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3,324,061

PREPARING AQUEOUS SOLUTIONS OF
POLYPYRROLIDONE

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This invention relates to the dry-spinning of polypyrrolidone and particularly to compositions, processes and apparatus useful for the dry-spinning thereof.

The potential value of polypyrrolidone for articles such as fibers, filaments, films and molded articles is well recognized. In particular, its value for use in textiles is outstanding because for such purposes polypyrrolidone possesses certain of the advantages of natural fibers with the strength of some of the synthetic fibers heretofore utilized.

The polymerization of pyrrolidone is well known and forms no part of the present invention. It is ordinarily carried out under anhydrous conditions in the presence of a basic catalyst and of a small amount of a suitable activator. The resultant polymer is usually washed very thoroughly and dried.

Shaping the polypyrrolidone, which term includes formation of fibers, sheets and molded articles, is commonly carried out by melting and extruding or injecting the molten thermoplastic polymer under pressure. Considering fibers particularly, there are three techniques generally applicable to thermoplastics, referred to as melt spinning, dry spinning and wet spinning. The technique of melt spinning is employed with some difficulty for polypyrrolidone, as mentioned by Cox, U.S. Patent No. 2,980,641, who states that dry-spinning and wet spinning have also been used and describes a process of wet spinning employing aqueous phytic acid. Another method of wet spinning is described by Barnes et al., U.S. Patent No. 2,711,398, employing anhydrous formic acid.

Each procedure offers certain advantages and disadvantages. Thus, melt spinning subjects the polymer to relatively high temperatures (of the order of 260° C., which is the accepted approximate melting point, or higher), pressure and mechanical stress and tends to result in degradation of polypyrrolidone with reversion to monomer and decrease in molecular weight of the polymer in the fibers. This has adverse effects on the properties of the fibers. In addition there is a loss of polymer thus causing lower yields of fibers. Because heretofore-known solvents for polypyrrolidone for use in dry spinning are relatively high boiling liquids, somewhat the same disadvantages have applied to this technique. Wet spinning as heretofore practiced has necessitated rather extensive chemical treatment and manipulation of the fibers which is found to have a deleterious effect on the properties. In particular it is noted that both acid and alkali may tenderize the fibers to subsequent heating.

It is an object of this invention to provide a process for the production of fibers, filaments and films of polypyrrolidone employing temperatures below about 250° C.

It is an other object of this invention to provide a process for the production of fibers, filaments and films of polypyrrolidone while avoiding subjecting said polypyrrolidone to potential chemical alterations.

A further object of the invention is to provide a process for spinning filaments of polypyrrolidone having improved properties.

A still further object of the invention is to provide spinnable compositions comprising polypyrrolidone.

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A yet further object of the invention is to provide spinnable compositions the non-volatile portion of which consists essentially of polypyrrolidone.

Further objects of the invention will become apparent from a reading of the disclosure hereinbelow.

It has been found that these and other objects of the invention are accomplished by the preparation of compositions consisting essentially of solutions of normally water-insoluble polypyrrolidone in water at elevated temperatures and pressures, and employing such solution in dry spinning and other fabricating processes. It is surprising that polypyrrolidone is soluble in water up to about 50% and even up to about 75% in water at temperatures below its melting point. At higher concentrations, about 80% and more, the water is apparently dissolved in the polypyrrolidone and on release of the pressure a foamed polymer may be obtained. Although solutions of about 5 to 50% by weight of polypyrrolidone in aqueous phytic acid or aqueous solutions of salts of the same acid have been described, it was not to be expected that the non-volatile co-solvent could be dispensed with entirely and a purely aqueous solution of polypyrrolidone prepared. It was further quite unexpected that such solutions could be extruded at temperatures above the boiling point of water under pressure into air without formation of bubbles or other imperfections.

