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54 **Process for melt spinning acrylonitrile polymer fibres.**

57 The invention provided a process for melt spinning acrylonitrile polymer fibers in which fusion melts of acrylonitrile polymer and water are melt-spun through spinnerettes of high capillary density without sticking together of the individual filaments. High capillary density may be obtained by closer spacing of conventional counterbores and capillaries, by using closely spaced counterbores and capillaries of smaller size, or by providing multiple capillaries per counterbore. The fusion melt is extruded through the spinnerette directly into a steam-pressurized solidification zone maintained under conditions such that the rate of release of water from the nascent extrudate avoids deformation thereof.

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TITLE:- Process For Melt Spinning Acrylonitrile Polymer  
Fibres

This invention relates to a process for melt-spinning fiber-forming polymers at an increased production rate per spinnerette. More particularly, this invention relates to such a process wherein a spinnerette with more orifices per given area than previously possible is employed. The greater density of orifices may arise from closer crowding of conventional sized orifices and associated counterbores, from close crowding of smaller orifices and associated counterbores, or by employing multiple orifices per counterbore.

In conventional melt-spinning of fibers, a fiber-forming polymer is heated to a temperature at which it melts, is extruded through a spinnerette plate to form filaments which rapidly cool to become solid, and the resulting filaments are then further processed to provide the desired fiber. The spinnerette plate that is employed in such processing must contain capillaries to provide the desired filaments while satisfying two additional requirements. The capillaries must be of such dimensions as to satisfy back-pressure requirements and must be sufficiently spaced from one another as to prevent premature contact between the emerging fibers that would result in sticking together or fusion of filaments with one another. To satisfy the back-pressure requirements, the capillaries are provided with counterbores of sufficient diameter and depth.

Recent developments in the field of fiber spinning, especially acrylic fibers, has led to the development of

fusion melts which can be extruded through a spinnerette plate to provide filaments. These fusion melts comprise a homogeneous composition of a fiber-forming polymer and a melt assistant therefor. The melt assistant is a material which enables the polymer to form a melt at a temperature below which the polymer would normally melt or decompose and becomes intimately associated with the molten polymer so that a single phase melt results. The melt assistant must be used in proper proportions with the polymer to provide the singly-phase fusion melt. If a low boiling melt assistant is used the melt assistant in proper amounts and the polymer often must be heated at pressures above atmospheric pressure to provide the fusion melt. Since the temperature at which the fusion melt forms is above the boiling point of the melt assistant at atmospheric pressure, consequently super-atmospheric pressures are necessary to keep the melt assistant in the system. Such fusion melts have been effectively spun into fiber using spinnerette plates similar to those employed in conventional melt-spinning.

Because of the requirement for adequate spacing of the capillaries in spinnerette plates used for melt-spinning to prevent premature contact between the nascent filaments which would result in their sticking together, the number of capillaries that can be provided in a given spinnerette plate is greatly restricted. As a result, production capacity of a spinnerette with a given surface area is limited and usually large tow bundles can only be produced by combining the outputs from a series of spinnerettes. This, in turn, requires costly installations of additional spinnerettes, specially designed conduits and spin packs to ensure an even distribution of the melt to all spinning holes, provision of space for installation, and further power consumption to operate the increased number of spinnerettes.

There exists, therefore, the need for processes for providing fiber by melt spinning which enables the productivity of spinnerettes to be increased. Such provision would fulfill a long-felt need and constitute a significant advance in the art.

In accordance with the present invention there is provided a process for melt-spinning an acrylonitrile polymer fiber which comprises providing a homogeneous fusion melt of a fiber-forming acrylonitrile polymer and water at a temperature above the boiling point of water at atmospheric pressure and at a temperature and pressure which maintains water in single phase with said polymer and extruding said fusion melt through a spinnerette assembly containing a spinnerette plate having an orifice density of at least 18 per square centimeter directly into a steam-pressurized solidification zone maintained under conditions such that the rate of release of water from the nascent extrudate avoids deformation thereof.

In a preferred embodiment, the spinnerette plate has orifices of 60 to 160 microns and the acrylonitrile polymer has a kinematic molecular weight in the range of 30,000 to 60,000.

In another preferred embodiment, the spinnerette plate has a plurality of counterbores within each of which are contained at least 3 capillaries.

Another preferred embodiment includes the step of stretching the nascent extrudate while it remains within said solidification zone to provide desirable textile properties. In such embodiment, it is generally preferred to conduct such stretching in at least two stages with the first stage being conducted at a stretch ratio less than that of the subsequent stage.

