Jan. 14, 1964 A. L. BREEN 3,118,011

PROCESS FOR PREPARING HELICALLY CRIMPED COMPOSITE FILAMENTS

Filed July 3, 1962 2 Sheets-Sheet 1

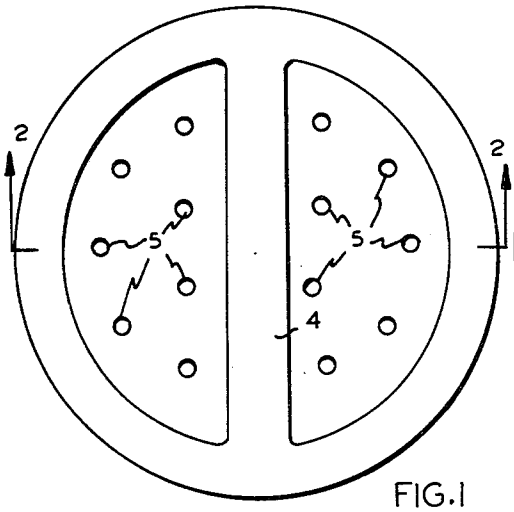

FIG. 1

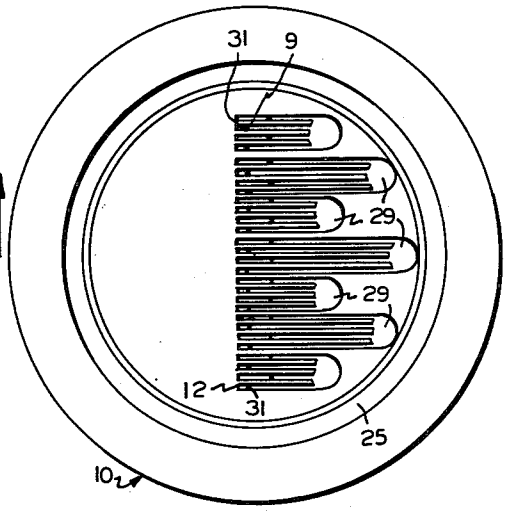

FIG. 4

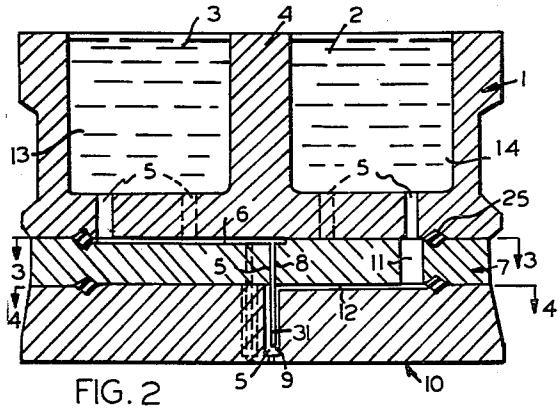

FIG. 2

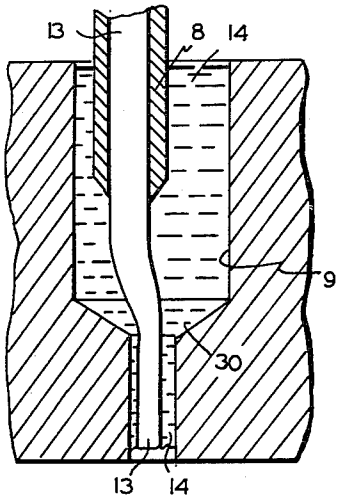

FIG. 5

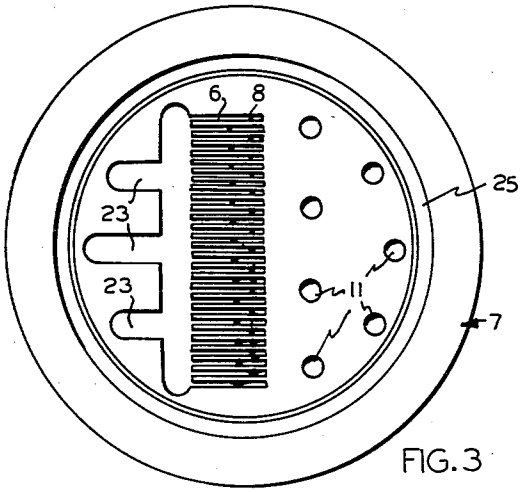

FIG. 3

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PROCESS FOR PREPARING HELICALLY CRIMPED COMPOSITE FILAMENTS

Filed July 3, 1962 2 Sheets-Sheet 2

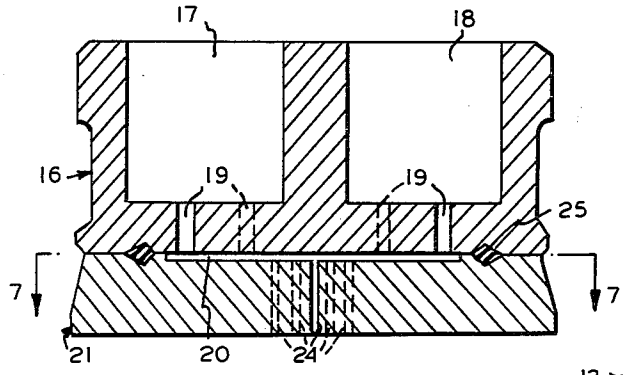

FIG.6

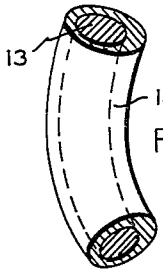

FIG.10

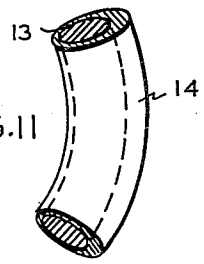

FIG.11

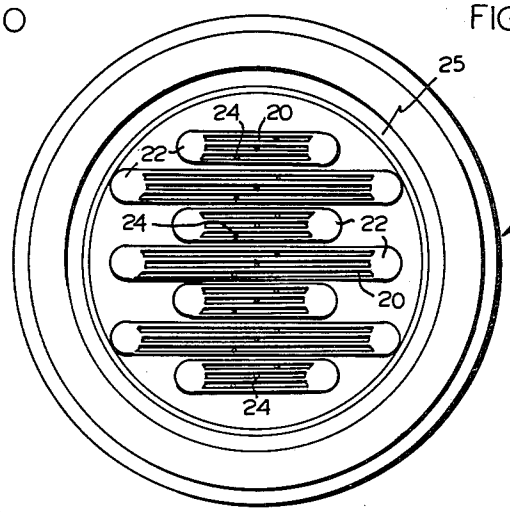

FIG.7

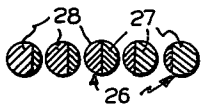

FIG.9

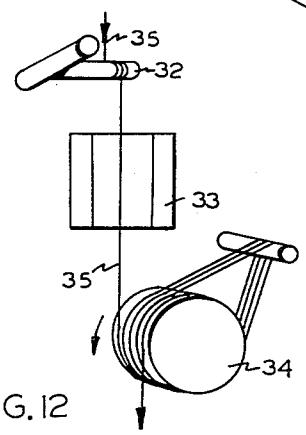

FIG.12

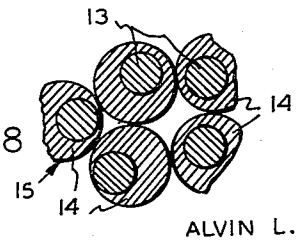

FIG.8

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PROCESS FOR PREPARING HELICALLY CRIMPED COMPOSITE FILAMENTS

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Filed July 3, 1962, Ser. No. 207,304
5 Claims. (Cl. 264—168)

This invention relates to the preparation of synthetic textile fibers and particularly textile fibers possessing a permanent crimp.

Various methods have been proposed and used to produce crimped synthetic filaments. The principles of these crimping methods comprise mechanical treatment of the filaments spun in normal fashion as well as application of specific conditions of spinning or after-treating which bring about differential physical properties over the cross-section of the single filaments.

Newer proposals of producing an improved crimp in synthetic fibers comprise the spinning of two or more different materials together so that they form a unitary filament which contains the components in an eccentric relation over the cross-section of the filaments. When, for instance, two materials are used together which possess substantially different physical properties, for example, different residual shrinkage, a crimp is brought about by the application of a suitable after-treatment to the spun and drawn composite filaments. These crimped filaments may be quite satisfactory as long as only relatively small tensions are applied during their use. However, with the application of higher tensions, the crimped filaments of the prior art do not possess the optimum properties and the highest possible crimp retention. Perhaps this is the reason that none of these composite crimped filaments have been commercially produced and used.

It is, therefore, an object of the present invention to provide crimped two- or multi-component composite filaments which have improved recovery properties and higher crimp retention. It is another object of the invention to produce crimped filaments with improved mechanical properties. It is another object to produce crimped filaments having on application of high tensions, as they occur in practical manufacture of fabrics therefrom, a considerably higher crimp retention than heretofore obtainable. Further objects will appear as the description of the invention proceeds.

