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FORMATION OF POLYPYROMELLITIMIDE FILAMENTS

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13 Claims. (Cl. 260—47)

ABSTRACT OF THE DISCLOSURE

Polypyromellitimide filaments having high strength in both straight and transverse directions are obtained by dry-spinning a solution of a polyamide-acid of pyromellitic dianhydride and bis(4-aminophenyl)ether or bis(4-aminophenyl)sulfide, then converting the polyamide-acid to the polyimide and drawing. The dry-spun filaments may be drawn partially before and partially after the conversion step.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of our application Ser. No. 355,943, filed Mar. 30, 1964.

BACKGROUND OF THE INVENTION

This invention relates to certain high melting polypyromellitimide filaments and to the method of obtaining them which involves dry-spinning polypyromellitamide acid precursors, treating the resulting filaments to convert the polyamide-acid to the polyimide, and drawing. Drawing can be carried out either before or after, or partially before and partially after, conversion.

British Patent 903,271, published Aug. 15, 1962, discloses a process whereby a polyamide-acid polymer is formed into a shaped article and the article then treated to convert the polyamide-acid polymer to the polyimide thereof. The novel polyimide polymers so obtained are well suited for a variety of applications because they possess a unique combination of physical properties and chemical characteristics. Especially notable properties of these polyimide polymers include resistance to melting at temperatures up to 500° C. or more, resistance to corrosive atmospheres, and resistance to degradation by high energy particles and gamma ray radiation.

In the case of filaments comprising the novel polyimide polymers of the aforementioned British patent, however, it has been found that in some applications these tend to be deficient with respect to certain textile properties. In particular, the transverse tenacity and elongation properties of such polyimide filaments have been found to be unduly low, especially when the filaments have been exposed to a high temperature for a substantial period of time. The transverse tenacity of a filament, or "loop" strength as it is frequently called, is largely a measure of the brittleness of the filament. Although a fiber might retain quite acceptable values of straight tenacity and elongation after thermal aging, yet if it nevertheless suffers serious losses in transverse tenacity and elongation under the same conditions, it will be extremely brittle and hence will be generally unsuited in woven or knitted fabrics that must encounter severe use and temperature conditions. In this regard, it is pointed out in "The Journal of the Textile Institute," vol. 38, page T43 (1947), that fibers which, though of very high tensile strength, break very easily on bending, may be less serviceable in use in

twisted cord or woven fabrics than weaker more flexible fibers.

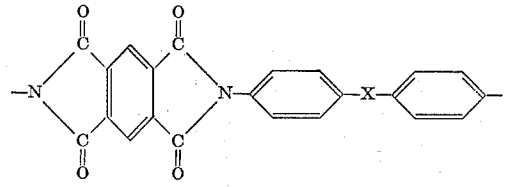
SUMMARY OF THE INVENTION

According to this invention there are provided high melting polypyromellitimides of bis(4-aminophenyl)ether and bis(4-aminophenyl)sulfide in the form of filaments exhibiting outstanding tensile strength in both straight and transverse dimensions. The filaments are characterized by a smooth, non-crenulated surface, as indicated by a roughness index (defined hereinafter) of less than 5. They are further characterized by a high degree of molecular orientation along the filament axis, as indicated by an imperfection index (also defined hereinafter) of less than 25.

Also according to the invention there is provided a process for producing the filaments which comprises spinning into a gaseous atmosphere a solution of a polyamide-acid of pyromellitic dianhydride and a diamine selected from bis(4-aminophenyl)ether and bis(4-aminophenyl)-sulfide to produce a polyamide-acid filament, and thereafter converting under a tension of 0–0.5 g./d. and drawing the filaments to produce the corresponding polypyromellitimide filaments, the total draw ratio in the process being at least 1.3×, preferably 1.4× to 3.4×.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The filaments of this invention ae composed of a polyimide of recurring units of the formula



wherein X is selected from the group consisting of O and S. On an average the number of such units per molecule should be sufficient to provide an inherent viscosity of at least 0.3. Filaments of the invention having the above formula wherein X is O, typically exhibit a straight tenacity of at least 3.0 g./d., a transverse tenacity of at least 1 g./d., and a flex life of at least 1000 cycles. The corresponding polypyromellitimide filaments wherein X is S exhibit similar properties except that the straight tenacity is generally somewhat lower, e.g. as little as 2.0 g./d.

The filaments of the invention are characterized in that they have a smooth, noncrenulated surface and a high degree of molecular orientation along the principal filament axis. These characteristics are expressed quantitatively by a roughness index of less than 5 and an imperfection index of less than 25.

For purpose of this invention roughness index is defined and measured as follows: A fiber cross-section is mounted in immersion oil of refractive index 1.550 and photographed through a microscope. The photograph is enlarged by means of an epidiascope (total magnification about 1500–3000×) and the periphery of the image recorded on paper. The area A of the cross-section is determined from the weight of the image or by integration with a planimeter. Then the area B of the plane figure with the smallest perimeter that can be drawn around the cross-section is obtained in the same manner. Cross-sections which are essentially symmetrical around a plane of symmetry or a twofold, threefold, . . . *n*-fold axis of symmetry are divided into two, three, . . . *n* segments of essentially equal size and shape, and each segment is treated as an individual cross-section. The average of areas A and B from all *n* segments are used to calculate the roughness index. The segments are selected so that the smallest possible roughness index is obtained. If the

perimeter of a cross-section or a section of a cross-section deviates from the smallest perimeter drawn around it in two or less places, the areas circumscribed by the two perimeters are considered identical for the purpose of this definition. The roughness index R is defined as

$$R=\frac{B-A}{B}\times 100$$

Measurements are made on at least five different cross-sections to give the mean roughness index of a fiber.

Imperfection index is measured by use of a polarizing microscope. A single filament or a piece of yarn is mounted in immersion oil of refractive index 1.55 (for filaments) or 1.63 (for yarns) and examined in longitudinal view in a polarizing microscope at a magnification of about 10 to 100×. The specimen is placed on the microscope stage between 90° crossed linear polars. The polar between the specimen and the light source is called the polarizer and the polar following the specimen is called the analyzer. Since the vibration direction of the analyzer is perpendicular to that of the polarizer, light is not transmitted by the analyzer when there is no specimen in the microscope. When a specimen (yarn or filament of this invention) is placed on the stage, however, it will "depolarize" at least a portion of the light from the polarizer and this "depolarized light" will be transmitted by the analyzer. When the stage is oriented such that the principal filament axis is parallel to the vibration direction of the polarizer (called the "extinction position") very little light will be depolarized because of the high degree of molecular orientation parallel to the axis; accordingly very little light will be transmitted by the analyzer, and the specimen will appear dark, with the exception of a few isolated bright spots. These bright spots are caused by imperfections, probably spherulitic inclusions and material around small voids which is not oriented parallel to the fiber axis, which depolarize the light. For a "perfect" fiber, the depolarization in the extinction position would be zero. When the stage is oriented such that the principal filament axis is at an angle to the vibration direction of the polarizer more of the light is depolarized, and the specimen appears bright since the analyzer transmits the light. Depolarization in the 45° position is taken to be the maximum possible.

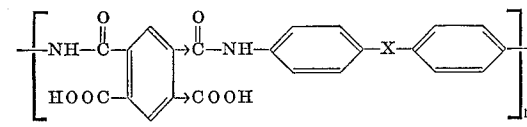
In determining imperfection index, the light intensity over the entire fiber width is measured with the specimen in the extinction position and again with the specimen in the 45° position. This is done by means of a photocell inserted into the camera slot of the microscope and connected to a Sinar-Six light meter (Gossen, Germany). The fiber must be carefully centered under the photocell. Measurements are made on three filament or yarn samples and the results averaged to give.

$$\text{Imperfection index}=\frac{\text{Light intensity with sample in extinction position}}{\text{Light intensity with sample in 45° position}}\times 100$$

Imperfection index for filaments of this invention is less than 25. In contrast, prior art filaments made by chemical spinning have a much higher imperfection index, due to depolarization in the extinction position by a large number of small, well-ordered regions which are randomly oriented with respect to the filament axis.

