn at a draw ratio of 3.0 times. The drawn filaments have a tenacity of 4.1 grams per denier at a break elongation of 26%.

When examined by optical microscopy at 200× magnification the filaments are found to have the smooth surface characteristic of melt spun fibers. No bumps, protuberances, or sections of enlarged diameter are apparent. The filaments are then examined in profile by electron microscopy and found to possess surface ripples which occur at a frequency of about 1270 ripples per inch along the filament and have an average height of about 0.07 micron. Examination of surface replicas by electron microscopy show these to be transverse ridges extending more than half-way around the filament in most instances. A control yarn prepared in the same manner, except that the first stage drawing step is omitted, is found to have a smooth surface by both optical and electron microscope examination.

Example XI

Polyethylene terephthalate is melt spun to produce a 34-filament yarn having a total denier of 210, a 15% aqueous solution of butyl stearate cracking agent is applied, the undrawn yarn is wound on a package and the package is stored for 3 weeks. The coated yarn is then drawn in two stages. In the first stage the yarn is passed over a feed wheel having a peripheral speed of 100 feet per minute, around a $\frac{3}{16}$ inch diameter unheated stationary ceramic snubbing pin, then around a draw roll rotating at 110 feet per minute. The 1.1× drawn yarn continues directly to the second stage draw, passing around a 1.25 inch ceramic stationary snubbing pin heated to a temperature of 90° C., around a second draw roll rotating at a surface speed of 330 feet per minute, and finally to a windup.

The drawn filaments are examined under a light microscope at 200× magnification and found to have a smooth surface with no significant number of ridges or nodules, and no visible voids or bubbles. Birefringence measurements indicate uniform molecular orientation along the length of the filaments. Examination by means of an electron microscope, using standard replica techniques, showed the surface to be characterized by randomly spaced, circumferential ridges at a frequency of about 1500 per inch of filament length, having an average height of about 0.09 micron. The filament diameter is about 14 microns.

The improvement in frictional properties is evaluated by determining the hydrodynamic friction coefficient in the following manner:

A test filament is hung over a $\frac{1}{2}$ inch diameter polished chrome-plated mandrel so that the filament contacts the mandrel over an arc of approximately 180°. A 0.3 gram weight is attached to one end of the filament (input tension) and a strain gauge is attached to the other end (output tension). The mandrel is rotated at a speed of 1,800 y.p.m. and the area of contact "flooded" with a drop of No. 50 mineral oil immediately before strain gauge readings are made. The coefficient f is calculated from the belt friction equation:

$$\frac{T_2}{T_1} = e^{af}$$

where f is the coefficient of hydrodynamic friction, T_1 is the input tension, T_2 is the output tension, and a is the angle of wrap.

The yarn of Example XI gives a value of $f=0.55$ in this test. When the first stage predraw is omitted a much higher value of $f=0.74$ is obtained. When yarn is treated as in Example XI except that the butyl stearate is omitted a value of $f=0.67$ is obtained.

Example XI is repeated using 15% aqueous solutions or emulsions of the following cracking agents, instead of butyl stearate, with the results indicated:

Cracking agent—	f
Polyethylene oxide (400 M.W.)-----	0.48
Polyethylene oxide (600 M.W.)-----	0.47
Poly(ethylene glycol)monolaurate-----	0.46
Oleyl alcohol/9 moles ethylene oxide-----	0.50
Copolymerized ethylene glycol/propylene glycol (random)-----	0.49
Eicosane -----	0.54
Isopropyl myristate-----	0.55

Example XII

A polyethylene terephthalate yarn (4.5 d.p.f., 140 filaments) is spun and a 15% emulsion of butyl stearate is applied to the moving threadline during spinning. After storage for 10 days, three portions of this yarn are drawn in the following manner: Sample A is passed around a set of feed rolls operating at a peripheral speed of 90 feet per minute, then S-fashion around a pair of stainless steel snubbing pins, then around a set of rolls rotating at a pe-

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ripheral speed of 96 feet per minute and providing a draw ratio of $1.06\times$. The yarn is then passed through an aqueous bath at 95°C . and then is drawn to a total draw ratio of $2.8\times$ on a third set of rolls operating at a peripheral speed of 250 feet per minute. The yarn is then relaxed for 6 minutes at 140°C . under no load. Item B is prepared similarly except that the yarn is not snubbed in the first draw zone. Item C is prepared similarly to items A and B except that no snub is used in the first stage and the speed of the second set of rolls is set at 90 feet per minute so that no drawing takes place in the first stage. The properties of these three yarns are tabulated below.

