Oct. 25, 1960 J. F. BOWLING 2,957,747

PROCESS FOR PRODUCING CRIMPABLE POLYAMIDE FILAMENTS

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Fig. 1

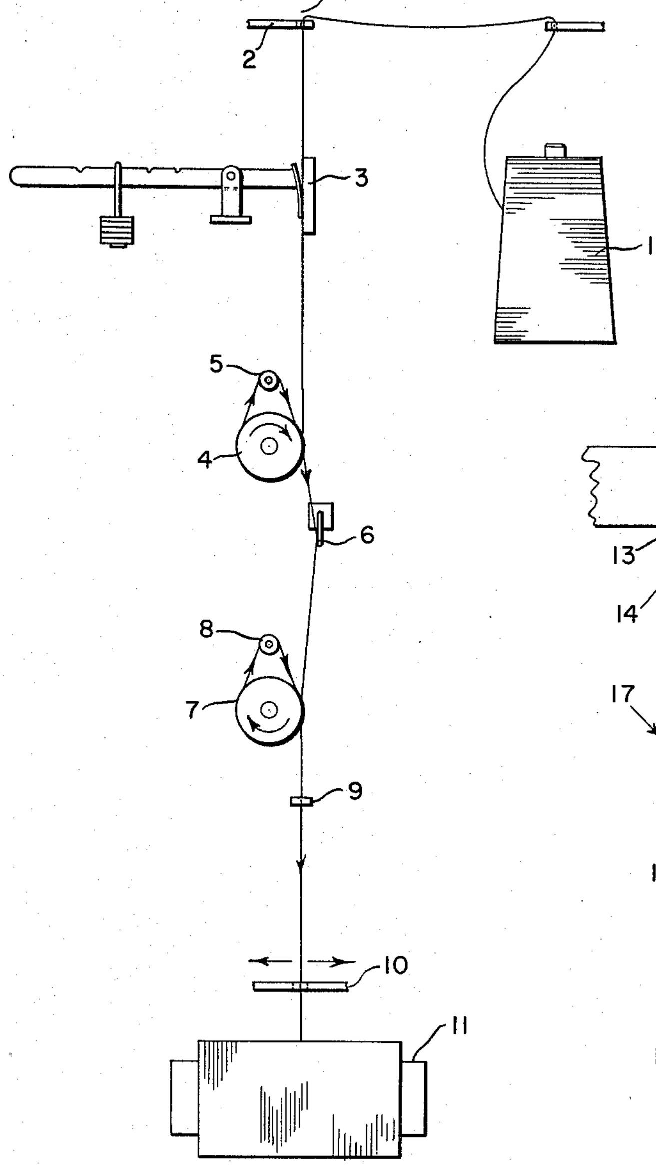

Fig. 2

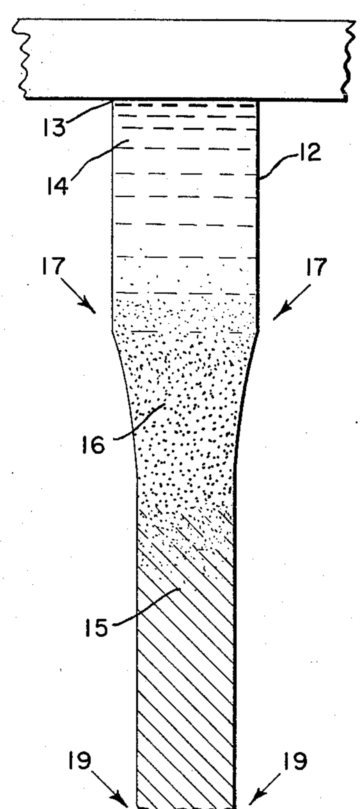

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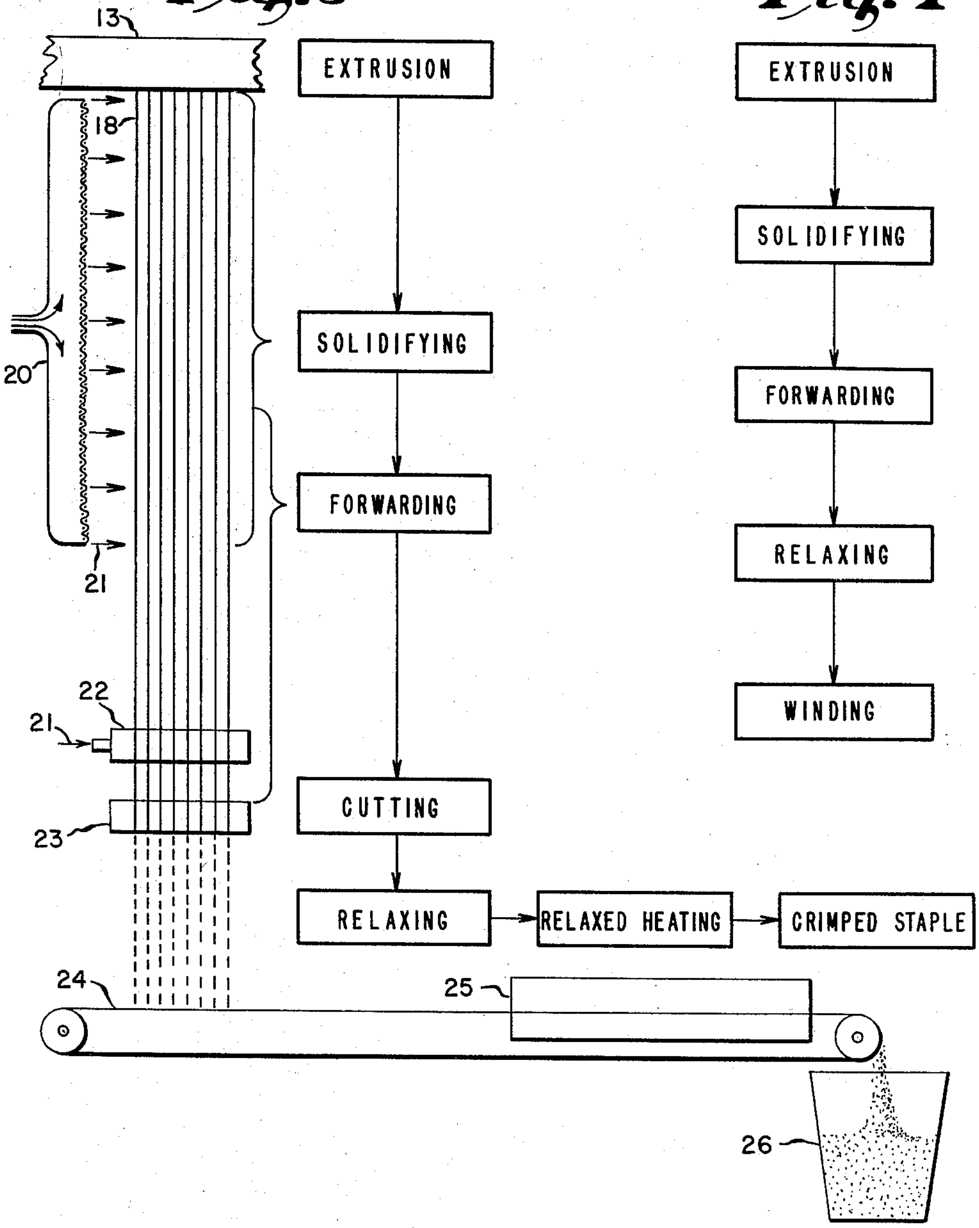
Fig. 3



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PROCESS FOR PRODUCING CRIMPABLE POLYAMIDE FILAMENTS

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3 Claims. (Cl. 18—54)

This invention relates to a process for preparing an oriented spontaneously crimpable polyhexamethylene adipamide yarn. More specifically, it is concerned with a process for preparing such a yarn, wherein the product possesses a relatively low initial tensile modulus combined with a relatively high dry tenacity.

By "spontaneously crimpable" is meant that when heated to a temperature between about 90° and 200° C. in a relaxed condition, the yarn or staple folds or plaits in small irregular undulation, to a degree suitable for mill processing. By the term "initial tensile modulus" (M_1) is meant the slope of the first reasonably straight portion of a stress-strain curve of a funicular structure, obtained by plotting tension on a vertical axis vs. fractional elongation ($\Delta 1/1$) on a horizontal axis as the structure is being elongated at the rate of 10% per minute under a standard condition of temperature (21° C.) and humidity (60% RH). In almost every instance, this first reasonably straight portion is also the steepest slope to be found on the curve. The values as used herein are in units of kilograms per square millimeter. This value is a measure of resistance to stretching and bending. The effects of the filament modulus are felt in a fabric chiefly when the fabric is folded or crushed in the hand or otherwise handled. If the modulus is too low, the fabric is "rubbery" or "limp"; with too high a modulus in the fibers, the fabric is "wiry" or "boardy." When the modulus is the proper range, a "soft" fabric results.