Certain points should be observed in connection with measurement of imperfection index as described herein. First, the filaments of this invention, if they possess inclusions, spherulites, voids, surface defects, or structural imperfections, will transmit light in the extinction (i.e. parallel) position. The scale of the Sinar-Six light meter is divided into 10 units with subdivisions between only the last nine. Thus, if the light intensity is so low that the meter indicates less than one unit (which is the case with filaments of this invention in the extinction position) the meter reading must be estimated. This of course introduces the possibility of some apparent variation in determining imperfection index for a given filament of the invention, but with care this can be kept to minimum. Second, in contrast with filaments of this invention, depolarization by prior art fibers is so great in the parallel position that the "extinction" position is difficult to establish. Therefore, the stage is oriented to the position which provides the minimum light intensity and this is taken as the parallel or extinction position. Third, prior art samples may be so opaque that optical measurements cannot be made. In this event the fibers are cut into short lengths so that the immersion oil can fill the voids and the fibers become transparent. Measurements are then taken on transparent areas of the fibers. Fourth, the intensity of light transmitted by a birefringent object between crossed polars is a function of volume. Hence, fibers of this invention (of the same sample) of different diameters (or volumes) will exhibit different intensities in the 45° position although the intensity for the parallel position, in both cases, is so near zero that no distinction between them can be observed. The result would be an apparent difference in imperfection index when in fact no such difference exists. Finally, because of small variations between filaments, the average fiber structure is more accurately described by imperfection indices of yarns than by single filament indices. However, whether measured on single filaments or yarns, imperfection indices for filaments of this invention are below the limiting value of 25.

In a preferred embodiment of the process of this invention pyromellitic dianhydride is first reacted with bis(4-aminophenyl)ether or bis(4-aminophenyl)sulfide in an organic solvent under anhydrous conditions while maintaining the temperature throughout the reaction below 65° C., advantageously below 50° C. There is thus provided a spinning solution of a polyamide-acid polymer having the formula



wherein → denotes isomerism, X represents oxygen or sulfur, and *n* is an integer sufficient to provide the polyamide-acid polymer with an inherent viscosity of at least 0.3.

A highly suitable process for the preparation of spinning solutions of the above polyamide-acid polymers involves portionwise addition of about 0.97 equivalent of solid pyromellitic dianhydride to a solution of about 1.0 equivalent of the appropriate diamine disolved in an organic solvent. The contents of the reaction vessel are desirably kept below 60° C., preferably below 50° C., at all times during the addition by externally cooling the contents so as to remove the evolved heat of polymerization. The resulting polymer solution is then adjusted to a suitable solution viscosity by incremental addition of a solution or slurry of pyromellitic dianhydride in the organic solvent. Reagents and solutions at all times should be kept under nitrogen to exclude moisture. For the same reason the reaction vessel should be also flushed with nitrogen prior to dissolution of the diamine in the solvent.

While many organic solvents are useful for preparing polyamide-acid polymers in solution form, those found especially suitable for use in the process of the invention for the preparation of polymer solutions and for the direct dry spinning of strong filaments therefrom are N,N-dimethylacetamide and pyridine, and mixtures thereof. N,N-dimethylacetamide is preferred species in most cases. The solvent and reactants should be essentially anhydrous because of the detrimental effect of water upon the polymerization process.

Polyamide-acid polymer spinning solutions containing from 12 to 25% or greater by weight solids can be employed in the process of the invention although spinning solutions of about 20% solids content are particularly

well suited. Molecular weight, as measured by the inherent viscosity of the polyamide-acid spinning solution, is not a particularly critical factor in preparing tough polyimide fibers by the process of this invention since high molecular weight polymers are readily achieved. However, solution viscosity is a factor of some importance in this respect. For example, in the spining of a dimethylacetamide solution of the polypyromellitamide-acid polymer prepared from pyromellitic dianhydride and bis(4-aminophenyl) ether it has been found that suitable filaments can be dry spun from solutions wherein the solution viscosity varies between 800 and 2400 poises at 30° C. The solution viscosity, as measured in poise units with a Brookfield viscometer, increases sharply as equivalence is approached and, in accordance with the preferred process of preparing these solutions, final additions of the pyromellitic dianhydride solution or slurry must be made with care. Solution viscosity drops as the equivalence point is exceeded. It is, therefore, important for the stability of the polymer to avoid using an excess of pyromellitic dianhydride in preparing the spinning solution.

When the desired solution viscosity has been attained, the polyamide-acid spinning solution (which preferably is not handled for prolonged periods of time at temperatures above 80° C. prior to spinning) is extruded through a spinneret into a heated spinning column which is continuously being swept by a steady co-current flow of dry gas, e.g. nitrogen. Normally the gas will be heated to a temperature below 280° C., usually 200–280° C. Spinning conditions should be adjusted so that the freshly spun filaments contain about 20% to about 35%, preferably about 20% to 30% of the spinning solvent based on the total weight of the filament. The filaments are withdrawn from the spinning column at a rate of about 125–200 yds./min. and may then be treated with water or a finishing composition after they emerge from the spinning chamber.

The subsequent steps of the process for obtaining the strong, thermally stable polyimide fibers from the as-spun filaments need not be carried out in a fixed sequence, since several variations are possible within the scope of the invention. As previously noted, these post spinning steps involve filament drawing and complete conversion of the as-spun filaments to the polyimide species. Additional steps include tempering of the polyimide filaments at elevated temperatures, and, if desired, annealing of the filaments following the tempering step. As used herein, the term "tempering" refers to heat treatment of the filaments on the run by contact with a heated roll or plate and the term "annealing" refers to heat treating the filaments subsequent to tempering and at a higher temperature than that attained by the filaments in tempering. Filament drawing, within limits to be described more fully hereinafter, can be accomplished by drawing the as-spun filaments in air or water (distilled or deionized) prior to their complete conversion to the polyimide species. However, the drawing can also be fully performed after the conversion process at the same time the filaments are caused to undergo a tempering treatment in contact with a surface heated to at least 380° C. Prior to the initial drawing action or concurrently therewith, it is desirable that filaments spun from dimethylacetamide be at some time immersed in distilled or deionized water. Distilled or deionized water is highly preferred for use in the washing or wash-drawing baths at all times since apparently inorganic salts in the water can seriously affect the thermal stability of the polyimide products. Filament drawing according to the preferred embodiment of the process is performed in a manner which represents a combination of the two methods previously described. That is, the as-spun filaments are initially drawn a limited amount (preferably 1.3–2.5×) in water prior to their conversion to the polyimide species and the balance of the drawing is performed on the converted filaments during the tempering action. The presence of water appears to facilitate the initial drawing procedure by plasticizing the filaments and preventing their dehydration. Other drawing procedures are also possible, however, within the scope of this invention. The total draw ratio, regardless of the procedures employed, is at least about 1.3×, preferably 2.0–2.5×. It will be understood that the filaments should not be drawn to that extent which would cause filament breakage. For this reason a draw ratio of 3.4× should generally not be exceeded.

Conversion of the as-spun filaments to strong, thermally stable polyimide filaments by imidization of the polyamide-acid linkages in the polymer can be effected by either chemical or thermal means. Chemical conversion is most advantageously performed by immersing the as-spun filaments in a liquid bath comprised of a suitable dehydrating agent. Such suitable dehydrating agents can be the anhydrides of lower fatty monobasic acids, for example, acetic anhydride and propionic anhydride, or they can be anhydrides of aromatic carboxylic acids, for example, benzoic anhydride, or they can be carbodiimides, for example, dicyclohexylcarbodiimide. However, in its preferred embodiment the process of completely converting the dry spun filaments to the polyimide structure is performed by thermal, rather than chemical, means. Thermal conversion not only is simpler because it eliminates the need for a washing step to remove excess cyclizing agent prior to tempering, but also it eliminates certain fume problems inherent in the use of the liquid dehydrating baths. Moreover, diffusion of the cyclizing agent into the as-extruded filaments is somewhat slow at room temperature and thus hinders completion of the imidization step. Although the diffusion can be hastened by maintaining the cyclizing baths at higher temperatures, such is frequently accompanied by degradation of the yarn since the anhydride cyclizing agent may tend to attack the polymer at temperature even as low as 40° C.

