

PATENT SPECIFICATION (11)

1 452 400

1 452 400

- (21) Application No. 2985/74 (22) Filed 22 Jan. 1974 (19)
 (31) Convention Application Nos. 329 479 (32) Filed 5 Feb. 1973
 337 506 2 March 1973
 344 463 23 March 1973
 349 877 10 April 1973
 376 778 5 July 1973 in



- (33) United States of America (US)
 (44) Complete Specification published 13 Oct. 1976
 (51) INT. CL.² B29D 7/02 D01F 6/04 6/08 6/14 6/16 6/18 6/60
 (52) Index at acceptance

B5B 230 350 352 35Y 367 368 369 401 402 412 422 540
 614 714 725 728 72Y 785

(54) MELT SPINNING OF REFRACTORY POLYMERS

(71) We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for melt-spinning shaped articles of refractory polymer, for example acrylonitrile polymer. Refractory polymers are polymers which are difficult or impossible to soften under heat without degradation or use of excessively high temperatures.

In general, shaped articles, such as synthetic filaments, fibers, films, etc., can be produced from polymeric materials by melt-spinning, dry-spinning, or wet-spinning processes. In the "melt-spinning process" for forming synthetic filaments, polymer liquefied by melting is extruded through spinnerette orifices or slots to form an extrudate which is coagulated by cooling. Typically, polyamide, polyester, and polyolefin, fibers or films are produced by melt-spinning. In the "dry-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a volatile solvent is extruded through spinnerette orifices to form an extrudate which is coagulated by evaporation of the volatile solvent. Typically, cellulose acetate solutions in acetone, acrylonitrile polymer solutions in dimethylformamide, etc. are spun into fibers by dry-spinning. In the "wet-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a solvent is extruded through spinnerette orifices or slots to form an extrudate which is coagulated by removal of solvent in a liquid coagulating medium. In wet-spinning fibers of some polymers, such as from solutions of acrylonitrile polymers in aqueous nitric acid, aqueous salt, or organic solvents,

the solvent is removed by leaching it out of the extrudate in an aqueous coagulant. In wet-spinning fibers or films of other polymers, such as from viscose (aqueous sodium hydroxide solution of cellulose xanthate), the solvent is removed by chemical reaction with an aqueous sulfuric acid coagulant.

For various reasons, it has been recognized that melt-spinning processes are preferable to dry-spinning or wet-spinning processes whenever a choice is possible. Among the reasons for such preference are (a) the increased speed of operation when cooling rather than solvent diffusion (evaporation or leaching) is involved as the solidification mechanism, and (b) the extremely high spin draw-down ratios or jet stretches achievable permitting spinning fine denier fibers from the relatively large spinnerette orifices required to avoid excessive extrusion pressure when spinning the very viscous polymer melt. Further reasons for preferring melt-spinning processes include avoidance of the need for washing the product free of residual solvent, and avoidance of solvent recovery from coagulation liquids or gases. However, since acrylonitrile polymers do not readily melt without degradation, melt-spinning processes have not been available for spinning acrylonitrile polymers, and major attention has been directed to wet-spinning and dry-spinning processes for spinning such polymers.

Recognizing the desirability of melt-spinning processes, attempts have been made to find ways of liquefying acrylonitrile polymers so they could be extruded and then solidified by cooling alone. Such pseudo-melt-spinning processes have utilized latent or partial solvents which could be used, in combination with acrylonitrile polymers, to form liquids at elevated temperatures, which liquids could solidify, after extrusion, merely on cooling. However, such products still had to be washed free of latent or partial solvent and still required solvent recovery systems,

50

55

60

65

70

75

80

85

90

whereby such pseudo-melt-spinning processes still do not possess all the advantages and desirable characteristics of true melt-spinning processes.

- 5 The present invention seeks to provide a process for melt-spinning acrylonitrile polymer and other refractory polymers.

The melt-spinning process in accordance with the present invention comprises: extruding a single phase fusion melt consisting essentially of refractory polymer and melt assistant at a temperature T , which is above the single phase fusion melt melting point temperature M and also above the boiling point at atmospheric pressure of said melt assistant though a spinnerette directly into a pressurized solidification zone wherein the following conditions obtain: (1) there is a partial pressure of melt assistant such that the composition profile across the cross-section of the nascent extrudate so produced remains relatively flat; (2) the concentration of melt assistant retained in said nascent extrudate remains at a value at least 70% of the concentration of melt assistant in said single phase fusion melt; and (3) the temperature of the nascent extrudate is below said temperature T , but not lower than 20°C. below said temperature M .

30 While the process of this invention can be used for melt-spinning other single phase fusion melts of melt assistant and refractory polymer, such as the various cellulose acetates, polyvinyl halides (e.g. polyvinyl chloride, polytetrafluoroethylene, polytrifluorochloroethylene, polyvinylidene chloride, etc.), polyvinyl alcohol, very high molecular weight polyamides, polyimides, and polyesters, refractory polyamides, polyimides, and polyesters derived from aromatic monomers, the further description herein will be principally directed toward the commercially important acrylonitrile polymers. It will be understood that the invention is not so limited in its application, but can be useful for melt-spinning a wide variety of refractory polymers wherein the melt assistant makes melting possible or reduces the melting point of such polymer.

50 A melt assistant is a material or substance which is capable, when used under pressure sufficient to prevent boiling at temperatures above its atmospheric boiling point, of reducing the melting point of the refractory polymer when used in the proper concentration, to a temperature preferably below the degradation range for the polymer to form a single phase fusion melt. In the case of acrylonitrile polymers, there are excluded from use as melt assistants substances normally considered good solvents for acrylonitrile polymers, such as dimethylformamide, dimethylacetamide, ethylene or propylene carbonate, dimethyl sulfoxide, dimethylsulfone, tetramethylenesulfone, concentrated

nitric acid, very concentrated aqueous solutions of salts of strongly hydrated ions such as thiocyanate salts, zinc chloride, calcium or lithium bromide, iodide salts, alkali metal perchlorates, etc., or other solvents, such as those mentioned in such prior art as United States Patents 2,140,921; 2,356,767; 2,404,713—728; 2,648,648—9; etc.

We have arrived at certain theoretical considerations useful in selecting substances which are useful as melt assistants. According to our theory, melt assistants can be selected on the basis of certain thermodynamic properties, viz., the solubility parameter, the hydrogen bond strength, and the dipole moment. The solubility parameter of a substance, which is defined as the square root of the cohesive energy density, is preferably greater than about 8.7 for a melt assistant for acrylonitrile polymer. The cohesive energy density is the latent heat of vaporization in calories per mole divided by the molar volume or alternatively, is the latent heat of vaporization in calories per gram times the specific gravity of the liquid. The hydrogen bond strength for a melt assistant for acrylonitrile polymer is greater than zero, and preferably greater than about 4. If the solubility parameter is toward the lower values, such as between about 8.7 to about 11, then the hydrogen bond strength is preferably higher, i.e., above about 12. The dipole moment for a melt assistant for acrylonitrile polymer is greater than zero.

