United States Patent [19]

Rochina et al.

[11] **3,717,696**

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[54] **PROCESS FOR THE PREPARATION OF POLYAMIDE-IMIDE FILAMENTS**

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[21] Appl. No.: **114,082**

Related U.S. Application Data

[63] Continuation of Ser. No. 829,914, June 3, 1969, abandoned.

[30] **Foreign Application Priority Data**

June 4, 1968 France.....6850063

[52] **U.S. Cl.**.....**264/205**, 264/210 F, 264/290 R

[51] **Int. Cl.**.....**D01d 5/04**, D01f 7/04, D02j 13/00

[58] **Field of Search** .....264/205, 210 F, 290; 260/78 TF

[56] **References Cited**

UNITED STATES PATENTS

3,415,782	12/1968	Irwin et al.	264/205 X
3,260,691	7/1966	Lavin et al.	260/78 TF UX
3,314,923	4/1967	Muller et al.	260/78 TF

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[57] **ABSTRACT**

This invention provides a process for producing polyamide-imide filaments which are heat-stable and have high tensile strength by solvent spinning under specified conditions. In a preferred embodiment the polyamide-imide polymers in solution are extruded into filaments and fibers through a spinneret maintained at a temperature between 60° C. and 180° C. heated at a temperature higher than 160° C. up to about 240° C. at a constant length for 2 to 6 hours, and subsequently drawn at a drawing ratio of at least 3:1 at a temperature generally in the range of about 220° C. up to about 420° C.

10 Claims, 6 Drawing Figures

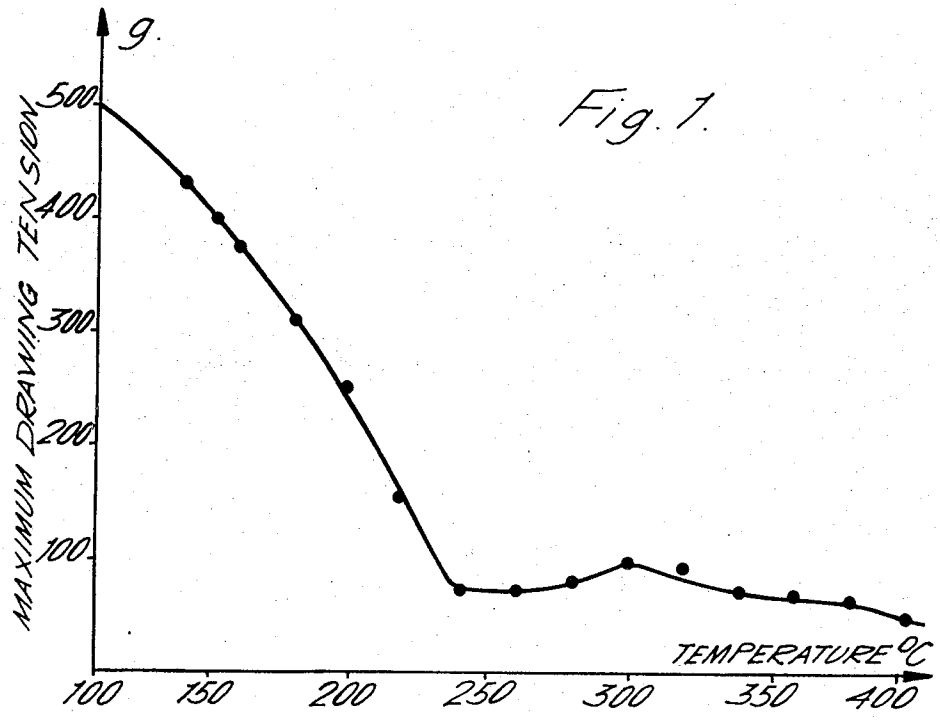

Fig. 1.

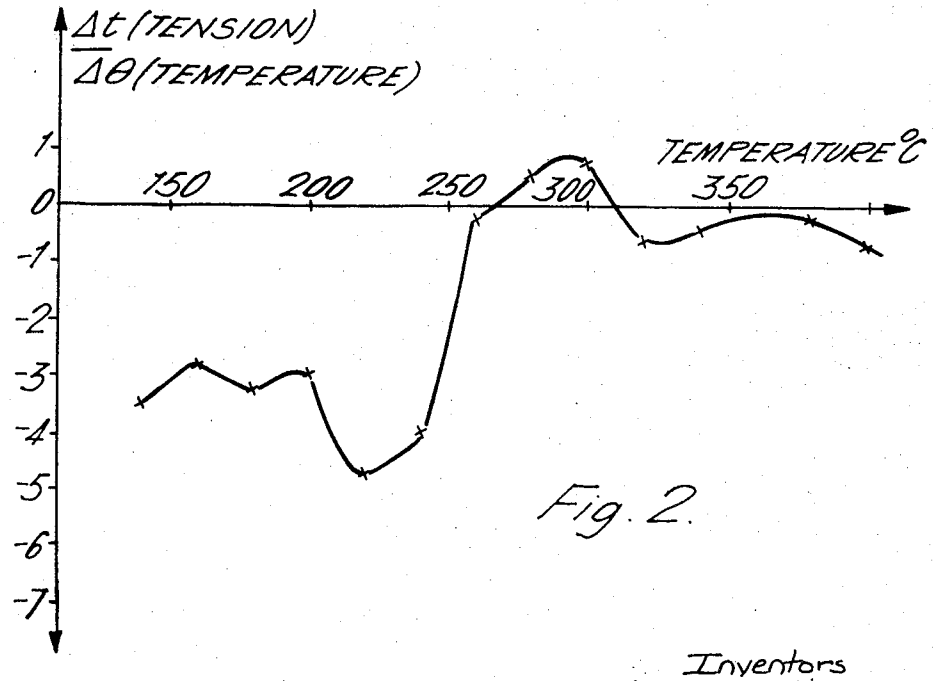

Fig. 2.

