

Jan. 26, 1971

E. H. OLSON

3,558,760

PROCESS FOR SPINNING TWO COMPONENT POLYAMIDE FILAMENTS

Filed Dec. 17, 1969

4 Sheets-Sheet 1

Fig. 1.

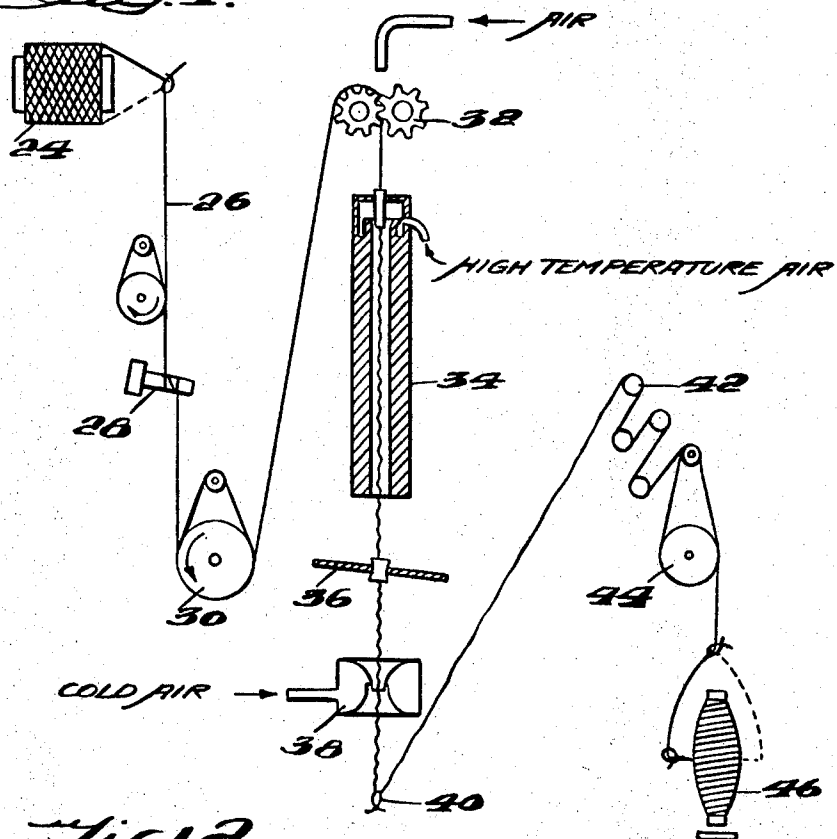
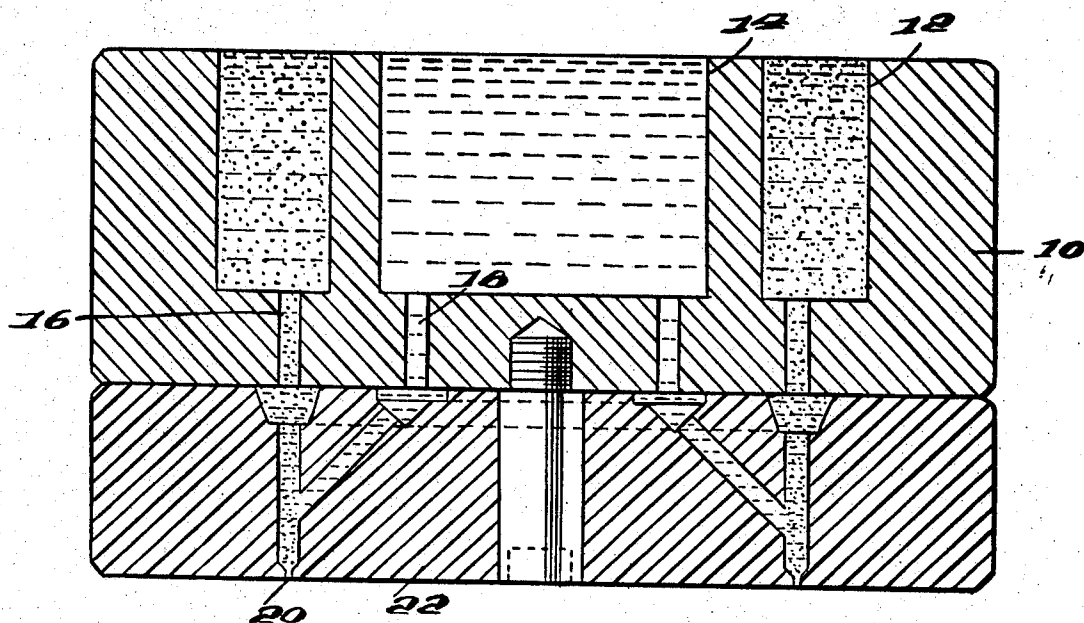


Fig. 2.



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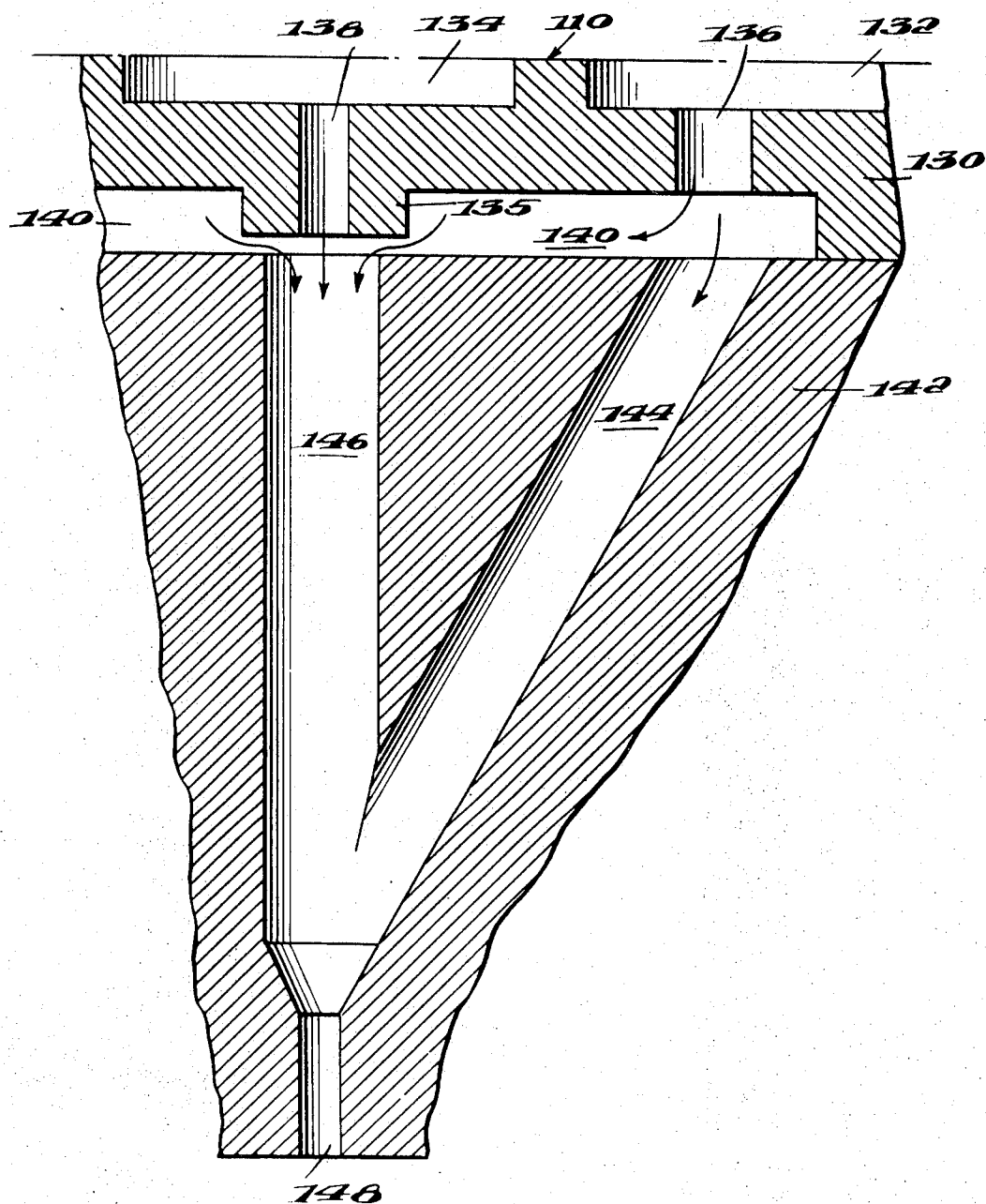
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Fig. 3.