An important feature of the thermal conversion procedure is the requirement to keep the filaments under low tension during the conversion, that is, under a tension of from about 0.0 gram per denier to 0.5 gram per denier, preferably from 0.0–0.2 gram per denier. Unless this requirement is met during the conversion step the filaments become severely weakened and highly susceptible to breakage. Under this condition of low tension, thermal conversion of the drawn filaments is preferably accomplished by heating the filaments at temperatures of at least 200° C. The thermal conversion is preferably effected at a temperature of 260 to 350° C. The period required for complete conversion to occur, usually 1 minute to 120 minutes, will vary depending upon the temperature employed. In general lower time periods are used at higher temperatures and vice-versa. This is shown by the following values obtained for typical conversions performed in accordance with the method of the invention.

Single Stage Heating Step Temperature (° C.)	Length Of Heating Period, minutes	Percent Conversion
200	60	94
200	90	100
250	45	100
300	10	100

To convert at a low tension the drawn filaments may be fed onto a moving belt and in this supported condition be transported through a heated atmosphere where conversion takes place (for example, in air warmed by means of infrared sources). The filaments may also be led over a series of heated rolls or through a heated atmosphere on a series of pulleys in order to accomplish the conversion. In addition, the filaments can be made up into skeins which are placed in a heated atmosphere, under sufficient support, for the conversion step. When treated in the form of skeins as is preferred, the filaments are under essentially zero tension. It will be understood that thermal conversion can be accomplished by incremental stages.

When the process of converting the as-spun filaments to the polyimide structure is completed, the filaments are tempered by briefly passing them into contact with a surface having a temperature of at least 380° C. or by longer heating on a bobbin at a temperature of at least 300° C. This heated surface may be a heated metal block or plate, e.g., a block of chromium-plated copper or of aluminum plated with stainless steel. This tempering action contributes significantly to the high strength of the polyimide filaments. A simultaneous drawing of the filaments may also be accomplished during this tempering step in the event the desired draw ratio has not yet been fully obtained. For example, by initially drawing the as-spun filaments 1.5× in a heated aqueous bath followed by a post-conversion drawing of 1.5× during the tempering step, polyimide filaments with outstanding physical and chemical properties are provided. Subsequent annealing of the filaments at a temperature above the temperature reached by the filaments during tempering improves the already excellent thermal and tensile properties.

The filaments of the invention may be of normal textile denier, i.e., up to 10 denier per filament or more, and of various shapes. Thus the filaments be of round, cruciform, delta-shaped, ribbon, dumb-bell, or other non-circular cross-section. The filaments may range from relatively short-length staple fibers to continuous length fibers and may be assembled into various forms such as yarn, tow, sliver, or other filamentary bundles. Moreover, the filaments may comprise loose fibrous masses as well as non-woven, woven, and knitted fabrics. Typical uses for the filaments because of their excellent thermal stability and resistance to burning include fabrics for high temperature electrical insulation, cable wrapping, protective clothing, curtains, packings, linings, etc.

The filaments of the invention may be modified by typical additives such as pigments, dyes, finishes, anti-static agents and the like. In some cases these may be advantageously provided in the filaments by inclusion directly in the spinning solution. For the most part care should be exercised in avoiding iron-containing additives or contaminants as these tend to lower the thermal stability properties of the polyimide filaments when the amount of iron exceeds about 55 parts per million.

The dry spun polyimides of the invention exhibit a high level of properties with respect to tenacity and flex life. They typically exhibit a transverse tenacity of at least 1 g./d. and a flex life of at least 1000 cycles. As will be apparent from the examples, corresponding wet spun filaments are extremely deficient with respect to these properties.

The polyimide filaments of this invention are also highly resistant to hydrolysis by boiling water, steam, and dilute acids and retain their excellent tensile properties even after lengthy exposure to such hydrolysis conditions.

The filaments of the invention exhibit excellent light stability as witnessed by the behavior of polyimide yarns after prolonged exposure to an intense light source. For testing this light durability, samples of the yarns were exposed to the light emitted by a xenon-filled lamp (type Osram XBF–6000) inserted in a Model FDA–R Fade-Ometer (Atlas Electric Devices Co., Inc., Chicago, Ill.), which was operated in accordance with a procedure similar to the standard testing procedure for dyed textiles (ASTM designation D506–55). When a polyimide fiber prepared according to the general method of Example 1 herein was subjected to this testing procedure, the fiber was found to retain over 33% of its original straight tenacity (5.6 g./d.) after being exposed for nearly 950 hours.

The thermal stability of the polyimide fibers of this invention is readily manifested by measurements which show that the fibers retain their tensile properties both during and after exposure to high temperatures. A meaningful definition of thermal stability for a fiber should take into account the property of the fiber, essential to its tensile use, which is subject to the most adverse change when the fiber is heated. In this respect, loop tenacity measurements taken on single filaments or yarn provide a rigorous test of the transverse strength of a fiber since quite acceptable values of straight tenacity and percent elongation may be retained even after a fiber is subjected to extreme conditions of thermal aging.

Thermal stability measurements (taken in air) for the fibers of this invention, and for polyimide fibers prepared by prior art methods, were obtained under several conditions. For example, fiber specimens were held at an elevated temperature (e.g., 300° C.) and the tensile properties measured at that temperature. In another test, respective fiber specimens were thermally aged by exposure for various periods of time to a constant temperature (e.g., 400° C.) after which they were each returned to room temperature for evaluation of tensile property retention after such exposure conditions. Details of these test procedures are given in subsequent paragraphs.

Tensile strength, elongation, and initial tensile modulus properties are reported in the following examples for the fibers of this invention in terms of both straight (or linear) and transverse measurements determined under both elevated temperature and room temperature conditions (21.1° C., 65% relative humidity). Unless otherwise, specified, properties are reported for room temperature conditions. These physical properties were determined by conventional procedures using an Instron tester (a product of the Instron Engineering Corp., Canton, Mass.). Unless otherwise specified, these measurements were obtained from yarn samples which were 10 inches in length, were twisted 3 turns per inch, and were subjected to a load sufficient to cause elongation to occur at the rate of 100% per minute. Loop stress-strain measurements were obtained by looping two yarns over each other so that both ends of one yarn are in the upper clamp of the Instron tester and both ends of the other yarn are in the lower clamp of the testing device, after which a regular stress-strain curve is made.

Measurement of these properties at elevated temperatures (e.g., at 300° C.) was performed as described above except that, prior to elongating a given sample, the yarn resided in the test atmosphere for a period of 1 minute in order to bring it to equilibrium with the test atmosphere. Determination of the loop tenacity change of a fiber sample at a given temperature (e.g., 400° C.) was performed by holding given specimens in air at that temperature for various periods of time, after which the specimens were cooled to room temperature conditions whereat the tensile properties were determined as described above.

A measure of the transverse properties and brittleness of a fiber may be obtained by determining the flex resistance of individual filaments. The flex resistance of the polyimide fibers of this invention is measured by repeatedly bending individual filaments through an angle of 180 degrees over a 0.003 inch diameter stationary tungsten wire while under tension and is reported as the number of cycles required to break 11 of 21 filament samples undergoing simultaneous testing. The test is somewhat denier-dependent since larger filaments tend to give lower results. However in normal textile deniers the products of the invention will generally exhibit flex life values in excess of 1000 cycles. The test is performed simultaneously on 21 filament samples (each conveniently about 7.5 cm. in length) which have been conditioned for at least 16 hours at 21.1° C. and 65% relative humidity. Each of these specimens has a denier within ±10% of the average denier of the entire test group. One end of each filament is drawn up into a small loop through which is wound a length of 0.0625 inch diameter lead wire sufficiently heavy to apply a tension of 0.6 g. per denier to the filament during testing. The other end of this filament is carefully placed within one of a series of clamps contained in an electrically-driven oscillating apparatus which flexes the free-hanging filament samples over the stationary tungsten wire

through an angle of 180 degrees at the constant rate of 149 cycles per minute. The number of cycles required to break 11 of the filaments under the above-cited conditions is determined from a cycle-recording counter which is part of the apparatus and is reported as the flex resistance of the fiber.

Inherent viscosities (η_{inh}) are determined at 30° C. in accordance with the following equation:

$$\eta_{inh}=\frac{\ln \eta_{rel}}{C}$$

The relative viscosity (η_{rel}) may be determined by dividing the flow time in a capillary viscometer of a dilute solution of the polymer by the flow time for the pure solvent. The concentration term (C) is 0.5 gram of polymer per 100 ml. of solution.