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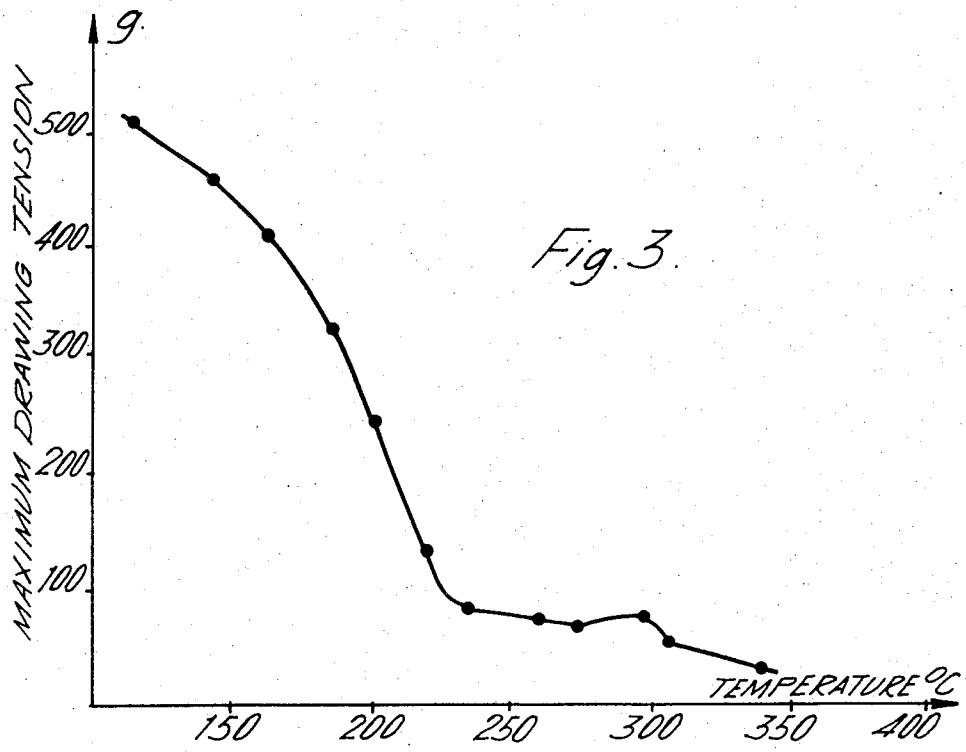

Fig. 3.

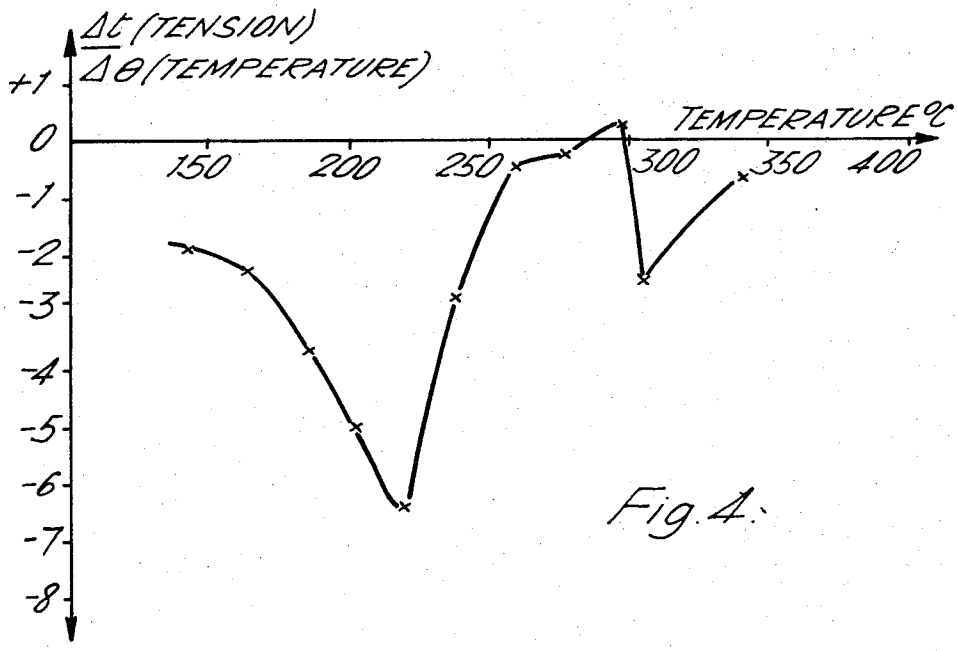

Fig. 4.

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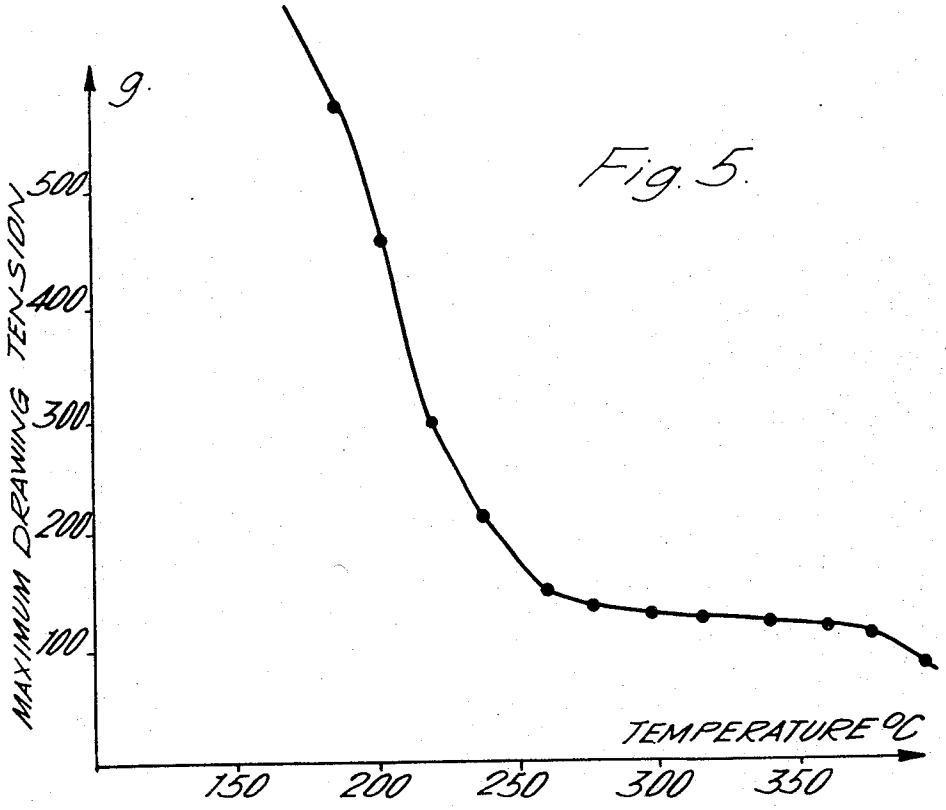

Fig. 5.

