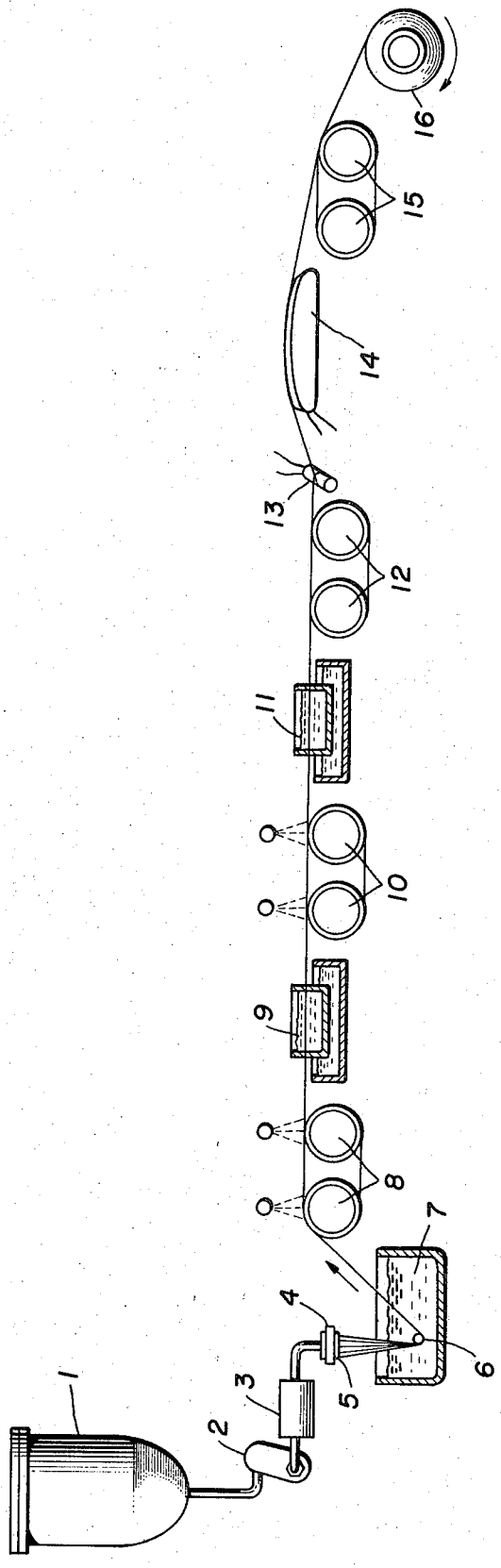
Feb. 15, 1972 H. S. MORGAN, JR 3,642,706

PROCESS FOR SPINNING WHOLLY AROMATIC POLYAMIDE FILAMENTS

Filed March 3, 1970



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United States Patent Office 3,642,706 Patented Feb. 15, 1972

3,642,706

PROCESS FOR SPINNING WHOLLY AROMATIC POLYAMIDE FILAMENTS

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Filed Mar. 3, 1970, Ser. No. 16,265
Int. Cl. C08g 20/00; D01f 1/02
U.S. Cl. 260—78 S 15 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for preparing filaments, films and the like shaped objects from wholly aromatic polyamides is provided. A spinning solution of such polyamide is extruded into at least one stream that passes through a coagulating bath. The resulting filaments are withdrawn from the bath and then washed, dried, and drawn. Improvements result from incorporating in the solution a small but effective amount of a wax having a melting point above 25° C. and being retained at least in part in the filaments at least until the filaments are drawn.

BACKGROUND

Synthetic linear condensation polymers, such as polyesters and polyamides in strand form, have found wide applications in textile and other industrial end uses requiring high tensile strength, abrasion resistance and resistance to thermal and other degradative conditions. In recent years the need for polymers having even better thermal degrading resistance has been met through the provision of wholly aromatic polyamide compositions, as well as various heterocyclic polymers and copolymers. These wholly aromatic or heterocyclic polymers cannot be spun into filaments by melt spinning techniques because the high temperatures required foster side reactions to such an extent that degradation occurs before the polymers become sufficiently fluid for spinning. The production of strand products such as fibers, films and the like from these polymers is necessarily limited to the use of solution employing techniques, such as wet, dry or dry jet-wet spinning.