Substances which meet the foregoing criteria and which are relatively volatile, i.e., which have boiling points at atmospheric pressure which are below the temperature to which they can depress the acrylonitrile polymer melting point, and therefore have boiling points below the extrusion temperature of the single phase fusion melt, can be selected from low molecular weight members of various classes of materials, such as alcohols, halogen-substituted alcohols, amino-substituted alcohols, nitroalkanes, heterocyclic nitrogen compounds, cyanoalkanes, fatty acids, acylacetones, aldehydes, alkenyl sulfones, alkynyl sulfones, singly-etherified glycols, mercaptans, thiocyanalkanes, cyclic ethers, amides, etc. Compounds of relatively low atmospheric boiling point which contain a hydroxyl group form an especially useful subgrouping of these materials because the hydroxyl group imparts to the molecule a dipole moment, hydrogen bonding properties, and good solubility parameters. In general, compounds of these types may, if desired, also contain other substituents thereon to lower their boiling points. Also, mixtures of these compounds with each other, with water, or with other compounds may be used to lower their boiling points or to lower the melting temperature of single phase fusion melts made utiliz-

ing them. Also, the melt assistant may have incorporated therein minor amounts (e.g., less than 50%) of materials which are solvents for the acrylonitrile polymer to further depress the melting point of the polymer.

Melt assistants selected in accordance with the foregoing principles which are useable in the practice of this invention with acrylonitrile polymers include water, methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, t-butyl alcohol, nitromethane, nitroethane, pyridine, piperidine, morpholine, n-butylamine, isobutylamine, sec-butylamine, t-butylamine, acetonitrile, propionitrile, acetic acid, formic acid, acetylacetone, ethylene glycol monoethyl ether, 1,3-dioxane, dimethylfuran, sylvan, 1-chloro-2-hydroxyethane, propyl mercaptan, butyl mercaptan, methyl thiocyanate, diallyl sulfone, and mixtures of these compounds with each other or with known solvents or swelling agents for acrylonitrile polymers, such as dimethylformamide-water, acetonitrile-water, dimethylacetamide-water, methyl alcohol-water, methyl alcohol-dimethylformamide, phenol-water, phenol-methanol, glycol-water, glycerol-water, dilute aqueous solutions of sodium thiocyanate, zinc chloride, lithium bromide, guanidine thiocyanate, nitric acid, etc. While all these melt assistants are useful in the practice of the present invention to produce the melt-spinning advantages of high speed of operation and extremely high spin draw-down ratios or jet stretches, water is the one melt assistant greatly preferred since it also produces the added melt-spinning advantages of avoiding the need for washing the product free of melt-assistant and, therefore, also avoiding the need for recovery systems for recovering melt assistant.

To obtain the required extrudate conditions in the pressurized solidification zone, the ambient conditions therein are preferably controlled and maintained as follows: (1) the absolute partial pressure p of melt assistant therein is preferably from 56% to 110%, and more preferably from 80% to 100%, of the absolute vapor pressure of melt assistant at the extrusion temperature T_e ; (2) the temperature T in the pressurized solidification zone is at least equal to the saturation temperature of the melt assistant at a vapor pressure equal to the partial pressure p in the solidification zone and may range upwardly to a temperature at which substantial decomposition of the nascent extrudate occurs, although it is preferred to maintain the temperature T near the lower end of the indicated range; (3) the total pressure P in the solidification zone must be at least equal to the partial pressure p but preferably should not exceed 25 times said partial pressure p ; even higher total

pressures may be used but such are not usually desired. The excess of the total pressure P over the partial pressure p , if any, comprises other fluids, such as air, nitrogen, sulfur dioxide, etc. Preferably, the total pressure P is equal to or does not appreciably exceed the partial pressure p and very little, if any, other fluids are present. Use of the foregoing three conditions within the solidification zone results in boundary control of the rate of evaporation of melt assistant from the nascent extrudate. The term "boundary control" of evaporation means that the rate of evaporation of melt assistant from the surface of the nascent extrudate is equal to or less than the rate of diffusion of melt assistant from within the nascent extrudate to its surface, as a consequence of which, the composition across the cross-section of the nascent extrudate is relatively uniform while within the solidification zone.

While in said solidification zone, it is preferred that the nascent extrudate is given a spin draw-down or jet stretch at a stretch ratio of 25 to 250, preferably 35 to 150. The linear speed through the spinnerette is computed by dividing the volume per unit time of melt being extruded by the total cross-sectional area of all orifices in the spinnerette. The jet stretch or spin draw-down ratio is the linear speed of the shaped articles as they pass a pulling device (such as driven godet or thread-advancing rolls wherein the peripheral speed of such pulling rolls is taken as the linear speed of the shaped articles) divided by the linear speed through the spinnerette. Outside of the temperature, pressure, and composition conditions previously specified for the solidification zone environment, such extremely high jet stretches are not obtained. While the spin draw-down occurring in the solidification zone be accomplished in a single stage, it is also possible to achieve the total spin draw-down in two stages, namely a first stage at a stretch ratio of 5 to 150 followed by a second stage at a stretch ratio of about 1.1 to 30, or even more, to produce the total spin draw-down within the solidification zone.

In melt-spinning organic polymer fibers, such as polyamides, polyesters, and polyolefins, and in wet-spinning or dry-spinning acrylonitrile polymers, the filaments after extrusion and spin draw-down or jet stretch must be later subjected to a secondary stretching or after drawing to orient the polymer molecules therein followed by a relaxation step to ease internal strains whereby the characteristic good fiber properties are developed. Surprisingly and unexpectedly, as one advantage of the present invention, filaments spun by the process of the present invention do not usually need any secondary stretching or after drawing pro-

cess steps. The filaments issuing from the solidification zone may be collected directly or they may be relaxed in a free-to-shrink condition by any of the known procedures for so doing, such as by passing them over heater feed roll to a slower moving thread-advancing roll or by passing them on a conveyor belt through an atmosphere of saturated steam under pressure. In this way, the characteristic good fiber properties of acrylonitrile polymer fibers can usually be obtained with the process of the present invention without use of any secondary stretching or after drawing steps.