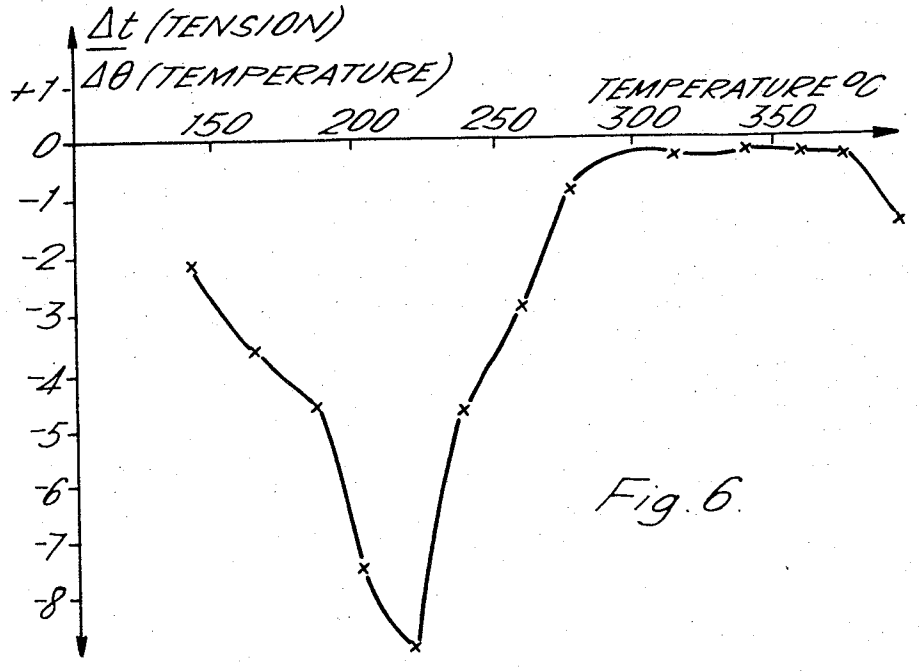

Fig. 6.

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PROCESS FOR THE PREPARATION OF POLYAMIDE-IMIDE FILAMENTS

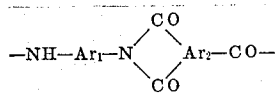
This is a continuation of application, Ser. No. 829,914, filed June 3, 1969, now abandoned.

This invention relates to the preparation of heat-stable synthetic filaments of high tensile strength from polyamide-imides.

Conventional synthetic fibers possess a high degree of strength and a good flexibility compared with inorganic or metallic fibers, but their heat stability is insufficient for many applications. Attempts have therefore been made in recent years to obtain filaments from fibers from already known or newly discovered heat-stable polymers. The latter can be schematically divided into two principal classes; aromatic polyamides, and polymers containing heterocyclic nuclei.

The present invention relates to a process for the preparation of fibers from a polymer containing in the chain both amide and imide linkages derived from a tricarbonyl compound such as a tri-acid or acid-anhydride.

The present invention provides heat-stable filaments and fibers of a polyamide-imide having an inherent viscosity greater than 0.4, the said filaments having a tensile strength of at least 30 g/tex, a low moist absorption, a very good dimensional stability and a good resistance to acids. According to the invention, these filaments and fibers are made by a process which comprises extruding through a spinneret maintained at 60° to 180°C in an evaporatory atmosphere, maintained at a temperature about or greater than the boiling point of the solvent, a solution in an organic polar solvent having an inherent viscosity greater than 0.4 and containing amide-imide linkages of the formula



and optionally also amide linkages of the formula — NH — Ar_1 — NH — CO — R — CO — in which R represents a divalent aromatic, aliphatic, cycloaliphatic, or arylaliphatic radical, Ar_1 represents a divalent aromatic radical (optically with a minor proportion of divalent aliphatic or cyclcaliphatic radicals), and Ar_2 represents a trivalent aromatic radical containing at least six carbon atoms; heating the filaments obtained to a temperature higher than 160° C; and drawing the filaments at a temperature higher than the temperature corresponding to the maximum in absolute value of the first derivative of the function expressing the variation of the maximum drawing tension as a function of the temperature, and preferably near or above the temperature corresponding to the maximum algebraic value of this derivative.

The solutions of these polymers, which will hereafter be referred to for clarity simply as "polyamide-imides," can be obtained by reaction in substantially stoichiometric proportions in a polar organic solvent of at least one aromatic diisocyanate and an acid reactant containing at least an aromatic anhydride-acid and optionally also at least one di-acid which may be aromatic, aliphatic, cycloaliphatic, or acylaliphatic.

Suitable diisocyanates which can be used to obtain these polymers include, more particularly, monocyclic diisocyanates such as tolylene diisocyanate and the

bicyclic preferably symmetrical, diisocyanates, such as diphenylmethane diisocyanate, diphenylpropane diisocyanate, and diphenylether diisocyanate. An aliphatic or cycloaliphatic diisocyanate may optionally be added to the aromatic diisocyanate in minor proportions so as to improve certain properties of the polymer such as solubility, or the flexibility or elasticity of articles made from it.

As the anhydride-acid trimellitic acid anhydride is preferably used. Suitable diacids include preferably terephthalic acid, isophthalic acid, adipic acid, sebacic acid and succinic acid. The proportion of the diacid in the mixture should generally be from 5 to 95 mol percent, preferably 20 to 80 mol percent, with reference to the mixture of anhydride and diacid.

The solution of polyamide-imide can also be obtained by reaction in substantially stoichiometric proportions in a solvent of a diamine on at least one compound carrying an acid chloride function and an anhydride function, and optionally at least one diacid dichloride of an aromatic, aliphatic or cycloaliphatic diacid.

The polyamide-imide solution can also be obtained by reaction in a solvent medium of a diisocyanate on a diacid containing imide linkages.