In U.S. Pat. 3,414,645 there is described a solution spinning of aromatic polyamides using a so-called dry jet-wet spinning process. In this process the polymer solution immediately after extrusion is led through a gaseous medium for a short distance, say about ⅛ to 1½ inches, before entering the coagulation bath. Although highly successful for the production of fibers and filaments having excellent tensile properties from wholly aromatic polyamides, the dry jet-wet spinning process is generally restricted to the production of filaments of rather low total denier and a denier per filament of about six or less. For many end uses and for economic reasons, i.e., desirability of increased production rates, the spinning of large numbers of filaments from a given spinnerette is highly desirable, as is also the spinning of filaments with large individual deniers. By the present invention one is able to spin wholly aromatic polyamide solutions into dense attenuated filaments of unusually high crystallinity, orientation and thermal stability at high rates of production.

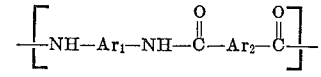
SUMMARY OF THE INVENTION

A process for the preparation of improved filaments and the like from wholly aromatic polyamides, especially from those polyamides having a pronounced tendency toward preorientation and random crystallization, is provided. A solution of such polyamide is extruded from a spinnerette or other type of extrusion nozzle into a spin bath also called a coagulating bath. In one preferred

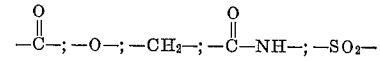
embodiment the point of extrusion is disposed a short distance of about ⅛ to 1½ inches above the liquid level in the bath. The resulting filaments are withdrawn from the coagulating bath and then washed and dried. Thereafter, the filaments are hot drawn. Improvements result from incorporating in the solution prior to extrusion a small but effective amount of a wax. The wax preferably has a melting point above 25° C. and is obtained by the reaction of a saturated fatty acid having about 8–28 carbon atoms with a hexahydric alcohol in an amount of about 0.1% to 5.0% based on the weight of the polyamide in solution.

DETAILED DESCRIPTION

Typical of polymers useful in carrying out the process of this invention are those wholly aromatic polyamides, having recurring structural units as follows:



wherein Ar_1 and Ar_2 are divalent unsaturated carbocyclic ring radicals. The polyamides may be generally described as having no aliphatic linkages or segments in their regularly recurring structural units. The term "unsaturated carbocyclic ring radicals" as used herein refers to any resonance-stabilized ring system whether benzene-aromatic or hetero-aromatic. The term "benzene-aromatic" refers to single, multiple or fused ring residues, such as phenylene, biphenylene and naphthalene and also applies to aromatic ring systems which have been modified by internal aromatic amide block units. Ar_1 and Ar_2 may be the same or different and may be substituted or unsubstituted. The substituents may be nitro, halogen, lower alkyl groups and the like. In the above formula, either one or both of the Ar groups may contain optionally linkages other than carbon-to-carbon, such as



etc. Specific examples of such polymers include: poly(m-phenylene isophthalamide); poly-N,N'-m-phenylenebis (m-benzamido)-4,4'-biphenyldicarbonamide; poly - 4,4'-bis(p-aminophenyl)-2,2'-bithiazole isophthalamide poly-2,5-bis(p-aminophenyl)-1,3,4-oxadiazole isophthalamide; poly-3,4'-diaminobenzanilide isophthalamide and poly-4,4'-diaminobenzanilide terephthalamide. Two preferred wholly aromatic polymers are poly[N,N'-m-phenylene bis(m-benzamide) naphthalene-2,6-dicarboxamide] and poly[N,N' - m - phenylene bis(m-benzamide)]terephthalamide.