The present invention, by employing a fusion melt of an acrylonitrile fiber-forming polymer and water at a temperature above the boiling point of water at atmospheric pressure and at a temperature and pressure that maintains water and the polymer in a single phase and by extruding the fusion melt directly into a steam-pressurized solidification zone maintained under conditions such that the rate of release of water from the nascent extrudate avoids deformation thereof, provides filamentary extrudates which do not stick together as they emerge from the spinnerette orifices. Since the filaments have no tendency to stick together as they emerge from the spinnerette, the orifices of the spinner-

ette plate can be located closer together and more orifices can be provided in the spinnerette plate. As a result, the producticity of a spinnerette can be greatly increased without negatively affecting the quality  
5 of the resulting fiber.

The present invention also enables the use of orifices of reduced cross-section relative to those conventionally employed in melt-spinning. As a result an even greater number of orifices can be present in the  
10 spinnerette plate. In order to overcome back-pressure difficulties that would arise with the orifices of narrow cross-section, the process of the present invention in this embodiment employs fiber-forming polymers of lower molecular weight than conventionally employed. Unexpectedly,  
15 the fiber obtained possesses good fiber properties in spite of the low molecular weight of the fiber-forming fiber. It is believed these good fiber properties are the result of processing steps employed.

The spinnerette plate used in the process of  
20 the present invention contains a much greater density of orifices per unit area than do conventional spinnerette plates used in melt spinning by conventional procedures. Typically, prior art melt-spinning spinnerette plates have a density of about 5-10 orifices per square centimeter  
25 at most. In the process of the present invention the spinnerette plate contains at least about 18 orifices per square centimeter, preferably at least 25, 50 or more per square centimeter. This enables the process of the present invention to provide a substantial increase  
30 in productivity from a given spinnerette. Since processing of the melt is under conditions which lead to nascent extrudates which do not stick together or deform, the higher density of spinnerette orifices is possible.

Conventional, melt-spinning spinnerette plates have orifices of about 200-400 microns or larger diameter at their exit ends. The process of the present invention may employ orifice of such conventional diameters but  
5 preferably uses orifices in the range of about 60-160 microns diameter at their exit ends. This provision not only allows a greater number of orifices to be positioned in the spinnerette plate to increase productivity but also enables finer denier fiber to be provided at a  
10 given stretch ratio.

In another preferred embodiment, the spinnerette plate of the present invention contains a number of capillaries located within each counterbore. The counterbores are necessary to enable the spinnerette plate to operate at  
15 a suitable level of back-pressure. The spinnerette plate as a whole will contain a substantially greater number of capillaries than the prior art spinnerette plates associated with melt spinning because the problem of sticking together of nascent extrudates is eliminated. Increased productivity is  
20 provided by increasing the density of capillaries in the spinnerette plate and the number of capillaries in each counterbore beyond the operative limits of conventional melt-spinning spinnerette plates which have restrictions as to hole density imposed by fusing of individual filaments.

25 It is possible to provide larger counterbores than are normally associated with a capillary and provide numerous capillaries therein although this has often been found to be unnecessary. It is preferable to provide a pattern of counterbores more closely spaced than those in the prior art spinnerette plates for melt spinning in a pattern providing uniform  
30 extrusion of the spinning melt through the spinnerette plate. The combination of more closely spaced counterbores with a plurality of capillaries within each counterbore gives rise to a substantial increase in the total number of capillaries for a given spinnerette surface, and hence in the pro-  
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ductivity of the spinnerette.

In carrying out the process of the present invention, it is necessary to provide a homogeneous fusion melt of a fiber-forming acrylonitrile polymer that can form a fusion melt with water at a temperature above the boiling point of water at atmospheric pressure and at a pressure and temperature sufficient to maintain water and the polymer in a single fluid phase, can be used in the process of the present invention. Polymers falling into this category are known in the art. Preferred acrylonitrile fiber-forming polymers are those having kinematic molecular weights ranging from about 30,000 to 60,000, as defined below. The fusion melt is prepared at a temperature above the boiling point at atmospheric pressure of water and eventually reaches a temperature and pressure sufficient to maintain water and the polymer in a single, fluid phase.

The homogeneous fusion melt thus provided is extruded through the spinnerette plate of the present invention directly into a steam-pressurized solidification zone that controls the rate of release of water from the nascent filaments so that deformation thereof is avoided and the process is able to provide filaments which solidify without sticking together one with another in spite of the close proximity of adjacent capillaries. The extruded filaments may be processed according to conventional procedures to provide desirable filamentary materials which may have application in textile and other applications.