In the process of the present invention it is possible to use the polyamide-imide solution in the form in which it is obtained, or to separate the polymer so as to remove by-products formed in the course of the polycondensation, and then to re-dissolve the polymer before it is extruded.

Suitable polar organic solvents which can be used in the present invention include dimethylformamide, dimethylacetamide, hexamethylphosphotriamide, tetramethylenesulphone, and preferably N-methylpyrrolidone.

The polyamide-imides used in the present invention must have an inherent viscosity greater than 0.4, but preferably not greater than 1.6. This inherent viscosity is measured at 25° C. on an 0.5 percent weight for volume solution in the solvent used in the preparation of the polyamide-imide Polymers having an inherent viscosity from 0.8 to 1.4 are preferably used.

The polyamide-imide solutions used in the new process preferably have a viscosity of 300 to 6,000 poises at 25° C (measured with a Drage viscometer using speed II and mobile 47.2) Preferably the solution has a viscosity from 1,500 to 3,000 poises to ensure stable spinning together with good filtration and easy transport of the solution. The solution spun should contain a polymer concentration of 15 to 35 percent by weight and preferably 19 to 30 percent by weight, and it can also contain various adjuvants such as pigments and dulling agents.

The circuit through which the solution is fed to the head of the spinneret can be heated or not depending on the viscosity of the polymer solution. Generally, for solutions having a viscosity of 1,500 to 2,500 poises at 25° C., which are preferably used, the temperature of the feed circuit is kept at about ambient temperature.

The temperature of the solution on extrusion must be between 60° and 180° C., and is preferably between 90° and 180° C.

For the extrusion, the spinneret may be in any form desired, for example a plate or cup provided with ori-

fices, the dimensions of which can vary within wide limits, for example from 0.08 to 0.50 mm in diameter.

On leaving the spinneret, the filaments traverse an atmosphere maintained at a temperature near or above the boiling point of the solvent. It is not necessary that this atmosphere be constituted by an inert gas, and hot air is generally used, for example in the form of a current circulating in the same direction as the filaments.

The speed of spinning can vary within wide limits, and may be generally fixed between 100 and 400 meters per minute, preferably 150 to 200 meters per minute. This speed is chosen as a function of the titre of each filament and the number of strands spun.

The filaments contain from 5 to 30 percent of solvent on leaving the evaporation chamber. If desired, the filaments may be subjected, either in the spinning cell or immediately after leaving it, to a predrawing operation to a small degree before receiving the thermal treatment in accordance with the new process.

It is an essential feature of the process of the invention that the filaments receive, a thermal treatment before being drawn. This thermal treatment at a temperature higher than 160° C. can be carried out in an inert gas such as nitrogen or carbon dioxide or in a mixture of air and inert gas, optionally under reduced pressure. It can be effected using any appropriate apparatus. For example, the filament can be collected on metallic supports which are then introduced into a zone heated to more than 160° C. This zone is preferably sealed and connected to an evacuation device so that the pressure in the zone can be reduced. The zone can also be provided with tuyeres so that air, nitrogen, carbon dioxide or another inert gas can be swept through the zone.

The thermal treatment can also be effected on heated rolls rotated at a speed such that the treatment can be carried out continuously. If desired, these rolls can be enclosed in a zone in which hot air or inert gas is circulated and optionally the pressure is reduced.

The thermal treatment is preferably carried out while the filaments are maintained at constant length.

This treatment causes in the polymer constituting the filaments physical and/or chemical modifications which cause the filaments to possess, after drawing, excellent mechanical properties. In the course of the treatment, the solvent content of the filaments is reduced to the levels of the order of 3 percent or less. This reduction in solvent content is not, however, the only cause of the substantial increase in tensile strength which is conferred by the process of the invention on the filaments obtained after drawing. In fact, if the solvent is removed by washing with boiling water to a level identical with that obtained after the thermal treatment, it is not possible to obtain by drawing filaments possessing such good tensile strength.

It has been established that the inherent viscosity measured on filaments obtained starting from the polymer solutions of low viscosity is higher after thermal treatment than that of the starting polymer. However, this postcondensation phenomenon which occurs in certain cases cannot be considered as the sole cause of the remarkable properties of filaments produced in accordance with the invention, since it is only produced to a small extent when the filaments are obtained from polymer solutions of high viscosity.

The duration of the heat treatment varies as a function of the temperature and the titre of the filaments. At 160° C., it lasts for at least 2 hours.

After the heat treatment it is possible to subject the filaments to a prestretching to a small degree, before the proper drawing in accordance with the invention takes place. After the heat treatment, the filaments are drawn at a temperature higher than the temperature corresponding to the maximum value in absolute terms of the first derivative of the function expressing the variation of maximum drawing tension as a function of temperature. Preferably, the temperature of drawing should be close to or even greater than the temperature corresponding to the maximum algebraic value of the first derivative of said function expressing the maximum drawing tension as a function of temperature.

To measure the maximum drawing tension, the filaments are made to pass over feed rolls in a furnace heated to the temperature desired and then over drawing rolls. The tension of the filaments is measured thus before rupture using an appropriate apparatus such as a Rothschild tensiometer, while the speed of the drawing rolls is made to increase.

The polyamide-imide filaments and fibers obtained according to the invention have a good tensile strength of at least 30 g/tex, a low moisture absorption, a good dimensional stability, and a very good resistance to acids. They can be used for all usages where these qualities are particularly important, such as in medical and hospital use where good resistance to successive sterilizations is required, and for work garments for foundry workers, glass workers and chemists.

The following Examples illustrate the invention. In the Examples the percentages are by weight except where otherwise indicated. The Drage viscosity is measured with a Drage viscometer using speed II and mobile 47.2. The inherent viscosity is measured at 25° C. on a 0.5 percent weight for volume solution in N-methylpyrrolidone.

EXAMPLE 1

A 26.5 percent solution in N-methylpyrrolidone of a copolyamide-imide is obtained by reaction of diphenylmethanediisocyanate (50 molar parts), trimellitic anhydride (40 molar parts), and terephthalic acid (10 molar parts). The Drage viscosity at 25° C. of this solution is 2,380 poises and the inherent viscosity of the polymer is 0.93.