The determination of viscosities in poise units, also performed at 30° C., is performed by use of a Brookfield viscometer according to standard test procedures.

Fiber properties of tenacity, elongation, and initial modulus, for both straight and loop measurements, are coded as T/E/M_i and are in conventional units of grams per denier, percent, and grams per denier, respectively.

The following examples will further illustrate the invention. Therein all parts are by weight unless otherwise indicated.

Example 1

This example demonstrates wash-drawing of as-spun filaments prior to their thermal conversion, while in the form of skeins to the polyimide species. The converted filaments are further drawn during subsequent tempering.

A solution consisting of anhydrous bis(4-aminophenyl) ether (3.4 kg., 17 moles) in 27.8 l. of anhydrous dimethylacetamide is prepared in a glass-lined reaction vessel under a nitrogen atmosphere. The temperature of this solution is kept within 15–18° C. by external cooling and continuous stirring during dissolution of the diamine. Anhydrous pyromellitic dianhydride (3.5 kg., 16.2 moles) is added, in portions, to the well-stirred diamine solution during an interval of about 100 minutes, during which period the solution is kept at a temperature within 18°–28° C. by external cooling. When the prepolymer ingredients have completely reacted, the solution is pumped, under nitrogen, to a second reaction vessel equipped with an efficient stirring apparatus. An additional quantity of dry pyromellitic dianhydride (80 g., 0.37 mole) is then added to the nitrogen-blanketed solution while keeping the solution temperature below 35° C. This polymer solution is brought to the desired spinning viscosity of 1,960 poises (η_{inh}=1.3) at 30° C. by the incremental addition, under nitrogen, of about 800 ml. of a 10% slurry of pyromellitic dianhydride in dimethylacetamide during a 100 min. period. After its preparation this spinning solution is stored under nitrogen at a temperature below 0° C. It is then pumped to another storage vessel wherein it is kept at 15° C., under nitrogen, prior to being pumped through a pancake filter to the head of the spinning cell. At the latter point the solution is maintained at 62° C. by a cold water coil. The polymer solution is then extruded at the rate of about 45.5 ml./min. through a spinneret having 60 holes of 0.006 inch diameter into a drying column whose walls are kept at a temperature of 202° C. The column is swept with a co-current stream of dry nitrogen gas which enters the column at 265° C.

The emerging yarn, of approximately 400 denier, is wound up on a bobbin at the rate of 180 yd./min., with about 150 ml./min. of water being applied to the threadline at it emerges from the spinning cell. About 8% of the polyamide linkages present in the polymer prior to spinning are converted to polyimide linkages in preparing this yarn, as determined by infrared analysis. The wet as-spun yarn, containing about 38% dimethylacetamide and about 95% water by weight (based on the dry weight of the yarn) is stored at room temperature in polyethylene bags prior to being drawn. (Yarn stored in this manner is preferably drawn not more than 2 days after spinning.) The yarn is then removed from the bobbin at the rate of 75 yd./min. and is led through a bath of distilled water, 3 feet in length and kept at 75° C., wherein the yarn is drawn 1.5×. The yarn is subsequently dried by passing it over drying rolls heated to 140° C. (yarn contact time is about 1.0 sec.), after which it is wound onto cardboard tubes by a traversing friction drive roll. The yarn has a dimethylacetamide content of about 18% at this point.

From the tubes the yarn is made into skeins which are suspended from racks and exposed in an oven for 30 min. at 100° C. and 275° C. for 15 min. This thermal treatment converts the drawn, as-spun yarn to the polyimide composition. The converted yarn is again transferred to a bobbin from whence it is led, at a rate of 55 yd./min., into contact with a heated plate maintained at 550° C. On the plate the yarn is further drawn 1.5× to provide 220 denier polyimide yarn having T/E/M_i values of

3.5/11.7/50

and loop T/E values of 3.1/12.0.

Example 2

This example illustrates the preparation of polyamide-acid filaments which are subjected to single-stage drawing in air prior to their thermal conversion to the corresponding polyimide composition.

A solution consisting of bis(4-aminophenyl)ether (12.0 g., 0.06 mole) dissolved in 100 g. of dry dimethylacetamide is prepared within a dry box. To this stirred solution, kept under dry nitrogen, is added, in portions, a quantity of anhydrous pyromellitic dianhydride (12.8 g., 0.059 mole) over a 5 min. interval. The resulting polymer solution is brought to the desired spinning viscosity (η_{inh}=2.03) by the careful, slow addition of incremental qualities of a 5% solution of anhydrous pyromellitic dianhydride in dry dimethylacetamide. The polyamide-acid spinning solution, kept at a temperature within 50–60° C., is extruded from a closed cylinder at the rate of 2.92 ml./min., via an adapter maintained at 124–126° C., by an oil-driven piston under a pressure of 175 p.s.i. through a spinneret having 10 holes of 0.005 inch diameter. A drying column, swept by a co-current flow (5 cu. ft./min.) of dry nitrogen gas at a temperature of 200–215° C., permits evaporation of the solvent. The resulting filaments are wound at a rate of 125 yd./min. onto a bobbin which is intermittently wetted with distilled water.

The bobbin of as-spun fibers is immersed for 45 minutes in a bath of distilled water at room temperature after which the filaments are unwound from the bobbin, stretched 1.5× in room temperature air, and rewound on a second bobbin. The drawn filaments are then converted to the polyimide on the bobbin by heating the bobbin under the following conditions: 20 min. at 200° C., 20 min. at 250° C., 20 min. at 300° C., 5 min. at 400° C., and 9 min. at 500° C. The filaments are loosened between each of these heating stages and are then tightly rewound prior to the next heating period. This process affords polyimide filaments of 2.3 denier having T/E/M_i values of 5.6/17.0/56 and loop T/E values of 1.7/4.5.

The use of a polyamide-acid spinning solution containing 25 solids (η_{inh}=1.07, dynamic viscosity=1,750 poises) in the process of this example produces polyimide filaments possessing tensile properties similar to those reported in the previous paragraph.

Example 3

This example illustrates wash-drawing of as-spun polymer filaments, followed by drawing and converting the filaments on heated plates to furnish polyimide filaments having a high value of straight tenacity.

A polyamide-acid spinning solution, comprising 20% solids (η_{inh}=1.22), is prepared by the procedure of Example 2 herein. This solution, maintained at 38–40° C., is extruded from a closed cylinder at the rate of 4.1 ml./min. by an oil-driven piston under a pressure of 275 p.s.i. through a spinneret having 10 holes of 0.005 inch diameter into a drying column swept by a co-current flow (5.25 cu. ft./min.) of dry nitrogen at a temperature of 200–245° C. The filaments thus produced are wound onto a bobbin under the conditions described previously in Example 2.

The bobbin of as-spun filaments is immersed in water as in Example 2. The filaments are then unwound and led through a water bath heated to 75° C. wherein they are drawn 1.7× and are rewound on a second bobbin located outside the water bath. The wash-drawn filaments are removed from the second bobbin at the rate of 10.5 ft./min. and passed into contact with a heated, curved plate, 18 inches in length, which has a temperature gradient spanning 175° C.–255° C. The filaments are drawn 1.1× during their passage over the plate. The filaments are led into contact with a second plate heated to 500–510° C. whereon they are drawn 1.04× during their 10 second time of contact with this plate. Polyimide filaments produced by this technique have straight T/E/M_i values of 8.6/11.9/75 and loop T/E values of 1.3/2.1.

Example 4

The utilization of the process of this invention for the preparation of strong filaments of the polyimide obtained from bis(4-aminophenyl)sulfide and pyromellitic dianhydride is hereby illustrated.