Satisfactory methods for preparing these wholly aromatic polyamides are well known in the art. Although these polymers may be prepared using interfacial techniques, the use of solution polymerization is preferred because the resulting polymer solutions can be spun directly into filaments. When the solution preparation method is employed, representative members of this class of polymers may be prepared conveniently and preferably by the reaction of an aromatic diacid halide with an aromatic diamine at low temperatures in a lower dialkyl N-substituted amide solvent, such as N,N-dimethylformamide and N,N-dimethylacetamide. In addition to the lower dialkylamides, solvents suitable for preparing the polymers and spinning solutions of this invention include N-methyl-2-pyrrolidone, hexamethyl phosphoric triamide, trifluoroacetic acid and the like. Mixtures of solvents are also contemplated. Concentrated sulfuric acid and dimethyl sulfoxide may also be used for redissolving polymers which have been isolated and purified, as for example, when interfacial techniques are used to prepare the polymers. Preferably, the same solvent is used for both polymer preparation and spinning.

When the polymer is prepared in part from an aromatic halide, the hydrogen halide formed during the polymerization should be neutralized or removed from the polymer solution prior to spinning in order to prevent its harmful effect on the resulting product and corrosive effect on the spinning equipment used. Neutralization may be conveniently accomplished, by adding an alkali or alkaline earth metal base to the polymer solution. Specific examples of such bases include lithium carbonate, lithium hydroxide, calcium, hydroxide, calcium carbonate, calcium acetate and magnesium carbonate.

As a result of the neutralization reaction, the polymers are dissolved in the solvent, preferably a lower dialkyl amide, containing an amount of salt and water proportional to the amount of hydrogen halide formed during the polymerization. The salt contributes to the polymer solubilization and varies in amount with the chemical structure and molecular weight of the polymer, but generally ranges from about 1% to about 8% based on solution weight.

The polymer spinning solutions may also be prepared by dissolving a washed isolated polymer, such as one prepared by the interfacial technique, in a solvent containing from about 1% to about 8% of an alkali or alkaline earth metal chloride or bromide at a temperature of about 60–90° C. Suitable salts are lithium chloride, lithium bromide, calcium chloride, zinc chloride and the like. Of these, calcium chloride and lithium chloride are preferred. Although it is not essential, the addition of up to about 4% water to these spinning solutions will improve their stability.

Attempts to spin solutions of wholly aromatic polyamides using conventional wet spinning techniques at economically high spinning rates have been found not to be too successful. Fibres obtained, using numerous combinations of spinning conditions, have poor structural quality, contain numerous voids, and could not be stretched or hot drawn to a desired extent. The attainment of a high total orientation stretch during the after-treatment is necessary to obtain dense void-free filaments having excellent physical properties and thermal stability. In addition pre-orientation and random crystallization in the freshly coagulated filaments also contribute to the poor results.

It has now been found that any preorientation and random crystallization in the freshly coagulated filaments can be minimized by the addition of certain waxy additives to the hereindescribed polymer solutions prior to spinning. Also the total drawability of the filaments is enhanced resulting in increased productivity.

Typical of the additives that may be used in the practice of this invention are esters of hexahydric alcohols and the anhydro derivatives thereof such as sorbitol, mannitol, dulcitol, sorbitan, mannitan, sorbide, mannide and the like. The fatty cadi portion of the ester is advantageously derived from the long-chain fatty acids including lauric, myristic, palmitic, stearic, oleic, ricinoleic, and the like. The esters may be either predominantly mono-, di-, tri-esters, or mixtures thereof and should have a melting point about about 25° C. Examples of specific esters are sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan trioleate, sorbitan tristearate, sorbitan monolaurate, sorbitol tetrastearate, mannitan monopalmitate, mannide monooleate, sorbide dipalmitate, sorbide distearate, sorbide monomyristate, and sorbide monostearate. Also alkoxylated derivates of these esters can be employed such as polyoxyethylene (20 ethylene oxide units) sorbitan monopalmitate, polyoxyethylene (40 ethylene oxide units) sorbitan monostearate, polyoxyethylene (20 ethylene oxide units) monooleate, polyoxyethylene (20 ethylene oxide units) sorbitol oleate, polyoxyethylene (20 ethylene oxide units) sorbitol palmitate. In addition, mixtures of one or more of these additives with similar additives such as ethoxylated castor oil, glycerol monostearate, glycerol monopalmitate, polyoxyethylene glycerol monostearate can be employed.