It is an object of the present invention to provide a process for the preparation of an oriented spontaneously crimpable polyhexamethylene adipamide yarn.

Another object is to provide a novel process for the preparation of crimped polyhexamethylene adipamide staple fiber.

A further object is to provide a process for the preparation of a spontaneously crimpable polyhexamethylene adipamide yarn possessing a relatively low initial tensile modulus combined with a relatively high dry tenacity.

These and other objects will become apparent in the course of the following specification and claims.

The invention will be more readily understood by reference to the drawings.

Figure 1 is a diagrammatic representation of the conventional process employed in the preparation of oriented polyhexamethylene adipamide yarn.

Figure 2 is a diagrammatic representation of a single strand of extruded mass illustrating the various stages in its transition from liquid to solid.

Figure 3 is a diagrammatic representation showing the preferred embodiment in the process for the preparation of crimpable polyhexamethylene adipamide staple fiber in accordance with the present invention.

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Figure 4 is a diagrammatic representation showing the preferred embodiment in the process for the preparation of crimpable polyhexamethylene adipamide continuous filament fiber in accordance with the present invention.

The production of high tenacity polyhexamethylene adipamide yarn is conventionally performed by extruding a molten mass of polymer through a suitably shaped orifice followed by quenching of the extruded form as a solid filament, the solidified filament being thereafter subjected to a drawing operation, generally over a pin, which may be hot or at room temperature. The drawing operation of such a process is illustrated in Figure 1. The source of solidified yarn **1**, which may be either a package or the solidified extruded mass fed directly from a spinneret, is led through guide **2** into tensioning device **3** and on to feed roller **4** and separator roller **5**. Thereafter it passes over the non-rotatable snubbing pin **6** (which may be maintained either at room temperature or heated). The drawing operation occurs as the yarn is removed from the snubbing pin due to the stretching action of drawing roller **7** which is operated at a higher speed than feed roller **4**. From the drawing roller the yarn then passes over separating roller **8** through guide **9** and is fed by means of the traversing guide **10** upon the wind-up bobbin **11**. Such a process is described in United States Patent No. 2,289,232, dated July 7, 1942. Other drawing processes are known to the prior art which avoid the use of a snubbing pin, employing a system of draw rolls such as disclosed in United States Patent No. 2,611,923, dated September 30, 1952. However, as pointed out previously, it is characteristic of all of the prior art processes to first produce a solidified, uniformly unoriented fiber form and thereafter orient it in the drawing operation. Such a fiber is not spontaneously crimpable.

In accordance with the present invention, an oriented spontaneously crimpable polyhexamethylene adipamide yarn is produced without first preparing an extruded solidified unoriented fiber form by a process which comprises attenuating the extruded flow from a spinneret orifice, said flow having a jet velocity of from about 1 to 100 yards per minute, in its area of non-tacky impressionable tractability by forwarding, within a minute or two after attenuation, the portion of shaped yarn form beyond the position of impressionable tractability at a rate of from about 3000 to about 6000 yards per minute into a relaxed stage wherein tension is withdrawn from the yarn. The oriented yarn, after attenuation, may be forwarded directly as a continuous filament into the relaxed stage or it may be sent to a cutter to be cut into staple before it is allowed to relax. Thereafter the yarn, either as continuous filament or as staple fiber is spontaneously crimpable by being heated while relaxed to a temperature within the range of from about 90° C. to about 200° C. The product retains its crimp on cooling.

By the term "area of non-tacky, impressionable tractability" is meant that area of extruded mass wherein the soldifying product is in a transistional, high plasticity stage between the liquid and solid states. This concept is illustrated in Figure 2. As the extruded stream **12** flows from the orifice of spinneret **13** it is initially a liquid, as represented by dashes **14**. As quenching occurs the viscosity increases and concurrent plasticity of product appears which on further quenching provides a solid, illustrated by the cross-hatching **15**. The area of transitional high plasticity is shown by dots **16**. In this area a state of non-tackiness is attained and it is apparent that the stress resulting from the application of the forwarding means at **19** carries back and is effective in this area as shown by arrows **17**. This point of applying the forwarding means is readily found in practice by shifting the forwarding means along the length of the extruded mass until the said means operates at its highest efficiency without adherence of adjacent filaments. Solidification occurs rapidly after the drawing due to the change in crystalline structure wrought by the molecular orientation and the increase in quenching efficiency resulting from decreased diameter of the filament. Contrary to the abrupt "necking down" observed in pin drawing operations, the draw of the present invention occurs gradually.