A solution of anhydrous bis(4-aminophenyl)sulfide (16.2 g., 0.075 mole) in 90 g. of dry dimethylacetamide is prepared in a resin flask and pyromellitic dianhydride (15.7 g., 0.072 mole) is slowly added, portionwise, thereto. The resulting polymer solution is brought to the desired spinning viscosity (η_{inh}=1.63) by the incremental addition of a 10% slurry of pyromellitic dianhydride in anhydrous dimethylacetamide. This polyamide-acid spinning solution, kept at 30–32° C., is extruded from a closed cylinder, at the rate of 4.7 ml./min., by an oil-driven piston under a pressure of 425–500 p.s.i. through a spinneret having 10 holes of 0.005 inch diameter and into a drying column swept by a co-current flow (5.5 cu. ft./min.) of dry nitrogen at temperature of 255–265° C. The filaments thus produced, having a round cross-section, are wound up at 190 yds./min. Distilled water is intermittently applied to the fibers on the wind-up bobbin.

The as-spun filaments are treated as in Example 2 and are removed from the windup bobbin at the rate of 100 ft./min., passed through a water bath heated to 75° C. wherein they are drawn 1.35×, and are then rewound as they emerge from the bath. The bobbin of wash-drawn yarn is converted to the polyimide structure by being heated, while still on the bobbin, under the following conditions: 100° C. for 4 hours, 275° C. for 25 min., and 400° C. for 25 min. The converted filaments are subsequently removed from the bobbin at the rate of 100 ft./min. and are drawn 1.6× while being tempered during contact with an 18 inch long heated plate having a 250° C.–420° C.–250° C. temperature profile. The final polyimide filaments possess the following properties: T/E/M_i=2.8/25.7/31 and loop T/E=1.2/8.1.

Example 5

A polyamide-acid solution is prepared and filaments spun therefrom according to the procedure of Example 2 herein. The as-spun filaments are washed and drawn 1.75× in a water bath kept at 75° C. The drawn filaments are dried and converted to the polyimide form by passage over the following system of hot plates at an input rate of 75 ft./min.:

Plate No.	Plate Temperature, ° C.	Contact Distance, ft.	Contact Time, sec.
1	205	2.5	2.0
2	(1)	1.5	1.2
3	310	4.5	3.6
4	500	2.0	1.6

[1] Gradient of 175°–270°.

This treatment produces polyimide filaments of T/E/M_i=5.7/14.5/53 and loop T/E/M_i=2.7/6.7/53.5.

Example 6

A polyimide-acid solution is prepared and filaments spun and wash-drawn therefrom as in Example 2. The filaments are then dried and converted to the polyimide over the following system of plates and rolls: At an input rate of 50 yd./min., yarn is passed over a 2 ft. diameter, gas-heated roll for three-wraps (contact time 7.5 sec.), at 170–180° C.; then for a similar contact time over the same drum at 215–230° C.; then for a contact time of 2.5 sec. over the same drum at 250–255° C. and finally over a hot shoe (contact time 0.2 sec.) at 485–500° C. with a 1.15× draw over the shoe. This gives yarn with T/E/M_i=4.2/12/63 and loop T/E=2.1/4.5.

Example 7

The dry spinning of filaments from a pyridine solution of a polyamide-acid polymer is exemplified herein.

Anhydrous pyromellitic dianhydride (50.8 g., 0.23 mole) is slowly added with vigorous stirring, under nitrogen, to a solution of bis(4-aminophenyl)ether (48 g., 0.24 mole) in 650 ml. of anhydrous pyridine. This polymer solution (14% solids) is brought to the desired spinning viscosity (4,500 poises, η_{inh}=1.65) by the careful incremental addition of an appropriate quantity of a 5% pyromellitic dianhydride solution in pyridine. The solution, kept at 45–50° C., is extruded from a closed cylinder at the rate of 3.2–3.5 ml./min., via an adapter maintained at 70–80° C., by an oil-driven piston under a pressure of 350–400 p.s.i. through a protrusion type spinneret having 10 holes of 0.005 inch diameter. A drying column, swept by a co-current flow (5.5 cu. ft./min.) of dry nitrogen gas at a temperature of 185–200° C., permits evaporation of the solvent. The resulting filaments are wound at the rate of 92 yd./min. onto a bobbin while a finish comprising "Ultrasense"[1] "Dow Corning Fluid 200"[2] "Span 20"[3] in a ratio of 80/20/10 parts by weight is applied to the filaments.

The as-spun filaments are converted to the polyimide by heating them on the bobbin under the following successive conditions: 15 hr. at 70° C., 24 hr. at 170° C., and 3 hr. at 300° C. The polyimide filaments are then drawn 1.3× at 400° C. over a plate (total draw is 1.3×) to provide 5.0 denier filaments having straight T/EM_i values of 3.5/25.3/45.0 and loop T/E values of 1.5/5.6.

Example 8

This example illustrates the dry spinning of a pyridine solution of a polyamide-acid. Filament drawing is performed prior to the thermal conversion step.

A polyamide-acid spinning solution, comprising 15.6% solids, is prepared and spun as in Example 7 with the exception that the nitrogen gas in the drying column is at a temperature of 152–190° C. The finish composition of Example 7 is again applied to the filaments as they are wound onto the bobbin. The filaments are subsequently drawn 1.5× in air and are rewound onto a second bobbin whereon they are subjected to heating for 25 hr. at 80° C. and 16 hr. at 160° C. Conversion of the filaments to the polyimide species is completed by

[1] Atlantic Refining Co.'s deodorized petroleum product.
[2] Dow Corning Co.'s inert, liquid silicone product.
[3] Atlas Chemical Industries' sorbitan monolaurate wetting agent.

further heating them for 3 hr. at 300° C., after which they are tempered on the bobbin by heating for 4 min. at 600° C. This treatment affords 3.0 denier filaments having straight T/E/M_i values of 5.3/24/49 and loop T/E values of 2.0/6.

Example 9

Chemical conversion of as-spun, wash-drawn filaments to the corresponding polyimide species is illustrated herein.

A spinning solution is prepared and spun as in Example 2. The as-spun filaments are wash-drawn 1.8× in water according to the procedure of Example 2, after which samples of the drawn filaments are converted to the polyimide form by subjecting them, on separate bobbins, to one of the following treatments:

(a) A bobbin of filaments is immersed at 25° C. in a mixture of acetic anhydride/pyridine (70/30 by volume) for 15 hrs., after which it is removed from the liquid mixture and is heated in an oven under the following conditions: 15 hr. at 80° C., 30 min. at 200° C., 30 min. at 250° C., and 30 min. at 300° C.

(b) A bobbin of filaments is immersed at 25° C. in a mixture of acetic anhydride/triethyl amine (70/30 by volume) for 15 hrs., after which it is removed from the liquid mixture and heated in an oven under the following conditions: 5 hr. at 80° C., 30 min. at 200° C., 30 min. at 250° C., and 30 min. at 300° C.

Polyimide filaments produced by the above procedures exhibit properties similar to those of filaments obtained through the thermal conversion techniques described herein.

Example 10

This example demonstrates the improvement produced in polyimide filament tensile properties by postconversion annealing.

PART A

A polyamide-acid spinning solution containing 25% solids is prepared, spun, and the resulting fibers drawn 1.2× as in Example 2. The fibers are then converted to the polyimide form by being successively heated in an oven under the following conditions: 18 hr. at 80° C., 30 min. at 200° C., 40 min. at 250° C., 30 min. at 300° C., and 8 min. at 400° C. The resulting polyimide fiber exhibits T/E/M_i values of 3.2/55/29. After these filaments are annealed on a bobbin for an additional 16 min. at 400° C., they exhibit straight T/E/M_i values of 4.5/26/37.

PART B

A polyamide-acid spinning solution in pyridine (20% solids, η_{inh}=0.88, dynamic viscosity=1,500 poises) is prepared and spun as in Example 7. The as-spun filaments are drawn 1.3× and are then converted to the polyimide species as in Example 7 to provide fibers having straight T/E/M_i values of 2.8/68/19. After these filaments are annealed on a bobbin for 4 min. at 600° C., they possess straight T/E/M_i values 3.75/22/31.

PART C

A polyamide-acid spinning solution is prepared and spun as in Example 1. The as-spun filaments are wash-drawn 1.6× and converted to the polyimide species as in Example 1. The converted filaments, as a yarn, are passed at 100 ft./min. over a plate heated to 200° C. and thence over a shoe heated to 500° C., being drawn 1.6× in the process. This treatment affords 170 denier/60 filament yarn having straight T/E/M_i values of 4.2/7.6/62. When an additional shoe, maintained at 525° C., is placed within the system immediately after the drawing section and the drawn yarn is passed over it (whiie shrinking 3%), the yarn's straight T/E/M_i values becomes 5.2/9.8/67.

Example 11

Presented in Table I below is a summary of polyimide yarn properties which are obtained as a result of variations in draw ratio, yarn processing speeds during drawing, and in plate and shoe temperatures when drawing is performed according to the process of this invention. In each instance, the polyimide is that obtained from pyromellitic dianhydride and bis(4-aminophenyl)ether.

Example 12

This example illustrates the preparation of filaments by both wet and chemical spinning of polyamide-solutions according to prior art procedures. The polyimide fibers ultimately obtained are shown to exhibit poor transverse tensile properties.

TABLE I

Feature	Draw Ratio		Total Draw	Yarn Input Speed To Plate, ft./min.	Temperature, ° C.		Yarn Property	
	Wash-Draw	Post-Conversion Draw			Plate	Shoe	T/E/M_i	Loop T/E
High Total Draw	1.5×	2.25×	3.38×	25	285	575	6.6/9.0/77	2.8/4.5
High Input Speed	1.5×	1.7×	2.55×	375	----------	----------	4.2/9.8/67	3.8/7.6
Low Wash-Draw, High Post-Draw	(1)	2.5×	2.5×	----------	----------	490	5.8/16.9/54	2.4/4.9

[1] None.

PART A

Anhydrous pyromellitic dianhydride (53 g., 0.24 mole) is slowly added with effective stirring, under nitrogen, to a solution of bis(4-aminophenyl)ether (50 g., 0.25 mole) in a mixture of dry pyridine/dimethylacetamide (40/60 by volume). This polymer solution (18% solids) is brought to the desired spinning viscosity (η_{inh}=1.5) by the careful addition of the appropriate amount of an 8% pyromellitic dianhydride solution in the same solvent mixture. This spinning solution, kept at room temperature, is extruded by an oil-driven piston at the rate of 4.7 ml./min. through a spinneret having 20 holes of 0.004 inch diameter into a bath of acetic anhydride maintained at 21° C. After 5 traverses through the bath (total length travelled is 12 ft. in a bath-contact time of 48 sec.), the filaments are wound on a metering roll at 15 ft./min. and are drawn in air 2.06× between the metering roll and a windup bobbin. The white, as-wound filaments slowly become orange upon standing on the bobbin. The filaments are completely converted to the polyimide species by heating them in an oven under the following successive conditions: 3 hr. at 100° C., 30 min. at 300° C., and 15 min. at 400° C. The dark orange-brown 13 denier polyimide filaments have the following properties: straight T/E/M_i=3.6/12.6/59.5 and loop T/E=0.7/2.4. Although the filaments can be stretched slightly over a hot plate, no improvement in tensile properties results.

PART B

A polyamide-acid spinning solution comprising 20% solids is prepared according to Example 2. This solution is spun by the procedure of Example 12A into a room temperature water bath. After traversing the bath for a total time of 48 sec., the filaments are wound onto a bobbin at the rate of 15 ft./min. The filaments are dried on the bobbin by heating for 3 hr. at 80° C. The polyamide-acid filaments are then converted to the polyimide by being heated on the bobbin for 30 min. at 300° C. and 30 min. at 400° C. The dark brown, 712 denier polyimide filaments have straight T/E/M_i values of 1.53/6.4/52.8 and loop T/E values of 0.19/1.3. In polyamide-acid form the filaments are too weak to be drawn successfully. Drawing the polyimide filaments only weakens them further.

Example 13

This example demonstrates that fibers prepared by the process of this invention retain their excellent tensile properties during exposure to conditions of high temperature.

A polyamide-acid spinning solution is prepared and processed as in Example 1, with the exception that the converted filaments are postdrawn 2.05× while in contact with a plate maintained at 525° C., filament input speed to this plate being 25 ft./min. This treatment produces a 166 denier/60 filament polyimide yarn exhibiting the following tensile properties at 21° C.: straight T/E/M_i=5.14/9.0/68.5 and loop T/E=4.0/6.7. When the tensile properties of this yarn are measured at 300° C. by the procedure hereinbefore described, the following results are obtained: straight T/E/M_i=2.55/8.8/39.5 and loop T/E=1.6/4.4.

Example 14

This example further demonstrates that the polyimide filaments prepared by the process of this invention possess enhanced levels of transverse tensile properties and are characterized by a lack of brittleness, as measured by their resistance to breaking when subjected to the flexing test described hereinbefore.

In the following Table II, the column headed "Filament" indicates the example whose procedure is employed to obtain the respective filaments being tested and the column headed "Flex Resistance" indicates the number of flexing cycles required to break 11 of the 21 filament specimens tested, as previously noted.

TABLE II

Filament	Average Filament Denier	Flex Resistance, cycles
Example 1	2.65	204,861
Example 4	2.37	39,705
Example 12A		(1)

[1] Less than 10 cycles.

Example 15

This example demonstrates the comparative thermal stability properties (in air) at 400° C. of polyimide filaments prepared by the process of this invention. In the following Table III, the column entitle "Filament" indicates the preparative method for the filament being tested, and the column headed "Time, Hr." records the exposure hours at 400° C. which produce the corresponding loop tensile properties recorded under "Loop T/E" and measured after the respective filament specimens have been returned to room temperature.

TABLE III

Filament	Time, hr.	Loop T/E
Example 2	0.0	3.7/17.3
	3.25	1.02/2.3
Example 9A	0.0	3.0/9.7
	2.0	1.35/2.8
	2.5	0.9/2.3
	3.25	0.84/1.8
Example 9B	0.0	2.45/8.4
	2.0	1.21/3.0
	2.5	1.32/3.0
	3.75	0.76/1.8
	4.25	0.57/1.4
Example 12A	0.0	0.72/2.4
	1.25	(1)
	3.0	(1)

[1] Too brittle to test.

Example 16

A solution consisting of anhydrous bis(4-aminophenyl)ether (170.0 g., 0.85 mole) in 1385 ml. anhydrous dimethylacetamide is prepared in a resin kettle under nitrogen. Anhydrous pyromellitic dianhydride (181.0 g., 0.83 mole) is added, in portions, to the well-stirred diamine solution during an interval of about 60 minutes, during which period the solution is kept at 15° C. by external cooling. Last traces of pyromellitic dianhydride are washed from the additon flask into the resin kettle with 50 ml. dimethylacetamide. The resin kettle is then removed from the cooling bath and the polymer solution is brought to the desired spinning viscosity of 960 poises (η_{inh}=1.2) at 30° C. by the incremental addition, under nitrogen and at a solution temperature below 35°, of about 31 ml. of a 3.5% solution (weight/weight) of pyromellitic dianhydride in dimethylacetamide during a 30 minute period. The polymer solution (20% solids) is stirred at about 25° C. for 30 minutes prior to being filled into the spinning cell.

In the spinning cell, the solution is maintained at 27–35° C. by a cold water coil. The polymer solution is then extruded at the rate of about 8.2 ml./min. through a spinneret having 17 holes of 0.005 inch diameter into a drying column whose walls are kept at a temperature of 160° C. The column is swept with a co-current stream of dry nitrogen gas which enters the column at 105–108° C. The emerging yarn, of approximately 160 denier, is wound up on a bobbin at the rate of 124 yd./min. with water being applied to the thread-line as it emerges from the spinning cell. The as-spun yarn, containing about 34% dimethylacetamide by weight (based on the total weight of the water-free yarn) is stored at room temperature in polyethylene bags prior to being drawn. (Yarn stored in this manner is preferably drawn not more than 2 days after spinning.)

The bobbin of as-spun fibers is emmersed for 15 minutes in a bath of distilled water at room temperature after which the filaments are unwound from the bobbin, stretched 1.5× in room temperature air, and rewound on a second bobbin. The drawn filaments are then converted by heating the bobbin under the following conditions: 20 min. at 200° C., 20 min. at 250° C., 20 min. at 300° C., and 5 min. at 400° C. The fiaments are loosened between each of these heating stages and are then tightly rewound prior to the next heating period. This process affords polyamide filaments of 4.5 denier having T/E/M_i values of 3.2/46.4/35.6 and loop T/E values of 2.1/13.0. Additional heating at 500° C. for 9 min. gives polyimide filaments of 3.3 denier having T/E/M_i values of 2.8/6.6/53.2.