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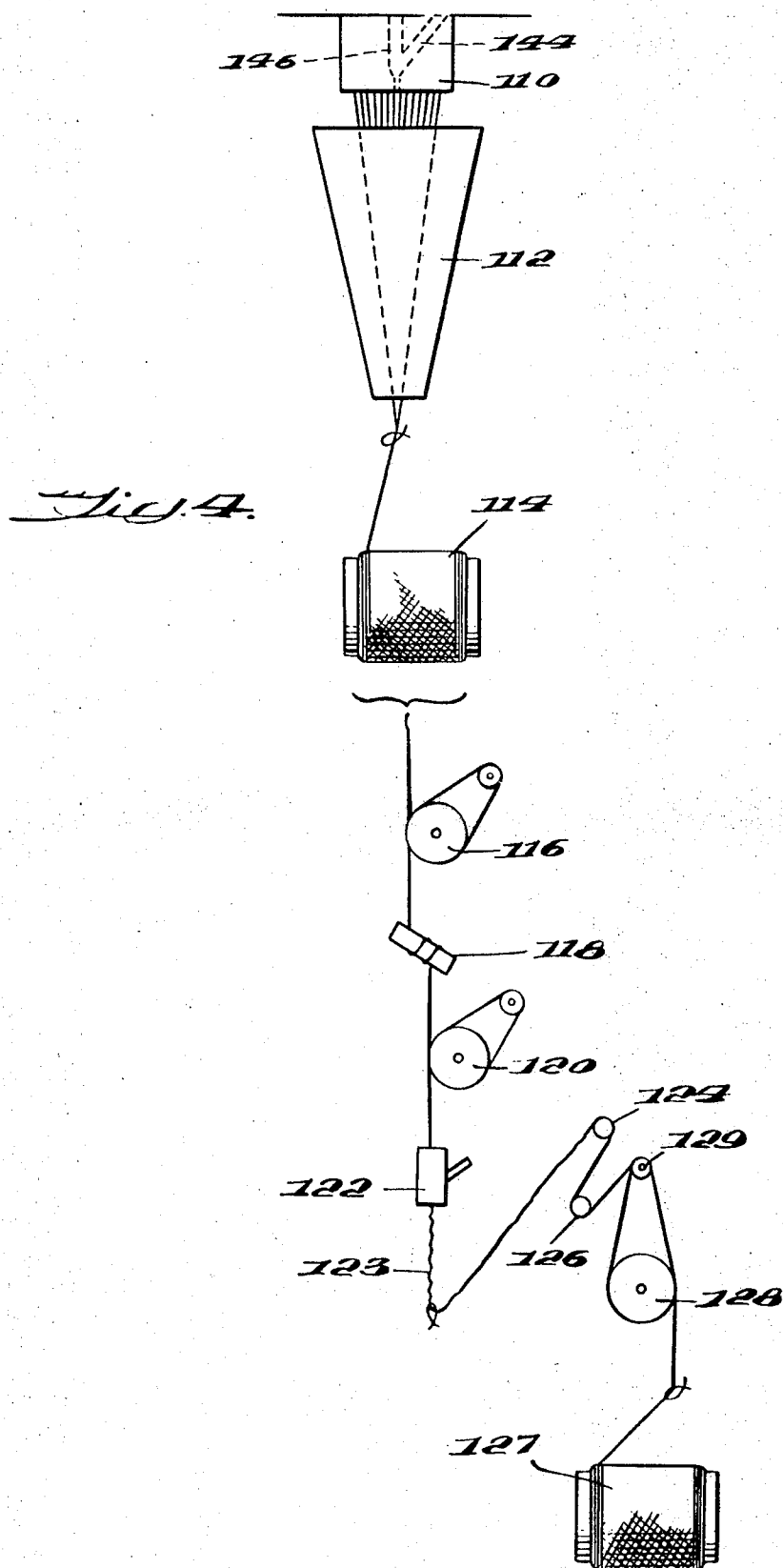
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PROCESS FOR SPINNING TWO COMPONENT POLYAMIDE FILAMENTS

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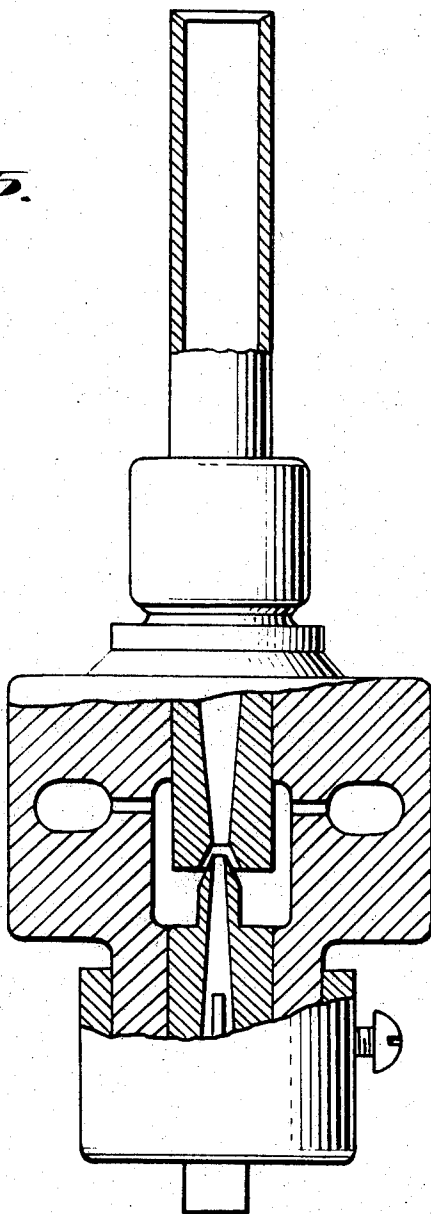
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Fig. 5.



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3,558,760

PROCESS FOR SPINNING TWO COMPONENT POLYAMIDE FILAMENTS

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Continuation-in-part of application Ser. No. 754,828, Aug. 23, 1968, which is a continuation-in-part directed to subject matter divided from application Ser. No. 465,121, June 18, 1965, now Patent No. 3,399,108, the latter being a continuation-in-part of application Ser. No. 335,187, Jan. 2, 1964, which is a continuation-in-part of application Ser. No. 202,611, Jan. 14, 1962, which in turn is a continuation-in-part of application Ser. No. 132,449, Aug. 18, 1961, all abandoned. This application Dec. 17, 1969, Ser. No. 886,034

Int. Cl. B29f 3/10; D01d 5/22

U.S. Cl. 264—168

9 Claims

ABSTRACT OF THE DISCLOSURE

The production of a crimpable filament by drawing, heat relaxing, cooling and stretching a melt spun composite of eccentrically disposed, differentially shrinkable components of different nylon compositions. Crimp developed in the heat relaxing step is pulled out in the stretching step, leaving the filament crimpable.