The pressurized solidification zone used in the process of the present invention is a critical feature of the process. If this pressurized solidification zone is omitted, water is so rapidly released from the nascent filaments which would emerge into atmospheric conditions that the filaments would become inflated or deformed and interfere with neighboring filaments and necessitate reduction in the number of operative spinnerette capillaries which would defeat the object of the invention. On the other hand, by employing the pressurized solidification zone operating at suitable steam pressure, the rate of release of water can be controlled as the nascent filaments solidify so that foaming and deformation thereof is avoided and optimum stretching is possible.

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The particular pressure of steam will vary widely depending upon the polymer employed, the spinning temperature employed and the like. The useful values for given systems are those values which minimize or avoid foaming or other forms of deformation of the filaments and provide optimum stretching. These values can readily be determined for any given system of polymer and water taking into account the teachings herein given.

A particularly preferred embodiment of the process of the present invention is drawing the nascent extrudate while it remains in the steam-pressurized solidification zone. Such drawing can be accomplished in one or more stretches and can eliminate any subsequent drawing normally required for fiber orientation. It is particularly preferred to conduct drawing in two stages with the stretch ratio of the second stage being larger than that of the first stage. It is also preferred to relax the drawn fiber in steam generally under conditions which provide from about 20% to 35% filament shrinkage.

The invention is more fully illustrated in the examples which follow wherein all parts and percentages are by weight unless otherwise specified.

Kinematic average molecular weight ( $M_k$ ) is obtained from the following relationship:

$$\mu = \frac{1}{A} \bar{M}_k$$

wherein  $\mu$  is the average effluent time (t) in seconds for a solution of 1 gram of the polymer in 100 milliliters of 53 weight percent aqueous sodium thiocyanate solvent at 40°C. multiplied by the viscometer factor and A is the solution factor derived from a polymer of known molecular weight and in the present case is equal to 3,500.

#### COMPARATIVE EXAMPLE A

A single phase fusion melt was prepared using a copolymer containing 89.3% acrylonitrile and 10.7% methyl methacrylate and having an intrinsic viscosity of 1.52. This fusion melt was extruded through a spinnerette having 1266 capillaries each of diameter 200 microns. Each of the capillaries was centered in a counter bore of 2.0 millimeters in

diameter and dispersed at a spacing of 4.0 millimeters center-to-center in the spinnerette plate, the density of orifices being 5 per square centimeter of spinnerette plate extrusion surface. Extrusion was conducted at 176°C. and the extrudate issued directly into a solidification zone maintained at 25 psig (130°C.) with saturated steam. The extrudate was subjected to a first stage of stretching at a stretch ratio of 3.2 and a second stage of stretching at a stretch ratio of 13.6 while the extrudate remained in the solidification zone. The stretch ratio was the speed of the extrudate take-up relative to the linear flow of fusion melt through the spinnerette. The total stretch ratio obtained was 43.5. The extrudate, representing a bundle of filaments, which emerged from the solidification zone was relaxed in saturated steam at a pressure of 18 psig (124°C.) during which a shrinkage of 285 occurred. The fiber before relaxation was 5.4 denier/filament and 7.2 denier/filament after relaxation. Relaxed fiber properties were as follows:

	Straight tenacity (grams/denier)	6.5
20	Straight elongation (%)	33.0
	Loop tenacity (grams/denier)	4.2
	Loop elongation (%)	24.0

EXAMPLE 1

Following the procedure of Comparative Example A in every material detail except for the spinnerette plate employed, an additional extrusion run was made. In this example, a smaller spinnerette plate was employed but it contained 2937 orifices each of 200 micron diameter centered in counterbores of 1.0 millimeter diameter, the density of orifices being 67 per square centimeter of spinnerette plate extrusion surface.

Extrusion was conducted without any sticking together of individual filaments and fiber identical to that obtained in Comparative Example A was obtained.

35 COMPARATIVE EXAMPLE B

The procedure of Example 1 was repeated in every material detail except that a polypropylene melt free of melt assistant and designated as fiber grade having a melt index

of 3 (Trademark Rexene PP-3153) was employed and extrusion was conducted at 260-280°C. directly into air. The extrudates stuck together as they emerged from the spinnerette and the desired individual filaments could not be obtained.