The concentration of the additive used may be in the range of from about 0.1% to about 5% and preferably from about 0.1% to about 1% by weight based on the weight of polymer in the solution. Obviously, the optimum amount of additive is dependent on the spinning conditions employed such as rate of spinning, dope temperature, spin bath concentration and temperature, fiber denier and number of filaments and polymer variables such as composition, molecular weight and concentration.

The method used for adding the wax to the polymer is not of critical importance. For convenience and ease of mixing, the additives may be dissolved in a small amount of the solvent used as the polymerization solvent and added to the polymer solution at an elevated temperature. In a preferred mode of operation, the additives may be incorporated immediately following completion of the polymerization step and prior to the neutralization step.

The presence of the wax additives in the spinning solution is thought to prevent the polymer solution from coagulating too rapidly in the spin bath. Although the exact mechanism is not known presently, it is believed that the wax additives reduce the rate of coagulation by controlling the rate of diffusion of water and solvent into and from the coagulating filaments, which are maintained in a substantially amorphous state. As a result of the controlled coagulation and diffusion rates, the major portion of the residual salt in the spining solution is thus removed by the coagulation bath.

Extruded streams of solutions of wholly aromatic polyamides containing no wax additives are believed to coagulate rapidly at the surface in the vicinity of the extrusion nozzle resulting in an undesirable skin-core effect in the filaments. The rapidly coagulated skin reduces the diffusity of water into the filaments and inhibits the removal of salt and solvent therefrom. The differing rates of coagulation between the skin and core are believed responsible for preorientation and random crystallization. As a result of the skin-core effect, filaments emerging from the bath have a high degree of orientation, some random crystallization and retention of considerable amounts of salts. These factors are responsible for poor fiber structure and void formation, both of which reduce the maximum orientation stretch obtainable.

In certain instances, particularly those having virtually all para-orientation, such as the polyamide hydrazide derived from p-aminobenzhydride and terephthaloyl chloride or poly-4,4'-diamino benzanilido terephthalamide, random crystallization in the spin bath is not a serious problem. However, spinning of solutions of most para-polyamides results in a pronounced tendency of spin orientation in the polymer. The term "spin orientation" as used herein refers to orientation resulting from the shear effect produced by the flow of a viscous solution through a spinneret orifice. The term "pre-orientation" refers to the combined effect of spin orientation plus the added orientation produced by the drag of the spin bath liquid on freshly coagulated filaments. The term pre-orientation refers to those cases in which random crystallization predominantly occurs in the spin bath and spin orientation in those cases in which orientation in the spin bath is a dominant factor and random crystallization is a negligible factor.

When random crystallization occurs, the filaments coming from the spin bath are weak, delustered and brittle and cannot be processed satisfactorily. On the other hand when high spin orientation develops, the filaments may be strong but the maximum orientation stretch is considerably reduced, thereby resulting in a lower productivity and physical strength.

The use of the wax additives in accordance with the present invention results in a pronounced reduction in random crystallization and a reduction in pre-orientation. Furthermore, the additives often improve the stability of

the polymers from having a tendency to develop gel formation on standing and heating. Thus, the spinnability of spinning solutions containing the additive is enhanced.

Reference is now made to the accompanying drawing where a spinning system useful for the practice of the present invention is shown. This system was used in the illustrative examples given below unless otherwise indicated. Numeral 1 denotes a spinning solution supply tank. A wholly aromatic polyamide is prepared and dissolved in a suitable solvent. The resulting polymer solution is the feed material supplied to tank 1. The percent of polymer in the solution is conveniently from about 5 to about 30. Preferably the solution contains about 6 to about 18 percent polymer. For best results, as well as for increased productivity, it is generally desirable to use as concentrated polymer solution as possible and practical. Of course, the solubility of the aromatic polyamides varies inter alia with the structure of the polymer and with regard to the solvent used. The polymers should have an inherent viscosity of from about 0.6 to 3.0 or higher, and preferably about 1.2 as measured at 30° C. as a 0.5% solution in N,N-dimethylacetamide containing 5% lithium chloride.

The polymer solution is moved from tank **1** by means of pump **2** and is conveyed through an in-line filter **3** to an extrusion head or spinnerette assembly **4**. The solution containing a sufficiently high concentration of polymer can be extruded at temperatures of from about 40° C. to about 120° C., and preferably from about 60–90° C. The polymer concentration can be increased or decreased within the preferred limits of 6 to 18 percent in order to provide a suitable viscosity for spinning. Additionally, the viscosity at a given concentration can be adjusted by heating or cooling the polymer-containing spinning solution.

The spinning solution is forced through a suitable number of holes provided in a spinnerette **5**. As shown the extrusion face of the spinnerett is disposed just above the liquid level of the spin bath, although it may very well be submerged in the spin bath. The polymer streams emerging from the spinnerette pass around guide **6** and move through the spin bath composition **7**. Spin baths, suitable for use in the present invention for converting the extruded viscous polymer solutions into strand-like objects may be comprised of water or a mixture of water and a lower alkylamide solvent. The spin bath composition may vary over a wide range, depending on the composition of the polymer and solvent being used in the spinning solution, as well as on other factors. For example, when spinning solutions of polymers having a pronounced tendency toward pre-orientation and random crystallization, such as for example, polymers of N,N'-m-phenylene bis(m-aminobenzamide) terephthalate, a spin bath consisting of about 35–45% N,N-dimethylacetamide in water is preferred. However, when spinning solutions of polymers having a tendency toward spin orientation such as for example 4,4-diaminobenzanilide terephthalamide polymer and the polyamide hydrazide derived from p-aminobenzhydrazide and terephthaloyl chloride, a spin bath of from about 0–20%, preferably 0–10% of N,N-dimethylacetamide in water is desirable. For convenience of solvent recovery, the solvent used in making up the spin bath should be the same as that used for dissolving the polymer. Other solvents, useful as coagulation baths, when mixed with water, include ethylene glycol, polyethylene glycol, dimethylsulfoxide and the like.

In order to maintain an essentially constant environment for coagulation in the bath, the solution should be circulated and maintained at the optimum concentration by the continuous addition of water while maintaining a constant volume of liquid bath coagulation media. The temperature of the spin bath may be from about −10° C. to about 50° C., and preferably from about 15° C. to 25° C. during coagulation.

When coagulated as taught herein, void-free filaments emerging from the spin bath have a low birefringence, or orientation, and low salt content which permits their conversion by further processing into useful filaments.

After coagulation the filaments are washed, stretched, dried and stretched again. The filaments are conveyed by a set of drums **8** under spray heads provided with a shower of washing liquid, preferably hot water. From these drums the filaments are moved through a wash bath **9** by means of a second set of drums **10** also provided with spray heads. The filaments may be stretched from about one to four times their length in bath **9** containing hot water having a temperature of about 50–100° C. The amount of washing depends on the salt concentrations present in the polymer solutions, the total denier of the threadline, and other factors.

The washed, drawn filaments are next passed through an optional aqueous finish bath **11** containing conventional yarn lubricants and/or antistatic agents. A third set of drums **12** are used to pull the filaments through the bath. Drums **12** are heated so that drying of the filaments is accomplished. The temperature of these drying rolls are preferably maintained from about 100–160° C.

Following the drawing operation, the filament bundle may be heated even higher by passing over a heated draw pin **13** as shown or through a heated enclosure such as an oven, furnace or hot block slot where the filaments are continuously conditioned at about 300–500° C., and preferably about 400–450° C. The filaments are then drawn from one to four times over a heated surface such as that of a hot metal shoe **14** at about 300–450° C. A fourth set of drums **15** is shown as providing the traction sufficient to draw the bundle of filaments. When it is desirable to reduce shrinkage and further stabilize the filaments, the filaments may be heat relaxed prior to being collected in package form **16**.

The following examples are illustrative of the present invention. Parts are on a weight basis uness otherwise stated.