This is a continuation-in-part of my copending application Ser. No. 754,828, filed Aug. 23, 1968, which was a continuation-in-part directed to subject matter divided from my application Ser. No. 465,121, filed June 18, 1965, now U.S. Pat. 3,399,108. The latter was a continuation-in-part of application Ser. No. 335,187, filed Jan. 2, 1964, which was a continuation-in-part of application Ser. No. 202,611, filed Jan. 4, 1962, which was a continuation-in-part of application Ser. No. 132,449, filed Aug. 18, 1961, all now abandoned.

Avoidance of various difficulties encountered with earlier hosiery yarns has been attributed, in the above-identified applications, to the crimp retractive force of a crimpable, composite, nylon filament comprised of continuous, adherent, eccentric, fiber-forming components of a crystalline polyamide and a nonisomorphic, random copolyamide. This invention relates to a process for the preparation of such filaments.

When polymer unit combinations are selected and the filaments are processed in accordance with the teachings of the present invention, the nonisomorphic copolyamide component is characterized by equatorial X-ray reflections similar to those exhibited by the crystalline homopolyamide. The filaments have the further characteristic of crimping helically with the copolyamide component as the load bearing member when subjected to steam, the crimp retractive force being sufficient to cause the filament to crimp when under a slight tension, e.g., when in a fabric. For use in hosiery leg yarn, the monofilaments should retract by at least 12% of their length upon exposure to 100° C. steam at atmospheric pressure (hereinafter referred to as "atmospheric steam") while under a restraint of 0.0012 g.p.d. They should have a retraction due to crimping of at least 24% upon exposure to a 118° C. steam atmosphere while under a restraint of 0.0012 g.p.d.

Such crimpable filaments are prepared by extruding the homopolyamide and random copolyamide components in eccentric relationship to form a composite filament, drawing the filament under conditions such that the homopolyamide component becomes crystalline and oriented and subsequently relaxing while simultaneously heating

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the filament, thus producing a crimped composite structure in which both components exhibit the equatorial X-ray reflections characteristic of a crystalline homopolyamide. Both components must be of fiber-forming molecular weight to give the desired level of processability and fiber properties. Preferably, the filaments are heated with very low or no tension applied in the heating-relaxing step, cooled as the running length advances through a room temperature environment and then stretched to remove crimp induced by differential shrinkage in the heat relaxation step. The time-temperature relationship of the heat relaxation step is sufficient to produce the desired X-ray diffraction appearances in the nonisomorphic copolyamide component. For this purpose, a temperature of at least 140° C., but below the softening point of either component, is applied for a sufficient period of time to permit the filament to crimp to the desired extent.

When reheated, the stretched filaments have sufficient crimping force to develop crimp after having been incorporated into a hose fabric and to thereby impart stretchability to the hose.

When employed in fabrics where increased bulk and covering power are desired, multifilament yarns processed in accordance with this invention crimp, when heated in the fabric, with the crimps out-of-phase relative to crimps in adjacent filaments. Prior art bicomponent yarns, when crimped in the fabric, develop in-phase crimps and thus provide much less bulk and covering power.

Objectives and advantages of the process will be apparent from the following specification and examples wherein reference is made to the accompanying drawings

FIGS. 1 and 4 are schematic representations of equipment which was used in processing the spun filaments exemplified hereinafter;

FIGS. 2 and 3 are fragmentary transverse sectional views of spinnerets employed in the spinning steps; and

FIG. 5 is a plan view of the jet device shown schematically in FIG. 4, parts having been broken away and shown in section to reveal details of construction.

As used herein, the term "eccentric" is meant to include both side-by-side and truly eccentric sheath-core structures.

The expression "relative viscosity" signifies the ratio of flow time in a viscometer of a polyamide solution containing 8.2±0.2% by weight of polymer relative to flow time of the solvent by itself. Measurements of relative viscosity are made with 5.5 grams of polyamide in 50 ml. of 90% formic acid at 25° C.

The X-ray measurements referred to herein may be made in the following manner. The composite filaments are exposed on a Hilger semi-micro-focus diffraction unit using a flat plate Norelco micro-camera similar in design to that described by Fankuchen and Mark, J. Applied Physics 15, 364 (1944). Side-by-side composite filaments are mounted in the camera, with the aid of a microscope, in such a manner as to place only one component in the path of the X-ray beam. In the case of eccentric sheath-core filaments, the filament is mounted so that the X-ray beam passes through only one half, or preferably somewhat less than one half, of the filament. If the microscopic location technique should prove unsatisfactory, the sheath-core filament is then rotated 45° around its long axis and the measurement repeated. This is continued until eight measurements have been made. If any one of these measurements indicates a lack of crystallinity, the measurements should be repeated. If confirmed, the measurement indicates that one of the components does not have the required crystallinity.

The degree of crystallinity is determined from radial densitometer traces along the equator of the X-ray diagram. Such a trace, for a polyamide with well-developed 100 and 010, 110 reflections, will show two distinct peaks.

As the degree and perfection of crystallinity decreases, these peaks move together and broaden. For samples of very low crystallinity, they merge into a single peak. A parameter indicating crystal perfection is the ratio of the equatorial distance of separation of the outside peaks (010, 110 planes) to the equatorial distance of separation of the inside peaks (100 plane). When this peak ratio becomes less than 1.10 some difficulty may be encountered in determining the ratio with a high degree of accuracy.

As discussed more fully hereinafter, some nonisomorphic copolyamides do not develop a truly crystalline structure but do develop a crystal-like structure which gives the equatorial X-ray reflections characteristic of a truly crystalline structure. It is to be understood that where reference is made to crystalline structure, such crystal-like structures are meant to be included, i.e., any structure which gives equatorial X-ray reflections characteristic of a crystalline structure is considered to be crystalline for the purposes of this invention.

EXAMPLE I

An evaporator is charged with 296 pounds of a 36.2 percent aqueous solution of hexamethylenediammonium sebacate (6-10 salt solution prepared from hexamethylene diamine and sebacic acid, the sebacic acid containing about 8% by weight of a mixture of undecanedioic and dodecanedioic acids as impurities) and 225 pounds of a 48.9% aqueous solution of hexamethylenediammonium adipate (6-6 salt solution) and 159 pounds of water are removed by evaporative heating at atmospheric pressure. After adding 230 grams of 25% aqueous acetic acid solution to the salt solution as a viscosity stabilizer, the solution is transferred to an autoclave, heated to a temperature of about 210° C. and brought to a pressure of 250 p.s.i.g. At this point, 1295 grams of a 20% aqueous slurry of titanium dioxide are added. The solution is then heated at 250 p.s.i.g. for a period of 3 hours, the temperature increasing to 274° C. during this time. Pressure is reduced over a period of 130 minutes to atmospheric and the temperature is increased to 279° C. The polymer is then held for 60 minutes at this temperature, extruded under 75 p.s.i.g. nitrogen in the form of a ribbon, quenched on a water cooled casting wheel and cut into 3/8 inch flakes in the conventional manner. The non-isomorphous copolymer consisting of 50% polyhexamethylene adipamide and 50% polyhexamethylene sebacamide/undecanedioamide/dodecanedioamide has a relative viscosity of 54.

Polyhexamethylene adipamide (6-6 nylon) flake having a relative viscosity of 45 is prepared in the conventional manner. The two flakes (6-6 and 6-6/6-10/6-11/6-12) are melted separately and pumped to a spinneret assembly of the type shown in FIG. 2. This assembly includes a block 10 provided with a first ring-shaped cavity 12 and a second cavity 14. Each cavity discharges through one of the passages 16, 18 to each of the several holes 20 in spinneret plate 22. The spun filaments are air quenched and each is wound into a package 24 (FIG. 1) in the conventional manner. The filament 26 is subsequently withdrawn from the package, drawn at 770 yards/minute to a ratio of 5.3 over a draw pin 28 heated to 105° C. and passed from the draw roll 30 through a pair of meshing nylon gears 32. As shown in FIG. 1, these gears are rotated by means of an air jet and function to pull the drawn yarn from the draw roll, to prevent back wrapping and to overfeed the yarn into a crimping chamber 34 in the form of a narrow elongated channel where low tension exists. In chamber 34, the yarn is crimped into helical form by a concentric jet of heated air which passes through the channel with the yarn and is controlled in such a manner as to give an air temperature of 155° C. (311° F.) at the chamber exit. The yarn is then passed through an eyelet in a baffle plate 36 which functions to deflect most of the hot ex-

haust air away from a cold air aspirator 38. The yarn is then cooled by passing it through aspirator 38 in which room temperature air is drawn over the yarn. From the cold air aspirator, the crimped yarn is led through a lower guide 40 and then around four snubbing pins 42 where tension is applied to remove the crimp before the yarn passes around withdrawal roll 44 to package 46. It is permitted to retract by 22% of its as-drawn length between draw roll 30 and withdrawal roll 44.