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Example 1 compared to Comparative Example A shows that the process of the present invention provides desirable fiber using closely spaced orifices. Comparative Example B compared to Example 1 shows that other melt-spinning compositions are not effectively processed using closely spaced orifices.

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EXAMPLES 2 - 5

Again following the procedure of Example 1, a series of runs were made in which the spacing of the orifices in the spinnerette plate was varied. In each instance fiber of substantially the same properties as those of the fiber of Example 1 was obtained. Example numbers and spinnerette plate details are given below:

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Example	Overall		Capillary		Density	Counterbores	
	Plate Diameter (mm)	Diameter (mm)	Diameter (mm)	No.		Diameter (mm)	Spacing* (mm)
2	381	200	200	5,016	18	1.8	2.2
3	279	200	200	9,060	25	1.5	1.7
4	279	200	200	5,016	18	2.0	2.2
5	432	200	200	30,000	54	1.2	1.3

\* Spacing of counterbores center to center.

EXAMPLE 6

A fusion melt of 14% water and 86% of an acrylonitrile polymer of the following composition was prepared:

Acrylonitrile	84.98
Methyl methacrylate	12.0%
Polyvinyl alcohol (Trademark Elvanol 71-30G)	3.0%
Acrylamidomethylpropane sulfonic acid	0.1%

This polymer had a kinematic molecular weight value of 40,000.

The fusion melt was spun through a spinnerette plate having the following characteristics:

Capillary Diameter	120 microns
Capillary spacing, center to center	1.3 millimeters
Counterbore Diameter	1.2 millimeters
Counterbore spacing center to center	1.2 millimeters
Capillary Density	54 per square centimeter

The extrusion temperature was 170°C. and extrusion was directly into a steam-pressurized solidification zone maintained at 13 pounds per square inch gauge. The extrudates were stretched at a stretch ratio of 4.2 in a first stage and 9.8 in a second stage, dried at 138°C. and steam relaxed at 116°C. No filament breakage or sticking occurred. The fiber obtained had the following properties:

Denier per filament	3.15
Straight tenacity	3.2 grams/denier
Straight elongation	30%
Loop tenacity	2.6 grams/denier
Loop elongation	23%

COMPARATIVE EXAMPLE C

Following the procedure of Example 6 in every material detail, an additional run was made using a polypropylene melt free of melt assistant and designated as fiber grade having a melt index of 3 (Trademark Rexene PP-3153) in place of the fusion melt of example. Extrusion was conducted at 260-280°C. directly into air. The extrudates stuck together as they emerged from the spinnerette and the desired individ-

ual filaments could not be obtained.

EXAMPLES 7 - 11

Again following the procedure of Example 6 in every material detail except for the spinnerette plate, a series of runs were made using spinnerettes of the characteristics given in Table II which also indicates the example number. In each instance, no filament breakage or sticking occurred and the fiber obtained had properties substantially similar to those of the fiber of Example 6.

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TABLE II

Example	Overall Plate Diam. mm	Capillary		SPACING mm	DENSITY* NO./cm <sup>2</sup>	COUNTERBORES	
		Diameter $\mu$	Total No.			DIAM. mm	SPACING mm
7	381	200	5016	2.2	18	1.8	2.2
8	279	120	9060	1.7	25	1.5	1.7
9	279	100	5016	2.2	18	2.0	2.2
10	76	85	2937	1.2	67	1.0	1.2
11	432	120	30000	1.3	54	1.2	1.3

\* Spinnerette capillary density was calculated based on effective area of plate used (flange area not included).

EXAMPLE 12

The process of Example 6 was again repeated in every material detail except that the polymer employed was a copolymer of 94% acrylonitrile and 6 methyl acrylate having a kinematic molecular weight of 48,000. No filament breakage or sticking occurred during extrusion and the fiber obtained had substantially the same properties as those of Example 6.

EXAMPLE 13

A fusion melt of 15% water and 85% of an acrylonitrile polymer of the following composition was prepared at autogeneous pressure and 170°C.:

Acrylonitrile	89.3%
Methyl methacrylate	10.7%
Molecular weight, kinematic	58,000

The fusion melt was spun at 170°C. through a spinnerette assembly having orifice characteristics as follows:

Capillary diameter	200 microns
Capillary spacing <sup>1</sup>	0.47 millimeters
Capillaries per counterbore	7
Counterbore diameter	1.2 millimeters
Counterbore spacing <sup>1</sup>	4.1 millimeters
Capillary density	62 per sq. cm.