A preferred embodiment of the process of the present invention is illustrated in Figure 3. Essentially parallel streams of molten polyhexamethylene adipamide **18** are extruded from the orifices of spineret **13**, at a jet velocity in the orifice of from about 1 to about 100 yards per minute, into a quenching chimney **20** which cools the molten streams by a cross flow of air shown by arrows **21**. Forwarding air jet device **22** received the extruded mass beyond its area of non-tacky impressionable tractability and, by virtue of the action of the jet of air along the path of travel of the portion of shaped yarn beyond the position of intractability, forwards the yarn at a rate of from about 3000 to about 6000 yards per minute. The oriented yarn is then fed to a high speed cutter **23** which drops the staple upon a conveyor belt **24**. Thereafter the oriented staple is subjected to a temperature within a range of from about 90° to about 200° C. by means of hot air tunnel **25**. The fiber crimps spontaneously upon reaching this temperature range and within a period of about 1 to 15 minutes, for a 4 inch mat of staple, the crimped, oriented product is collected in baler **26**.

The same process as applied to a continuous filament is diagrammatically shown by Figure 4.

In a preferred embodiment of the present invention, the continuous filament of Figure 4 is, after attenuation, forwarded directly to the relaxed stage and cooled to a temperature not substantially above room temperature. The continuous filament is then sent to a cutter to be cut into staple fiber. As was hereinbefore pointed out, however, the cutting may precede the relaxed stage and the fiber still be spontaneously crimpable when heated to a temperature of about 90° to about 200° C.

In accordance with the process of the present invention, synthetic filaments and yarns are produced which have an initial modulus well below 100 kilograms per square millimeter (generally between 50 and 85) but tenacities of at least about 1.4 grams per denier, which are satisfactory for staple fibers. This compares with "as-spun" (i.e. with no drawing operation) tenacities of from about 0.2 to 0.8 grams per denier at elongations of several hundred percent and with conventionally produced fiber (subjected to drawing) tenacities of as high as 4 to 10 grams per denier. The high tenacity of the conventionally produced yarn is always accompanied by a very high initial modulus, in the order of 200 kilograms per square millimeter. Any attempt to reduce the initial modulus, for instance by reducing the conventional draw ratio, causes a sharp drop in dry tenacity. For instance, a fiber produced by conventional procedure and possessing an intial modulus of around 100 kilograms per square millimeter (produced by drawing the spun filament only about two times its extruded length) usually has a dry tenacity of less than 1.0 grams per denier and is not spontaneously crimpable. Furthermore, the synthetic fibers of the present invention have the desirable low modulus throughout the fiber length. This is accomplished by means of this invention because the filaments receive uniform treatment throughout their length during formation and subsequent processing. In the separate drawing step required in the conventional process, it is particularly difficult to obtain the proper uniformity along the fiber length at low draw ratios.

The polyhexamethylene adipamide yarn of the present invention requires a relaxing of the yarn within a few minutes after attenuation if it is to thereafter be spontaneously crimpable when subjected to heat. This is in sharp contrast to polyethylene terephthalate yarns which may be collected under tension from the forwarding means and thereafter crimped by heating.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner. The apparatus and technique described above under the discussion of Figure 3 is employed with slight variation in the step of spontaneous crimping. Spinning speed and crimping conditions are varied as indicated in Table 1 and the characteristics of the yarn produced are reported. The physical properties of the fibers are measured after the fiber samples are boiled in water for an hour. The fibers of each example are prepared from a polymer of 30 relative viscosity, prepared substantially as taught in Example 1 of United States Patent 2,163,584. Extrusion is through a 30 hole spinneret at a temperature of 285° C.

Table 1

Jet Velocity, y.p.m.	Ex.	Forwarding Speed [1]	Denier Filament	Orifice Diameter, Inches	Tenacity [2]	Tensile Strength [3]	Percent Elongation at Break	M_1	Crimping Conditions
14	1	4,200	3.6	0.015	1.5	15.4	132	51.3	Boiling water, 15 min.
16	2	4,600	3.8	0.015	1.6	16.4	125	55.4	125° C. air, 3 min.
15	3	4,900	3.3	0.015	1.7	17.4	108	63.6	Do.
18	4	5,300	3.7	0.015	1.7	17.4	95	67.6	Do.
13	5	5,500	2.7	0.015	2.0	20.5	87	63.6	30 p.s.i. steam, 5 min.
38	6	4,400	6.1	0.012	1.6	16.4	130	53.3	125° C. air, 4 min.
67	7	3,000	8.9	0.009	1.4	14.3	175	51.3	Do.
37	8	4,700	3.1	0.009	2.7	27.6	73	80.0	Do.
39	9	4,700	3.3	0.009	1.4	14.3	82	82.0	Do.
5	10	4,200	3.6	0.025	1.6	16.4	130	52.3	Do.

[1] Yards per minute.
[2] Grams per denier.
[3] Kilograms per square millimeter.

The forwarding speed can be varied over a wide range above 3,000 yards per minute. Lower forwarding speed results in lower tenacity yarns of limited utility. Above 3,000 yards per minute, the forwarding speed can be increased up to speeds where excessive filament breakage occurs. For example, at extrusion rates of 15,000 denyards (denier times yards per minute) the upper limit is about 6,500 yards per minute. At higher extrusion rates the forwarding speed can also be higher without excessive filament breaking at the spinneret. The upper practical limit for extrusion rate is about 41,000 denyards per spinneret hole. However, there is little to be gained in going above 6,000 yards per minute in forwarding speed in the production of a low-modulus yarn.

As shown in the table of examples, the physical properties of the yarns prepared by forwarding in the range of 3,000 to 6,000 yards per minute do not vary appreciably. Accordingly, the actual operating speed within this range will be dictated primarily by the denier per filament to be spun. Filament deniers of around 4 and less are conveniently spun at speeds approaching 6,000 yards per minute, while higher filament deniers should be spun at speeds nearer the 3,000 yards per minute end of the range.

The forwarding speeds of the process of this invention may be obtained by several methods. For instance, a driven bobbin, a high-speed pirn take-up, or an air jet may be used as the tensioning and forwarding device so that the yarn can be forwarded directly to a staple cutter without any intermediate wind up. When using an intermediate bobbin or pirn take up, provision must be made to permit the relaxation of the forwarded yarn, preferably while cooling to a temperature not substantially above room temperature, before the winding.

By "polyhexamethylene adipamide" is meant a polyamide which contains at least 90 mol percent of the recurring unit formed by the reaction of hexamethylenediamine and adipic acid or an amide-forming derivative thereof. During the preparation of this polyamide, minor amounts of a modifying material may be added, for example, a mordant, a dye, a delustrant, a viscosity stabilizer, another diamine, another dicarboxylic acid and the like. Thus suitable materials comprised essentially of polyhexamethylene adipamide, may have in the polymerization mass up to 10 mol percent of a modifying monomer or mixture of such monomers, such as octamethylenediamine, decamethylenediamine, sebacic acid, azelaic acid, hexahydroterephthalic acid and the like. These modifiers may be added as one of the initial reactants during the polymerization process, but the modifying materials may also be polymerized separately and then melt-blended with the polyhexamethylene adipamide. In either case, the total amount of modifier in the final polymeric material should not exceed about 10 mol percent. While the polymerization process is preferably carried out in the melt, it may also be performed in the solid phase, or in solution or emulsion by conventional procedures. A typical polymerization process for the type of polyamides comprehended herein is disclosed in U.S. Patent No. 2,130,948.

As explained above, after preparation of the polymer, it is extruded by conventional procedure through a spinneret into a cooling area. The molten polymer may be extruded through a spinneret at temperatures within the range of 260° to 310° C. For optimum results this extrusion temperature should be between 280° to 295° C. although properties of the final yarns vary but little over the entire range. The preferred temperature range is from 10° to 20° C. lower when copolymers of hexamethylene adipamide are used, depending on the copolymer, and typically in the range of 270° to 275° C. When the molten polymer is extruded into room temperature air, the resulting filaments, when 3 denier, should be allowed to travel at least 45 to 50 inches before they reach the forwarding means. This distance is required for sufficient solidification to prevent adherence or other damage to the filaments and is a function of the filament denier, e.g. for 1 denier filaments the distance should be at least about 33 inches and for 6 filaments at least about 75 in. When the distance is less, fused filaments often result with an otherwise standard spinning procedure because of inadequate quenching time. The means for forwarding the filaments at about 3000 to about 6000 yards per minute may comprise a high speed wheel, roll or pinch rolls, an air jet or other suitable means. Under the impetus imposed by the forwarding means, the filaments elongate in the distance between the spinneret face and the point of complete solidification. The inertia of the material apparently provides sufficient drag on the filaments to induce orientation of the polymer molecules in the solidification range. Actually, no useful orientation takes place until the filamentary streams begin to solidify. For several inches from the spinneret, the filaments appear to be just dangling from the spinneret. In the solidification range, the filaments can be seen to accelerate and become taut fibers, moving along their length at high speeds. The phenomenon can further be detected by feeling the air dragged along with the filaments, beginning at the solidification range. It is the completely uniform partial orientation taking place at this point which accounts for the low modulus and other useful properties of the yarn spun by the process of this invention.