This solution is extruded downwardly at a temperature of 132° C. through a spinneret having 60 orifices each 0.15 mm in diameter into a vertical spinning cell 7 meters high and 200 millimeters in diameter, the walls of which are maintained at 245° C. A current of hot air is introduced at the top of the cell and a mixture of air and solvent withdrawn at the lower part of the cell.

The filaments leave the cell at a speed of 150 meters per minute and are then taken up on a roll at a speed of 155 meters per minute and finally wound up on a metallic support at a speed of 160 meters per minute. The filaments on the support are then introduced into a zone maintained at 240° C. containing nitrogen under reduced pressure, where they remain for 6 hours. During this treatment the pressure in the zone is periodically varied in the following manner: 1–2 mm Hg for 45 minutes; 50 mm Hg for 15 minutes; and this alternation

of pressures is maintained for the duration of the treatment.

The maximum drawing tension of the filaments during their passage through an oven heated successively to different temperatures is measured. For each temperature the tension of the filaments is measured just before rupture using a Rothschild tensiometer. The curve expressing the variation of this maximum drawing tension as a function of temperature is then drawn. It is shown in FIG. 1 of the accompanying drawings. The derivative of this curve at each point is then calculated and FIG. 2 shows that this derivative has a maximum absolute value at 220° C −4.75 and a maximum algebraic value at about 300° C. (+0.75). In other words, the drawing temperature being higher than the temperature corresponding to the maximum absolute value of the curve expressing the rate of change of maximum drawing tension with temperature against the temperature, the rate of change being determined by measuring the slope of the curve of maximum drawing tension versus temperature. See FIGS. 1 and 2.

The filaments, after the heat treatment, are introduced at a speed of 10 meters per minute into a tube, 1.5 meters long and 8 mm in diameter, heated electrically, in which it is drawn 4 times in air at 380° C. The thread obtained has the following characteristics:

titre	160 dtex
dry tensile strength	41.6 g/tex
dry elongation at break	12.5 %
moisture absorption at 22°C. and 65% relative humidity	2.1%
heat resistance, loss of strength after ageing in a heated and ventilated oven:	
300 hours at 177°C.	17 %;
1000 hours 177°C.	34 %;
300 hours at 260°C.	57 %;
1000 hours at 260°C.	67 %;
dimensional stability: shrinkage	
10 minutes at 100°C. in dry air	0%
10 minutes at 150°C. in dry air	0%
10 minutes at 200°C. in dry air	0.4%
5 minutes in boiling water	0.2%
Acid resistance; loss of tensile strength	
100 hours in water vapor and sulfur dioxide at 175°C.	16%
100 hours in 60% sulphuric acid at 60°C.	16%
20 hours in 10% hydrochloric acid at 95°C.	48%

EXAMPLE 2

A 23.1 percent solution in N-methylpyrrolidone is prepared of a copolyamideimide obtained by reaction of diphenylmethane diisocyanate (50 molar parts), trimellitic anhydride (40 molar parts), and terephthalic acid (20 molar parts). The Drage viscosity at 25° C. of this solution measured as described above is 1,840 poises. The inherent viscosity of the polymer is 1.01.

This solution is extruded at a temperature of 110° C. through a spinneret having 60 orifices each 0.10 millimeters in diameter downwardly in a vertical spinning cell 7 meters long and 200 mm in diameter, the walls of which are maintained at 245° C. A current of hot air enters the upper part of the cell, and a mixture of air and solvent is withdrawn at the lower part of the cell. A 650 dtex thread is obtained at a speed of 150 meters per minute. Eight identical threads are combined and wound up at a rate of 20 Z turns per meter on a metallic support. The filaments on their support are treated for three hours at 240° C. under a pressure of 1–2 mm Hg. The thread then possesses the following characteristics:

titre	4500–3900 dtex
dry tensile strength	13.6 to 15.1 g/tex
dry elongation at break	108 to 113%

The filaments are then drawn 3.3 times in air at 340° C. that is to say at a temperature higher than the temperature corresponding to the maximum algebraic value of the curve in FIG. 2, by passage through a tube 1 meter long and 8 mm in diameter, heated electrically, which they leave at a speed of 24 meters per minute. The thread then possesses the following characteristics:

titre	1303 dtex
dry tensile strength	45 g/tex
dry elongation at break	18.6%

They have the same qualities of moisture absorption, heat stability, dimensional stability and resistance to acids as the thread obtained in Example 1.

EXAMPLE 3

A 23.9 percent solution in N-methylpyrrolidone is prepared of a copolyamide-imide obtained by reaction of diphenylether diisocyanate (50 molar parts), trimellitic anhydride (20 molar parts), terephthalic acid (10 molar parts), and isophthalic acid (20 molar parts). The Drage viscosity of this solution is 2,500 poises and the inherent viscosity of the polymer is 1.0.

This solution is extruded at a temperature of 130° C. through a spinneret having 12 orifices each 0.1 mm in diameter into the same spinning cell and under the same conditions of temperature and circulation of air as in Example 1. The filaments leave the spinning cell at a speed of 194 meters per minute and are taken up on a roll turning at 199 meters per minute and are finally wound up on a metallic support at a speed of 200 meters per minute. Five identical threads are assembled and the wound assembly on the metallic support is introduced into a zone at 240° C. where it is treated as described in Example 1 for 6 hours.

The variations of the maximum drawing tension of this thread as a function of temperature is measured as in Example 1 and the curve shown in FIG. 3 is drawn from the results obtained. From this curve the variations in the derivative are calculated and the curve shown in FIG. 4 is drawn. From the latter curve, it can be seen that the temperature corresponding to the maximum absolute value of the derivative is 220° C. (−6.38) and that corresponding to the maximum algebraic value is 297° C. (+0.25).

The thread is drawn 3.8 times after the heat treatment in air at 320° C. in the same tube and at the same speed as in Example 1. The thread obtained has the following characteristics:

titre	158 dtex
dry tensile strength	40.5 g/tex
dry elongation at break	10.9 %
take-up of moisture at 22° C. and 65% relative humidity	3.4 %

heat stability: loss of strength after ageing in a heated oven	
300 hours at 177°C.	7 %
300 hours at 260°C.	30 %
dimensional stability: shrinkage	
10 minutes at 100°C. in dry air	0 %
10 minutes at 150°C. in dry air	0 %
10 minutes at 200°C. in air	0.17%
5 minutes in boiling water	0.39%

The filaments have good resistance to acids.