Example I

Polymeric [N,N'-m-phenylene bis(m-benzamide)] terephthalamide was prepared. 209 parts of N,N'-m-phenylene bis-(m-aminobenzamide) was charged to a reactor along with 57 parts of powdered calcium carbonate. The reactor was closed and swept with nitrogen gas. 1300 parts of dry N,N-dimethylacetamide was then added to the reactor, and the previously added aromatic diamine dissolved with stirring. A coolant bath at −20° C. was placed around the reactor. After 1½ hours 122 parts of terephthaloyl chloride was added with rapid stirring. The diacid chloride was rinsed into the reactor with 60 parts of dimethylacetamide. After stirring for 30 minutes, the temperature of the reaction mixture was raised to 35° C. A solution composed of 200 parts of dimethylacetamide and 11 parts water was added and stirred. The resulting solution was degassed and cooled to room temperature. The polymer had an inherent viscosity of 2.29. The solution contained 15.5% polymer.

This polymer solution at 70° C. was spun into a spin bath to produce filaments. The spin bath composition was 55% water by volume and 45% dimethylacetamide and had a temperature of 25° C. The spinneret face was below the spin bath surface. Under optimum conditions the calculated jet stretch accomplished between the spinneret and the first set of rolls was only 0.22. While being washed with water at 60° C., the filaments were stretched 1.21×. After a lubricant was applied and the filaments dried, the threadline was hot drawn 2.75×. The maximum total draw was 0.73. The filament denier was 8.5 and the filaments had a tenacity of 2.4 grams per denier and an elongation of 13.9 percent.

To the same polymer solution 1% sorbitan monopalmitate based on the polymer weight was added and the resulting solution was spun under identical spinning con-

ditions. The optimum jet stretch was 0.60×. While being washed with water at 60° C., the filaments were stretched 2.0×. After the application of the lubricant and drying of the filaments, the threadline was drawn 1.47×. The maximum total draw was 1.76×. The filament denier was 4.6 with a tenacity of 3.15 and an elongation of 30.4 percent.

Therefore, by having the wax additive present in the polymer-containing spinning solution, one is able to obtain spinning solution, one is able to obtain a higher total draw of wholly aromatic polyamide filaments. In addition, significantly higher work is required to break the filaments prepared in accordance with the present invention.

Photomicrographs were taken of the filaments samples produced with the wax additive and without the additive. The improved void-free structure of the filaments produced from the wax containing polymer solution was readily noted.

Example II

A polymer solution was prepared as described in Example I; and sorbitan monopalmitate was added in an amount of 0.25% based on the weight of the polymer. Spinning conditions were the same as in the first example. The total stretch was 1.85. Filaments having an individual denier of 3.0 were prepared. The tenacity thereof was 5.1 grams per denier and the elongation was 15.2 percent. Again it is seen that greater work is required to break the filaments spun in the presence of the wax additive employed as compared to the filaments prepared without the presence of the additive.

Example III

A polymer solution was prepared as described in Example I; and sorbitan monopalmitate was added in an amount of 0.50% based on the weight of the polymer. Spinning conditions were the same as in the first example. The total draw was 1.89. Filaments having an individual denier of 3.3 were prepared. The tenacity thereof was 5.8 grams per denier and the elongation was 12.1%. Again it is seen that greater work is required to break the filaments spun in the presence of the wax additive as compared to the filaments prepared without the additive.

Example IV

With polymer and solution preparation being identical to that described in Example I, 1% by weight polyoxyethylene sorbitol oleate (about 20 ethylene oxide units per mol) was added to the spinning solution instead of sorbitan monopalmitate. Spinning and aftertreating conditions identical to that of Example I were used to produce filaments. The optimum jet stretch was 1.0×. While being washed with water at 60° C. the filaments were stretched 2.0×. After the application of the lubricant and drying of the filaments, the threadline was drawn 1.65×. The maximum total draw was 3.3×. The filament denier was 3.6 with a tenacity of 3.9 grams per denier and an elongation of 17.8. Again it is seen that greater work is required to break the filaments spun in the presence of the wax additive employed as compared to the filaments prepared without the presence of the additive.