It is essential to attain the property of spontaneous crimpability, that the yarn or fiber be relaxed after the forwarding operation and prior to winding under tension on a bobbin; or prior to forwarding under tension where such forwarding takes more than about 1 minute before release of the forwarding tension. Thus if the yarn is taken immediately from the forwarding means under tension and wound upon a bobbin or the like, under tension, without an intermediate relaxing stage, it will not thereafter be spontaneously crimpable. Therefore, if the feed from the forwarding means is fed substantially immediately to a cutter to form relaxed staple it may thereafter be immediately subjected to high temperature to give spontaneous crimping.

The product of the present invention is spontaneously crimpable, i.e., it may be crimped by subjecting it to relaxed heating at a temperature of from about 90° to 200° C. Suitable heating media for crimp induction include hot air, hot or boiling water, saturated or superheated steam, and various hot solutions that exert a mild plasticizing action on the polyamide material. This heat treatment also stabilizes the yarns and increases the degree of crystallization while at the same time reducing residual shrinkages. In general a period of from about 1 to about 15 minutes is sufficient within this range to attain the desired crimp.

The outstanding advantage of the products of the process of the present invention is that valuable polyhexamethylene adipamide fibers and yarns having suitable strength for use as staple combined with a low modulus are produced directly without the necessity of after-drawing operation. The spinning process also operates at exceptionally high speeds. Both of these advantages contribute to increased production and a saving in manpower and equipment.

The low-modulus yarns produced by the process of this invention have great utility in the apparel field. They are useful particularly in staple form in soft felts of various kinds, including paper-maker's felts, knitting yarns, and in woven and knit goods such as sweaters and socks. Relatively heavy denier per filament yarn (6 to 10 denier per filament) may be used in the preparation of knit and woven goods which have a soft and pleasing hand. The pilling tendency of garments, such as socks and sweaters, made from the low modulus staple fibers of this invention, is eliminated at the high denier per filament level and greatly minimized at the lower denier per filament level.

This case is a continuation in part of United States applications Serial No. 212,494, filed February 23, 1951 and Serial No. 545,334, filed November 7, 1955.

What is claimed is:

1. A process for producing a yarn containing at least 90 mol percent of polyhexamethylene adipamide which comprises extruding the molten polymer through a spinneret, attenuating the extruded flow from the spinneret orifice, said flow having a jet velocity of from about 1 to about 100 yards per minute, in its area of non-tacky impressionable tractability, by forwarding, within a few minutes after attenuation, the portion of the shaped yarn from beyond the position of impressionable tractability at a rate of from about 3000 to about 6000 yards per

minute and cooling the forwarded yarn in a relaxed state to a temperature not substantially above room temperature.

2. A process for producing a crimped yarn containing at least 90 mol percent of polyhexamethylene adipamide which comprises extruding the molten polymer through a spinnert, and attenuating the extruded flow from the spinneret orifice, said flow having a jet velocity of from about 1 to about 100 yards per minute, in its area of non-tacky impressionable tractability, by forwarding, within a few minutes after attenuation, the portion of the shaped form beyond the position of impressionable tractability at a rate of from about 3000 to about 6000 yards per minute into a relaxed stage wherein tension is released from the yarn and thereafter heating the product to a temperature within the range of from about 90° to about 200° C.

3. A process for producing a crimped yarn containing at least 90 mol percent of polyhexamethylene adipamide which comprises extruding the molten polymer through a spinnerer, and attenuating the extruded flow from the spinneret orifice, said flow having a jet velocity of from about 1 to about 100 yards per minute, in its area of non-tacky impressionable tractability, by forwarding, within a few minutes after attenuation, the portion of the shaped yarn form beyond the position of impressionable tractability at a rate of from about 3000 to about 6000 yards per minute, cooling the forwarded yarn in a relaxed state to a temperature not substantially above room temperature and thereafter heating the product to a temperature within the range of from about 90° to about 200° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,252,684 Babcock ---------------- Aug. 19, 1941
2,604,689 Hebeler ---------------- July 29, 1952