In addition to homopolyacrylonitrile, acrylonitrile polymers which can be used in the practice of this invention also include copolymers or blends of polymers containing greater than 50% combined acrylonitrile. Amongst the acrylonitrile copolymers which may be used are copolymers of acrylonitrile with one or more of the following copolymerizable mono-olefinic monomers: acrylic, alpha-chloroacrylic and methacrylic acids; the methacrylates, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl bromide, vinyl chloride, vinyl fluoride, vinylidene bromide, vinylidene chloride, allyl chloride, 1-chloro-1-bromoethylene; methacrylonitrile; allyl alcohol; acrylamide and methacrylamide; alpha-chloroacrylamide, or mono-alkyl substitution products thereof; methyl vinyl ketone; vinyl carboxylates, such as vinyl formate, vinyl acetate, vinyl chloroacetate, vinyl propionate, vinyl stearate, and vinyl benzoate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic esters; N-vinylcarbazole; vinylfuran; alkyl vinyl ethers; vinyl sulfonic acids, such as vinyl sulfonic acid, styrene sulfonic acid, methallyl sulfonic acid, p-methallyloxy benzene sulfonic acid and their salts; ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethyl citraconate, diethyl mesaconate; styrene; dibromostyrene; vinylnaphthalene; vinyl-substituted tertiary heterocyclic amines such as the vinylpyridines and alkyl-substituted vinylpyridines for example, 2-vinylpyridine, 4-vinylpyridine and 2-methyl-5-vinylpyridine; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, vinyl-pyrrolidone, vinylpiperidone, and other mono-olefinic copolymerizable monomeric materials. The acrylonitrile polymers or blends of polymers may contain varying quantities of one or more comonomers, as, for example, a total of about 5, 10, 15, 20, 25, 30, or 40% comonomer content based on the total acrylonitrile polymer composition and may have

molecular weights ranging from 10,000 to 200,000, as for example, about 20,000; 40,000; 50,000; 60,000; 70,000; 85,000; 100,000; 130,000; etc. The quantity of comonomer and the molecular weights may vary outside these indicated ranges since the present invention does not depend upon these features although the consideration of the properties of the products for their end uses may indicate such variations.

The degradation range for acrylonitrile polymer refers to the range of temperatures wherein acrylonitrile polymers suffer degradation, usually evidenced by discoloration, on exposure to such temperatures for the time normally required for fluidizing and extruding the polymer. Usually, this degradation range starts at about 180°C. to about 220°C., depending on polymer composition, etc. and extends upwardly therefrom. Where the quality of the polymer in the product is not critical and some polymer degradation can be tolerated, the single phase fusion melt may be heated to more elevated temperatures into the degradation range in the practice of this invention. However, in general, it is preferred to operate at lower temperatures to avoid degradation and usually the extrusion temperature is not more than 30°C. above the minimum fusion temperature (M).

In accordance with one preferred embodiment of the present invention, wherein water is the melt assistant, the process is further characterized by drying said fibers at a temperature above 90°C. while substantially preventing loss of water from the freshly melt-spun fibers at any temperature below 90°C. until said drying step, thereby minimizing the tendency of such fibers to form voids and micro-voids therein.

In the years that acrylonitrile polymer fibers have been commercially available from wet-spinning and dry-spinning processes, and even before, it has become recognized that it was desirable that the fibers be as free of voids and micro-voids as possible for many reasons, among which are the better tensile and abrasion properties, the preferred aesthetics, and the higher apparent dyeability of the denser fibers free of voids.

As will be described in more detail hereinafter, a single phase fusion melt of acrylonitrile polymer and water suitable for melt-spinning contains somewhere between about 10% and about 35% water, depending on acrylonitrile polymer composition and other variables. In the melt-spinning process, the material being formed into fibers during passage through the spinnerette orifices, therefore, contains somewhere between about 10% and about 35% water. Somewhere during subsequent processing, whether immediately or remotely, this water must be evaporated to produce the dry acrylonitrile polymer fibers one finds in the finished pro-

(14)

ducts, such as clothing, blankets, carpets, etc. As used herein, "dry" fibers are those which contain about the equilibrium moisture regain they assume on exposure to ambient conditions or less moisture. For acrylonitrile polymer fibers, this means the dry fibers contain less than about 5% moisture regain. We have found that the formation of micro-voids in the fibers results from improper drying of the nascent fibers. When the nascent fibers are permitted to cool and partially or completely dry at moderate or low temperatures, this improper drying leads to the formation of the voids and micro-voids. Proper drying to minimize or prevent this requires that the nascent fibers be prevented from losing water until they are dried at elevated temperature, i.e., above 90°C.

One type of process sequence incorporating proper drying according to this preferred embodiment of the present invention involves drying the nascent fibers, after leaving a hot, pressurized, steam-containing pressurized solidification zone, by passing them directly into and through a heated chamber wherein they are dried in an environment maintained at above about 100°C., which heated chamber may contain air at about the same temperature and pressure as the steam in the solidification zone.

Another type of process sequence incorporating proper drying according to this preferred embodiment of the present invention involves keeping the nascent fibers wet even though they be cooled to below 90°C. until such time as they are dried at elevated temperature, i.e., above 90°C. Illustrative of this process sequence, the nascent fibers, after leaving a hot pressurized solidification zone, are cooled in a water bath, and thereafter, are reheated while still wet in a drier operating to dry the fibers at above 90°C. In this process sequence, if the nascent fibers are crimped while still wet prior to the initial drying step, the crimp obtained can be very stable, resisting loss of crimpiness during textile processing on cards, etc. and even during exposure to hot water, as in a dye-bath.

During tests related to this second type of process sequence, a surprising phenomenon was observed. When the nascent fibers, after leaving the spinnerette, were cooled to room temperature, the fiber became white and opaque due to formation of voids and micro-voids therein. When these white opaque fibers were heated on a hot plate at about 120°C., they became transparent due to the redissolving of the water into the polymer with disappearance of the voids and micro-voids. When these transparent fibers were cooled to room temperature immediately after becoming transparent, the white opaque appearance reappeared due to the water "precipitating" out of the polymer to re-

create voids and micro-voids. This phenomenon can be repeated for several hot-cold cycles. However, once the fiber has lost enough water at elevated temperature to become dry, cooling the fiber still results in a transparent fiber free of voids and micro-voids.

To locate the proper conditions for preparing a single phase fusion melt consisting essentially of refractory polymer and melt assistant for any specific combination thereof, a mixture of the polymer and melt assistant is prepared and heated, under pressure, to a temperature sufficient to cause fusion of the polymer. If a single phase fusion melt is produced, the minimum temperature to cause fusion (temperature M) is noted. By way of illustration, reference will now be made to Figure 2 of the accompanying drawings which is a phase diagram relating to an acrylonitrile polymer with water being employed as the melt assistant (see Example 1). Referring to Figure 2, point A is first located, then lines ABF and ACG are located, after which the preferred portion ABC is determined to locate the range of conditions from which the shaped articles may be melt spun.