Example 17

A bobbin of as-spun polyamide-acid fibers from Example 16 is immersed in distilled water for 15 min. The filaments are then unwound and led through a water bath heated to 75° C. wherein they are drawn 1.8× and are rewound on a second bobbin located outside the water bath. The wash-drawn filaments are removed from the second bobbin at the rate of 10.5 ft./min. and passed into contact with a heated, curved plate, 18 inches in length, which has a temperature gradient spanning 160° C.–240° C. The filaments are drawn 1.1× during their passage over the plate. The filaments are led into contact with a second plate heated to 490°–495° C. whereon they are drawn 1.04× during their 13 second time of contact with the plate. Polyimide filaments produced by this technique have straight T/E/M_i values of 8.9/7.6/114.7 and loop T/E values of 1.0/1.3.

Example 18

A solution of anhydrous bis(4-aminophenyl)sulfide (16.2 g., 0.075 mole) in 95 ml. (89 g.) of dry dimethylacetamide is prepared in a resin flask and pyromellitic dianhydride (15.7 g., 0.072 mole) is slowly added, portionwise, thereto. The resulting polymer solution is brought to the desired spinning viscosity (η_{inh}=1.63) by the incremental addition of a 10% slurry of pyromellitic dianhydride in anhydrous dimethylacetamide. This polyamide-acid spinning solution, kept at 30–32° C., is extruded from a closed cylinder, at the rate of 4.7 ml./min, by an oil-driven piston under a pressure of 425–500 p.s.i. through a spinneret having 10 holes of 0.005 inch diameter and into a drying column swept by a co-current flow (5.5 cu. ft./min.) of dry nitrogen at a temperature

of 255–265° C. The filaments thus provided, having a round cross-section, are wound up at 190 yds./min. Distilled water is intermittently applied to the fibers on the windup bobbin.

The bobbin of as-spun fibers is immersed in distilled water. The filaments are then unwound and led at the rate of 100 ft./min. through a water bath heated to 75° C. whereon they are drawn 1.35×, and are then rewound as they emerge from the bath. The bobbin of wash-drawn yarn is converted to the polyimide structure by being heated, while still on the bobbin, under the following conditions: 100° C. for 4 hours, 275° C. for 25 min., and 400° C. for 25 min.

The converted filaments are subsequently unwound from the bobbin at the rate of 50 ft./min. and are drawn 1.6× while being tempered during contact with an 18 inch long heated plate having a 220°C.–420° C.–280° C. temperature profile. The final polyimide filaments possess the following properties: $T/E/M_i$=2.3/20.0/24.3 and loop T/E=1.2/8.0.

Example 19

As-spun polyamide-acid fibers from Example 16 are immersed in distilled water for 15 min. and wash-drawn 1.8× in a water bath kept at 75° C. The drawn filaments are dried and converted to the polyimide form by passage over the following system of hot plates at an input rate of 25 ft./min.:

Plate No.	Plate Temperature, ° C.	Contact Distance, ft.	Contact Time, sec.
1	200	1.0	2.4
2	(1)	1.5	2.4
3	290	1.5	3.6
4	495	1.25	3.0

[1] Gradient of 175°–255°.

During this treatment the fibers are drawn 1.12×. This treatment produces polyimide filaments of $T/E/M_i$=2.9/11.5/47.1 and loop T/E=0.9/2.2.

Example 20

As-spun polyamide-acid fibers from Example 16 are wash-drawn 1.5× as in Example 16. The drawn filaments are then dried and converted to the polyimide over the following system of plates and rolls: At an input rate of 50 yds./min., yarn is passed over an 8 in. diameter, electrically heated roll for nine wraps (contact time 7.6 sec.), at 170° C., then for a similar contact time over the same drum at 215° C., then for a contact time of 2.5 sec. over the same drum at 250° C. and finally, at an input rate of 16.7 yds./min., over an 18 in. long curved plate with a 160° C.–245° C.–185° C. temperature gradient (contact time 0.6 sec.) and a hot shoe (contact time 0.6 sec.) at 500° C. with a 1.1× draw over the shoe. This gives yarn with $T/E/M_i$=3.2/6.0/66.9 and loop T/E=2.0/3.7.

Example 21

Anhydrous pyromellitic dianhydride (53.4 g., 0.245 mole) is slowely added with vigorous stirring, under nitrogen, to a solution of bis(4-aminophenyl)ether (50.0 g., 0.25 mole) in 505 ml. of anhydrous pyridine. Last traces of pyromellitic dianhydride are washed from the addition flask into the resin kettle with 50 ml. pyridine. This polymer solution (16% solids) is brought to the desired spinning viscosity (2,100 poise, η_{inh}=1.49) by the careful incremental addition of an appropriate quantity of a 5% pyromellitic dianhydride solution in pyridine. The solution, kept at 40–45° C., is extruded from a closed cylinder at the rate of 5.0–5.3 ml./min., via an adapter maintained at 50–55° C., by an oil-driven piston under a pressure of 260–500 p.s.i. through a protrusion type spinneret having 10 holes of 0.005 inch diameter. A drying column, swept by a co-current flow (4.0 cu. ft./min.) of dry nitrogen gas at a temperature of 70–75° C., permits evaporation of the solvent. The resulting filaments are wound at the rate of 99 yd./min. onto a bobbin while a finish comprising "Ultrasene"[4] "Dow Corning Fluid 200"[5] in a ratio of 100/20 parts by weight is applied to the filaments.

The as-spun filaments are converted to the polyimide by heating them on the bobbin under the following successive conditions: 15 hr. at 80° C., 24 hr. at 160° C., and 3 hr. at 300° C. The polyimide filaments are then drawn 1.3× at 400° C. over a plate to provide 4.4 denier filaments having straight $T/E/M_i$ values of 3.8/44.6/34.9 and loop T/E values of 1.5/6.8. If the polyimide filaments are drawn 1.6× at 400° C. over a plate the resulting 3.8 denier filaments have straight $T/E/M_i$ values of 4.5/25.5/49.1 and loop T/E values of 2.1/6.7.

Example 22

As-spun polyamide-acid fibers from Example 21 are drawn 1.5× in air and are rewound onto a second bobbin whereon they are subjected to heating for 25 hr. at 80° C. and 16 hr. at 160° C. Conversion of the filaments to the polyimide species is completed by further heating them for 3 hr. at 300° C., after which they are annealed on the bobbin by heating 4 min. at 575° C. This treatment affords 3.7 denier filaments having straight $T/E/M_i$ values of 5.9/13.2/54.3 and loop T/E values of 1.0/2.8.

Example 23

As-spun polyamide-acid fibers from Example 16 are immersed in distilled water for 15 min. after which the filaments are unwound from the bobbin, stretched 1.8× in room temperature air, and rewound on a second bobbin. Samples of the drawn filaments are converted to the polyimide form by subjecting them, on separate bobbins, to one of the following treatments:

(a) A bobbin of filaments is immersed at 25° C. in a mixture of acetic anhydride/pyridine (70/30 by volume) for 15 hrs., after which it is removed from the liquid mixture and is heated in an oven under the following conditions: 5 hrs. at 80° C., 30 min. at 200° C., 30 min. at 250° C., and 30 min. at 300° C. This gives 3.0 denier polyimide filaments having straight $T/E/M_i$ values of 2.5/30.8/45.9 and loop T/E values of 2.1/16.8.

(b) A bobbin of filaments is immersed at 25° C. in a mixture of acetic anhydride/triethylamine (70/30 by volume) for 15 hrs., after which it is removed from the liquid mixture and heated in an oven under the following conditions: 5 hrs. at 80° C., 30 min. at 200° C., 30 min. at 250° C., and 30 min. at 300° C. Polyimide filaments of 3.3 denier produced by this technique, have straight $T/E/M_i$ values of 2.3/23.4/46.0 and loop T/E values of 2.0/18.1.

Examples 24

PART A

As-spun polyamide-acid filaments from Example 16 are drawn 1.2× according to the procedure of Example 16. The filaments are converted to the polyimide on the bobbin by heating under the following conditions: 20 min. at 200° C., 20 min. at 250° C. and 20 min. at 300° C. This produces polyimide filaments having straight $T/E/M_i$ values of 3.3/52.1/42.3. After these filaments are annealed on a bobbin for 16 min. at 400° C., they possess straight $T/E/M_i$ values of 3.2/45.4/30.3.