Example V

A polyamide hydrazide from p-aminobenzhydrazide and terephthaloyl chloride was prepared. A stirred reaction vessel was charged with 57 parts of p-aminobenzhydrazide to which 1300 parts of dimethylacetamide had been added. The hydrazide dissolved rapidly and completely. The temperature of the vessel was reduced to −10° C. whereupon 76 parts of solid terephthaloyl chloride was added thereto. Upon completion of the polymerization 66 parts of calcium acetate monohydrate, 13 parts of water and 304 parts of dimethylacetamide were added to the vessel. The solution was heated to 70° C. and divided into two parts to provide material for wet spinning filaments. To one part was added 0.5% sorbitan monopalmitate. Both samples spun very well and could be hot drawn using spinning and aftertreating conditions set forth in Example I. The filaments produced by using the spinning solution containing the sorbitan additive could be drawn over 1.6× at 300° C., whereas the filaments produced by using the spinning solution containing no additive could be drawn only 1.3× at most even at slightly higher temperature. Photomicrographs of the two types of filaments revealed that the spun filaments containing the sorbitan additive were void-free and clear, whereas the structure of the filaments containing no additive was slightly granular.

Example VI

Polymeric N,N'-m-phenylene bis(m-benzamide)terephthalamide was prepared as described in Example I. The polymer had an inherent viscosity of 2.43. This polymer was dissolved in dimethylacetamide to provide 13% polymer solids. To this solution was added 0.5% sorbitan monopalmitate based on the weight of the polymer. The spinning solution at 110° C. was pumped through a hundred hole spinnerette immersed in a spin bath having a temperature of 20° C. and being composed of 55% water and 45% dimethylacetamide. The diameter of the spinnerette holes was 3 mils. The coagulated filaments had an immersion length in the bath of 42 inches. The calculated jet stretch was 0.53×. The freshly spun filaments were washed with hot water and stretched while wet 2.52×. The filaments were then coated with a lubricant, dried and hot stretched at 300° C. 1.36×. The total draw was 1.8. The filament denier was 3.0 and the filaments had a tenacity of 5.1 grams per denier and an elongation of 15.2%.

Example VII

A polyamide hydrazide from p-aminobenzhydrazide and terephthaloyl chloride with an inherent viscosity of 1.4 was prepared as described in Example V. The polymer was polymerized in dimethyl acetamide to provide 6% polymer solids. To this solution was added 1.0% sorbitan monopalmitate based on the weight of the polymer. The solution was divided into two equal parts. The first part was used in a conventional wet spinning procedure wherein the spinnerette is 2 inches below the level of the spin bath. The second part was used in a wet spinning procedure wherein the extrusion surface of the spinnerette is disposed ½" above the level of the spin bath.

At a temperature of 60° C. the first part was extruded through a fifteen hole spinnerette with the diameter of the holes being 6 mils. The spin bath had a temperature of 20° C. and a concentration of 99% water and 1% dimethylacetamide. The coagulated filaments had an immersion length of 31 inches. The calculated jet stretch was 0.47×. The freshly spun filaments were washed with hot water (85° C.) and stretched while wet 1.31×. The filaments were then coated with a lubricant, dried and hot stretched over a 12 inch hot shoe at 350° C. 1.29×. The total draw was 0.79. The filament denier was 11 and the filaments had a tenacity of 8.5 grams per denier and an elongation of 2.2%.

At a temperature of 60° C. the second part was extruded through the same fifteen hole spinnerette. The extruded streams after passing through the one-half inch air gap moved 31 inches through a spin bath having a temperature of 20° C. and a concentration of 99% water and 1% dimethylacetamide. The calculated jet stretch was 0.43×. The freshly spun filaments were washed with hot water (85° C.) and stretched while wet 1.44×. The filaments were then coated with a lubricant, dried and hot stretched over a 12 inch hot shoe at 350° C. 1.41×. The total draw was 0.87. The individual filament denier was 10.0 and the filaments had a tenacity of 19.3 grams per denier and an elongation of 4.3. It is readily apparent that when the spinnerette is disposed outside the spin bath

one obtains filaments requiring considerable more work to break.

Example VIII

To the polymer solution described in Example VI a blend consisting of 60% by weight sorbitan monopalmitate and 40% by weight castor oil ethoxylated with 20 moles of ethylene oxide in an amount to provide 1% additives by weight based on the polymer. The resulting spinning solution at 65° C. was extruded through a fifteen 7 mil hole spinneret. The extruded streams after passing through a one-half inch air gap moved 25 inches through a spin bath having a temperature of 25° C. and a concentration of 99% water and 1% dimethylacetamide. The calculated jet stretch was 2.17×. The freshly spun filaments were washed with ethylene glycol at 135° C. and stretched 2.7×. The filaments were washed and dried and hot stretched 1.05× at 370° C. The individual filament denier was 6.4 and the filaments had a tenacity of 6.6 grams per denier and an elongation of 20%. The total stretch was 6.2×.

Example IX

To the polymer solution described in Example VI a blend consisting of 60% by weight sorbitan monopalmitate and 40% by weight castor oil ethoxylated with 200 moles of ethylene oxide in an amount to provide 0.5% additives by weight based on the polymer. The resulting spinning solution at 65° C. was extruded through a thirty 5 mil hole spinnerette. The extruded streams after passing through a one-half inch air gap moved 25 inches through a spin bath having a temperature of 23° C. and a concentration of 99% water and 1% dimethylacetamide. The calculated jet stretch was 1.67×. The freshly spun filaments were washed with ethylene glycol at 135° C. and stretched 2.74×. The filaments were washed and dried and hot stretched 1.47× at 370° C. The individual filament denier was 4.6 and the filaments had a tenacity of 5.6 grams per denier and an elongation of 34%. The total stretch was 6.7×.

I claim:

1. A composition of matter comprising
(a) a fiber-forming wholly aromatic polyamide and
(b) about 0.1 to 5.0% based on the weight of the polymer of a wax having a melting point above 25° C. and obtained by the reaction of a saturated fatty acid having at least about 8 carbon atoms with a hexahydric alcohol.

2. A filament shaped from the composition of claim 1.

3. A composition of matter consisting of
(a) polymeric fiber-forming N,N'-m-phenylene bis(m-benzamide) terephthalamide; and
(b) about 0.1 to 5.0% based on the weight of the polymer of sorbitan monopalmitate.

4. A composition of matter consisting of
(a) polymeric fiber-forming N,N'-m-phenylene bis(m-benzamide) terephthalamide; and
(b) about 0.1 to 5.0% based on the weight of the polymer of polyoxyethylene (about 20 ethylene oxide units) sorbitol oleate.

5. A composition of matter consisting of
(a) a polyamide hydrazide prepared from p-aminobenzhydrazide and terephthaloyl halide; and
(b) about 0.1 to 5.0% based on the weight of the polymer of sorbitan monopalmitate.

6. In a process for the preparation of filaments and the like from wholly aromatic polyamides having a pronounced tendency toward preorientation and random crystallization in which a solution of said polyamide is extruded into at least one stream that passes through a coagulating bath, the resulting filaments are withdrawn from the coagulating bath and then washed and dried and thereafter the filaments are hot drawn, the improvement of incorporating in the solution prior to extrusion a wax having a melting point above 25° C. obtained by the reaction of a saturated fatty acid having at least about 8 carbon atoms with a hexahydric alcohol in an amount of about 0.1% to 5% based on the weight of the polyamide in solution, said wax being retained in the filaments at least until the filaments are hot drawn.

7. The process of claim 2 wherein the polyamide is polymeric N,N'-m-phenylene bis(m-benzamide) terephthalamide.

8. The process of claim 6 wherein the solvent used to form the spinning solution is N,N-dimethylacetamide.

9. The process of claim 8 wherein the solvent contains about 1–8% alkali or alkaline earth halide salt.

10. The process of claim 9 wherein the salt is lithium chloride.

11. The process of claim 6 wherein the wax is sorbitan monopalimitate.

12. The process of claim 6 wherein the wax is polyoxyethylene (about 20 ethylene oxide units) sorbitol oleate.

13. The process of claim 6 wherein the polyamide is the polyamide hydrazide prepared from p-aminobenzhydrazide and terephthaloyl halide.

14. The process of claim 13 wherein the wax sorbitan monopalmitate.

15. The process of claim 6 where the extruded streams move through a gaseous medium for a short distance before entering the coagulating bath.

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

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