To determine point A, a series of polymer samples is exposed to saturated steam in an autoclave for five minutes each. Each sample is exposed to increasing temperatures. The melting point of the polymer in saturated steam is the minimum temperature where flow has occurred. The surface of melted polymer appears glassy and particles of polymer are strongly bonded together. This minimum temperature establishes the line AE shown in Figure 2.

Once the melting line DAE is known, the minimum water content necessary for fusion at that temperature is determined. This minimum water content and temperature is point A. At this point all water is hydrogen-bonded to the acrylonitrile polymer and no free water as a second phase exists. A sample of polymer mixed with a known quantity of water is placed into a steel cell equipped with a glass window. The cell is sealed to retain the pressure generated by the test. The cell is heated in an oil bath so that the sample can be observed at all times. In separate tests, samples containing various water-to-polymer ratios are placed in the cell and heated to the temperature indicated by line DAE. When excess water is present, two phases are visible when the polymer melts. Samples of progressively lower water contents are tested until a sample exhibiting only one phase is visible, establishing point A at that concentration. With further reduction in water-to-polymer ratio, melting will not occur at the temperature established by line DAE.

To determine the phase fusion region, it is necessary to establish the lines ABF and

ACG as shown in Figure 2. This is done by placing in the steel cell samples of polymer whose water content in one case contains approximately 5—10% more water than the concentration at point A. Line ABF is determined by locating the point which represents the temperature and concentration at which the mixture of polymer and water having the lower amount of water melts into a single phase. Line ACG is established by locating the point at which the two-phase mixture of polymer and water having the greater amount of water become a single phase after passing through a two-phase liquid state. Since physical mixing is difficult to obtain in the sealed cell, this latter point may be time consuming to obtain.

After locating point A and lines ABF and ACG, line BC is drawn at a temperature about 30°C. above the temperature of point A. Thus, the preferred portion ABC of the single phase fusion melt region is defined.

Generally, the single phase fusion melt compositions will be located somewhere in the region of about 10% to about 35% water, with correspondingly, about 90% to about 65% acrylonitrile polymer. If the single phase fusion melt composition range for an specific acrylonitrile polymer water extends over a wide range of compositions having usefully low melting points (viz., below the polymer degradation temperature range), it is preferred, in accordance with the present invention, to select a composition toward the side of such composition range having the lower amounts of water.

Sometimes, the quantity of water can vary outside this range and still form a single phase fusion melt. For instance, more water may be used if there is added a third material (such as a polymer soluble in the water; a hydrophilic polymer which, with the water, forms a melt; a finely divided hydrophilic solid; or a hydrophilic liquid) which binds up excess water leaving the acrylonitrile polymer as a single phase fusion melt. This third material must not significantly interfere with the formation of a single phase fusion melt with the water. This third material may be compatible with the acrylonitrile polymer and the products produced may be a uniform blend or may have the third material as permanent inclusions therein. This third material may be incompatible making the products readily fibrillatable. This third material may be readily removable, as by washing with water or organic liquid, to leave a porous structure. Such third materials include hydroscopic or water-soluble polymers, such as polyvinyl alcohol, polyethylene glycol, polyacrylamide and derivatives thereof, polyacrylic acid, polyvinyl pyrrolidone, polyelectrolytes, proteins, such as gelatin, casein, and finely divided hygro-

scopic solids, such as silica gel, starch, aluminum chlorohydrate, alumina gel, diatomaceous earths, kaolin clays, and molecular sieves, and other water binders, such as anhydrides, such as acetic anhydride, and inorganic salts, such as anhydrous sodium sulfate, calcium chloride, sodium phosphate, etc.

The invention will now be described further with reference to Figure 1 of the accompanying drawings which is a schematic drawing illustrating one embodiment of the process of this invention as applied to making continuous filaments.

In Figure 1, there is shown generally an extruder 11 provided with a spinnerette 12 at its outlet and a pressurized solidification chamber 13 positioned to receive extrudate issuing from spinnerette 12. As illustrated, extruder 11 is shown as a piston extruder wherein cylinder 15 is provided with a closely fitted piston 16 moveable by means, not shown, to force the contents of cylinder 15 through spinnerette 12 directly into pressurized solidification chamber 13. With cylinder 15, single phase fusion melt 17 is heated to the proper temperature by heating means, not shown, such as steam jackets or electrical heaters in the walls of cylinder 15. Cylinder 15 is also provided with a thermometer 18 and a pressure gauge 19 for monitoring the temperature and pressure within extruder 11 during melt-spinning. While extruder 11 is shown as a piston extruder, other types of extruders, such as screw extruders, gear pumps, etc., as are known for melt-spinning other organic polymers, may be used.

At the outlet of extruder 11, a spinnerette 12 is mounted. Spinnerette 12 may be provided with circular or non-circular orifices for spinning filaments or fibers or with slots for spinning ribbons or films. The extrudate issuing from spinnerette 12, here shown as filaments 21, goes directly into pressurized solidification chamber 13 from which it is drawn, under tension, by rapidly rotating godet or thread-advancing rolls 22 which produce the extremely high jet stretches of this process. Pressurized solidification chamber 13 is provided with an inlet 24 through which fluid under pressure and at elevated temperature can be admitted, an outlet 25 from which liquid can be withdrawn as necessary, and a thermometer 26 and a pressure gauge 27 for monitoring the temperature and pressure within chamber 13. Chamber 13 is also provided at its outlet with a pressure seal 28, illustrated herein as a long thin slot only slightly larger than the diameter of the bundle of filaments 21 passing therethrough. Other pressure sealing devices may be used, illustrative of which are those described in United States Patents 2,708,843; 2,920,934; 2,932,183; 3,012,427; 130

3,027,740; 3,037,369; 3,046,773; 3,066,006; 3,083,073; 3,118,154; 3,126,724; 3,137,151; and 3,152,379, all of which relate generally to continuous relaxation of filaments of acrylonitrile polymers under superatmospheric steam pressure at elevated temperatures.

From godet or thread-advancing rolls 22, which may optionally be located within pressurized chamber 13 or outside thereof as illustrated, filaments 21 may be wound up on yarn package 30 by a suitable winder, not shown, or preferably, filaments 21 may be relaxed in steam chamber 33 wherein steam under superatmospheric pressure and at elevated temperature is permitted to contact filaments 21 in a relaxed free-to-shrink condition as described in United States Patents listed in the preceding paragraph. In steam chamber 33, filaments 21 are fed through inlet pressure seal, not shown, by inlet rolls 35 onto a conveyor belt 36 where they are conveyed through steam chamber 33 to exit rolls 37 which feed the relaxed filaments through exit pressure seal, not shown, out of steam chamber 33 to be wound onto yarn package 40 by a suitable winder, not shown.