In general, solution is effected by heating polypyrrolidone prepared by the processes described in the art, and washed to remove catalyst, monomer and soluble concomitants with the requisite amount of water to produce the desired concentration, in a pressure vessel. The polymer used is of such molecular weight that it is normally insoluble in water, and preferably at least of molecular weight which permits formation of continuous films. Agitation accelerates the rate of solution and assists in maintaining a uniform temperature and it is preferred that solution be effected with mechanical agitation, but avoiding entrainment of air. The temperatures used may vary from about 265° to about 450° F. It will readily be appreciated that the higher temperatures are necessary in the formation of more concentrated solutions, i.e. about 60% to 75%, but temperatures as high as 350° F. may be desirable to accelerate solution when solutions containing less than 50% polypyrrolidone are being prepared. Pressure in the vessel is largely autogenous and must be maintained sufficiently high to prevent ebullition and occlusion of bubbles in the lines leading to the extrusion die. It is sometimes convenient to apply additional pressure, e.g. with nitrogen, to facilitate transfer of the solution. For use in extrusion, the pressure vessel is connected by suitable fittings and a gear pump to an extrusion die.

After forming the solution it is maintained above its melting point by suitable heating means during passage through the gear pump, and the other accessories before extrusion. If cooled prematurely the solution hardens with or without expulsion of water depending on the concentration.

A remarkable and unexpected property of the compositions of the invention is their relatively low viscosity, particularly as compared to melts of the polymer. Accordingly, one of the great advantages of dry spinning employing these compositions is that the viscosity in pumping and extrusion stages is reduced. Viscosity studies show values of the order of about 1 to about 15 poises for compositions of the invention as compared to values of about 100 to 1000 poises for melted polypyrrolidone at much higher temperatures. This results in less consumption of mechanical work and less mechanical and thermal degradation of the polymer than in the melt spinning processes heretofore most commonly employed.

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As stated hereinabove, the spinnable compositions of the invention consist essentially of solutions of polypyrrolidone in water at temperatures in the range of about 256° to about 450° F. (about 130° to about 225° C). Concentrations of polypyrrolidone range from about 20 to about 75% by weight of the solutions. A particularly preferred range is from about 25% to about 40%. The solutions are preferably prepared using distilled or deionized water but water having relatively low mineral content may be employed without serious effects if no especially corrosive materials are present and if the content of iron (which may stain the fibers) is very low.

In addition to the polypyrrolidone and water the compositions of the invention may contain up to about 5 to 10% of other ingredients such as volatile and water miscible co-solvents; plasticizers, for example, pyrrolidone; delustrants such as titania; dyestuffs; pigments; anti-static agents and the like materials employed to affect the properties of the fibers. In general only the co-solvents are employed in amounts of 5 to 10%; the other materials individually are employed in lesser amounts although the total of all such materials may be up to about 5 to 10%. It will be understood that additives are chosen to be stable under the conditions in which the compositions are to be employed. Modifications which may be necessitated in the equipment due to such additions will be readily apparent to those skilled in the art.

The characteristic feature of the dry-spinning process of the invention is that the hot aqueous solution of polypyrrolidone under pressure is forced through a die into air forming a filament which dries to less than about 35% water content by weight before being taken up and reeled.

Modifications of the process within the scope of the invention are readily made. For example, a gear pump is very satisfactory for the purpose, but other types of pumps may be used if desired. It is found convenient to provide several sources of heat to maintain the temperature of the solution at the desired point during passage to the die. In addition, heating the die may be desirable. When initially starting the operation it is found that the assembly is conveniently preheated by passing hot glycerine through the various passages, the pump and the die; a valve permitting switchover to the hot solution to be extruded is therefore desirable but other mechanical equivalents may be employed and other liquids may be employed for the preheating including, for example, glycols and pyrrolidone. This preheating performs another important function since it prevents precipitation of polymer in the system which may occur initially as the result of flashing off of water when the solution is first released from the autoclave. Polymer which precipitates under these conditions may plug the lines, filter or spinneret orifices.