A skein of the 15 denier monofil is prepared by winding 50 loops to give a 1500 denier skein of about 55 cm. length when suspended with a weight attached. The skein is hung on a hook with a 500 gram weight (0.33 g.p.d.) suspended from its other end. After one minute, the length (a) of the skein is measured and found to be 55.8 cm. The 500 gram load is removed and a 1.8 gram load is applied in its place so that the skein is under a tensile load of 0.0012 g.p.d., i.e., a tension slightly in excess of that on the yarn when knitted into a fabric. Steam at atmospheric pressure is then applied over the entire length of the skein for one minute and the skein is allowed to dry in air for 10 minutes, after which the skein length (b) is measured and found to be 43.3 cm. The retraction in length is due to the initial shrinkage of both components followed by additional shrinkage of the copolyamide component which results in the development of a spiral crimp. The 1.8 gram load is then removed, a 500 gram load is again applied for one minute and the length (c) of the skein again determined and found to be 55.0 cm. The crimp retraction and shrinkage of the filament are then calculated as follows:

$$\begin{aligned} \text{Crimp retraction, percent} &= 100 \times \frac{c-b}{c} \\ &= 100 \times \frac{55-43.3}{55} = 21.3 \end{aligned}$$

$$\text{Shrinkage, percent} = 100 \times \frac{a-c}{a} = 100 \times \frac{55.8-55}{55.8} = 1.43$$

For purposes of comparison, it is noted that drawn 15 denier monofil of the same composition which have not been heat relaxed were tested in atmospheric steam and found to have crimp retractions ranging from 1-5%. Hose knitted from monofil having such a low level of crimp retraction would not show any appreciable improvement in fit and comfort over available hose of conventional construction.

In another test, crimp retraction of 22% heat relaxed filaments of the same composition is determined according to the same procedures except that the skein, bearing the 1.8 gram load, is subjected to steam at 118° C. (245° F.) in a conventional hosiery boarding oven. Under these conditions, the crimp retraction is 32.5% and the shrinkage is 8%. The helix spacing and diameter of these filaments are measured under a tension of 0.0012 g.p.d. by taping one-inch lengths of the crimped, tensioned filament on a microscope slide and projecting the magnified image on a grid covered screen by means of a projection microscope. The average helix diameter is found to be 9 mils and the average spacing of the helices is 26 mils.

Forty total denier, 13-filament crimpable yarn is prepared as described above except that the draw ratio is 3.82, the drawpin temperature is 98° C. and the yarn is permitted to contract only 18% in the relaxation-cooling-stretching steps. The crimp developed in the individual filaments is generally out-of-phase relative to crimp in adjacent filaments, and this characteristic persists when the yarn is crimped in hose. This yarn has a crimp retraction of about 6.5% in atmospheric steam. Since it is used in the welt, heel and toe of the hose, the higher crimp retraction possessed by the 22% relaxed monofilaments is not required.

X-ray measurements on each component of the 22% relaxed composite filaments are made as previously described. Values, where determinable, for filaments after

drawing as well as after heat treatment, cooling and stretching, are reported in the following table:

TABLE 1

6-6 component:	Peak ratio
(1) After drawing -----	1.092
(2) Final filament -----	1.137
6-6/6-10/6-11/6-12 component:	
(1) After drawing -----	1.00
(2) Final filament -----	1.139

The 100 and 010, 110 peaks on the densitometer trace were separated to some extent in the case of the 6-6 component after drawing, as signified by the peak ratio of 1.092 which indicates a substantial degree of crystallinity. No separation of the peaks occurred in the case of the copolymer component after drawing, as signified by the 1.00 ratio which indicates a very low degree of crystallinity. After the relaxed heat treatment, however, distinctly separate peaks were observed as indicated by the higher ratios.

Women's hose are knitted using the 15 denier monofil, except in the welt, heel and toe where the 40 total denier 13 filament yarn is employed. The course count, as measured on a volumetric hose board, is kept in the range of 45 to 70 courses per inch over the knee, calf and ankle sections of the hose. The hose feet are knitted ½ size larger than the finished size desired. The hose are wrapped loosely in cheese cloth, boiled off in hot water for ten minutes and put on a hose board. It is found that when a standard hose board is used the resultant hose is narrower than desired. This condition is corrected by boarding on a standard board and measuring the resulting width at the various parts of the hose. The ratio of standard board width obtained is then multiplied by the desired hose width to give the board width required at this location in the hose. It is also found that the optimum boarding length is 4-5 inches shorter than the knitted length. Boards are then constructed to this design and the hose placed on the board and steamed for 10 minutes with 5 p.s.i.g. steam. The manner in which the hose shrink to the board is indicative of the extent of crimp retractive force developed in the two-component filaments. The hose are dyed in the conventional manner, placed while damp on the hose board and steamed as before.

The finished hose are somewhat similar in appearance to nonstretch hose although slimmer and slightly shorter but have the fit and comfort of stretch hose. The clarity of stitch is greatly superior to that of stretch hose so that the hose of this invention have a much better appearance when displayed for sale, as well as on the wearer's leg.

The two components of each filament adhere sufficiently to prevent filament splitting and the resultant undesirable effects when the hose are placed in use.

EXAMPLE II

Example I is repeated except that the pin 28 is only heated to 40° C. and the yarn is passed at a speed of 843 y.p.m. upwardly from draw roll 30 through an inverted crimping chamber 34, carried through the crimping chamber by the hot air stream, advanced over a pin located at about the same position as gears 32 (FIG. 1), which are omitted, and then passed downwardly to guide 40, the baffle plate 36 and aspirator 38 being omitted. From guide 40, the yarn advances as shown in FIG. 1. Air temperature at the exit of the inverted chamber 34 is 195° C. and the yarn is permitted to retract 22% between draw roll 30 and withdrawal roll 44. Between snubbing pins 42 and roll 44, it is placed under tension to remove the crimp. Cooling of the yarn is achieved in the room temperature environment between crimping chamber and snubbing pins 42. When the yarn is tested as described in Example I, the results are substantially the same except that the crimp retraction under 0.0012

g.p.d. load is 14.4% with atmospheric steam and 27% with 118° C. steam.

When the above procedure is repeated except that the yarn is passed directly from the guide pin above the inverted chamber 34 to and over one of the pins 42 and thence directly to windup package 46 where the yarn is wound at a tension of 3-5 grams, the crimping action in the heated zone is largely eliminated and the resulting yarn has a crimp retraction in atmospheric steam of only 5-6%. Hose from this yarn do not provide a satisfactory fit.

EXAMPLE III

A two-component filament is extruded and processed as described in Example I except that polycaproatamide (6 polymer) of 45 relative viscosity is substituted for the 6-6 homopolymer component. The results are substantially the same except that the shrinkage is about 2% and the crimp retraction under 0.0012 g.p.d. is about 20% with atmospheric steam and about 33% with 118° C. steam.