<sup>1</sup>center to center

The extrusion was directly into a solidification zone pressurized with saturated steam at 15 pounds per square inch. The extruded filaments were stretched in a first stage at a stretch ratio of 3.8 and in a second stage at 6.7 for a total stretch of 25.5 x. The filaments were dried at 138°C. and relaxed in steam at 116°C. Fiber of about 12 denier per filament was obtained having the following properties:

Straight tenacity grams/denier	3.4
Straight elongation %	35
Loop tenacity grams/denier	2.1
Loop elongation %	13

No sticking together of the filaments occurred and continuous processing was accomplished.

COMPARATIVE EXAMPLE D

Using the spinnerette assembly described in Example

13, a melt of polypropylene (Rexene Grade PP 3153) of fiber grade having a melt index of 3 dg/min. was prepared at 260°C. and extruded into static air at 25°C. The melt emerging from the union of the individual filaments issuing from single capillaries. Thus, filaments of the desired denier were not obtained using this spinnerette plate design.

EXAMPLE 14

The procedure of Example 13 was again followed with the following exceptions: The polymer had a kinematic molecular weight value of 40,000 and the spinnerette assembly had the following characteristics:

Capillary diameter	85 microns
Capillary spacing	0.40 millimeter
Capillary per counterbore	19
Counterbore diameter	2.0 millimeters
Counterbore spacing	1.4 millimeters
Capillary density	875 per sq. cm.

Continuous spinning was conducted with no sticking together or fusion of the individual filaments and fiber of substantially the same properties as obtained in Example 13 was obtained.

When the polypropylene melt described in Comparative Example D was extruded, extensive fusion of the individual filaments occurred and it was not possible to provide the desired filament denier.

EXAMPLES 15 - 17

Following the procedure of Example 13, a number of runs were made using spinnerette assemblies of different design in each run as shown in Table III which also gives the example number. In each instance, continuous spinning was effected with no sticking together of the individual filaments.

TABLE III

<u>Example</u>	<u>Capillaries</u>		<u>Density<sup>3</sup></u>	<u>Diameter<sup>4</sup></u>	<u>Spacing<sup>5</sup></u>	<u>Counterbores Capillaries Per Counterbore</u>
	<u>Diameter<sup>1</sup></u>	<u>Spacing<sup>2</sup></u>				
15	85	.42	213	1.0	1.2	3
16	85	.59	87	1.2	2.8	5
17	85	.47	337	1.2	1.4	7

1 Microns

2 Millimeters, center to center

3 Holes per square centimeter

4 Millimeters

5 Millimeters, center to center

CLAIMS

1. A process for melt-spinning an acrylonitrile polymer fiber which comprises providing a homogeneous fusion melt of a fiber-forming acrylonitrile polymer and water at a temperature above the boiling point of water at atmospheric pressure and at a temperature and pressure which maintains water in single phase with said polymer and extruding said fusion melt through a spinnerette assembly containing a spinnerette plate having an orifice density of at least 18 per square centimeter directly into a steam-pressurized solidification zone maintained under conditions such that the rate of release of water from the nascent extrudate avoids deformation thereof.

2. The process of Claim 1 wherein the spinnerette plate has orifices of a diameter of 60 to 160 microns and the acrylonitrile polymer has a kinematic molecular weight in the range of 30,000 to 60,000.

3. The process of Claim 1 or Claim 2, wherein the spinnerette plate has a plurality of counterbores within each of which are contained at least 3 capillaries.

4. The process of any preceding Claim, including the steps of stretching the nascent extrudate while it remains within said solidification zone to provide desirable textile properties.

5. The process of Claim 4 wherein said stretching is conducted in at least two stages, the first stage being at a stretch ratio less than that of the subsequent stage.

6. The process of Claim 4 or Claim 5, wherein the drawn fiber is relaxed in steam under conditions to provide from about 20-35% filament shrinkage.





DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p>* Abstract *</p> <p>--</p> <p>US - A - 4 094 948 (E.I. DU PONT DE NEMOURS)</p> <p>* Claims *</p> <p>--</p>	1	
P	<p>FR - A - 2 409 330 (AMERICAN CYANAMID)</p> <p>* Claims *</p> <p>--</p> <p>PATENT ABSTRACTS OF JAPAN, vol. 2, no. 89, 21 July 1978, page 1493-C-78.</p> <p>&amp; JP - A - 53 52 730 (ASAHI KASEI KOGYO)</p> <p>&amp; JP - A - 53 52 731 (ASAHI KASEI KOGYO)</p> <p>----</p>	1 1	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )