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W. W. BECK
QUENCHING PROCESS
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3,115,385

FIG. 1

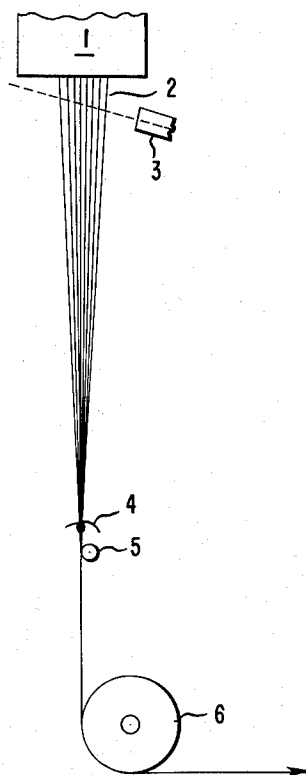
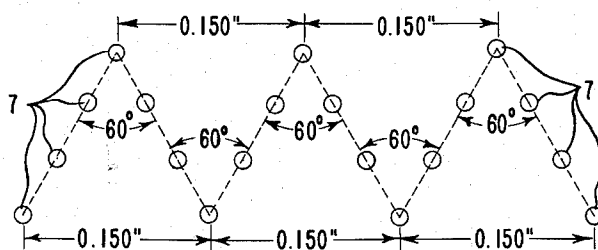


FIG. 2



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3,115,385

QUENCHING PROCESS

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7 Claims. (Cl. 18—54)

This invention relates to a process of melt-spinning and quenching of synthetic polymer to produce as-spun filaments of highly uniform physical properties. This is a continuation-in-part of my copending application Serial No. 810,321, filed May 1, 1959.

In the spinning of yarns from synthetic polymers, uniformity of the properties of the filaments, both from one filament to another, and from point to point of an individual filament, is of the highest importance to the properties of the yarn as a whole. The word "uniformity" refers here to any of the physical properties of the filaments, such as the denier, tenacity, orientation, or other. Uniformity of the as-spun yarn assures that in the subsequent processing steps, such as drawing, relaxing, and dyeing, each filament will respond in the same fashion.

The drawing step may be taken as an example of the manner in which as-spun uniformity governs the success of subsequent operations. One purpose of the drawing step is to increase the tenacity of the yarn bundle, and in general the greater the draw ratio, the higher the tenacity. Since for a yarn bundle the maximum draw ratio which can be achieved depends upon the maximum draw ratio of the least drawable filament, it is readily apprehended that uniformity of filaments in the bundle is critical for the preparation of high tenacity yarns. It is also true that a more uniform yarn bundle is in general drawable at a higher rate.

It is an object of the present invention to provide a process for preparing a highly uniform as-spun polyester or polypropylene yarn. It is a particular object to provide a process for spinning such yarns at high productivity. Other objects will become apparent from the specification and claims.

These objects are accomplished by continuously extruding a fiber-forming polyester or polypropylene in a molten condition through a spinneret having a high density of orifices to form a plurality of filaments and quenching the said filaments as they emerge from the said orifices by subjecting them to uniform treatment with a current of steam to cool them to a temperature below about 15° C. below the melting point prior to a point 2 inches below the spinneret.

By a "fiber-forming polyester" is meant a linear, fiber-forming resin in which the ester groups form part of the polymer chain. By a "spinneret having a high density of orifices" is meant a spinneret whose orifices are spaced less than 0.100 inch apart (measured center-to-center). The term "steam" is intended to include both wet and dry steam.

The invention may be better understood by reference to the drawing.

In FIGURE 1, molten fiber-forming polymer is extruded from spinneret 1 to form threadline 2 which passes through a current of steam directed upon it from nozzle 3. After being uniformly quenched by the steam, the threadline is converged by passing through guide 4. An antistatic agent may optionally be applied at finish roll 5, and the yarn is subsequently taken up on wind-up 6.

A high density of spinneret orifices can be employed to provide for high productivity per spinneret position. FIGURE 2 shows one arrangement of closely spaced

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holes 7 of uniform diameter. These holes are spaced apart at intervals of only 0.050 inch (center-to-center) in rows which intersect at 60° angles. The holes may be of diameters conventionally used for melt-spinning, e.g., about 0.005 to 0.030 inch in diameter. The pattern of holes is not important and other arrangements are illustrated in the examples.

Hole spacings of less than 0.100 inch apart from center-to-center are much closer together than had been considered practical in melt spinning. Difficulties encountered included fused filaments and non-uniform properties. It has been found that filaments can be kept from fusing with each other by directing a jet of gas or vapor at the filaments as they emerge from the spinneret. Quenching with gas instead of the steam used in the process of the present invention makes possible a remarkably high productivity per spinning position. However, the fibers so produced are not completely uniform across the yarn bundle owing to heating of the quenching medium as it traverses the bundle. For many purposes this is not a serious disadvantage, as when it is not necessary to raise the properties of the yarn to the highest achievable values.

By the use of steam, the present invention provides the unexpected and desirable result of spinning a highly uniform product at the exceedingly high productivity per spinning position of 4 to 40 g./min./cm.² of effective spinneret face area, and is especially useful for about 10 to 30 g./min./cm.² of effective spinneret area. A quenching stream of 0.5 to 6.5 pounds of steam per pound of polymer extruded can be used to provide the specified rapid rate of cooling, as illustrated in the examples. By the expression "effective spinneret face area" is meant the area within a quadrilateral defined by four straight lines between the centers of four adjacent orifices. Thus, if the orifices are arranged in a square pattern, the effective spinneret area is the square of the center-to-center spacing of the orifices.

In the following examples relative viscosities of polyethylene terephthalate are measured at a concentration of 8.73% in a solution of phenol/2,4,6-trichlorophenol (10/7). Example I demonstrates that the favorable results achieved by quenching with dry steam are not duplicated when other gases are used. Examples II and III illustrate the use of wet steam. Example IV illustrates the use of an alternative quenching arrangement. Relative viscosities are measured at 25° C.

EXAMPLE I

Polyethylene terephthalate with a relative viscosity of 32 is extruded from a melt at a temperature of 290° C. through a horizontal spinneret having 126 0.007-inch diameter holes arranged in a 7 x 18 rectangular pattern at a center-to-center distance of 0.050 inch. Polymer is extruded at a rate of 0.2 gram/min./hole. The quenching device is a flared tube 15 inches long, which receives the quenching medium from a ¼" I.D. pipe and discharges it from a nozzle having dimensions 1" x 2". The nozzle is oriented with its long dimension parallel to the long dimension of the spinneret pattern. It is situated so that the center of the orifice is 1" vertically distant from the face of the spinneret and 1½ inches horizontally distant from the center of the spinning threadline. It is tilted upward so that the quenching stream is at an angle of 20° with the horizontal. The quenched filaments are wound up at a speed of 1000 yards per minute as about 2 denier per filament as-spun yarn. The yarn is subsequently drawn at 90° C. over a hot pin at the maximum operable draw ratio. Yarn elongation is measured on the undrawn yarn. Maximum draw ratio and elongation are measures of yarn uniformity. In the following table, the values of these properties are compared as functions

of the nature and temperature of the quenching stream. The extrusion rate of 0.2 g./min./hole is equivalent to 12.4 g./min./cm.² of effective spinneret face surface area.

Table 1

Quenching Medium	Quenching Temperature (°C.)	Quenching Rate (lb./min.)	Draw Ratio	Elongation (percent)
Air-----	35	.24	2.6	225
	77	.24	2.4	215
	140	.24	2.7	232
Steam-----	105	.25	3.4	328
	125	.25	3.3	400
	140	.25	3.4	366
	185	.25	3.0	339
Carbon dioxide-----	144	.32	2.6	-----

At a hole spacing greater than 0.10 inch (center-to-center), no advantage derives from the use of steam as a quenching medium.

EXAMPLE II

Polyethylene terephthalate having a relative viscosity of 31.6 is extruded at a temperature of 290° C. from a 126-hole spinneret. The spinneret holes have a diameter of .0050 inch and are situated in a rectangular array 18 holes long by 7 holes wide, with a center-to-center separation of .050 inch. The filaments are quenched with wet steam which is delivered from a rectangular slot 1½ inches high by 3 inches wide at an upward angle of 15 to 20° with the horizontal at a rate of 1-2 pounds per pound of polymer. The slot is 2 inches distant from the threadline and one inch vertically downward from the spinneret, with its long dimension parallel to the long dimension of the spinneret pattern. The quenched filaments are wound up at speeds of 475 and 1050 yds./min. The properties of the as-spun yarn are given in Table 2. Properties of the same yarns, after drawing over a hot pin at a temperature of 90° C., are also given in the table. Wet steam refers to 100° C. steam at atmospheric pressure.

Table 2

Windup Speed (yds./min.)	As-Spun Props.				Draw Ratio	Props. After Draw			
	T	E	M _i	D		T	E	M _i	D
475-----	1.4	390	35	2.9	4.9	5.5	17	97	.64
1,050-----	1.9	330	38	1.5	2.7	4.1	59	68	.60
1,050-----	1.7	295	29	2.7	2.8	4.8	41	84	.83
1,050-----	1.5	370	31	4.0	3.1	4.1	41	69	1.5

T is the tenacity in grams/denier, E is the elongation in percent, M_i is the initial modulus in grams/denier, and D is the denier per filament.

Under comparable conditions, yarn which is spun at 1000 yards per minute and quenched with air at 23° C. instead of steam has a maximum draw ratio of only 2.2 to 2.3. In the above table, polymer throughput in g./min./cm.² of spinneret face surface area is 8.7, 10.0, 18.0, and 26.6, respectively, reading from top to bottom.

EXAMPLE III

Polyethylene terephthalate having a relative viscosity of 31.6 is extruded at a temperature of 290° C. through a spinneret having 40 holes of .009 inch diameter. These holes are placed at intervals of 0.050 inch (center-to-center) as shown in FIGURE 2. Extrusion is carried out at rates of 0.2, 0.35, 0.52, 0.64, and 0.80 gram per minute per hole. The quenching jet of Example I is used, being situated 1 inch below the face of the spinneret and 1½ inches horizontally distant from the center of the hole pattern. Wet steam is directed horizontally at the filaments at the rate of 2 pounds per pound of polymer. Filaments are wound up at a speed of 1000 yards per minute at a point 3½ feet below the spinneret. By way of comparison, fibers are spun in a fashion identical with the above with the exception that the quenching medium is air at room temperature delivered at a rate of 3.5

standard cubic feet per minute. The yarn samples are drawn over a hot pin at 90° C. at the maximum draw ratio consistent with continuity of the drawing operation. Subsequently, the yarns are boiled off in water for ½ hour in the relaxed state. Properties of the relaxed yarns are presented in Table 3. A standard cubic foot of air is the mass of one cubic foot of air at 70° F. and 1 atmosphere pressure.

Table 3

Quench Medium	Capillary Throughput (gm./mm.)	Draw Ratio	Tenacity (g.p.d.)	Elongation (percent)	Initial Modulus (g.p.d.)
Wet steam-----	.2	3.0	4.5	30	40
	.2	2.3	3.3	37	30
	.35	4.1	5.4	29	56
Air-----	.35	2.8	4.1	25	46
	.52	4.4	5.1	29	56
	.52	3.3	4.2	28	52
Wet steam-----	.64	4.4	4.9	31	63
	.64	3.6	4.0	37	54
	.80	4.4	4.7	32	62
Air-----	.80	4.0	4.2	27	58

In every case, the tenacity after drawing of the steam-quenched yarns is superior to the air-quenched yarn. In addition, the uniformity of the steam-quenched yarn is substantially better; for example, the coefficient of variation of the elongation when spun at 0.2 gram per minute per hole is 12% for the steam-quenched yarn as against 27% for the air-quenched yarn.

EXAMPLE IV

Polyethylene terephthalate having a relative viscosity of 31.6 is extruded at a temperature of 290° C. through a 187-hole spinneret. The holes are each .005 inch in diameter and are arranged in four concentric circles of 0.6, 0.7, 0.8, and 0.9 inch diameter having 37, 44, 50, and 56 holes, respectively. The spacing between holes along the circumference is in each case .050 inch, and adjacent holes in adjacent circles are less than 0.100 inch apart. Polymer is extruded at a rate of 9.3 grams/min./cm.², and forms a yarn which is wound up at 1500 yds./min. The filament bundle is quenched by wet steam which is delivered at the rate of 2 pounds per pound of polymer spun.

The quenching medium is delivered from a toroidal plenum situated ½ inch vertically downward from the face of the spinneret. The plenum encircles the filament bundle and is oriented such that its plane is perpendicular to the axis of the filament bundle. The toroid has a small diameter of one inch and a large diameter of four inches. The toroidal chamber is filled with screens to assist in providing an even distribution of the quenching medium. The quenching medium leaves the plenum by a cylindrical slot 1 inch high, being directed horizontally and radially inward toward the filaments.

The properties of the spun yarn are as follows:

Tenacity, g.p.d.-----	2.3
Elongation, percent-----	145
Modulus, g.p.d.-----	18

EXAMPLE V

Crystalline polypropylene of melt index 4 is extruded from a melt at a temperature of about 280° C. through a spinneret having 30 orifices of 0.015 inch diameter arranged in a 3 x 10 rectangular pattern at center-to-center distances of 0.095 inch. The extruded filaments are quenched radially and horizontally by steam from a screened slot 1 inch high and 2.25 inches in diameter in the plenum of Example IV centered about the thread line and located 0.25 inch below the spinneret face. The quenched filaments are forwarded by a feed roll located 60 inches below the spinneret to a faster moving draw roll to draw the filaments. The draw roll is operated at 500 to 800 yards per minute. The speed of the feed roll is adjusted to the slowest speed (i.e., highest draw ratio) that will afford good spinning continuity of 15 minutes

or more without breaking any filaments. The superior results obtained with steam as compared with air are shown in Table 4. The results using air (25° C.) are typical for the entire operable range of air velocities under the particular spinning conditions. In each case the use of a steam quench affords a greater draw ratio and a higher tenacity than obtained with air. The above extrusion rates of 0.4–0.6 gram/min./hole are equivalent to 6.9–10.3 grams/min./cm.² of effective spinneret face surface area. The steam pressures of 2.5 and 5.0 pounds per square inch gauge correspond to 0.1 and 0.16 pound of steam per minute.

Similar superior results are obtained in the above arrangement using various extrusion rates as high as 0.8 gram per hole and steam quenching rates from 0.5 to 6.5 pounds of steam per pound of polymer at steam pressures of 1 to 12 pounds per square inch gauge.

Table 4

Item	Quench		Extrusion Rate, gram/min./hole	Draw Ratio	Tenacity (g.p.d.)
	Medium	p.s.i.g.			
a-----	Steam-----	4.8	0.4	3.3	3.8
b-----	Air-----	-----	0.4	2.7	3.5
c-----	Steam-----	2.5	0.5	4.4	4.6
d-----	Air-----	-----	0.5	3.4	4.0
e-----	Steam-----	5.0	0.6	4.0	4.6
f-----	Air-----	-----	0.6	3.3	3.9

The polyesters to which the present invention is preferably applicable are those in which the portion of the polymer chain deriving from an acid is principally derived from terephthalic acid. Glycols which react with terephthalic acid to give fiber-forming polyesters include polymethylene glycols, HO(CH₂CH where x=2–10, and 1,4-cyclohexanedimethanol.

The quenching geometry is not critical. However, it is important that the quenching zone should be as close to the spinneret as possible. The quenching medium may be imposed, for example, unilaterally, bilaterally, radially inward, and radially outward. The length of the quenching zone will be a function of the rate at which polymer traverses the zone as well as of the temperature to which the polymer is to be quenched.

It is sometimes desirable that the temperature of the yarn be allowed to approach room temperature before being collected. This is easily accomplished by allowing the yarn a few feet of free travel from the point at which it leaves the quenching zone to the point at which it is wound up. However, if space is an important consideration, the yarn may be collected immediately after it leaves the quenching zone. Since the quenching zone itself may be very short, there is a saving of space when compared with conventional spinning.

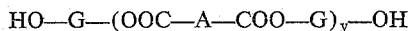
In the case of wet steam it is very surprising that the introduction of liquid droplets into the quenching stream should lead to a yarn of higher uniformity. In fact, quite the reverse effect would be expected, inasmuch as liquid droplets striking the filaments would be expected to cause strong local quenching, leading to non-uniformity in the filaments. However, in the operation of the present invention with wet steam, the droplet diameter is maintained at less than 0.5 of the diameter of the unquenched unextended filaments and preferably less than 0.1 of that diameter so that the droplets are apparently either completely vaporized or are deflected before striking a filament and causing a non-uniform section. A beneficial effect of the presence of the droplets is the heat balance in the quenching medium which is achieved in their presence. Heat which is removed from the filament bundle during the quenching process acts to evaporate liquid from the surface of the droplets. As the quenching medium traverses the filament bundle there need be no rise in temperature, but only the evaporation of a portion of the droplets.

Thus, when wet steam is used, the present process pro-

vides a method for positive temperature control of the spinning environment which heretofore has not been achieved in melt spinning. This temperature control in the quenching region makes possible improved uniformity of the product.

Yarns and tows prepared in accordance with this invention may be converted into woven and non-woven fabrics by methods well known to those skilled in the art.

The preferred polyesters used in this invention are linear terephthalate polyesters. These should be fiber forming and having a relative viscosity of at least about 12. Such polymers may be represented in a more general way by the formula



where —G— and —A— are divalent organic radicals corresponding, respectively, to the radicals in the initial glycol, G(OH)₂, and to the initial dicarboxylic acid, A(COOH)₂, and y is a whole number sufficiently large that the polymer is of fiber-forming molecular weight. Preferably at least about 75% of the —A— radicals are terephthalate radicals and preferably at least about 75% of the —G— radicals are ethylene radicals. The terephthalate radical may be the sole dicarboxylate constituent of the recurring structural units, or up to about 25% of the recurring structural units may contain other dicarboxylic radicals, such as the adipate, sebacate, isophthalate, 5-(sodium sulfo)isophthalate, bibenzoate, hexahydroterephthalate, diphenoxyethane - 4,4' - dicarboxylate, or p,p'-sulfonylbibenzoate radicals, derived from the corresponding dicarboxylic acids or ester-forming derivatives thereof. Similarly, ethylene glycol may be the sole glycol constituent of the polyester, or another glycol may be used, such as tetramethylene glycol, hexamethylene glycol, decamethylene glycol, 2,2-dimethylpropanediol, trans-p-hexahydroxylylene glycol, diethylene glycol, bis-p-(β-hydroxyethoxy)benzene, bis-1,4-(β-hydroxyethoxy) - 2,5 - dichlorobenzene, or bis-[p-(β-hydroxyethoxy)phenyl]difluoromethane alone or in mixtures.

Suitable polypropylene is highly crystalline as shown by sharp and distinct X-ray diffraction patterns and characterized by a melt index (ASTM Standards, 1958, D-1238-57T, part 9, page 378) of 0.1 to 200 and preferably from 1.0 to 25.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. In the process for melt-spinning polymer into filaments, the improvement for spinning filaments selected from the group consisting of linear polyester filaments and polypropylene filaments at high rates of productivity per spinning position which comprises extruding the polymer in a molten condition through a spinneret having a high density of orifices spaced less than 0.100 inch apart from center-to-center to spin a plurality of filaments from the face of the spinneret, cooling the extruded filaments to a temperature below about 15° C. below the melting point of the polymer prior to a point 2 inches below the spinneret by directing in front of the spinneret face, to form a uniform quenching medium adjacent to the spinneret, a current of steam selected from the group consisting of dry steam and wet steam wherein the droplets have maximum diameters less than 0.5 of the diameter of the filaments extruded, said medium being otherwise free from liquid, and passing the filaments as they emerge from the spinneret orifices through said medium so as to be uniformly treated.

2. The process as defined in claim 1 wherein said polymer is polypropylene.

3. The process as defined in claim 1 wherein said polymer is polyethylene terephthalate.

4. The process for melt-spinning a linear terephthalate polyester into filaments at a high rate of productivity per spinning position which comprises extruding the polyester in a molten condition through a spinneret having a high density of orifices spaced less than 0.100 inch apart from center-to-center to spin a plurality of filaments from the face of the spinneret, cooling the extruded filaments to a temperature below about 15° C. below the melting point of the polyester prior to a point 2 inches below the spinneret by directing in front of the spinneret face, to form a uniform quenching medium adjacent to the spinneret, a current of steam selected from the group consisting of dry steam and wet steam wherein the droplets have maximum diameters less than 0.5 of the diameter of the filaments extruded, said medium being otherwise free from liquid, and passing the filaments as they emerge from the spinneret orifices through said medium so as to be uniformly treated to produce as-spun

polyester filaments of highly uniform physical properties.

5. The process as defined in claim 4 wherein said polyester is polyethylene terephthalate.

6. The process as defined in claim 4 wherein said steam is dry steam.

7. The process as defined in claim 4 wherein said steam is wet steam.

References Cited in the file of this patent

UNITED STATES PATENTS

2,335,922	Dreyfus	Dec. 7, 1943
2,377,810	Robbins	June 5, 1945
2,708,813	Bourgeaux	May 24, 1955
2,821,744	Spohn	Feb. 4, 1958

FOREIGN PATENTS

809,273	Great Britain	Feb. 18, 1959
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