EXAMPLE IV

48% aqueous solution of hexamethylene diammonium adipate (6-6 nylon salt) is charged to an evaporator. A 40% aqueous solution of hexamethylene diammonium isophthalate (6-I), prepared by combining equimolar proportions of hexamethylene diamine and isophthalic acid, is added to the evaporator in sufficient amount to provide 27% by weight of hexamethylene diammonium isophthalate based on the total weight of dry salt present. The salt solution is then evaporated to a 75% concentration level, at which point the temperature is about 138° C. The 75% salt solution is charged to an autoclave and heated to a temperature of about 242° C. and 250 p.s.i.g. pressure, about 85 to 90 minutes being required for this operation. The pressure is then reduced over a period of 85 minutes to atmospheric pressure and the temperature is increased to 270-275° C. The copolymer is held for 40 minutes at this temperature, extruded in the form of a ribbon, quenched on a water-cooled casting wheel and cut into ½ inch flakes in the conventional manner. The copolymer has a relative viscosity of 39.

6-6 nylon flake prepared as described in Example I and the 6-6/6-I flake are melted separately, extruded together to form side-by-side filaments which are quenched, wound, subsequently withdrawn from the package, drawn to 15 denier at a ratio of 4.67, crimped by heating under low tension, cooled and stretched to remove the crimp, all as described in Example I.

The filaments are then crimped while under a tension of 0.0012 g.p.d. and the crimp retraction, determined as in Example I, is found to be 20% in atmospheric steam and 34.5% in 118° C. steam. The shrinkage of the filament in 100° C. steam is 5%. The shrinkage of the filament in boiling water in a relaxed state is 10%. When hose are knitted and treated, the results are substantially the same as observed in Example I.

X-ray measurements are made on each component of the composite filament, as in Example I. The results, reported in Table 2 below, indicate that both components, after relaxed heat treatment, show the equatorial X-ray reflections which are characteristic of crystalline homopolyamides.

TABLE 2

6-6 component:	Peak ratio
(1) After drawing -----	1.092
(2) Final filament -----	1.137
6-6/6-I component:	
(1) After drawing -----	1.00
(2) Final filament -----	1.133

EXAMPLE V

After charging an evaporator with 3230 g. of a 35.0% aqueous solution of hexamethylenediammonium do-

decanedioate (6-12 salt solution) and 2360 grams of a 48.5% aqueous solution of hexamethylenediammonium adipate (6-6 salt solution), 1780 grams of water are removed by evaporative heating at atmospheric pressure. The solution is then transferred to an autoclave, heated to a temperature of 215° C. and brought to a pressure of 250 p.s.i.g. At this point, 35 grams of a 20% aqueous slurry of titanium dioxide are added. The solution is then heated at 250 p.s.i.g. for a period of two hours, the temperature increasing to 270° C. during this time. The pressure is reduced over a period of sixty minutes to atmospheric and the temperature is increased to 278° C. The polymer is then held for 60 minutes at this temperature, extruded under 75 p.s.i.g. nitrogen to form a ribbon, quenched on a water-cooled casting wheel and cut into $\frac{3}{16}$ " flake in the conventional manner. The copolymer consisting of 50% polyhexamethylene dodecanedioamide units and 50% polyhexamethylene adipamide units has a relative viscosity of 53.

The above flake (6-6/6-12) and polyhexamethylene adipamide (6-6) flake having a relative viscosity of approximately 45 were then spun as side-by-side two-component filaments, drawn, heat-relaxed, cooled and stretched, as described in Example I. Crimp retraction and shrinkage values substantially equivalent to those of Example I were obtained.

X-ray measurements on the 6-6/6-12 and the 6-6 components were made separately as previously described. The values for these two-component filaments show essentially the same relationship as between the 6-6 and 6-6/6-10 components of Example I. The degree of crystallinity of the 6-6/6-12 component has been changed from low up to a satisfactory level.

TABLE 3

6-6 component:	Peak ratio
(1) After drawing	1.110
(2) Final filament	1.151
6-6/6-12 component:	
(1) After drawing	1.069
(2) Final filament	1.194

The crimp retraction in atmospheric steam is 17.4% and in 118° C. steam is 32%.

Women's hose were knit and treated in a manner similar to Example I, except that they were treated with atmospheric steam rather than hot water before boarding. They displayed the advantages in appearance, fit and comfort shown in Example I.

EXAMPLE VI

An evaporator is charged with 370 gallons of an aqueous solution of hexamethylenediammonium sebacate (6-10 salt solution prepared as in Example I) containing 1,132 pounds of dry salt and 260 gallons of an aqueous solution of hexamethylenediammonium adipate (6-6 salt solution) containing 1,163 pounds of dry salt and the resulting solution is heated at 13 p.s.i.g. until the temperature reaches 132° C., giving a salt concentration of approximately 75%. The solution is then transferred to an autoclave, heated to a temperature of about 205° C. and brought to a pressure of 250 p.s.i.g. At this point, sufficient 20% aqueous titanium dioxide slurry is added to give a concentration of 0.3% TiO₂ in the final polymer. The solution is then heated at 250 p.s.i.g. until the temperature reaches 225° C. The pressure is then reduced over a period of 80 minutes to atmospheric and the temperature is increased to 250° C. The polymer is then held, at atmospheric pressure, for 30 minutes at a temperature of 250-260° C., extruded under 90 p.s.i.g. nitrogen in the form of a ribbon, quenched on a water-cooled casting wheel and cut into $\frac{5}{16}$ -inch flake in the conventional manner. The copolymer, consisting of 50% polyhexamethylene adipamide and 50% polyhexamethylene sebacamide/undecanedioamide/dodecanedioamide, has a relative viscosity of 45.

Polyhexamethylene adipamide (6-6 nylon) flake having a relative viscosity of 46.5 is also prepared in the conventional manner. The two flakes (6-6 and 6-6/6-10/6-11/6-12) are fed separately to a dual screw melter where the flake is first conditioned by exposure to humidified nitrogen at 125° C. and then melted and pumped to a spinneret assembly of the type shown in FIGS. 3 and 4. The relative viscosity of the 6-6 flake after conditioning is 50 and that of the copolymer flake is 55. The melt temperature of the 6-6 is 290° C. and that of the copolymer is 282° C. The two polymers are extruded, with the copolymer as the core, to form eccentric sheath-core hosiery monofilaments containing equal amounts of the copolymer and homopolymer. The sheath, at its thinnest point, has a thickness equivalent to about 1% of the total filament diameter. The clearance between the projection 135 on pack 130 and spinneret plate 142 is 0.003 inch. The filaments are set by quenching, using a 60-inch chimney and an air temperature of 45° C., steam conditioned as described in U.S. Pat. No. 2,289,860 and each is wound into a package 114 (FIG. 4) at 461 y.p.m. That monofilament is subsequently withdrawn from the package and drawn to a ratio of 4.95 over an unheated draw pin 118 situated between rolls 116 and 120 to give a final denier of 15. It is passed from the second draw roll through a tubular crimping chamber 122, three inches in length, at 563 y.p.m. As shown in FIG. 5, the crimping chamber is an elongated conduit on a jet device or gas delivery means to which 0.5 cubic feet/minute of heated air at 30-38 p.s.i.g. is introduced to give an air temperature of 201-208° C. at the exit. The yarn which is under low tension in the crimping chamber is crimped into helical form as indicated at 123 and then led over snubbing pins 124 and 126 to remove the crimp by stretching the yarn slightly. The crimpable monofilament is then wound into a package 127. The relative speeds of rolls 120 and 128 permit 22% retraction in the length of the yarn between these points.

When yarn from package 127 is exposed to hot water or steam it crimps in a very uniform fashion and the crimp diameter and crimp elongation are quite uniform. The crimp retraction at a load of 0.0012 g.p.d., determined as described in Example I, is 14% in atmospheric steam and 27.5% in 118° C. steam. The average crimp spacing and diameter, measured as in Example I, are about 8.5 mils and 27 mils, respectively. When the crimpable yarn is knit into women's semi-stretch hose, in combination with 45 denier, 7 filament welt yarn having 13.5% crimp retraction in 118° C. steam, the hose have a very uniform texture and perform well, being similar to the hose of Example I in fit and appearance. When the crimp retraction test at 118° C. is applied to the drawn filament before the relaxed heat treatment, the retraction under 0.0012 g.p.d. load is only 16.6%. In addition, hosiery fabric knit from monofilament which has not been subjected to the relaxed heat treatment has a very poor appearance as compared to fabric from monofilament prepared as described above. When the monofilament is passed through the heated chamber at constant length, the crimp retraction is reduced to 6.5%. Treatment of this filament in a relaxed state with steam at 102° C. increases the crimp retraction to its original level of 16.6%, but does not produce a filament satisfactory for the purposes of this invention.

EXAMPLE VII

An evaporator is charged with 2,345 lbs. (1062 kg.) of a 49.5% aqueous solution of hexamethylenediammonium adipate (6-6 salt solution) and 3,635 lbs. (1648 kg.) of a 31% aqueous salt solution prepared by reacting equimolar proportions of hexamethylenediamine and a mixture of acids prepared by adding 15% by weight of dodecanedioic acid to technical grade sebacic acid which contains about 2% by weight of undecanedioic acid and about 3% by weight of dodecanedioic acid. The salt solution is then evaporated to a 75% concentration level, at which point the temperature is about 132° C. at a

pressure of 13 p.s.i.g. (0.91 kg./sq.cm.). The 75% salt solution is charged to an autoclave and heated to a temperature of about 210° C. and brought to a pressure of 250 p.s.i.g. (17.6 kg./sq. cm.). At this point 30 lbs. (13.6 kg.) of a 20% aqueous slurry of titanium dioxide is added. The solution is then heated to a temperature of about 225° C. at 250 p.s.i.g. (17.6 kg./sq. cm.) pressure, about 60 minutes being required for the heating operation. The pressure is then reduced over a period of 80 minutes to atmospheric pressure and the temperature is increased to 260–265° C. The copolymer is held for 30 minutes at this temperature, extruded in the form of a ribbon, quenched on a water-cooled casting wheel and cut into ½" (1.27 cm.) flake in the conventional manner. The copolymer has a relative viscosity of about 46.

Following the procedure of Example VI, sheath-core monofil is prepared with the copolymer, prepared as above, as the core and 6–6 flake having a relative viscosity of about 46 as the sheath. The crimp retraction of the monofil at a load of 0.0012 g.p.d., determined as described in Example I, is 32.5% in 118° C. steam. The crystallinity of the core is found to be similar to that of the sheath. The crimp spacing and diameter, determined as described in Example I, are 25 mils and 8.5 mils, respectively.

When the monofil is made into women's miniature hose and finished at 118° C., the hose are found to provide improved fit for various leg sizes as compared to women's semi-conventional hose and are superior in appearance on the leg as compared to conventional stretch hose. The miniature hose prepared from the monofil of this example are found to be superior to similar hose prepared from the monofil of Example VI with regard to improved fit.

EXAMPLE VIII

Example VI is repeated except that the ratio of the copolymer to homopolymer is varied to give 60% core and 40% sheath in one test and 70% core and 30% sheath in another. The 60:40 ratio filaments exhibit a crimp retraction at 118° C. of 32.4% while the 70:30 ratio gives a retraction of 34.2%.

EXAMPLE IX

Nylon 6–6 flake having a relative viscosity of 36.5 and 6–6/6–I flake having a relative viscosity of 29.3 and containing 30% of 6–I (polyhexamethylene isophthalamide) are prepared following the procedure of Example IV. Following the procedure of Example VI, the 6–6 and 6–6/6–I flakes are extruded to form a sheath-core monofil with the 6–6 polymer as the sheath, drawn, heat-treated and wound into a package. The draw ratio is 4.6 and the air temperature at the crimping chamber exit is 190° C. When the monofil contains 50% sheath and 50% core, the crimp retraction at 118° C. is 26.4%. When the flow of 6–6 and 6–6/6–I polymers is adjusted to give 60% core and 40% sheath, the crimp retraction at 118° C. is 30.2%. When the monofil is knit into women's semi-stretch hose, the results are substantially the same as found for the hose of Example I. The monofil having 60% core is also knit into women's miniature stretch hose. These hose are found to provide excellent fit for various leg sizes and are superior in appearance on the leg as compared to conventional stretch hose.

EXAMPLE X

Following the general procedure of Example VII, a copolymer is prepared from an aqueous solution of hexamethylenediammonium adipate (6–6 salt) and a salt prepared from hexamethylene diamine and a mixture of 38 parts by wt. of dodecanedioic acid and 62 parts by wt. of technical grade sebacic acid. The latter acid contains about 5% by wt. of a mixture of undecanedioic and dodecanedioic acids as an impurity. The copolymer contains 50% by wt. of 6–6 polymer units and has a relative viscosity at extrusion of about 46.

Following the general procedure of Example VI, an undrawn sheath core monofilament is prepared with the above copolymer as the core and 6–6 polymer having a relative viscosity of about 44 as the sheath and packaged. About 56% by wt. of the filament is core and about 44% is sheath. The monofilament is drawn at a ratio of 5.3 over an unheated draw pin with a draw roll peripheral speed of 167 yds./min. From the draw roll, the monofilament is fed downwardly by air-driven gears of the type shown in FIG. 1 to a ¾" x ¾" x 6½" long slot in an aluminum bar which is electrically heated to temperatures of 150 and 170° C. in two experiments. In each experiment, the bicomponent filament is crimped by the action of the heat as it slides through the slot which is inclined at an angle of about 60° relative to the path of the feed yarn. After the filament is cooled by passage through room temperature air, it is passed through a metal snubbing device where it successively contacts six snubbing surfaces, each having a radius of curvature of about ¼ inch. The filament contacts each of the snubbing surfaces over an angle of 180° to give a cumulative snubbing angle of 1080°. From the snubbing device, the filament is passed to and around a power driven withdrawal roll rotating at peripheral speeds of 76 yds./min. for the experiment at 170° C. temperature and 99 yds./min. for experiment at 150° C. temperature and then to a winding device where it is wound into a package. The extent of relaxation or retraction between the draw roll and withdrawal roll is 55% for the 76 yds./min. speed and 41% for the 99 yds./min. speed. The filament is stretched sufficiently between the snubbing pins and the withdrawal roll to remove crimp. The denier of the final filament is about 15, and the crimp retraction in 100° C. steam under 0.0012 g.p.d. load is 56% for the filament which was heated at 170° C. and 60% for the filament heated at 150° C.

EXAMPLE XI

An undrawn yarn is prepared as in Example X except that two filaments are extruded and processed to form a yarn which after drawing has a denier of 17. The yarn is drawn at a ratio of 5.09 over an unheated pin at a draw roll peripheral speed of 690 yds./min. From the draw roll, the yarn is passed upwardly through a jet device of the type shown in FIG. 5. The jet device has a plastic extension tube eleven inches in length and about 1½ inches inside diameter, whence the yarn passes over a change-of-direction guide and downwardly to a series of snubbing pins of ¾ in. diameter. The yarn then passes to a power driven withdrawal roll rotating at the peripheral speed of 496 yds./min. for yarns A, B, C, D and E and 449 yds./min. for yarns F, G and H and then to a conventional winding device where the yarn is wound into a package in the usual manner. Heated air is passed into the jet device at the rate of 0.47 cu. ft./min., the temperature of the inlet air being as shown in Table 4 below. The number of snubbing pins is varied to give various degrees of snubbing, as reported in the table. In each test, the snubbing was adjusted to the maximum operable level. The crimp retraction in 100° C. steam under 0.0012 g.p.d. load for yarns produced at various jet temperatures and various degrees of snubbing are shown in the table. Two levels of retraction (28 and 35%) between the draw roll and withdrawal roll are shown in the table. It was found that higher degrees of snubbing were permissible with the lower retraction.

When the above-prepared yarns are removed from the packages, they exhibit little tendency to crimp, i.e., they are substantially straight. However, after the yarns are knit into ladies' hose in the conventional manner, it is found that the yarns produced at the higher jet temperatures and with the higher degrees of snubbing produce greige hose of reduced size due to the fact that the yarn attempts to crimp in the fabric after knitting, thus re-

ducing the relaxed fabric area. These reductions in fabric areas are reported in Table 4.

TABLE 4

	Yarn							
	A	B	C	D	E	F	G	H
Jet inlet air temp., ° C.....	175	200	230	265	298	230	265	298
Snubbing, °..... ¹	180	875	1,190	1,250	1,230	965	1,190	1,190
Retraction, percent.....	28	28	28	28	28	35	35	35
Crimp retraction, percent.....	12	30	40	51	50	40	50	49
Knit tubing area, sq. in.....	93	47	33	29	33	32	30	33

¹ In this case, the only snubbing was the contact of the yarn with the change of direction guide referred to above.

EXAMPLE XII

Following the general procedure of Example XI, a 45-denier, 7-filament yarn is prepared. The draw roll speed is 690 yds./min., the draw ratio is 4.28, the jet air temperature is 265° C., the flow rate is 0.47 cu. ft./min., the number of snubbing pins is six, the cumulative angle of contact with the pins is 1260°, and the retraction between the draw roll and the withdrawal roll is 28%. The crimp retraction in 100° C. steam of the final yarn is 36%. When this yarn is knit into the panty section of ladies' panty hose in combination with 17-denier, 2-filament leg yarn of the type described in Example XI, the garment exhibits excellent fit characteristics.

The improved performance level and other advantages of filaments processed in accordance with the present invention are apparent from the foregoing examples. Non-isomorphic copolyamides must be employed since isomorphic copolymers are similar in behavior to homopolymers and do not shrink enough to give the desired crimping.

Filaments which are particularly suitable for the production of hosiery are produced by adjusting the relative amounts of different polymer units in the copolyamide so that the crimp retraction and retractive force are in the desired range. In most instances, the copolymer should contain at least 20% of each of two polymer units. For optimum results, the 6-6/6-10 copolymer should contain 30-70% of the 6-6 polymer units while the 6-6/6-12 copolymer should contain 40-60% of the 6-6 units and the 6-6/6-I copolymer should contain 60-80% of the 6-6 units. The optimum compositions for other copolyamides within the scope of this invention can readily be determined by one skilled in the art.

For the production of sheath-core filaments for use in the preparation of miniature stretch hose, it may be desirable that the copolymer contain more than two polymer units. Thus, as illustrated in Example VII, the addition of a certain amount of dodecanedioic acid to the sebatic acid enhances the crimp retraction. This increased crimp retraction is highly desirable for sheath-core filaments where it is difficult to obtain the retraction required for optimum results in miniature stretch hose. This procedure may also be used in the production of side-by-side filaments, however, it is usually unnecessary since side-by-side filaments characteristically develop a higher crimp than do sheath-core filaments. The maximum amount of dodecanedioic, undecanedioic, or other dibasic acid permissible in the acid mixture is dictated only by the effect on the crystallinity of the copolymer component since too large an amount may inhibit crystallization. Where mixtures of closely related acids are employed (see Examples I and VII) in forming one portion of the copolymer, the individual identities are not considered and all acids (and resulting polymers) are considered to be the major acid present in determining whether 20 percent of each of two polymer units is present. This course is followed where a mere technical grade of acid is employed (Example I, where the 8% of 11 and 12 carbon atom acids are considered as sebatic acid) or where a substantial acid addition is made (Example VII) to provide enhanced properties. In the production of sheath-core filaments from aliphatic polymers, where high crimp retraction is re-

quired, it is desirable that the core polymer have a higher relative viscosity than the sheath polymer.

In order to provide hose which have the necessary ability to stretch, the filament must have the ability to crimp, i.e., have the necessary retractive force when subjected to the tension imposed by the fabric construction. This tension has been found to be about 0.001 g.p.d. Therefore a filament which has a crimp retraction value of at least 12% in atmospheric steam and at least 24% in 118° C. steam after being crimped under a tension of 0.0012 g.p.d. is entirely satisfactory in knit fabrics such as hosiery leg yarn. Sheath-core multifilament yarns with at least 6.5% crimp retraction in atmospheric steam are satisfactory for hosiery welt yarns.

For use in hosiery leg yarn, the preferred bicomponent monofilaments are those having a crimp helix diameter of about 6-11 mils (optimum 7-11 mils) and a helix spacing of about 16-50 mils (optimum 24-38 mils) when crimped in 118° C. steam since this type crimp gives a uniformly rounded stitch in the hose and consequently a much better appearance. In order to achieve these dimensions, temperatures of 140° C. or higher are required in the heat relaxing steps.

As recorded in Examples I and V, the 6-6/6-10 and 6-6/6-12 copolymers develop a crystal-like structure and exhibit X-ray diffraction characteristics similar to those of 6-6 nylon but, because of the differences in chemical repeat distance (or spacing of hydrogen bonds in the crystal structure), it is not believed that such a copolymer system can form a truly crystalline structure. It is theorized that the crystallinity indications observed in the 6-6/6-10 copolymer results from the formation of sheets of 6-6 polymer chains and other sheets of 6-10 polymer chains, the sheets being stacked in a regular fashion and held together by Van der Waals forces while the polymer chains within the sheets are held together by hydrogen bonds. In connection with the 6-6/6-I copolymer of Example IV, it is theorized that the crystallinity indications are those of the 6-6 units in the copolymer and that the 6-I structure is not such as to interfere with the crystalline behavior of the 6-6 in the concentrations employed.

In addition to the copolymers exemplified, other crystallizable, nonisomorphic copolymers in which the 6-6 polymer units are replaced with units such as octamethylene oxamide (8-2), tetramethylene suberamide (4-8), hexamethylene suberamide (6-8), decamethylene sebamic acid (10-10), p-xylylene azelamide (PXD-9), 2-methylhexamethylenexoxamide and epsilon-caproamide may be employed. Some specific hexamethylene adipamide/caproamide (6-6/6) copolymeric ratios which are operable have been disclosed by Anton and Volcheck in U.S. Pat. No. 3,418,199.

The homopolyamide component in the composite filament must be crystallized. Otherwise, the shrinkage of this component may be so high that the necessary shrinkage differential between the two components will not be achieved. Crystallization and orientation of this component should take place to a substantial degree by the end of the drawing step in order to insure the desired relatively low shrinkage rate in the subsequent crimping step. This component should consist essentially of the homopolyamide but the addition of another polymer as a melt blend or another copolyamide in a very small amount obviously would not seriously impair its function. Suitable crystallizable homopolyamides in addition to those

exemplified include: polyheptanamide, polyundecanamide, polyoctamethylene oxamide, polytetramethylene suberamide, polyhexamethylene suberamide, polyxylylene azelamide and poly-2-methyl-hexamethylene terephthalamide. Crystallizable isomorphous copolymers such as the copolymer of polyhexamethylene adipamide and polyhexamethylene terephthalamide may be used in place of the homopolyamide component.

Both components of the filament of this invention must be extruded from polymer of fiber-forming molecular weight in order to avoid processing difficulties and provide filaments which have satisfactory crimpability. In side-by-side extrusion the use of a low molecular weight component leads to bending of the filaments as they emerge from the spinneret orifice and commercial operability is not obtained. In either side-by-side or sheath-core extrusion, it is found that the surface tensions of the two molten polymers must be approximately equal to obtain filaments having the desired high crimping force. For practical production of hosiery filaments, one component must have a relative viscosity of at least about 35 at extrusion in order to avoid severe processing difficulties. Preferably, the two components differ in relative viscosity by no more than 10 units.