It is well known to incorporate various additives in extruded shaped articles by including such additives in the liquefied polymer prior to extrusion. These additives are normally utilized to modify the properties of the shaped articles so produced or to improve spinnability. Such additives may be stabilizers, such as light stabilizers, heat stabilizers, antioxidants, gas-phase stabilizers, ultra-violet stabilizers, etc., pigments, dyes, brighteners, whiteners, flame-retardants, anti-bacterial agents, delusterants, luster enhancers, antistatic agents, dyesite-containing materials, porosity promoters, fibrillation enhancers, soil retardants, fillers, reinforcing agents, microencapsulated materials, latexes, etc. In the practice of the present invention, minor amounts (e.g. up to about 25%) of such materials may be incorporated in the single phase fusion melt prior to melt-spinning providing (a) they have particle sizes small enough to permit them to pass freely through the extrusion orifices or (b) they have melting points near or below the minimum fusion temperature (M) of the polymer in the presence of melt assistant or are soluble in the fusion melt. Among such additives are such polymers as polyvinyl alcohol, polyvinyl chloride, polyacrylamide, polyacrylic acid, polyalkylene glycol ether, etc. These polymers may have molecular weights from about 1,000 to above 100,000. Other additives which may be utilized include haloalkyl phosphate flame retardants, titanium dioxide pigments, cationic dyes, anionic dyes, disperse dyes, silica, aliphatic or aromatic halogen compounds, organic phosphorus compounds, antimony oxides,

etc. as will be readily apparent. These additives normally do not affect the location of the single phase fusion melt region of the phase diagram; however, if any such are utilized, the phase diagram should be re-determined with them present to be certain of the boundaries of this region to be used for the melt-spinning process.

Optionally, the process sequence described above may include additional steps, such as secondary stretching or after drawing (although as previously noted these particular steps are not essential in the present invention), crimping, restretching, washing, treating with antistatic agents, anti-soiling agents, fire-retardants, adhesion promoters, lubricants, etc., dyeing, post-treating chemically, as for cross-linking, staple cutting, and the like to produce such product modifications as these conventional steps are known to produce. Some of such additional steps may be performed within the same physical structure as the solidification zone, if desired, although under ambient conditions outside those required for the solidification zone. Illustrative of such additional steps performable within the same physical structure as contains the solidification zone may be mentioned secondary stretching or after drawing, relaxing, restretching, pressure dyeing, drying, etc. Usually, but not necessarily, such additional steps would be performed under elevated pressure.

Also, a plurality of single phase fusion melts may be extruded concurrently through the spinnerette to make composite or multi-component shaped articles, such as side-by-side, sheathcore, or random, bi-, tri-, or multi-component fibers using known apparatus for such purpose. The single phase fusion melts used for this purpose may be of the same or similar polymer, e.g. all acrylonitrile polymers, or may be of different polymers. The single phase fusion melts may be incompatible to form fibers which easily split apart or they may be compatible to remain permanently adhered together in the shaped articles. Additionally, hollow fibers can be prepared by extruding a sheath of single phase fusion melt about a gaseous more. In all these various embodiments, the extrusion takes place directly into a solidification zone having the defined conditions.

The invention is illustrated by the Examples which follow. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

This example first illustrates a method for determining a phase diagram to locate the single phase fusion melt region thereof. The example then illustrates melt-spinning an acrylonitrile polymer in accordance with the present invention and, for comparison, in accordance with a melt-spinning process

outside the scope of the present invention.

The phase diagram, illustrated in Figure 2, for an acrylonitrile polymer-water system wherein the acrylonitrile polymer was a polymer of 89.3% acrylonitrile and 10.7% methyl methacrylate having a molecular weight of approximately 58,000 was determined by the following series of tests.

A 1 gram bone dry sample of the acrylonitrile polymer was placed in an aluminum dish and autoclaved in saturated steam at 135°C. for 5 minutes. The sample was removed and cooled. The polymer was readily crumbled into a powder, had a dull appearance and microscopically no fused particles were observed. The procedure was repeated at 140°C. and 145°C. with substantially the same result. The procedure was again repeated at 150°C. This time the polymer would not crumble, appeared completely fused, and had a shiny surface. Under the microscope this sample had a continuous surface and no individual particles were observed. The procedure was repeated again at 155°C., 160°C., and 165°C. with no apparent change from the 150°C. sample except for a somewhat increased yellowness in the polymer. Line DAE of Figure 2 was therefore established at 150°C.

A polymer/water mixture was prepared consisting of 40% polymer and 60% water. The mixture was placed into a sealed cell, as previously described, and heated in an oil bath to 150°C. for 10 minutes. The sample was observed through the window as two phases. The sample was cooled and removed from the cell. The two phases were found to be fused polymer and free water. This procedure was repeated with mixtures of polymer and water consisting of 60%, 70%, 75% and 80% polymer, the balance being water. Two phases were observed in each case. When the procedure was again repeated using a mixture of 85% polymer and 15% water only one phase could be observed at 150°C.; and, after cooling and removal of the sample, only partial fusion of the polymer was observed in spite of the fact that only one phase was observed. This test was repeated again using a polymer sample containing 82% polymer and 18% water. When heated to 150°C. only one phase was observed. After cooling and examination, it was found that the polymer had undergone complete fusion or melting. Point A of Figure 2 was now established to be at about 18% water and 82% polymer at 150°C. There may, of course, be a small range of perhaps 17% to 19% water at 150°C. designating point A. In no case, however, is it as low as 15% or as high as 20% water for this particular polymer at 150°C.

Point A, the minimum single phase fusion melt melting point, having been established, it was next necessary to establish phase

boundary lines ABF and ACG of Figure 2.

Sufficient water was added to bone dry polymer to form a mixture of 88% polymer and 12% water. When placed in the sealed cell and heated to 150°C. no fusion or phase separation was observed. In separate tests, the sample was heated to 155°C., 160°C., 165°C., and 170°C. There was an increasing tendency of the sample to partially fuse with increasing temperature. Complete fusion or melting was not observed, however, until the sample was heated to 170°C. In all cases only one phase was observed. This series of tests locate a point on the line ABF at 12% water and 88% polymer at 170°C. Additional points on the line ABF of Figure 2 can be determined in the same manner using other compositions, such as 85% polymer, 15% water.

The procedure was repeated using a polymer mixture of 75% polymer and 25% water. At 150°C. two phases are observed. In separate tests the sample was heated to 155°C., 160°C., 165°C., 170°C., 175°C., and 180°C. In all cases, two phases were observed. In each case the polymer was fused or melted and in each case a layer of excess free water was noted. The procedure was repeated by heating a sample to 185°C. As the polymer fused, only one phase was observed and no excess or free water could be detected. Upon cooling and examination, the sample was found to be completely fused or melted and no water was detected in the sample cell. A point on the line ACG was therefore located at 25% water and 75% polymer at 185°C. Additional points on the line ACG of Figure 2 can be determined in the same manner using other compositions, such as 22% water and 78% polymer.

Having determined the phase diagram for mixtures of this polymer with water, as shown in Figure 2, the following experimental melt-spinnings were made, using apparatus substantially as schematically illustrated in Figure 1.

To 15 grams of dry polymer was added 3.3 grams of water thus providing an acrylonitrile polymer-water mixture containing 18% water. The mixture was sealed in a jar and mixed on a roll mill for 30 minutes to ensure complete blending. The blended mixture was then placed into a piston extruder 11 equipped with a spinnerette 12 having a single orifice of 16 mils diameter and 128 mils orifice length. The orifice opening was temporarily sealed to prevent any premature loss of moisture during start-up. The extruder 11 and spinnerette 12 were heated to 154°C. under sufficient pressure to prevent water vaporization. The spinnerette orifice was unsealed and 800 psi of force was applied by piston 16 in order to extrude a filament. In a first run, for comparison purposes, pressurized solidification chamber 130

13 was left open to the atmosphere so the filaments 21 extruded into a region of ambient temperature and pressure. Pressure on the piston 16 was adjusted so that the flow rate of single phase fusion melt through the spinnerette orifice was 0.446 meters per minute. The resulting filaments were taken up directly on yarn package 30 (without use of godet rolls 22) on a rotating winder. After starting up, the speed of the rotating winder was gradually increased until a maximum, determined by continuing filament breakage, was reached. The maximum take-up speed achieved was 1.16 meters per minute for spin draw-down ratio or jet stretch ratio of 1.16/0.446 or 2.6 (260% jet stretch).

In a second run, in accordance with the present invention, pressurized solidification chamber 13 was sealed and saturated steam was introduced through inlet 24 until a pressure of 38 psi gauge, corresponding to a temperature of 140°C., was reached. This temperature was about 14°C. below the single phase fusion melt temperature in the extruder and about 10°C. below the minimum melting temperature of 150°C. for this melt. Under these conditions, which were otherwise a duplication of the first run, the maximum take-up speed achieved was 38 meters per minute for a spin draw-down ratio or jet stretch ratio of 85 (8,500% jet stretch). A quantity of fiber so produced, having a denier per filament of 15, was collected and exposed to saturated steam under pressure at 127°C. in a relaxed free-to-shrink condition in an autoclave. The denier increased to 19.5, indicating about 23% shrinkage was achieved. Physical properties of this relaxed fiber were:

Straight Tenacity ...	3.5 grams/denier
Straight Elongation...	43.0%
Loop Tenacity ...	1.98 grams/denier
Loop Elongation ...	19.0%
Initial Modulus ...	58.0 grams/denier

EXAMPLE 2

The example illustrates this invention applied to melt-spinning acrylonitrile polymer filaments of finer denier than Example 1.

The second run of Example 1 was repeated except that the flow rate of single phase fusion melt through the spinnerette orifice was 0.792 meters per minute and the pressure of the saturated steam in solidification chamber 13 was increased to 49 psi gauge, corresponding to a temperature of 147°C. This temperature was about 7°C below temperature in the extruder and about 3°C below the minimum single phase fusion melt melting temperature of 150°C. for this composition. At these conditions, the maximum take-up speed achieved was 89 meters per minute for a spin draw-down ratio or jet

stretch ratio of 112 (11,200% jet stretch). The denier of the filaments obtained was 6.4, thus illustrating that a larger range of deniers is possible with a single size of spinnerette orifice. In the practice of this invention, using different sizes of spinnerette orifices, acrylonitrile polymer fibers may be prepared having deniers between 0.5 and 80, or even higher if desired.

COMPARATIVE EXAMPLE A

The first run of Example 1 was repeated except that a strip heater was installed along the full length of solidification chamber 13. With chamber 13 vented to the atmosphere, and the strip heater set to provide an air temperature in the chamber 13 of about 150°C., closely simulating the conditions utilized in conventional melt-spinning of other organic fibers to obtain high spin draw-down ratios or high jet stretch ratios, a filament-like material was obtained which appeared to be completely filled with bubbles, resembling an elongated foam. The maximum jet stretch ratio achieved was no higher than the first run of Example 1 (no heat, no steam under pressure) and frequently was less due to breakage of this highly non-uniform material. This demonstrated that elevated temperature and a melt assistant in the melt but without the environment of melt assistant under pressure in chamber 13 was not capable of providing the extremely high jet stretches obtainable in the present invention, but, instead, produces a degraded product.

COMPARATIVE EXAMPLE B

The second run of Example 1 was repeated except that nitrogen under ambient temperature was used, instead of steam, to pressurize chamber 13. As the pressure of nitrogen was increased to 56 psi gauge, with the linear velocity of single phase fusion melt through the spinnerette orifice being 0.634 meters per minute, the maximum take-up speed for the uniform filaments produced which could be achieved was 2.9 meters per minute for a spin draw-down ratio or jet stretch ratio of 4.6 (460% jet stretch), slightly higher than the jet stretch ratio achieved at ambient temperature and pressure (the first run of Example 1), but nowhere the extremely high jet stretch ratios achieved by the present invention (the second run of Example 1 and Example 2). This demonstrated that elevated pressure without the environment in chamber 13 of melt assistant at elevated temperature was not capable of providing the extremely high jet stretch ratios of the present invention.

COMPARATIVE EXAMPLE C

Comparative Example B was repeated using the strip heater described in Com-

parative Example A to heat the pressurized nitrogen at 56 psi gauge in chamber 13 to various temperatures. As the temperature of the nitrogen environment was raised to 140°C., the maximum spin draw-down ratio achieved was raised from about 4.6 to about 10.1 (1,010% jet stretch) without formation of the bubbles of Example A. Continued heating to 150°C. did not result in any increase in spin draw-down ratio achievable. Heating to above 150°C. caused filament melting resulting in fiber discontinuity and breakage. This demonstrated that elevated temperature and elevated temperature without the environment of melt assistant, while producing some improvement in spin draw-down ratio, still was not capable of providing the high jet stretch ratios achievable by the present invention.

COMPARATIVE EXAMPLE D

To 15 grams of dry polymer of 89.3% acrylonitrile and 10.7% methyl methacrylate having a molecular weight of approximately 58,000 was added 3.3 grams of water, thus providing an acrylonitrile polymer-water mixture containing 18% water. The mixture was sealed in a jar and mixed on a roll mill for 30 minutes to ensure complete blending. The blended mixture was then placed in a piston extruder provided at the outlet thereof with a spinnerette having a single orifice of 16 mils diameter and 128 mils orifice length. The orifice opening was temporarily sealed to prevent premature loss of moisture during start-up. The extruder and spinnerette were heated to 154°C. under sufficient pressure to prevent water vaporization, thereby converting the acrylonitrile polymer-water mixture to a single phase fusion melt. The spinnerette orifice was unsealed and 800 psi of force was applied by the piston of the piston extruder to extrude a filament through the orifice. The pressure on the piston was then adjusted so the flow of single phase fusion melt through the spinnerette orifice was 0.446 meters per minute. The resulting filaments, after passage through and cooling in ambient air from the spinnerette to a yarn winder, were collected on a yarn package at a jet stretch of slightly below the maximum attainable jet stretch ratio of about 2.6 and allowed to dry at room temperature. These filaments were opaque, white, and had a high gloss. On microscopic examination they were found to contain many voids and micro-voids.

EXAMPLE 3

The procedure of Comparative Example D was repeated except that the nascent filaments extruding through the spinnerette orifice entered directly into a pressurized chamber containing steam at a pressure of 38 psi gauge and a temperature of 140°C.

The resulting filaments, after passage through the steam pressure zone, were collected on a yarn package on a yarn winder at a jet stretch of slightly below the maximum attainable jet stretch ratio of about 85. These filaments were then relaxed in a free-to-shrink condition in an autoclave in steam under pressure at 127°C. These filaments were also opaque, white, and had a high gloss. On microscopic examination they were found to contain many voids and micro-voids. However, they did have physical properties which were acceptable for use as textile fibers.

COMPARATIVE EXAMPLE E

The filaments of Comparative Example D, after drying at ambient conditions, were heated in an oven in an attempt to make the voids and micro-voids disappear. There was no change in appearance noted. Relaxation in steam under pressure at 127°C. after the heating in the oven also did not change the appearance of these filaments.

EXAMPLE 4

Repeating the procedure of Example 3 except that the filaments, directly as they leave the steam-pressurized chamber, pass through a second pressurized chamber containing air or nitrogen at 38 psi gauge and 140°C. where they are dried produces, in accordance with this invention, filaments which are free of voids and micro-voids, are transparent, and have a luster similar to commercially available acrylic fibers. This illustrates drying the freshly spun acrylonitrile polymer while still hot from spinning before permitting cooling to below about 90°C.

EXAMPLE 5

In accordance with this example, the procedure of the second run of Example 1 is modified to produce fibers possessing a crimp which is stable to textile processing. Within the pressurized chamber containing steam at a pressure of 38 psi gauge and a temperature of 140°C., there are disposed a first set of thread-advancing rolls which serve to stretch the nascent filaments emerging from the spinnerette orifice to impart a jet stretch ratio of about 75 and a second set of thread-advancing rolls rotating at a lower speed which serve to relax the filaments. From the second set of thread-advancing rolls, the filaments are fed to a stuffing-box crimper which serves as a pressure seal in a wall of the pressurized chamber. Within the stuffing box of the crimper, the crimped fibers are quenched with cold water. After exiting from the crimper, the filaments are kept wet until they are dried in an oven at 110°C. Filaments so produced, in accordance with this invention, are transparent, free of voids and micro-voids, and have good luster.

EXAMPLE 6

This example illustrates melt-spinning acrylonitrile polymer filaments according to the process of this invention using other melt assistants.

Using the same apparatus as in Examples 1 and 2, the acrylonitrile polymer of Example 1 can be spun into filaments under the following conditions:

A. A single phase fusion melt of acrylonitrile polymer and methanol (about 75% acrylonitrile polymer and about 25% methanol) at 155°C. can be extruded through the spinnerette orifice at a flow rate of 0.792 meters per minute directly into a solidification zone containing an atmosphere of methanol vapour at a temperature of 148°C. and a pressure of 164 psi gauge to yield filaments to which a spin draw-down ratio or jet stretch of 100 times can be imparted.

B. A single phase fusion melt of acrylonitrile polymer and acetonitrile (about 80% acrylonitrile polymer and about 20% acetonitrile) at 155°C. can be extruded at 0.792 meters per minute directly into a solidification zone containing an atmosphere of acetonitrile vapor at a temperature of 141°C. and a pressure of 66 psi gauge to yield filaments spin drawable to at least 100 times.

C. A single phase fusion melt of acrylonitrile polymer and dilute aqueous sodium thiocyanate solution (about 75% acrylonitrile polymer, about 19% water, and about 6% sodium thiocyanate—such aqueous sodium thiocyanate solution being denominated "dilute" because it is of a concentration which will not normally dissolve the acrylonitrile polymer and is, in fact, sufficiently dilute to be used as a coagulant in wet-spinning acrylonitrile polymers) at 141°C. can be extruded at 0.792 meters per minute directly into a solidification zone containing steam at 140°C. and 38 psi gauge to yield filaments jet stretchable at least 100 times.

D. A single phase fusion melt of acrylonitrile polymer and acetic acid (about 77% acrylonitrile polymer and about 23% acetic acid) at 155°C. can be extruded at 0.792 meters per minute directly into an atmosphere of acetic acid vapor at a temperature of 145°C. and a pressure of 17 psi gauge to yield filaments spin drawable at least 100 times.

WHAT WE CLAIM IS:—

1. A process for melt-spinning shaped articles of refractory polymer comprising: extruding a single phase fusion melt consisting essentially of refractory polymer and melt consisting essentially of refractory polymer and melt assistant at a temperature T_1 ,

which is above the single phase fusion melt melting point temperature M and also above the boiling point at atmospheric pressure of said melt assistant through a spinnerette directly into a pressurized solidification zone wherein the following conditions obtain: (1) there is a partial pressure of melt assistant such that the composition profile across the cross-section of the nascent extrudate so produced remains relatively flat; (2) the concentration of melt assistant retained in said nascent extrudate remains at a value at least 70% of the concentration of melt assistant in said single phase fusion melt; and (3) the temperature of the nascent extrudate is below said temperature T_1 but not lower than 20°C. below said temperature M .

2. A process as defined in Claim 1, wherein said refractory polymer is an acrylonitrile polymer.

3. A process as defined in Claim 2, wherein said melt assistant comprises an organic melt assistant.

4. A process as defined in Claim 2, wherein said melt assistant comprises an aliphatic alcohol of 1 to 4 carbon atoms, acetonitrile, formic acid or acetic acid.

5. A process as defined in Claim 2, wherein said melt assistant comprises or consists of water.

6. A process as defined in Claim 2, wherein the melt assistant in said single phase fusion melt is a solution of a higher boiling solute in a lower boiling solvent for such solute and the melt assistant in said solidification zone comprises said solvent.

7. A process as defined in Claim 6, wherein said solute is an inorganic salt and said solvent is water, said solution being of a concentration too dilute to serve as a solvent for said acrylonitrile polymer.

8. A process as defined in any preceding claim, wherein the following conditions obtain in said pressurized solidification zone: (1) the partial pressure of melt assistant is from 56% to 110% of the vapor pressure of the melt assistant at temperature T_1 ; (2) the temperature T is at least equal to the saturation temperature of the melt assistant at a vapor pressure equal to said partial pressure p ; and (3) the total pressure P is at least equal to said partial pressure p ; said conditions ensuring boundary control of any evaporation of melt assistant from the nascent extrudate produced.

9. A process as defined in Claim 8, wherein the partial pressure p is from 80% to 100% of the vapor pressure of water at temperature T_1 and the total pressure P is equal to or does not substantially exceed such partial pressure p .

10. A process as defined in any preceding claim, wherein said solidification zone contains steam under pressure.

11. A process as defined in any preceding

EXAMPLE 6

This example illustrates melt-spinning acrylonitrile polymer filaments according to the process of this invention using other melt assistants.

Using the same apparatus as in Examples 1 and 2, the acrylonitrile polymer of Example 1 can be spun into filaments under the following conditions:

A. A single phase fusion melt of acrylonitrile polymer and methanol (about 75% acrylonitrile polymer and about 25% methanol) at 155°C. can be extruded through the spinnerette orifice at a flow rate of 0.792 meters per minute directly into a solidification zone containing an atmosphere of methanol vapour at a temperature of 148°C. and a pressure of 164 psi gauge to yield filaments to which a spin draw-down ratio or jet stretch of 100 times can be imparted.

B. A single phase fusion melt of acrylonitrile polymer and acetonitrile (about 80% acrylonitrile polymer and about 20% acetonitrile) at 155°C. can be extruded at 0.792 meters per minute directly into a solidification zone containing an atmosphere of acetonitrile vapor at a temperature of 141°C. and a pressure of 66 psi gauge to yield filaments spin drawable to at least 100 times.

C. A single phase fusion melt of acrylonitrile polymer and dilute aqueous sodium thiocyanate solution (about 75% acrylonitrile polymer, about 19% water, and about 6% sodium thiocyanate—such aqueous sodium thiocyanate solution being denominated "dilute" because it is of a concentration which will not normally dissolve the acrylonitrile polymer and is, in fact, sufficiently dilute to be used as a coagulant in wet-spinning acrylonitrile polymers) at 141°C. can be extruded at 0.792 meters per minute directly into a solidification zone containing steam at 140°C. and 38 psi gauge to yield filaments jet stretchable at least 100 times.

D. A single phase fusion melt of acrylonitrile polymer and acetic acid (about 77% acrylonitrile polymer and about 23% acetic acid) at 155°C. can be extruded at 0.792 meters per minute directly into an atmosphere of acetic acid vapor at a temperature of 145°C. and a pressure of 17 psi gauge to yield filaments spin drawable at least 100 times.

WHAT WE CLAIM IS:—

1. A process for melt-spinning shaped articles of refractory polymer comprising: extruding a single phase fusion melt consisting essentially of refractory polymer and melt consisting essentially of refractory polymer and melt assistant at a temperature T_1

which is above the single phase fusion melt melting point temperature M and also above the boiling point at atmospheric pressure of said melt assistant through a spinnerette directly into a pressurized solidification zone wherein the following conditions obtain: (1) there is a partial pressure of melt assistant such that the composition profile across the cross-section of the nascent extrudate so produced remains relatively flat; (2) the concentration of melt assistant retained in said nascent extrudate remains at a value at least 70% of the concentration of melt assistant in said single phase fusion melt; and (3) the temperature of the nascent extrudate is below said temperature T_1 but not lower than 20°C. below said temperature M .

2. A process as defined in Claim 1, wherein said refractory polymer is an acrylonitrile polymer.

3. A process as defined in Claim 2, wherein said melt assistant comprises an organic melt assistant.

4. A process as defined in Claim 2, wherein said melt assistant comprises an aliphatic alcohol of 1 to 4 carbon atoms, acetonitrile, formic acid or acetic acid.

5. A process as defined in Claim 2, wherein said melt assistant comprises or consists of water.

6. A process as defined in Claim 2, wherein the melt assistant in said single phase fusion melt is a solution of a higher boiling solute in a lower boiling solvent for such solute and the melt assistant in said solidification zone comprises said solvent.

7. A process as defined in Claim 6, wherein said solute is an inorganic salt and said solvent is water, said solution being of a concentration too dilute to serve as a solvent for said acrylonitrile polymer.

8. A process as defined in any preceding claim, wherein the following conditions obtain in said pressurized solidification zone: (1) the partial pressure of melt assistant is from 56% to 110% of the vapor pressure of the melt assistant at temperature T_1 ; (2) the temperature T is at least equal to the saturation temperature of the melt assistant at a vapor pressure equal to said partial pressure p ; and (3) the total pressure P is at least equal to said partial pressure p ; said conditions ensuring boundary control of any evaporation of melt assistant from the nascent extrudate produced.

9. A process as defined in Claim 8, wherein the partial pressure p is from 80% to 100% of the vapor pressure of water at temperature T_1 and the total pressure P is equal to or does not substantially exceed such partial pressure p .

10. A process as defined in any preceding claim, wherein said solidification zone contains steam under pressure.

11. A process as defined in any preced-



ing claim, wherein the shaped article is drawn while in said solidification zone at a linear speed of 25 to 250 times the linear speed of said single phase fusion melt through said spinnerette.

12. A process as defined in any one of Claims 1—11, wherein the shaped article is drawn while in said solidification zone at a linear speed of about 5 to 150 times the linear speed of said single phase fusion melt through said spinnerette in a first stage followed by a second state of about 1:1 to 30 times.

13. A process as defined in any preceding claim, wherein the shaped article is a filament.

14. A process as defined in any preceding claim, additionally comprising the step of relaxing the thus-drawn shaped article in a free-to-shrink condition.

15. A process as defined in Claim 5, wherein said shaped article is dried at a temperature above 90°C. while substantially preventing loss of water from the freshly melt-spun article at any temperature below 90°C., until said drying step, thereby reducing the tendency of voids and micro-voids to form therein.

16. A process for melt-spinning shaped articles of refractory polymer, as defined in Claim 1 and substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

17. A process for melt-spinning shaped articles of refractory polymer, as defined in Claim 1 and substantially as described in any one of the Examples herein.

18. A shaped article of a refractory polymer, whenever made by a process as defined in any preceding claim.

19. An acrylonitrile polymer fiber having a denier of from 0.5 to 80, whenever made by a process as defined in any preceding claim.

TREGEAR, THIEMANN & BLEACH,

Chartered Patent Agents,

Enterprise House,

Isambard Brunel Road,

Portsmouth, PO1 2AN,

and

49/51 Bedford Row,

London, WC1V 6RU,

Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1976.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY
from which copies may be obtained.

