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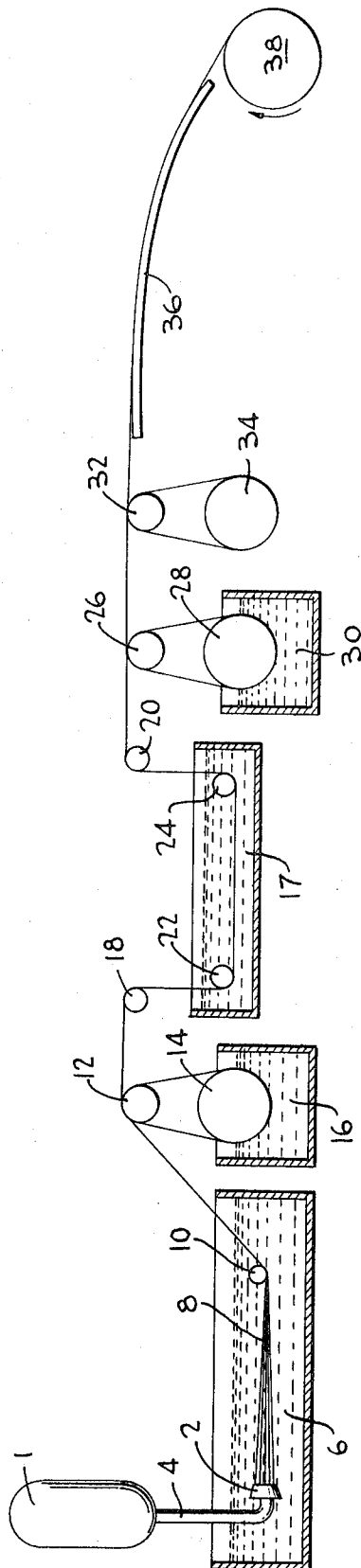
3,657,409

PROCESS FOR THE PRODUCTION OF ACRYLIC FILAMENTS

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2 Sheets-Sheet 1

FIG. 1



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2 Sheets-Sheet 2

FIG. 2

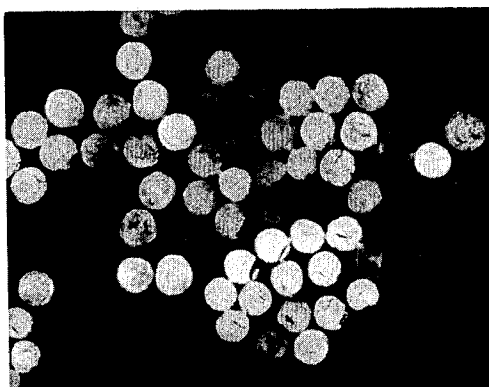
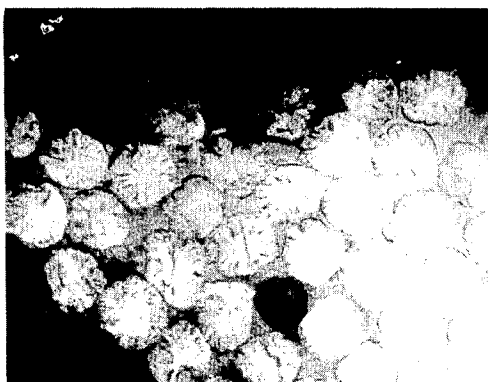


FIG. 3



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PROCESS FOR THE PRODUCTION OF
ACRYLIC FILAMENTS

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11 Claims

ABSTRACT OF THE DISCLOSURE

A process is provided for the production of substantially round acrylic filaments which are particularly suited as precursors for the formation of carbon filaments. A fiber-forming acrylic polymer, such as an acrylonitrile homopolymer, while dissolved in a dimethylacetamide containing lithium chloride solvent is extruded into an essentially non-aqueous coagulation bath consisting essentially of ethylene glycol and dimethylacetamide present in concentrations found capable of producing essentially round homogeneous (i.e. substantially free of voids and incursions) filaments. The resulting as-spun filaments are initially washed in relatively cool water, and are drawn to increase their orientation.

BACKGROUND OF THE INVENTION

In the past numerous processes have been proposed for the spinning of acrylic filaments. Such processes have included wet spinning techniques in which a solution of the acrylic polymer is extruded into a suitable coagulation bath to form a filamentary material, as well as dry spinning techniques in which a solution of the acrylic polymer is extruded into an evaporative medium in which the solvent is evaporated to form the resulting filamentary material. Experience has indicated, however, that the acrylic filaments produced in the prior art commonly possess non-uniform cross-sections. For instance, dry spun acrylic filaments spun from conventional high boiling solvents commonly exhibit what has been referred to as a dog bone cross-section. Additionally, acrylic filaments formed in accordance with the prior art commonly exhibit a non-uniform morphology such as an abundance of voids and/or radial incursions. For instance, when one utilizes aqueous coagulation baths which are commonly disclosed in the literature, an abundance of voids are commonly observed in the resulting fibers upon microscopic examination. Such voids often necessitate a separate healing treatment.

In the past procedures have been proposed for the conversion of fibers formed from acrylic polymers to modified forms possessing enhanced thermal stability. Such modification has generally been accomplished by heating the fibrous material in an oxygen-containing atmosphere at moderate temperatures. The resulting fibers may be utilized as intermediates in the formation of carbonized fibrous materials, or for direct utilization as fire-resistant fibers. If the carbonized fibrous materials are subjected to more highly elevated temperatures in an inert atmosphere they may optionally be converted to carbon fibers which exhibit an X-ray diffraction pattern characteristics of graphitic carbon. Such graphite fibers are particularly suited for use as a reinforcing medium for incorporation in a suitable matrix to form composite structural elements. The non-uniform characteristics exhibited by acrylic precursors commonly produced in accordance with the prior art, however, have tended to adversely influence the tensile properties of any carbonaceous fibers ultimately derived therefrom. Accordingly, any composite structures which in-

corporate such carbonaceous fibers as a reinforcing medium by necessity exhibit less than optimum structural characteristics.

It is an object of the invention to provide an improved wet spinning process for the production of acrylic filaments which are particularly suited as precursors for the formation of carbon filaments.

It is an object of the invention to provide an improved process for the production of acrylic filaments which possess substantially round cross-sections.

It is an object of the invention to provide a process for the production of substantially round acrylic filaments which are substantially free of voids and radial incursions.

It is another object of the invention to provide a process for the production of acrylic filaments exhibiting an essentially uniform and homogeneous microstructure.

It is another object of the invention to provide a process for the production of substantially round acrylic filaments which when carbonized may be uniformly loaded or packed into composite structures.

It is a further object of the present invention to provide a stable and readily controllable process in which substantially round acrylic filaments may be wet spun.

These and other objects as well as the scope, nature, and utilization of the invention will be apparent from the following description and appended claims.

SUMMARY OF THE INVENTION

It has been found that an improved wet spinning process for the production of round acrylic filaments which are particularly suited as precursors for the formation of carbon filaments comprises:

(a) Providing a spinning solution having a low shear viscosity of about 80 to 3000 poise measured at 25° C. comprising (1) a fiber-forming acrylic polymer in a concentration of about 15 to 30 percent by weight based upon the total weight of the solution selected from the group consisting of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent or one or more monovinyl units copolymerized therewith, (2) lithium chloride, and (3) a dimethylacetamide solvent,

(b) Extruding said spinning solution into a non-aqueous coagulation bath having a temperature of about 30 to 70° C. consisting essentially of about 55 to 85 percent by weight of ethylene glycol and about 15 to 45 percent by weight of dimethylacetamide,

(c) Washing the resulting as-spun filament in water to remove dimethylacetamide from the same, the washing being initially conducted for at least 25 seconds with the water at a temperature of about 10 to 50° C., and

(d) Drawing said washed filament to increase the orientation thereof.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of an apparatus arrangement suitable for carrying out the process of the present invention.

FIG. 2 is a photograph which illustrates the uniform cross-sectional configuration and morphology of a plurality of acrylonitrile homopolymer filaments formed in accordance with the present invention.

FIG. 3 is a cross-sectional photograph which illustrates the non-uniform nature of a plurality of acrylonitrile homopolymer filaments formed in accordance with a conventional wet spinning process of the prior art wherein a solution of the polymer dissolved in dimethylformamide is spun into an aqueous dimethylformamide coagulation bath.

DESCRIPTION OF PREFERRED EMBODIMENTS

The starting polymer

The fiber-forming acrylic polymer selected for use in the process may be either an acrylonitrile homopolymer or an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith. An acrylonitrile homopolymer is particularly preferred for use in the present process. Suitable copolymers commonly contain at least about 95 mol percent of recurring acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith. Representative monovinyl units which may be incorporated in the acrylonitrile copolymers include styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like. The acrylic polymers may be formed by standard polymerization processes which are well known in the art. When the acrylic fibers are intended for use as precursors in the production of carbon or graphite fibers, minor quantities of prooxidation or graphitization catalysts may optionally be incorporated in the bulk polymer prior to spinning.

The spinning solution

The solvent utilized to form the spinning solution employed in the present process is dimethylacetamide. This solvent is sometimes identified as N,N-dimethyl acetamide or DMAC, and has the chemical formula $\text{CH}_3\text{CON}(\text{CH}_3)_2$. The standard technical or commercial grade of dimethylacetamide may be employed as the solvent in the formation of the spinning solution.

The spinning solution may be prepared by dissolving sufficient acrylic polymer in the dimethylacetamide solvent to yield a solution suitable for extrusion containing from about 15 to 30 percent acrylic polymer by weight based upon the total weight of the solution, and preferably from about 18 to 25 percent by weight. In a particularly preferred embodiment of the invention the spinning solution contains the acrylic polymer in a concentration of about 20 to 22 percent by weight based upon the total weight of the solution. The low shear viscosity of the spinning solution should be within the range of about 80 to 3000 poise measured at 25° C. and preferably within the range of about 125 to 1500 poise measured at 25° C. If the spinning solution low shear viscosity is much below about 80 poise measured at 25° C., spinning breakdowns commonly occur. If the spinning solution low shear viscosity is much above about 3000 poise measured at 25° C., extremely high spinning pressures are required and plugging of the extrusion orifice may occur.

In a preferred embodiment of the present process the spinning solution additionally contains about 0.1 to 5.0 percent by weight based upon the total weight of the solution, and preferably about 0.5 to 2 percent by weight based upon the total weight of the solution of lithium chloride dissolved therein. Alternatively, one may employ a like quantity of an alkali or alkaline earth metal salt selected from the group consisting of calcium chloride, lithium bromide, sodium thiocyanate, and magnesium bromide or mixtures thereof, as disclosed in United States No. 2,632,750 to Justice which is herein incorporated by reference. The desired solution fluidity and mobility are accordingly efficiently maintained even upon the passage of time. For instance, it has been found that a solution comprising 22 parts by weight acrylonitrile homopolymer, 2 parts by weight lithium chloride, and 76 parts by weight dimethylacetamide solvent commonly exhibits a relatively constant low shear viscosity of about 150 poise measured at 25° C. after standing for 250 hours. A solution containing an even lesser concentration of acrylonitrile homopolymer and no lithium chloride (i.e. 20 parts by weight poly-

mer, and 80 parts by weight dimethylacetamide) tends to increase in viscosity upon standing and exhibits a low shear viscosity of about 1000 poise measured at 25° C. after about 2½ hours. One or more of the above-identified inorganic compounds (e.g. lithium chloride) may be dissolved in the dimethylacetamide solvent either simultaneously with the acrylic polymer or before or after the acrylic polymer is dissolved therein. When the acrylic fibers are intended for use as precursors in the production of carbon or graphite fibers, minor quantities of preoxidation or graphitization catalysts may optionally be incorporated in the spinning solution.

The spinning solution is preferably filtered, such as by passage through a plate and frame press provided with an appropriate filtration medium, prior to wet spinning in order to assure the removal of an extraneous solid matter which could possibly obstruct the extrusion orifice during the spinning operation.

Wet spinning

The spinning solution containing the fiber-forming acrylic polymer dissolved therein is extruded into a coagulation bath to form a substantially round filament having a surface which is substantially smooth and free of internal voids and radial incursions. The homogeneous nature of the resulting as-spun filament is preserved during the subsequent steps of the process.

It has been found that the objects of the present invention are accomplished when an essentially non-aqueous coagulation bath is selected having a temperature of about 30 to 70° C. (preferably 40 to 60° C.) which consists essentially of about 55 to 85 percent by weight of ethylene glycol and about 15 to 45 percent by weight of dimethylacetamide. When employing dimethylacetamide in the coagulation bath in concentrations much greater than about 45 percent by weight, then filament breakage tends to occur at the spinneret. When employing dimethylacetamide in the coagulation bath in concentrations much less than about 15 percent by weight, then the resulting filaments tend to lose their substantially round cross-section and exhibit a bean-shaped configuration. In a preferred embodiment of the invention the coagulation bath consists essentially of about 65 to 75 percent by weight of ethylene glycol and about 25 to 35 percent by weight of dimethylacetamide. In a particularly preferred embodiment of the invention the coagulation bath consists essentially of about 70 percent by weight of ethylene glycol and about 30 percent by weight of dimethylacetamide. The particularly preferred temperature for the coagulation bath is about 50° C. If the coagulation bath is provided at a temperature much below about 30° C., then the coagulation rate tends to be too slow. Coagulation bath temperatures much above about 70° C. tend to produce unduly rapid coagulation and impart voids to the resulting fibers. Any fibers which are insufficiently coagulated at the time of their departure from the coagulation bath may be flattened and lose their uniform round configuration in subsequent processing stages.

The temperature of the spinning solution at the time of its extrusion should be within the range of about 10° C. to about 90° C., and preferably at about 20 to 30° C. In a particularly preferred embodiment of the invention the spinning solution is provided at room temperature, e.g. about 25° C., which thereby facilitates expeditious handling and storage of the same.

The spinneret utilized during the extrusion may contain a single hole through which a single filament is extruded, and preferably contains a plurality of holes whereby a plurality of filaments may be simultaneously extruded in yarn form. The spinneret preferably contains holes having a diameter between about 50 to 150 microns when producing relatively low denier filaments having an as-spun denier of about 8 to 24 denier per filament and holes of about 300 to 500 microns when producing relatively high denier filaments having an as-spun denier of about 100

to 1500 denier per filament. Extrusion pressures between about 100 and 700 p.s.i.g. may be conveniently selected, and preferably between about 100 and 400 p.s.i.g. Spinning or extrusion speeds of about 5 to 80 meters per minute may be utilized, and preferably between about 10 to 20 meters per minute.

Throughout the extrusion process the coagulation bath is preferably circulated. A relatively constant composition within the coagulation bath may be maintained through the continuous withdrawal and purification of the same. Alternatively, additional ethylene glycol may be continuously added to the coagulation bath to preserve the desired proportion of dimethylacetamide to ethylene glycol within the same. The length of the coagulation bath is adjusted so that the resulting as-spun filaments are present within the coagulation bath for a residence time of at least about 3 seconds. For instance, residence times of about 3 to 120 seconds may be conveniently selected. Residence times for the as-spun filaments in the coagulation bath in excess of 120 seconds tend to yield no commensurate advantage. Particularly preferred residence times for the as-spun filament in the coagulation bath range from about 3 to 6 seconds.

Washing as-spun filament

The resulting as-spun filament is next washed with water to remove dimethylacetamide solvent from the same. The as-spun filament is preferably washed with water until substantially all residual amounts of solvent, coagulation bath, and inorganic compound (e.g. lithium chloride), if any, are removed from the same. It is essential that the filament first be exposed to a relatively cool water wash medium at a temperature of about 10 to 50° C. and preferably at about 10 to 30° C., and most preferably at room temperature (e.g. about 25° C.), for at least about 25 seconds. The entire wash treatment may be conducted at a temperature within the range of about 10 to 50° C. Alternatively the washing of the filament may be subsequently continued at a more highly elevated temperature, e.g. in excess of about 50° C. to remove additional solvent. In a preferred embodiment of the invention the initial cold water wash is conducted for at least about 50 seconds.

When the entire wash is conducted at a relatively cool wash temperature of about 10 to 50° C., wash times of about 25 to 240 seconds and preferably about 50 to 120 seconds, are commonly utilized depending upon the filament denier. Longer wash times tend to yield no commensurate advantage.