PART B

As-spun polyamide-acid fibers from Example 21 are drawn 1.5× in air and converted to the polyimide species on the bobbin by heating 25 hrs. at 80° C., 16 hrs. at 160° C., and 3 hrs. at 300° C. This produces polyimide filaments having straight $T/E/M_i$ values of 5.5/28.3/48.3. After these filaments are annealed on a bobbin for 4 min. at 575° C., they possess straight $T/E/M_i$ values of 5.9/13/54.

[4] Atlantic Refining Company's deodorized petroleum product.

[5] Dow Corning Company's inert, liquid silicone product.

PART C

As-spun polyamide-acid fibers from Example 16 are wash-drawn 1.5× according to the procedure of Example 1. The fibers are dried by passing them at a rate of 50 yd./min. over a roll maintained at 125° C. for a contact time of 0.84 sec. and are then converted according to the procedure in Example 1. The converted filaments, as a yarn, are passed at 100 ft./min. over a plate heated to 200° C. and thence over a shoe heated to 500° C., being drawn 1.6× in the process. This treatment affords 94 denier/34 filament yarn having straight T/E/M_i values of 4.1/8.7/67.0. When an additional shoe, maintained at 525–535° C., is placed within the system immediately after the drawing section and the drawn yarn is passed over it (while shrinking 2%), the yarn's straight T/E/M_i values become 4.9/9.9/68.3.

Example 25

PART A

The as-converted polyimide fibers from Example 24, Part C, are transferred to a bobbin from where they are led, at a rate of 25 ft./min., into contact with a heated plate maintained at 285° C. The filaments are drawn 1.5× during their passage over the plate. The filaments are then led to a shoe maintained at 550° C. whereon they are drawn 1.5× during their 1.8 second time of contact with this plate. Polyimide filaments produced by this technique have straight T/E/M_i values of 8.5/6.2/116.9 and loop values of 3.2/5.2.

PART B

The as-converted polyimide fibers from Example 24 Part C are led, at a rate of 300 ft./min., into contact with a heated plate maintained at 265° from where they are led to a slotted plate maintained at 550°. During their passage over both plates the filaments are drawn 1.7×. Polyimide filaments produced by this technique have straight T/E/M_i values of 4.5/7.4/77.9 and loop T/E values of 3.2/5.2.

Example 26

Anhydrous pyromellitic dianhydride (104.6 g., 0.48 mole) is slowly added with effective stirring, under nitrogen, to a solution of bis(4-aminophenyl)ether (100.0 g., 0.5 mole) in a mixture of dry pyridine/dimethylacetamide (40/60 by volume). This polymer solution is brought to the desired spinning viscosity (η_{inh}=1.0) by the careful addition of the appropriate amount of 5% pyromellitic dianhydride solution in dimethylacetamide. This spinning solution (18% solids), kept at room temperature, is extruded by an oil-driven piston at the rate of 2.0 ml./min. through a spineret having 20 holes of 0.0035 inch diameter into a bath of acetic anhydride maintained at 21° C. After 4 passes through the bath (total length travelled is 10 ft. in a bath contact time of 20 sec.), the filaments are wound on a metering roll at 30 ft./min. and are drawn in air 2.5× between the metering roll and a wind-up bobbin. The pale yellow, as-wound filaments slowly became orange upon standing on the bobbin. The filaments are completely converted to the polyimide species by heating them in an oven under the following successive conditions: 3 hr. at 100° C., 30 min. at 300° C., and 15 min. at 400° C. The dark orange-brown polyimide filaments have straight T/E/M_i values of 2.3/8.6/41.1.

Example 27

The as-converted polyimide fibers from Example 24, Part C, are post-drawn 2.05× while in contact with a plate maintained at 525° C., filament input speed to this plate being 25 ft./min. This treatment produces 71 denier/34 filament polyimide yarn exhibiting the following tensile properties at 21° C.: straight T/E/M_i=7.4/6.0/113.4 and loop T/E=3.4/3.2.

Table IV below shows roughness and imperfection indices for yarns of certain of the above examples.

TABLE IV

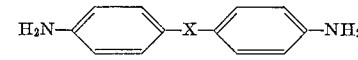
Example	Roughness Index	Imperfection Index	
		Filament	Yarn
1	0	5.9	9.5
12, Part A	10.4	50	36
17	0	5.8	12.0
18	0	7.0	10.5
21*	0	6.7	6.0
23a	0	8.5	10.9
25, Part A	0	6.5	14.0
26	9.1	43	66

*Drawn 1.6—.

It will be observed that yarns prepared by chemical spinning as taught in the prior art (Examples 12, Part A, and 26) exhibit roughness indices above 5 and imperfection indices above 25. In contrast, the other yarns, made in accordance with this invention exhibit roughness and imperfection indices below 5 and 25, respectively.

What is claimed is:

1. In a process for the production of polyimide filaments, the improvement, for providing a high level of strength properties in both straight and transverse directions, comprising forming polyamide-acid filaments by spinning into a gaseous atmosphere a solution of a polyamide-acid of pyromellitic dianhydride and a diamine of the formula



wherein X is selected from the group consisting of O and and S, and thereafter converting under a tension of 0–0.5 g./d. and drawning the filaments to produce the corresponding polypyromellitimide filaments, the total draw ratio in the process being at least 1.3×.

2. The process of claim **1** wherein at least a portion of said drawing is effected prior to the conversion of the polyamide-acid filaments, the total draw ratio being about 1.4–3.4×.

3. The process of claim **2** wherein said conversion is effected thermally by heating the polyamide-acid filaments to a temperature of at least 200° C.

4. The process of claim **1** wherein said polyamide-acid filaments are first converted to corresponding polypyromellitimide filaments and are thereafter drawn about 1.4 to 2.5×.

5. The process of claim **1** wherein said solution comprises the polyamide-acid dissolved in an organic solvent.

6. The process of claim **5** wherein said solvent is dimethylacetamide.

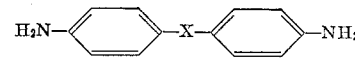
7. The process of claim **5** wherein said solvent is pyridine.

8. The process of claim **5** wherein said solution contains about 12 to 25% by weight of said polyamide-acid.

9. The process of claim **1** wherein said solution and said polyamide-acid filaments are maintained below 65° C. prior to said conversion.

10. Process for the production of polyimide filaments comprising the steps of:

(a) forming polyamide-acid filaments by spinning an organic solvent solution maintained at less than 80° C. of a polyamide-acid of pyromellitic dianhydride and a diamine of the formula



wherein X is selected from the group consisting of O and S, said spinning being effected into a gaseous atmosphere maintained at a temperature below about 280° C.

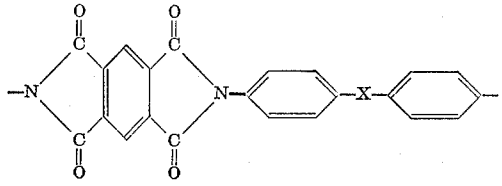
(b) drawing the polyamide-acid filaments about 1.3 to 2.5× in an aqueous bath at a temperature of 50° C. to 90° C.,

(c) thermally converting the drawn polyamide-acid filaments to the corresponding polypyromellitimide

by heating to a temperature of at least 200° C. while the filaments are under a tension of 0 to 0.5 g./d.,

(d) and tempering the filaments by passing same into contact with a surface having a temperature of at least 380° C. and further drawing same to give a total draw up to about 3.4×.

11. A filament composed of a polyimide of the formula



wherein X is a member of the group consisting of oxygen and sulfur, and being further characterized by a roughness index of less than 5 and an imperfection index of less than 25.

12. A filament as defined in claim **11** wherein X is oxygen, said filament having a straight tenacity of at least 3.0 g./d., a transverse tenacity of at least 1 g./d., and a flex life of at least 1000 cycles.

13. A filament as defined in claim **11** wherein X is sulfur, said filament having a straight tenacity of at least 2.0 g./d., a transverse tenacity of at least 1 g./d., and a flex life of at least 1000 cycles.

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