EXAMPLE 4

A 19.3 percent solution in N-methylpyrrolidone is prepared of a copolyamide-imide obtained by reaction of diphenylether diisocyanate (50 molar parts) trimellitic anhydride (35 molar parts), terephthalic acid (7.5 molar parts), and isophthalic acid (7.5 molar parts). The Drage viscosity of this solution is 2,080 poises, and the inherent viscosity of the polymer is 1.32. The solution is extruded at a temperature of 120° C. through a spinneret having 60 orifices each 0.15 mm in diameter, downwardly in the same spinning cell as in Example 1. The thread produced leaves the cell at a speed of 148 meters per minute and then passes over a roll where it is taken up at a speed of 154 meters per minute. It is wound up on a metallic support at a speed of 156 meters per minute. The thread on its support is then introduced into a zone at 240° C. containing nitrogen under reduced pressure where it remains for six hours. During this treatment the pressure in the zone is periodically varied in the following manner: 1–2 mm Hg for 45 minutes; 50 mm Hg. for 15 minutes; and so on throughout the duration of the treatment.

The thread is then passed at a speed of 10 meters per minute through a tube 1.5 meters long and 8 mm in diameter, heated electrically, where it is drawn 4.86 times in air at 380° C. that is to say, at a temperature above the temperature corresponding to the maximum algebraic value of the curve of FIG. 4. The thread obtained possesses the following characteristics:

titre	131 dtex
dry tensile strength	67 g/tex
dry elongation at break	10 %

The filaments possess the same qualities of moisture absorption, heat stability and dimensional stability as the filaments obtained in Example 3.

EXAMPLE 5

A 20 percent solution of N-methylpyrrolidone is prepared of a copolyamide-imide obtained by reaction of diphenylether diisocyanate (50 molar parts), trimellitic anhydride (40 molar parts), and terepthalic acid (10 molar parts). The inherent viscosity of the polymer is 1.0 and the Drage viscosity of the solution is 2,280 poises. This solution is extruded at a temperature of 120° C. through a spinneret having 12 orifices each 0.10 mm in diameter downwardly in the same spinning cell as in Example 1. The thread leaves the cell at a speed of 195 meters per minute and is then wound up on a metallic support at a speed of 200 meters per minute. The thread on its support is then introduced into an enclosure at 240° C. where it is treated in the same manner as in Example 1.

Ten identical threads are assembled and the combined thread obtained is then passed at a speed of 10 meters per minute through a tube 1.5 meters long and 8 mm in diameter, heated electrically, where it is drawn 4.75 times in air at 420° C. It then possesses the following characteristics:

titre	150 dtex
dry tensile strength	66.2 g/tex
dry elongation at break	11%
moisture absorption at 22°C. and 65% relative humidity	3.6%
heat stability: loss of strength after ageing in a ventilated oven:	
300 hours at 177°C.	18%
300 hours at 260°C.	27%
dimensional stability: Shrinkage	
10 minutes at 100°C. in dry air	0.18%
10 minutes at 150°C. in air	0%
10 minutes at 200°C. in dry air	0.48%
5 minutes in boiling water	0.17%

It possesses very good resistance to acids.

EXAMPLE 6

A 21.8 percent solution in N-methylpyrrolidone is prepared of a copolyamide-imide obtained by reaction of diphenylmethane diisocyanate (50 molar parts), trimellitic anhydride (40 molar parts), and terephthalic acid (10 molar parts). The Drage viscosity at 25° C. of this solution is 2,410 poises. The inherent viscosity of the polymer is 1.19. This solution is extruded at a temperature of 130° C. through a spinneret having 60 orifices, each 0.15 mm in diameter, downwardly in a vertical spinning cell 9 meters high having walls kept at 245° C., and which is swept by a current of hot air entering in the upper part and leaving mixed with solvent through the lower part. A 60 filaments 600 dtex thread is obtained at a speed of 150 meters per minute, having a dry tensile strength of 13 g/tex and a dry elongation at break of 90 percent. This thread is continuously treated for 50 seconds by passage over a group of two rollers turning at a speed of 40 meters per minute and having a surface temperature of 240° C.

For this thread examination of the first derivative of the function expressing the variation of maximum drawing tension with temperature shows that the temperature of drawing must be greater than 200° C., and preferably greater than 300° C.

The thread is fed at a speed of 10 meters per minute to a tube 1.5 meters long and 8 mm in diameter, heated electrically, in which it is drawn 4.3 times in air at 400° C. It then has the following characteristics:

titre	120 dtex
dry tensile strength	50.1 g/tex
dry elongation at break	14 %

If an otherwise identical thread which has been drawn at a temperature between 120° and 220° C. is examined, it is found that the tensile strength varies relatively little from 22.8 g/tex to 27.6 g/tex, while the tensile strength of the same thread drawn at temperatures from 300° to 400° C. increase enormously passing from 29 g/tex to 50.1 g/tex.

The thread obtained has the same qualities of water absorption, heat stability, dimensional stability and resistance to acids as the filament obtained in Example 1.

EXAMPLE 7

A 20.5 percent solution in N-methylpyrrolidone is prepared of a copolyamide-imide having an inherent viscosity of 1.28 obtained from the starting materials of Example 5. The Drage viscosity at 25° C. of this solution is 1,890 poises. This solution is extruded at a temperature of 150° C. through a spinneret having 90 orifices each 0.10 mm in diameter into a spinning cell 7 meters high, halving walls heated to 245° C. and traversed by a current of hot air entering in the upper part and leaving with solvent in the lower part. The filaments leave the cell at a speed of 150 meters per minute. They are then taken up on a roll turning at a peripheral speed of 240 meters per minute which confers on the filaments a predrawing of 1.6 times. The predrawn filaments are then introduced into a zone where they are treated at constant length for 6 hours in the same manner as that described in Example 1. The filaments thus treated are then fed at a speed of 10 meters per minute through a tube 1.5 long and 8 mm in diameter, heated electrically, where they are drawn 3.6 times in air at 340° C., that is to say at a temperature above that corresponding to the maximum algebraic value of the curve of FIG. 2. The thread obtained has the following characteristics:

titre	170 dtex
dry tensile strength	49 g/tex
dry elongation at break	15%

Here again the filament has the same qualities of moisture absorption, heat stability, dimensional stability and resistance to acids as the thread obtained in Example 1.