It has been found that the initial cool water wash described above is essential in order to preserve fiber homogeneity. During the cool water wash a one-way transfer of residual quantities of the dimethylacetamide spinning solvent out of the filament is believed to be promoted to the substantial exclusion of the passage of the molecules of the water wash medium into the filament. It has been found that if the as-spun filament is initially washed at a temperature substantially higher than about 50° C., then the resulting washed fiber tends to contain a significant number of voids and tends to flatten. At temperatures below about 10° C. the washing procedure tends to be unduly slow. The residual dimethylacetamide content of the washed filaments preferably is no more than about 5 percent dimethylacetamide by weight, and most preferably no more than about 0.1 percent by weight.

The water wash treatment of the present process is conveniently conducted in an in-line operation with the filament after it leaves the coagulation bath being continuously passed through a water wash medium which is continuously regenerated. Conventional filament wash rolls may be utilized. The filament additionally may be washed with water while wound upon a perforated bobbin, or by the use of other washing means as will be apparent to those skilled in the art.

Drawing washed filament

The as-spun and washed filament is drawn or stretched from about 1.5 times its original length up to the point at which the filament breaks to orient the same and thereby enhance its tensile properties. Total draw ratios above about 1.5:1 to 15:1 may commonly be selected. The drawing is commonly conducted at an elevated temperature and preferably at a total drawn ratio of between about 3:1 and 12:1. The dense uniform filament microstructure makes possible the use of the relatively high total draw ratios indicated. As will be apparent to those skilled in the art, the drawing of the as-spun and washed filament may be conducted by a variety of techniques. For instance, it is possible for the drawing to be conducted while the filament is (a) immersed in a heated liquid draw medium, (b) suspended in a heated gaseous atmosphere (e.g. at a temperature of about 120 to 200° C.) or (c) in contact with a heated solid surface (e.g. at a temperature of about 130 to 170° C.). If desired, the total draw imparted to the filament may be conducted by a combination of the foregoing technique. When draw techniques (b) and (c) are utilized, it is essential that the filament be provided to the draw zone in an essentially dry form in order to avoid void formation. When draw technique (a) is employed, the filament is subsequently washed to remove the draw medium and is dried. Additionally, the liquid draw medium may also serve a washing and/or coagulating function wherein residual quantities of dimethylacetamide are removed from the water washed fiber.

In a preferred embodiment of the invention the washed filament is at least partially drawn while immersed in a hot glycerin bath. In a particularly preferred embodiment of the invention the filament is drawn while immersed in a hot glycerin bath at a temperature of about 80 to 110° C. and at a draw ratio of about 1.5:1 to 3:1 (preferably at a temperature of about 90° C. and a draw ratio of about 2:1), washed in cool water (e.g. at a temperature of about 10 to 50° C.), and subsequently drawn at a draw ratio of about 3:1 to 6:1 while in contact with a hot shoe at a temperature of about 100 to 200° C., and preferably at a temperature of about 150 to 160° C.

The resulting drawn filament optionally may be relaxed. The relaxation step of the process renders the filament more highly extensible and greatly improves the knot strength of the same. The relaxation step may be conveniently conducted while passing the drawn filament through a muffle furnace for one or more passes or by passing the same over a hot shoe, or shoes. Other relaxation techniques will be apparent to those skilled in the art.

The drawn and optionally relaxed filaments may be plied to form yarns or tows of increased total denier as will be apparent to those skilled in the art.

Continuous lengths of the acrylic filaments may be stabilized (e.g. preoxidized) carbonized, and optionally graphitized in accordance with procedures known in the art. For instance, continuous lengths of the acrylic fibrous materials may be stabilized in accordance with the teaching of U.S. Ser. No. 749,957, filed Aug. 5, 1968 of Dagobert E. Stuetz and subsequently carbonized and graphitized in accordance with the teachings of U.S. Ser. No. 777,275, filed Nov. 20, 1968 of Charles M. Clarke. Each of the above-identified patents is assigned to the same assignee as the present invention and is herein incorporated by reference.

Alternatively, the uniform fibers produced in accordance with the present process may be employed directly in the formation of textiles and carpets and in similar use areas as will be apparent to those skilled in the art.

The following example is given as a specific illustration of the invention with reference being made to the drawings. It should be understood, however, that the invention is not limited to the specific details set forth in the example.