Item	T	E	Mi	100° C. Shrinkage	f
A	4.91	27.9	94	10.9	.45
B	4.92	28.0	97	11.5	.46
C	4.85	25.5	90	11.7	.69

It has been observed that different cracking agents or a single cracking agent used at different temperatures will cause different frequencies of cracking, and this in turn will give a modification of the number of cracks per inch and therefore the number of nodules or ridges per inch in the fully drawn and fully oriented yarn product. It is one of the desirable and attractive features of the present invention that these enlargements are not uniformly and precisely spaced, but are rather randomly distributed along the threadline. However, it may be observed that good cracking agents, such as those illustrated, will give a satisfactory high concentration of either nodules or smaller ridges if the proper attention is given to control of the amount of drawing performed in the presence of the cracking agent. It is necessary for the practice of the present invention that the amount of draw completed under the influence of the cracking agent be less than the full amount of draw available. Yarns drawn completely in the presence of the cracking agent are not nodular in character.

The following criteria may be used for selection of outstanding cracking agents suitable for use in aqueous solutions with polyester fibers. (1) The agent should be unsaturated or contain other sources of unpaired electrons. (2) The agent should be water soluble at least to the extent desired. (3) The agent should be liquid at the cracking temperature employed in the process to prevent crystallization of the agent in the fiber. (4) The agent should not be strongly self associating (e.g., that displayed by difunctional alcohols or amines) since this reduces possibilities for association with polymer which is postulated to be necessary. (5) The agent should be of fairly high molecular weight or of low volatility to avoid changes in bath composition with time.

No complete list of cracking agents can be given which are operable for all polymers. A simple test may be done by drawing a freshly spun undrawn fiber under the surface of the liquid to be tested a small amount (about $1.5\times$). By freshly spun is meant a fiber that is less than 1 week old. (This is for purposes of the test only since the process of this invention can be used on aged fibers.) Microscopic examination will show transverse cracks and/or multiple neck drawing as shown in the drawings if the liquid is a suitable cracking agent. It is characteristic of multiple-neck drawing that a lower drawing force (as much as 90% reduction or more) is required than in conventional cold drawing (single neck) under the same temperature and speed.

Use of the above criteria led to the use of the cracking agents illustrated, as well as such compounds as 2-methyl pyridine, dimethylpyridine, 4-methyl pyridine, 3-methyl pyridine, 2,4-dimethylpyridine, and benzyl amine with the activity of the agents increasing in the order given. Other suitable compounds include dimethoxyethane, propargyl alcohol, N-vinyl pyrrolidone, homologous alkyl benzenes, alcohols, acids, esters, ketones and olefinic compounds.

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Bundles of nodular filaments can be processed into staple-like fibers by rolling the filaments through the pinch of hard-surfaced rollers. Fabrics can be processed similarly.

Since the nodules are more readily influenced by swelling agents and the like, fabrics from nodular filaments may be bulked by treating the fabric with such agents to promote localized swelling and consequent increase in fabric bulk.

While the examples above show the application of the principles of the present invention in connection with polyester and polyamide filaments, it is obvious that any fiber which neck-draws, and which can be caused to crack by the use of a cracking agent in conjunction with proper heat and solvent treatments, can be employed to give nodular filament products. Thus, other polyamide filaments, as well as other polyester filaments, are also useful for providing the products of this invention. In addition, polyurethanes, for example, those from the interfacial reaction of piperazine and ethylene bischloroformate, are also suitable for the preparation of nodular filaments.

Because of their commercial availability, ease of processing and excellent properties, the condensation polymers and copolymers, e.g., polyamides, polysulfonamides and polyesters and particularly those that can be readily melt spun are preferred for application in this method. Suitable polymers can be found for instance among the fiber-forming polyamides and polyesters which are described, e.g., in U.S. Patents Nos. 2,071,250, 2,071,253, 2,130,523, 2,130,948, 2,190,770 and 2,465,319.

Polyamides may contain the repeating unit $-X-Z-$ $Y-Z-$ wherein $-X-$ and $-Y-$ represent divalent aliphatic or cycloaliphatic groups and $-Z-$ represents the



linkage as in polyhexamethylene adipamide, polycapromide, and polypiperazine adipamide. The group $-Y-$ may be replaced with a divalent aromatic radical ($-A-$) as in polyhexamethylene terephthalamide. Additionally, polyamides having repeating units such as $-A-Z-B-Z-$ and $-X-Z-B-Z-$ wherein $-B-$ is divalent alkaryl (such as xylylene) may be used.