EXAMPLE 8

A 19 percent solution of polymer in N-methylpyrrolidone is prepared from a polyamide-imide obtained by reacting trimellitic anhydride monochloride with 4,4'-diaminodiphenylmethane. The solution has a viscosity of 700 poises and the polymer an intrinsic viscosity of 1.34.

This solution is extruded at 120° C. through a spinneret with 12 0.20 mm diameter holes into a chamber 7 meters long, the walls of which are kept at 245° C. and through which passes a stream of hot air at 205° C. The filaments are collected at the rate of 150 m/minute and have a titre of 230 dtex, a tensile strength of 10 g/tex and an elongation at break of 90 percent.

These filaments are treated under tension for 3 hours at 240° C. under a pressure of 5 mm of mercury and then stretched in the ratio of 5.2 at 330° C.

The resulting filaments have the following characteristics:

Titre	44 dtex/12 filaments
Tensile strength	57 g/tex
Elongation at break	13 %

Moisture absorption at 22° C and 65 % humidity: 1.9 percent

Heat stability : loss of strength after ageing in a heated oven:

300 hours at 177° C : 7 % 1000 hours at 177° C : 50 %

Dimensional stability : shrinkage

10 minutes at 100°C. in dry air: 0 %
10 minutes at 150°C. in dry air: 0 %
10 minutes at 200°C. in dry air: 0.2 %
5 minutes in boiling water: 0.2 %

The thread has a good resistance to acids.

EXAMPLE 9

A 21.5 percent solution of polymer in N-methylpyrrolidone is prepared, from a polyamide-imide as described in Example 8. The solution has a viscosity of 1,810 poises and the polymer has an intrinsic viscosity of 1.10. This solution is extruded through a spinneret having 12 0.25 mm diameter holes and kept at 130° C. After passing through an evaporating atmosphere identical to that described in Example 8 the extruded filaments have a titre of 210 dtex/12 filaments. 5 threads are combined into a thread of 1,050 dtex which is treated for 3 hours at 240° C. under a pressure of 5 mm of mercury. The thread is stretched in a 1 meter tube at 340° C, in a ratio of 4.9. A thread having a titre of 215 dtex a tensile strength of 51 g/tex and 13 percent elongation at break is obtained. Its moisture absorption, heat stability and dimensional stability are identical with those of the filaments obtained in Example 8.

EXAMPLE 10

A 23.5 percent solution of polyamide-imide in N-methylpyrrolidone is prepared using a polymer obtained by reacting trimellitic anhydride with diisocyanatodiphenylmethane. The resulting solution has a viscosity of 2,800 poises and the polymer has an intrinsic viscosity of 1.02. This solution is extruded at 120° C. through a spinneret with 60 0.10 mm diameter holes into an evaporating chamber identical to that of Example 8. The thread wound up at 150 m/minute, shows the following characteristics :

Solvent content	15%
Titre	575 dtex
Tensile strength	11 g/tex
Elongation at break	95%

4 threads are combined and heat-treated at constant length for 3 hours at 240° C. under a pressure of 5 mm of mercury The intrinsic viscosity of the polymer forming the filament is then 12.

The thread displays the following properties:

Solvent content	2%
Titre	2,300 dtex
Tensile strength	14.3
Elongation at break	106%

The maximum drawing tension of the thread during its passage through an oven heated successively to different temperatures is measured. For each temperature the tension of the thread is measured just before break using a Rothschild tensiometer. The curve expressing the variation of this maximum drawing tension as a function of temperature is shown in FIG. 5. From this curve the derivative is calculated at each point and the derivative curve is shown in FIG. 6. It shows that the maximum absolute value of the derivative is at 220° C. (−8.88) and the maximum algebraic value is about 300° C. (−0.25).

The thread is stretched in a ratio of 4.5 in a 1 meter tube heated to 370° C. The properties of the thread are then as follows:

Titre	510 dtex
Tensile strength	55.2 g/tex
Elongation at break	17%
Moisture absorption at 22°C. and 65% humidity: 2.1%,	
heat stability: loss of strength after ageing in a heated oven,	
300 hours at 177°C:15%	
1000 hours at 177°C.:32%	
300 hours at 260°C.:54%	
1000 hours at 260°C: 63%	
dimensional stability: Shrinkage	
10 minutes at 100°C. in dry air	0%
10 minutes at 150°C. in dry air	0%
10 minutes at 200°C. in dry air	0.25%
5 minutes in boiling water	0%
Resistance to acids: loss of tensile strength	
100 hours in water vapor and sulphur dioxide at 175°C.	10%
100 hours in 60% sulphuric acid at 60°C.	18%
20 hours in 10% hydrochloric acid at 95°C.	66%

EXAMPLE 11

A 24 percent by weight solution in N-methylpyrrolidone of a polyamide-imide of intrinsic viscosity 1, derived from trimellitic anhydride and 4,4'-diisocyanato-diphenylmethane has a viscosity of 2,400 poises. This solution is converted into a 575 dtex 60 filaments thread under the conditions described in Example 10.

A sample of the filament is heat-treated for 3 hours at 240° C. under a pressure of 2 mm of mercury and then stretched on a plate: the maximum stretching ratio which can be achieved in practice at 330° C. is 3.6. The 160 dtex thread obtained has a tensile strength of 35 g/tex and an elongation at break of 12 percent. It presents the same qualities of moisture absorption, heat stability, dimensional stability and resistance to acids as the filament obtained in Example 10.

Another sample of the same thread is washed for 2 hours with boiling water, dried at 60° C. and then stretched at 330° C. Although the maximum practical stretching ratio is 4.2, the thread formed has a tensile strength of only 20 g/tex and an elongation at break of 11 percent.

It was confirmed that the solvent content of the yarns after heat treatment on one hand and washing with boiling water on the other and before stretching was about 3 percent in both cases.

EXAMPLE 12

A 23 percent solution of polyamide-imide of intrinsic viscosity 0.98, prepared from diisocyanatodiphenylether and trimellitic anhydride, has a viscosity of 2,350 poises.