7 EXAMPLE

Twenty-two parts by weight of polyacrylonitrile homopolymer, two parts by weight of lithium chloride, and seventy-six parts by weight of industrial grade dimethylacetamide are slurried at room temperature for 120 minutes by use of a stirred vessel. The slurry is heated to a temperature of 100° C. over a period of about 90 minutes where it is mixed with agitation for two hours. The resulting solution is passed four times through a conventional filter press while at 100° C. over a period of 19 hours in order to remove any solid contamination. The low shear viscosity (Brookfield) of the resulting spinning solution after degassing is found to be about 150 poise measured at 25° C.

The spinning solution is provided in dope bomb 1 under an atmosphere of nitrogen at 20 p.s.i.g. The spinning solution is conveyed to spinneret 2 via the line 4 where it is extruded into coagulation bath 6. The spinneret 2 is of the standard cup type and comprises a single circle of 80 holes each having a diameter of 100 microns. The spinning solution is conveyed to the spinneret 2 at a throughput volume of 8.7 cubic centimeters per minute.

The coagulation bath consists of 66 parts by weight ethylene glycol and 34 parts by weight dimethylacetamide and is provided at a temperature of 50° C. The coagulation bath is caused to flow concurrently with coagulated filament 8 and is maintained at a relatively constant composition by the continuous addition of ethylene glycol to the same and the continuous withdraw of a portion of the bath. The coagulation bath has a length of 35 inches and the coagulated filaments are maintained in the same for a residence time of about 4 seconds.

The coagulated filaments pass under guide 10 which is immersed in coagulation bath 6 and are conveyed to skewed roll 12 and wash roll 14 which is partially immersed in water bath 16 which is maintained at 16° C. The coagulated filaments are taken up on roll 12 at a rate of 15 meters per minute. The filaments are wrapped about skewed roll 12 and wash roll 14 for a residence time of about 50 seconds during which time the filaments are immersed in water for approximately 10 seconds and withdrawn with water adhering to the same during which time substantially all residual amounts of dimethylacetamide are removed from the same.

The washed filaments are next continuously passed through stretch bath 17 having a length of 15 inches which is provided with glycerin at 90° C. Rollers 18 and 20 situated outside the stretch bath and rollers 22 and 24 immersed within the stretch bath guide the filaments during the stretching operation. The filaments are next taken up on skewed roll 26 and wash roll 28 which is partially immersed in a water wash bath 30 provided at 16° C. which is identical to that of wash bath 16. The filaments are taken up on skewed roll 26 at a rate of 30 meters per minute and are accordingly drawn at a draw ratio of 2:1 while immersed in the glycerin stretch bath. The filaments are immersed in the water wash bath 30 for approximately 5 seconds during which time residual quantities of glycerin are substantially removed from the same. The water present in wash bath 30 is circulated and is constantly regenerated. The washed filaments are next passed to skewed roll 32 and drying roll 34 where residual quantities of moisture are expelled from the same. Dry roll 34 is steam heated and maintained at a constant temperature of approximately 95° C.

The washed and dried filaments are next passed over a two foot heated draw shoe which is provided at a constant temperature of 150° C. The residence time of the fiber while in contact with the hot shoe 36 is 0.5 second. The drawn fibers are collected on takeup roll 38 at a rate of 180 meters per minute.

FIG. 2 illustrates an enlarged cross-sectional view of a plurality of the filaments formed in the example and indicates the homogeneous uniform round cross-section

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achieved. The resulting filaments exhibit a denier per filament of 1.34, and elongation of 8.18 percent, a tenacity of 5.69 grams per denier, and an initial modulus of 144 grams per denier. The filaments illustrated have a diameter of about 30 microns.

The resulting filaments may be used as precursors for the formation of graphite fibers and may be initially stabilized in accordance with the teachings of U.S. Ser. No. 749,957, filed Aug. 5, 1968 and carbonized and graphitized in accordance with the teachings of U.S. Ser. No. 777,275, filed Nov. 20, 1968. The graphitized fibers exhibit a single filament tenacity of about 365,000 p.s.i., a single filament initial modulus of about 72×10^6 p.s.i., a specific gravity of about 1.9, and a denier per filament of about 0.9.

For comparison purposes data is presented with respect to acrylonitrile filaments wet spun by a conventional procedure from a solution of the same in dimethylformamide into a coagulation bath of aqueous dimethylformamide. FIG. 3 illustrates an enlarged cross-sectional view of the resulting filaments wherein numerous voids and incursions are visible. The fibers illustrated have a diameter of approximately 20 microns. Upon stabilization, carbonization, and graphitization the graphitized fibers exhibit a single filament tenacity of about 185,000 p.s.i., a single filament initial modulus of about 50×10^6 p.s.i., a specific gravity of about 1.81, and a denier per filament of about 0.6.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. An improved wet spinning process for the production of round acrylic filaments which are particularly suited as precursors for the formation of carbon filaments comprising:

(a) providing a spinning solution having a low shear viscosity of about 125 to 1500 poise measured at 25° C. comprising (1) a fiber-forming acrylic polymer in a concentration of about 18 to 25 percent by weight based upon the total weight of the solution selected from the group consisting of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith, (2) lithium chloride in a concentration of about 0.1 to 5 percent by weight based upon the total weight of the solution which lowers and preserves upon standing the viscosity of the solution, and (3) a dimethylacetamide solvent,

(b) extruding said spinning solution into an essentially non-aqueous coagulation bath having a temperature of about 30 to 70° C. consisting essentially of about 55 to 85 percent by weight of ethylene glycol and about 15 to 45 percent by weight of dimethylacetamide,

(c) washing the resulting as-spun filament in water to remove dimethylacetamide and lithium chloride from the same, the said washing being initially conducted for at least 25 seconds with said water at a temperature of about 10 to 50° C., and

(d) drawing said washed filament to increase the orientation thereof.

2. An improved wet spinning process according to claim 1 in which said acrylic polymer is an acrylonitrile homopolymer.

3. An improved wet spinning process according to claim 1 wherein lithium chloride is present in said spinning solution in a concentration of about 0.5 to 2 percent by weight based upon the total weight of the solution.

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4. An improved wet spinning process according to claim 1 wherein said essentially non-aqueous coagulation bath consists essentially of about 65 to 75 percent by weight of ethylene glycol and about 25 to 35 percent by weight of dimethylacetamide.

5. An improved wet spinning process according to claim 1 wherein said washing is initially conducted in water for at least 50 seconds with said water at a temperature of about 10 to 30° C.

6. An improved wet spinning process according to claim 1 wherein said washed filament is drawn at a draw ratio of about 3:1 to 12:1.

7. An improved wet spinning process according to claim 1 wherein said drawing is at least partially carried out in a hot glycerin bath at a temperature of about 80 to 110° C.

8. An improved wet spinning process for the production of round acrylonitrile homopolymer filaments which are particularly suited as precursors for the formation of carbon filaments comprising:

(a) providing a spinning solution having a low shear viscosity of about 125 to 1500 poise measured at 25° C. and present at a temperature of about 20 to 30° C. comprising (1) a fiber-forming acrylonitrile homopolymer in a concentration of about 20 to 22 percent by weight based upon the total weight of the solution, (2) lithium chloride in a concentration of about 0.5 to 2 percent by weight based upon the total weight of the solution which lowers and preserves upon standing the viscosity of the solution, and (3) a dimethylacetamide solvent,

(b) extruding said spinning solution into an essentially non-aqueous coagulation bath having a temperature of about 30 to 70° C. consisting essentially of about 55 to 85 percent by weight ethylene glycol

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and about 15 to 45 percent by weight of dimethylacetamide,

(c) washing the resulting as-spun filament in water to remove dimethylacetamide and lithium chloride from the same, the said washing being initially conducted for at least 25 seconds with said water at a temperature of about 10 to 50° C., and

(d) drawing said washed filament to increase the orientation thereof at a draw ratio of about 3:1 to 12:1.

9. An improved wet spinning process according to claim 8 wherein said resulting as-spun filament is initially washed in water for at least about 50 seconds with said water at a temperature of about 10 to 30° C.

10. An improved wet spinning process according to claim 8 wherein said drawing is at least partially carried out in a hot glycerin bath at a temperature of about 80 to 110° C.

11. An improved wet spinning process according to claim 8 wherein said essentially non-aqueous coagulation bath is provided at a temperature of about 40 to 60° C. and consists essentially of about 65 to 75 percent by weight of ethylene glycol and about 25 to 35 percent by weight of dimethylacetamide.

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

264—210 F