In the extrusion of sheath-core filaments, the homopolyamide is preferably extruded as the sheath to facilitate quenching of the filaments. Use of the copolyamide as the sheath results in slower quenching, frequently leads to filament sticking at high spinning speeds and results in excessive broken filaments during drawing. Where side-by-side filaments are extruded the filaments from a single spinneret should be similarly oriented with respect to the position of the components to insure uniform exposure to the quenching air which is usually blown across the filaments. Preferably the copolyamide component is on the side from which the quenching gas is blown.

The two components are preferably present in approximately equal amounts by weight of the filaments in side-by-side structures. However, with sheath-core filaments it may be desirable to employ a somewhat larger percentage of the higher shrinkage component. When the components are present in a ratio other than about 50:50, it is preferable that the copolyamide component be the greater of the two since it is the higher shrinkage component and therefore provides the necessary retractive force to produce crimping.

In producing sheath-core filaments, the core should be highly eccentric as illustrated in Example VI in order to develop the required retractive force on crimping. This means that part of the sheath will be very thin, i.e., the minimum thickness of the sheath will range from 5% of the filament diameter to 0.1% or less and is preferably no more than about 2% of the filament diameter.

In order to produce the requisite structure in the composite filament, it must be drawn under conditions which do not cause crystallization of the copolyamide to a substantial degree and, after drawing, it must be heated in a relaxed or partially relaxed state to crimp the filament and crystallize the copolyamide, and then cooled to consolidate the structure. The filament may be cold drawn or drawn at moderately elevated temperatures provided that the temperature is not sufficient to cause appreciable crystallization of the copolymer. The temperature, heating time and degree of relaxation required in the relaxation step may vary somewhat depending on the polymer system employed. The optimum conditions for drawing and relaxation are easily selected by one skilled in the art. In general the filaments should be heated in the relaxation step at a temperature of at least 140° C. (284° F.) but below the softening point of either of the components for a sufficient time to permit development of the crystalline structure. Where the filament is heated in a completely relaxed state or under very low tension, the extent of overfeed into the heat processing zone is adjusted to permit the maximum degree of crimp to develop in the

filament. In addition to high-temperature air, steam may also be employed as the heating medium and may be preferred with higher filament and/or yarn deniers and higher processing speeds.

After the filament is permitted to crimp in the relaxed heat treatment, it should be cooled to set the structure and the crimp removed by stretching. The stretching may also be adjusted to produce the desired degree of crimping when the filament is subsequently crimped in the fabric. Where snubbing pins are used in the stretching operation as illustrated in the drawings, application of a high friction finish to the filaments is desirable.

The amount of crimp which can develop in the heating zone will depend primarily on the amount of snubbing, the temperature at which the yarn is heated in this zone, and the amount of retraction permitted between the draw roll and withdrawal roll. At a given temperature of the heating zone, the snubbing must usually be increased if the retraction is decreased and vice versa, in order to maintain the same crimp retraction in the final yarn. In general, high levels of snubbing and high temperatures are desirable in order to achieve the highest crimp retraction in the yarn. At lower levels of snubbing, increased retraction between the draw roll and withdrawal roll in combination with high temperature in the heating zone will produce high levels of crimp in the yarn. In the production of hosiery leg yarns at commercial speeds, it is desirable to permit a yarn retraction between the two rolls of 22-35% and to have a cumulative snubbing angle of 720-1260°. For a given yarn at a given temperature, the relationship between retraction and snubbing is approximated by the equation:

$$\log \left(1 - \frac{\text{Retraction}}{\text{Max. retraction}} \right) = K (\text{snubbing angle}) + K'$$

where K and K' are constants for a given yarn. For 17-denier, two-filament yarn of the type described in Example XI, K and K' were found to be 7.1×10^{-4} and -1.2 respectively. The maximum retraction value is determined by varying the relative speeds of the draw roll and withdrawal roll with no snubbing, until the maximum retraction at which the yarn will run smoothly without accumulation and breakdown is found.

The relaxation step also serves to reduce the otherwise substantial shrinkage of the filament which takes place before crimp is formed in the fabric. In hosiery yarn, a shrinkage in boiling water in excess of 15% in the leg yarn is undesirable and lower shrinkages are required in the welt yarn. A heater may be provided integral with the crimping chamber to heat the crimping fluid to the pre-determined temperature.

Although hosiery filaments are usually of round cross section, other shapes can be employed for hosiery or other products and may indeed be particularly useful in certain end uses such as in tricot knit fabrics or certain woven fabrics. For such purposes, cross sections of trilobal shape as disclosed and claimed in U.S. Pat. No. 2,939,201 or shield shape as in U.S. Pat. No. 2,939,202 may be employed, as may others such as heart shape, cruciform shape, and various multilobal configurations. Either side-by-side or sheath-core filaments can be produced in any of the above shapes. Other variations and modifications of a similar nature will occur to those skilled in the art without departing from the spirit of my invention which, accordingly, is intended to be limited only by the scope of the appended claims.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. In a process including the steps of spinning, drawing and packaging a two-component filament in which one component is a fiber-forming crystalline polyamide and the other a nonisomorphous fiber-forming random copolyamide, the improvement comprising relaxing the drawn filament in its advance through a heated zone under low tension to produce crimp, cooling the relaxed crimped

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filament and then stretching the cooled filament in its departure from said zone to remove crimp, said stretched filament having been relaxed by a controlled percentage of its as-drawn length and being crimpable upon re-exposure to a heated atmosphere, said copolyamide component of the heat relaxed filament exhibiting X-ray diffraction characteristics similar to those of the polyamide component.

2. The process of claim 1 wherein said filament is heat relaxed in a substantially tensionless state, said zone includes a jet of heated air and said stretched filament is relaxed by at least 22% of its as-drawn length.

3. The process of claim 1 wherein said filament is relaxed at a temperature of at least 140° C.

4. The process of claim 3 wherein said filament is relaxed in heated air.

5. The process of claim 3 wherein said filament is relaxed in steam.

6. In the production of crimpable yarn from at least one filament comprised of differentially shrinkable, continuous, adherent, eccentric, nylon components, the steps of: drawing the composite filament; crimping the drawn filament by passing it, under low tension, through a high temperature zone, one component of said drawn filament being a fiber-forming crystalline polyamide, the other being a random fiber-forming nonisomorphic copolyamide; cooling the crimped heated filament by advancing it from said zone through a substantially room temperature environment to a snubbing device; and snubbing and stretching the cooled filament to remove crimp, said stretched filament having been relaxed by a controlled percentage of its as-drawn length and being crimpable upon re-exposure to a heated atmosphere.

7. In the production of crimpable yarn from at least

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one bicomponent nylon filament wherein one component is a crystalline polyamide and the other a nonisomorphic copolyamide, the steps of: drawing the filament; relaxing the drawn filament by advancing it in a substantially tensionless state through a jet of heated air, thereby producing helical crimps; cooling the relaxed crimped filament under very low tension; and then stretching the cooled filament to remove crimp, said stretched filament having been relaxed by a controlled percentage of its as-drawn length and being crimpable against restraint upon re-exposure to a heated atmosphere.

8. In the preparation of crimpable yarn from at least one filament comprised of differentially shrinkable, polyamide components, the coupled steps of drawing the yarn, relaxing the drawn yarn in its advance through a heated zone to produce a helical crimp configuration in each filament, cooling the heat-relaxed yarn, and then stretching the cooled yarn in its departure from said zone to remove said crimp configuration, said stretched yarn having been relaxed by a controlled percentage of its as-drawn length and being crimpable upon exposure to another heated atmosphere.

9. The process of claim 8 wherein said yarn is relaxed at a temperature of at least 140° C.

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U.S. Cl. X.R.

264—171, 290, 342; 28—72, 72.17