3 percent By weight relative to the polymer of carbon black are added to this solution which is then extruded through a spinneret with 60 0.10 mm diameter holes and kept at 115° C. into an evaporating chamber through which a stream of hot air is passed and the walls of which are kept at 245° C. The length of this chamber is 7 meters.

The thread, collected at 150 m/minute, has a gauge of 580 d/tex, a tensile strength of 10 g/tex, an elongation at break of 70 percent and a solvent content of 16 percent.

8 threads are assembled and twisted at 20 turns per meter, right-hand twist, and then treated at constant length for 3 hours under a pressure of 2 mm of mercury. They then display a tensile strength of 14 g/tex and an elongation at break of 80 percent.

The thread is stretched to a ratio of 3 at 365° C. in a 1 meter tube and has the following properties:

Titre	1,540 dtex
Tensile strength	50 g/tex
Elongation at break	13.5 %
Moisture absorption at 22° C. and 65% relative humidity 2.1%	
Heat stability: loss of strength after ageing in a ventilated oven	
300 hours at 177°C.	2%
1000 hours at 177°C.	3%
300 hours at 260°C.	0%
1000 hours at 260°C.	21%

The thread only begins to decompose at about 475° C.

Dimensional stability: Shrinkage	
10 minutes at 100°C. in dry air	0%
10 minutes at 150°C. in dry air	0%
10 minutes at 200°C. in dry air	0.1%
5 minutes in boiling water	0%
Acid resistance: loss of tensile strength	
100 hours in water vapour and sulphur dioxide at 175°C.	15%
100 hours in 60% sulphuric acid at 60°C.	23%
20 hours in 10% hydrochloric acid at 95°C.	47%

EXAMPLE 13

A 26 percent solution of a polyamide-imide of intrinsic viscosity 1.05 is prepared by reaction of trimellitic anhydride with diisocyanatodiphenyl-methane in N-methylpyrrolidone.

The solution, which has a viscosity of 4,200 poises, is extruded by the method described in Example 10.

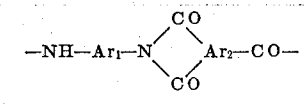
The threads collected are treated for 3 hours at 200° C. in a stream of nitrogen and then stretched to a ratio of 3.6 at 330° C; they then have the following properties:

Titre	188 dtex
Tensile strength	32.5 g/tex
Elongation at break	17%

This thread presents the same qualities of moisture absorption, heat stability, dimensional stability and resistance to acids as that of Example 10.

We claim:

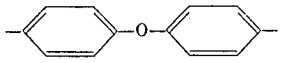
1. Process for producing heat stable filaments and fibers which comprises extruding through a spinneret maintained at a temperature between 60° and 180° C in an evaporatory atmosphere maintained at a temperature near or above the boiling point of the solvent, a solution in an inert organic polar solvent selected from dimethyl-formamide, dimethylacetamide, hexamethylphosphotriamide, tetramethylene-sulphone and N-methylpyrrolidone of a polymer having an inherent viscosity from 0.4 to 1.6 and consisting essentially of amide-imide linkages of the formula



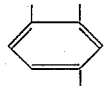
or of said amide-imide linkages and of amide linkages of the formula — NH — AR_1 — NH — CO — R — CO

— in which R represent a divalent benzene radical, Ar_1 represents a

or



radical, in which x is an integer from 1 to 3, and Ar_2 represents the radical

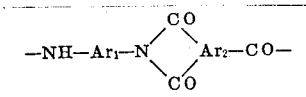


heating the filaments obtained to improve the physical and mechanical properties of said polymer at a temperature higher than 160° C. up to about 240° C. at substantially constant length and subsequently drawing the filaments at a drawing ratio of at least 3:1 and at a temperature higher than the temperature corresponding to the maximum absolute value of the curve expressing the rate of change of maximum drawing tension with temperature against the temperature the rate of change being determined by measuring the slope of the curve of maximum drawing tension versus temperature.

2. Process according to claim 1, wherein the drawing temperature is near or above the temperature corresponding to the maximum algebraic value of said curve.

3. A process according to claim 1, wherein the solvent is N-methylpyrrolidone.

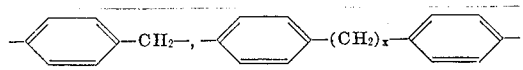
4. Process according to claim 1 which comprises extruding through a spinneret maintained at a temperature between 60° and 180° C. in an evaporatory atmosphere maintained at a temperature near or above the boiling point of the solvent, a solution in an inert organic polar solvent selected from dimethylformamide, dimethylacetamide, hexamethylphosphotriamide, tetramethylenesulphone or N-methylpyrrolidone of a polymer having an inherent viscosity from 0.4 to 1.6 and consisting essentially of amide-imide linkages of the formula



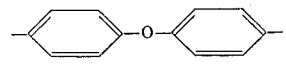
or of said amide-imide linkages and of amide linkages of the formula

$$— NH — Ar_1 — NH — CO — R — CO —$$

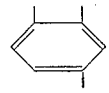
in which R represents a divalent benzene radical, Ar_1 represents a



or



radical, in which x is an integer from 1 to 3, and Ar_2 represents the radical



heating the filaments obtained to improve the physical and mechanical properties of said polymer at a temperature higher than 160° C. up to about 240° C. at constant length for 2 to 6 hours, and subsequently drawing the filaments at a drawing ratio from 3:1 to about 5.76:1 and at a temperature higher than the temperature corresponding to the maximum absolute value of the curve expressing the rate of change of maximum drawing tension with temperature against the temperature which is at least 220° C up to about 420° C.

5. Process according to claim 4 wherein the filaments are drawn at a drawing ratio from 3:1 to about 5.2:1.

6. A process according to claim 1 wherein the polyamide-imide solution has a viscosity of 300 to 6,000 poises at 25° C.

7. A process according to claim 1 wherein the polyamide-imide solution is 15 to 35 percent by weight.

8. A process according to claim 1 wherein the spinneret is maintained at 90° to 180° C.

9. A process according to claim 1 wherein the spinning speed is 100 to 400 m./minute.

10. A process according to claim 1 wherein the evaporating atmosphere consists of hot air or inert gas, or both.

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