After passage through the necessary filter packs and the die, the solution is spun by drawing through air at temperatures between about 60° F. and 400° F. or even higher depending upon rate of water-loss desired, relative humidity of the air, rate of flow of the air and the number and character of the fibers. The flow of air should be slow enough to avoid flicking of the extruded solution against the face of the die and fast enough to effect the desired degree of drying. When one or a few small filaments are being spun, the necessary rate of flow may be effected by convection. It will be apparent that gases other than air may be used but air is most economical. Nitrogen can be used to advantage if any ingredients of the solution are readily oxidizable.

The ratio between drawing rate and the rate of extrusion through the die determines whether the filament is heavier or finer than the diameter of the orifice. Under free fall conditions with substantially no drawing tension a heavier filament of relatively high denier is obtained. As the rate of drawing increases and exceeds the rate of extrusion greater draw down of the fiber occurs and smaller denier

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filaments are formed. The practical limit of draw down is determined by the cohesivity of the solution as extruded which increases with higher temperatures of extrusion and higher concentrations of polypyrrolidone in the solution.

The tension applied to effect draw down must obviously not be so great as to snap or break the filament in the zone immediately below the spinning die but may approach this value within a few percent.

By employing two drawing stages between the spinning die and the reel it is possible to effect both the initial drawn down of the filament to a finer denier and the subsequent orientation and further reduction in denier. When this double drawing is to be effected, the first draw down is carried out under conditions such that the fiber is brought to about 5-10% moisture content in passage through air.

During the drying phase of the process, the fibers apparently first dry exteriorly and subsequently water present on the inside diffuses outwardly and is evaporated. It is found that fibers formed by the process of the invention have a cross-section with a longer periphery than circular fibers of the same denier. This may take the form of a circle with more or less crenulate or crenate margin or periphery or in extreme cases may be of a flattened shape with parallel or even somewhat concave sides having enlarged ends and conveniently described as a dog-bone shape. Greater area of the surface for a given denier of fiber is often obtained as the concentration of the polypyrrolidone in the solution is decreased.

It is thus another advantage of the process of the invention that non-circular cross-sectional fibers are obtained employing standard circular-orificed dies or spinnerets. Such fibers are somewhat less lustrous than comparable fibers having substantially circular cross-sections.

The aqueous solution of lowest concentration which is found to be useful is about 20% by weight of polypyrrolidone. At concentrations below about 20% the extruded solution is not sufficiently viscous as extruded to be self-supporting during the drying phase and emerges as a water solution from which the polymer crystallizes as fibrils. The range of concentration which is preferred is from about 20% to 50% by weight of the polymer, in water. Higher concentrations up to about 75% may also be used, particularly in conjunction with short dwell times at the higher temperatures. At concentrations of about 80 to 90% the time required for solution is so great and the temperatures necessary so high that rather considerable hydrolysis of the polymer occurs. This is somewhat less at intermediate concentrations such as 70%.

After passage through the drying zone of the apparatus the filaments are collected and reeled in the conventional manner employing Godet rolls and reeling means known to the art. At this point, before passage over the first roll, lubricants and/or other treatments or finishes are conveniently applied to the filaments by conventional applicator techniques. Such treatments are employed to facilitate handling the filaments in desired subsequent processes and also the handling of the filaments in reeling or simultaneous orientation when desired.

Having thus described the composition and process of the invention broadly, it is now more particularly described by specific examples and embodiments intended to show the best mode presently contemplated of practicing the invention without being thereby limiting. In these examples and embodiments parts and percentages are by weight where not otherwise specified, temperatures are in degrees Fahrenheit in conformity with usual practice in the art and inherent viscosities are determined at about 0.2 g./deciliter in metacresol.

Example 1

This example illustrates an especially simple mode for practicing the process of the invention and making a composition of the invention.

A composition of the invention is prepared by outgassing and then heating a mixture of 420 parts of distilled water and 280 parts of polypyrrolidone having an inherent viscosity of 2.2 at about 320°–350° F. for about 1 hour. The composition is spun through 5 mil die holes and is oriented by hand drawing.

Example 2

An apparatus for preparation of compositions of the invention and the dry-spinning thereof by the process of the invention is constructed as follows.

A steam jacketed five gallon autoclave capable of containing and resisting pressures up to 1000 pounds per square inch (p.s.i.) constructed of stainless steel and having a suitable mechanical agitator, pressure gauge, connection with vacuum gauge and needle valve for application of vacuum or pressure and for venting, thermocouple well and inlet hand-hole at the top and outlet at the bottom is mounted so that the bottom outlet discharges into a filtering means such as a filter pack. The latter comprises a layer of screens or other filter medium and is of the type conventionally employed upstream of a gear pump as protection against fine particles. The filter pack and lines are sufficiently lagged or heated to maintain their temperature at that of the autoclave. Mechanical agitation in the autoclave is provided to prevent excessive thermal gradients which may result in precipitation of polypyrrolidone in the cooler portions. (It will be apparent that working pressures are considerably less than 1000 p.s.i. and autoclaves designed for lower pressures may be used equally satisfactorily.) The discharge from the filter pack which is at substantially the pressure and temperature of the autoclave passes through suitable heated valving means to a gear pump capable of delivering 42 cubic centimeters per minute at 100 to 300 p.s.i. The exact capacity of the gear pump is not critical provided it is capable of delivering at least the desired volume of solution at the necessary pressure. The gear pump, valving means and connections conveniently form a subassembly of the apparatus which is heated by external means to maintain its temperature. The effluent from the gear pump enters the discharge outlet of the subassembly still at substantially the temperature of the autoclave and at a pressure which may be substantially higher. It is convenient to provide the subassembly with a by-pass for the valve means so that the gear-pump can be by-passed and the effluent from the aforesaid filtering means can pass directly through the subassembly either under autogenous or superimposed pressure. Effluent at the outlet of the subassembly enters a narrow heat exchanger discharging into the spinning assembly, for example, about ¼ inch in internal diameter and 12 inches long, having an external jacket. This heat exchanger aids in maintaining or altering the temperature of the spinning composition as desired.

The spinning assembly consists of the body, a chamber, a filtering means and the attached spinneret plate. It is advantageously heated, e.g., electrically, to prevent excessive cooling of the spinning solution, because cooling of the spinneret face below about 225° F. may cause irregularities or breaks in the filaments or freeze-up of the orifices.

The autoclave (the lower outlet being closed) is charged with polypyrrolidone and water in the required proportions and the autoclave is then sealed. Agitation (at a very low rate) and heating is commenced. As the temperature within the autoclave rises, pressure is bled off through a vent from time to time during about 1 hour to remove air. Alternatively vacuum may be applied to the system before heating is commenced to remove entrained gases. While some water is lost in either outgassing procedure, this is not sufficient to have a significant effect on the subsequent process.

Because some air can be dissolved by the solution at elevated temperatures and pressure, which may cause difficulties when subsequently released in the orifices of the

spinneret or in the filaments, it is preferred to include this step of outgassing the polypyrrolidone.

The rate at which solution takes place is found to be dependent on the temperature employed. Some hydrolysis of the polymer may occur at elevated temperatures, and it is convenient to keep the time of heating to effect solution as short as possible. In practice, an hour of heating with moderate agitation is not considered excessive and a solution containing 20 percent by weight of polypyrrolidone is obtained at 300° F. in this time, or a solution containing about 50 percent of polypyrrolidone is obtained at 340° F. in this time. Higher temperatures result in more rapid solution of the polypyrrolidone.

When all of the polymer is in solution, the batch is ready for spinning. Hot glycerine is first pumped through the apparatus and the lower outlet of the autoclave is opened and the polymer solution forced through the first filtering means and into the hot glycerine under its autogenous pressure. Immediately the hot glycerine is shut off and from then on the solution is pumped, forcing the glycerine from the system.

The spinneret face should be maintained at about the temperature of the solution in the autoclave and not below about 225° F. While it is difficult to determine the actual temperature at the spinneret face, adjustments in the system such as supplemental heating of the spinneret when plugging of holes occurs can assure the proper temperature range. If the spinneret temperature drops lower than 225° F. the solution tends to solidify in the orifices, while if it is excessively high the polymer solution tends to foam on emerging from the spinneret. The solution itself, of course, provides some heat to the spinneret in passing therethrough.

When the solution emerges from the orifices a large part of the moisture (depending upon the original content of the solution) is lost by flashing off. This also requires a considerable amount of heat and tends to cool the spinneret face as well as the solution.

After formation of a filament at an orifice of the spinneret, the filament is drawn through air as before said. Conveniently and to promote consistency of results and prevent tangling of fibers due to stray air currents, a spinning tower (suitably a hollow stack) of some 8 to 10 feet in length or more and of a diameter of about 6–8 inches or more as desired is employed. While drawing through as little as 2 feet of air may be sufficient for some purposes, it is preferred to employ a stack of at least 8–10 feet. Greater lengths, for example, 20–30 feet, may be employed to provide somewhat longer dwell times with greater reduction in moisture content. Generally, larger diameters are used for longer columns.

The air in the stack is at a temperature from about 60° F. to about 400° F. or more varying through the length of the stack and being cooler toward the bottom. It will be apparent that if the filaments issuing from the bottom of the stack are excessively dry or excessively moist, the relative humidity and temperature of the air in the stack should be adjusted to counteract this effect.

As the filament emerges from the bottom of the stack, it is still moist and may contain from about 5 to about 35 percent by weight of water. The fiber is drawn over a yarn lubricant applicator and over Godet rolls as described hereinabove and reeled in conventional fashion. The speeds are adjusted to the rate of spinning so that the tension on the filaments is sufficient to produce up to about 2:1 draw down or more as desired but not sufficient to break the filaments or cause orientation. The spun filaments are subsequently conditioned for orientation or as described above the orientation process is effected concurrently with the spinning.

A number of lots of fiber are produced by the above described procedure employing polypyrrolidone and various proportions of water to produce compositions of the invention comprising from about 20 to 50 percent by weight of polypyrrolidone.

A group of 4 such lots designated A, B, C and D illustrate the process and fibers of the invention. The spinneret die hole size is 0.004 inch diameter. The draw down ratio is maintained very low so that relatively heavy filaments are obtained. The data are shown in tabular form (all temperatures in ° F. and pressures in p.s.i. gauge.).

Lot.....	A	B	C	D
Charge of water.....	3,200	2,100	1,800	2,500
Charge of polypyrrolidone.....	800	900	1,200	2,500
Inherent viscosity of polypyrrolidone.....	2.3	2.3	2.3	2.3
Solution concentration.....	20	30	40	50
Autoclave temperature.....	295	300	327	350
Temperature in valving subassembly.....	298	300	310	350
Temperature in heat exchanger.....	260	265	290	290
Temperature at die face.....	250	230	230	230
Pressure at die.....	100	50	125	110
Rate of spinning (grams solution per minute).....	4.44	2.0	2.67	2.39
Fiber character as spun.....	± Circular	Dog bone	Dog bone	Crenate
Properties of oriented fiber:				
Inherent viscosity.....	1.57	1.68	1.39	1.03
Density.....	1.260	1.258	1.254	1.257
Tenacity, grams per denier.....	1.4	1.2	2.1	1.2
Denier.....	25	26	29	32
Draw ratio (percent).....	(¹)	340	320	290
Elongation at break (percent).....	19	31	62	52

¹ Not measured, hand drawn.

Example 3

The procedure employed above is repeated employing solutions prepared as for lot B above containing additional materials. The three lots are designated E, F and G and are characterized as follows:

E

30 percent polypyrrolidone
6 percent pyrrolidone
64 percent water

F

30 percent polypyrrolidone (containing 2 percent titania (submicron sizes) added to polymerization and 1 percent Chlorantine Fast Red 5B Ex. Conc. added to polymer, both by weight)
70 percent water

G

30 percent polypyrrolidone containing 1 percent Chlorantine Fast Red 5B Ex. Conc. by weight
70 percent

The pertinent additional data on the dry spinning are:

Lot.....	E	F	G
Inherent viscosity of polypyrrolidone.....	2.3	1.6	2.3
Autoclave temperature (deg.).....	300	300	310
Temperature in valving subassembly (deg.).....	300	300	300
Temperature in heat exchanger (deg.).....	280	270	255
Temperature at die face (deg.).....	360	350	220
Pressure.....	100	75	200
Rate of spinning (grams per minute).....	3.39	4.0	4.0
Fiber character.....	Dog bone	Red, matte	Red, lustrous
Inherent viscosity of fiber.....	1.61	1.35	1.79

Example 4

A spinnable composition of the invention is prepared from 30 parts of polypyrrolidone having inherent viscosity of 3.5 and 70 parts of distilled water by heating together at 300 to 310° F. for 2 hours with gentle agitation. Before heating, the charge is outgassed by application of 15 inch vacuum for 10 minutes. The composition is estimated to have a viscosity of about 7 poises at about 300° F.

The composition is extruded through a spinneret having 4 mil hole size as described above. The valving sub-assembly is held at about 286° F. and the heat-exchanger

at about 250° F. The spinneret is held at a temperature, above about 230° F., so that no plugging occurs. The stack is heated by twelve 500 watt electrical heating units (Calrod) each about 2 feet long distributed over the outer surface of the stack from the bottom to within 2 feet of the top. The upper 1 foot section is removable

for access to the spinneret face. The heating units are not run at full capacity. The temperature in the air stack varies between about 75° F. at the lower open end which is at room temperature to about 650° to 700° F. as measured by thermocouples placed within the stack about 1½ inches from the wall and about 1 foot within each end of the heated zone. This temperature is probably that of the wall due to radiation as air above the heated zone is found to be about 400° F. The rate of extrusion is 3.3 grams of the solution per spinneret hole per minute. In about 9 feet through the stack approximately three-fourths of the water is evaporated and the moist fiber containing about 35 percent of water is reeled at a rate of 350 feet per minute. The moist fiber is then further conditioned on its reel at 65 percent relative humidity at 72° F. to 6 percent moisture content which is suitable for orientation. The fiber is oriented to 300 percent of the unoriented length and the properties of the oriented fiber determined by usual tests.

The inherent viscosity of the polypyrrolidone in the fiber is 1.68. The tenacity of the 22 denier filament is 2.4 grams per denier with elongation at break of 23

percent. The modulus at 1 percent elongation is 12 grams per denier.

The above-described spinning procedure is repeated employing polypyrrolidone having inherent viscosity of 1.3. Somewhat lower temperatures are sufficient for solution and maintaining solution up to the orifice. After extrusion the polypyrrolidone of the fiber is found to have an inherent viscosity of 1.12. While the compositions of the invention comprising polypyrrolidone having an inherent viscosity as low as 1.3 can be employed in the process of the invention, for spinning fibers of good strength it is preferred that the polypyrrolidone have an inherent viscosity of at least about 1.5. Superior results are ob-

tained when the polypyrrolidone as extruded has an inherent viscosity of at least about 1.4.

Films of polypyrrolidone are produced by extruding the solutions of the invention through a die with a slit-shaped orifice, under temperature conditions as set forth in these examples.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for the production of a dry-spinnable polypyrrolidone-containing composition which comprises the steps of:

A. outgassing a mixture comprising from about 20 percent to about 75 percent by weight of substantially neutral polypyrrolidone and from about 80 percent to about 25 percent by weight of water and

B. heating the said mixture with gentle agitation for from about 10 seconds to about 2 hours under the autogenous pressure of said mixture at a temperature in the range of from about 265° F. to about 450° F., the lower temperatures being employed with lower amounts of polypyrrolidone and the shorter times at the higher temperatures

whereby said mixture is liquefied without significant degradation of the said polypyrrolidone.

2. The process for extruding polypyrrolidone which comprises the steps of:

I. Forming a solution comprising polypyrrolidone and water by:

A. outgassing a mixture comprising from about 20 percent to about 75 percent by weight of substantially neutral polypyrrolidone and from about 80 percent to about 25 percent by weight of water and

B. heating the said mixture with gentle agitation for a period up to about 2 hours under the autogenous pressure of said mixture at a temperature in the range of from about 265° F. to about 450° F., the lower temperature being employed with lower amounts of polypyrrolidone and the shorter times at the higher temperatures, whereby said mixture is liquefied without significant degradation of the said polypyrrolidone

and, while maintaining the temperature of said solution at a temperature above the temperature at which crystallization of polypyrrolidone commences,

II. forcing the said solution through a spinneret plate maintained at a temperature of at least from about 225° F. and up to about 450° F. and not less than the crystallization temperature of the said solution into relatively dry warm air, to form a self-sustaining filament, and

III. collecting the said self-sustaining filament.

3. The process according to claim 2 wherein the solution is forced through the spinneret plate by its autogenous pressure.

4. The process according to claim 2 wherein the filament is dried to a water content of less than 35 percent by weight by a slow current of heated air.

5. The process according to claim 2 wherein the length of filament collected is not less than the length of self-sustaining filament extruded and is substantially un-oriented.

6. The process according to claim 2 wherein the filament is collected after tensioning and at least partial orientation.

7. The process according to claim 2 wherein the polypyrrolidone after extrusion has an inherent viscosity above about 1.3.

8. The process for extruding polypyrrolidone which comprises the steps of:

I. Forming a solution comprising polypyrrolidone and water by:

A. outgassing a mixture comprising from about 20 percent to about 75 percent by weight of substantially neutral polypyrrolidone and from about 80 percent to about 25 percent by weight of water and not more than about 1 percent of the weight thereof of solid materials and not more than about 6 percent of the weight thereof of a water-soluble relatively non-volatile plasticizer for polypyrrolidone

B. heating the said mixture with gentle agitation for a period up to about 2 hours under the autogenous pressure of said mixture at a temperature in the range of from about 265° F. to about 450° F., the lower temperature being employed with lower amounts of polypyrrolidone and the shorter times at the higher temperatures, whereby said mixture is liquefied without significant degradation of the said polypyrrolidone and, while maintaining the temperature of said solution at a temperature above the temperature at which crystallization of polypyrrolidone commences,

II. forcing the said solution through a spinneret plate maintained at a temperature of at least from about 225° F. and up to about 450° F. and not less than the crystallization temperature of the said solution into relatively dry warm air, to form a self-sustaining filament, and

III. collecting the said self-sustaining filament.

9. The process for the dry-spinning of polypyrrolidone dissolved in water in the substantial absence of dissolved gases at elevated temperatures and pressures to an extent of at least 20 percent by weight which comprises the steps of removing a substantial portion of the total amount of solvent water from the polypyrrolidone by:

I. flashing off a first portion of the water suddenly by reduction of pressure around a fine stream of solution emerging under pressure from an orifice of regular shape and, subsequently,

II. further reducing the water content of the fiber by gradual evaporation into air having a relative humidity below 100 percent

whereby a filament is produced having longitudinal striations and differing in cross-sectional shape from the said orifice.

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