In a preferred embodiment of the invention, the fiber-forming polymer is a synthetic linear condensation polyester of bifunctional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain include at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain (para-relationship in the case of a single 6-membered ring). The polyesters may be derived from any suitable combination of bifunctional ester-forming compounds. Such compounds include hydroxy acids such as 4-(2-hydroxyethyl)benzoic acid and 4-(2-hydroxyethoxy)-benzoic acid, or mixtures of the various suitable bifunctional acids or derivatives thereof and the various suitable dihydroxy compounds and derivatives thereof. The repeating structural units of the polymer chain comprise recurring divalent ester radicals separated by predominantly carbon atom chains comprising hydrocarbon radicals, halogen-substituted hydrocarbon radicals, and chalcogen-containing hydrocarbon radicals wherein each chalcogen atom is bonded to carbon or a different chalcogen atom, and no carbon is bonded to more than one chalcogen atom. Thus, the repeating units may contain ether, sulfonyl, sulfide, or carbonyl radicals. Sulfonate salt substituents may also be present in minor amount, up to about 5 mol percent total sulfonate salt substituents in the polyester based on the number of ester linkages present in the polyester. Other suitable substituents may also be present.

Among the various suitable dicarboxylic acids are terephthalic acid, bromoterephthalic acid, 4,4'-sulfonoyldiben-

zoic acid, 4,4'-diphenic acid, 4,4'-benzophenonedicarboxylic acid, 1,2-bis(4-carboxyphenyl)ethane, 1,2-bis(p-carboxyphenoxy)ethane bis-4-carboxyphenyl ether and various of the naphthalenedicarboxylic acids, especially the 1,4-, 1,5-, 2,6-, and 2,7-isomers. Isophthalic acid is also suitable, especially when used in combination with a 1,4-dihydroxyaromatic compound. Carbonic acid is similarly suitable.

Among the various suitable dihydroxy compounds are the glycols, such as ethylene glycol and other glycols taken from the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is 2 to 10; cis- or trans-p-hexahydroxyethylene glycol; diethylene glycol; quinitol; neopentylene glycol; 1,4-bis(hydroxyethyl)benzene; and 1,4-bis(hydroxyethoxy)benzene. Other suitable compounds include dihydroxyaromatic compounds such as 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, hydroquinone, and 2,5- or 2,6-dihydroxynaphthalene.

The products of the present invention, in addition to being useful in woven fabrics and knit fabrics, have obvious applications in the form of batts, felts, papers, and the like and are particularly desirable because the nodules cause a higher degree of stability of the structures thus formed.

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. The process of preparing substantially oriented filaments having at least 20 transverse ridges per inch of filament that extend in a circumferential direction on the filament surface, which comprises spinning a synthetic organic linear fiber-forming polymer, applying a crack-producing agent to the spun filament, partially drawing the filament from 1.01 to 2.5 times the undrawn length in the presence of the crack-producing agent to impart surface cracks transverse to the filament axis, dissociating the filament from the influence of the crack-producing agent and finally drawing the filament at least 1.5 times the partially drawn length.

2. A process as defined in claim 1 wherein the crack-producing agent is removed from the filament after the partial drawing step and prior to the final drawing step.

3. A process as defined in claim 1 wherein the partial drawing of the filament is at a temperature below 50° C. and the final drawing is at a temperature above 80° C.

4. A process as defined in claim 1 wherein the filament is partially drawn at a temperature of 0° to 30° C.

5. A process as defined in claim 1 wherein the partial drawing step starts with a substantially unoriented filament having a birefringence less than 10% of the maximum possible.

6. A process as defined in claim 1 wherein the filament is partially drawn from 1.1 to 1.5 times the undrawn length in the presence of the crack-producing agent.

7. A process as defined in claim 1 wherein the filament is drawn to a shrinkable condition and the final drawing step is followed by a step of shrinking the filament from 5% to 75% in length.

8. A process as defined in claim 1 wherein the crack-producing agent is an aliphatic hydrocarbon.

9. A process as defined in claim 1 wherein the crack-producing agent is ethanol.

10. A process as defined in claim 1 wherein the crack-producing agent is methyl isobutyl ketone.

11. A process as defined in claim 1 wherein the crack-producing agent is butyl stearate.

12. A process as defined in claim 1 wherein the crack-producing agent is a polymer of ethylene oxide.

13. A process as defined in claim 1 wherein the crack-producing agent is applied in aqueous solution.

14. A process as defined in claim 1 wherein the filament is coated with a high molecular weight crack-producing agent and stored for up to 3 weeks before drawing.

15. A process as defined in claim 1 wherein the filament is composed of polyethylene terephthalate.

16. A process as defined in claim 1 wherein the filament is composed of a linear polyamide.

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