The term "tensile recovery" is well known (cf. U.S. 2,604,689, Beste and Hoffman, Textile Research Journal vol. 20, No. 7, July 1950, page 441, and also Textile Fiber Yarns and Fabrics by E. R. Kaswell published by Rheinhold Publishing Corporation in New York City, 1953) and is defined as the extent to which a yarn recovers its original length after being stretched, a stress-strain curve being used to determine tensile recovery under the testing conditions. The determination is usually carried out at a constant rate of elongation. For example, a given sample of yarn may be elongated 5% at a rate of 1% per minute, held 30 seconds at the 5% elongation and then allowed to recover at the same rate which it was extended and the recovered length measured.

$$\text{The tensile recovery (in this instance for 5\% elongation)} = \frac{\text{elongation recovered}}{\text{total elongation}} \times 100$$

Since the extent of recovery varies with the elongation, the tensile recovery values are given for a stated total elongation. Typical values of tensile recovery from 5% elongation of some commercial fibers are as follows:

poly(hexamethylene adipamide), 89%; poly(ethylene terephthalate), 65%, and polyethylene, 80%.

The objects of this invention are effected by producing a crimped composite filament, in which the component having the higher tensile recovery properties is the component subjected to the higher strain on straightening the crimp by an external force. This component will be called the "load bearing" component in the following description of the invention. The new improved crimped filaments of this invention may be obtained by different methods. One method comprises spinning together two or more synthetic polymeric fiber-forming materials, of which the material having the higher shrinkage after drawing has the lower tensile recovery properties, in such a way that the materials form over the cross-section of the single composite filament two or more distinct zones which extend through the entire length of the filament in eccentric fashion, whereby only one, or part of, or all the components take part in forming the surface of the single composite filament, stretching the composite filament, length stabilizing the component or components with the higher shrinkage by the application of heat or other means to the drawn composite filament while it is kept under tension, which results in crystallization of this polymer without affecting the other component or components substantially, and subjecting the thus treated composite filaments in a substantially tensionless state to a shrinking treatment.

An important characterizing feature of this method of the present invention is the discovery that in composite synthetic crimped filaments wherein the load bearing component has the lower tensile recovery properties, the overall properties and particularly the crimp retention of the filaments can be greatly improved by subjecting the drawn composite filaments prior to the development of crimp to a treatment which results in crystallization and length stabilization of the normally load bearing component and which does not affect or only slightly affects the other component. Any treatment which meets these requirements may be used. Such treatments are, for instance, a taut heat treatment at a temperature high enough and for a time long enough to provide crystallization of the desired polymeric component. The temperatures applied in this heat treatment will generally be higher than the apparent minimum crystallization temperature (T_1) of the component which is to be length stabilized. The "apparent minimum crystallization temperature" (T_1) is defined as the lowest temperature at which the fiber may be treated to produce a substantial degree of crystallinity in its structure. This may be determined by measuring the rate of density change as the temperature is increased or by well known X-ray diffraction methods, both of which techniques will be described more fully hereinafter. In other instances, crystallization and length stabilization can preferably be brought about by a treatment of the taut composite fiber with certain polar organic liquids which are latent solvents for the amorphous regions of the component to be stabilized.

In the spinning, the polymers are not appreciably blended together in the melt but are fed separately to a shaped orifice where they are simultaneously extruded. The orifice is, then, adapted to receive the components separately for simultaneous extrusion to form a filament in which each component is substantially localized but is held to the other component in an eccentric relation. The extrusion can be such that the components are localized and held together in a "side-by-side" structure in which both components form part of the surface of the composite. The extrusion may also be such that one component forms a core and the other a sheath to form a composite referred to hereinafter as a "sheath-core" struc-

ture. In this structure only the sheath contributes to the surface of the composite. With the spinnerets described herein, melt spinning leads to composites which are generally smooth and have cross-sections which are substantially round with boundary lines that are regular.

The composite filaments are stretched and the resultant stretched filaments are subjected to the length stabilizing treatment and after that treatment they are given a shrinking treatment while they are in a free-to-shrink state. The crimp in the new crimped filaments of this invention is brought about not only by a differential in shrinkage in the components of the composite but by positioning the components in respect to helical crimps so that the component with the better tensile recovery properties is the load-bearing component.

In the figures:

FIGURE 1 is a plan view of the spinneret assembly shown in FIGURE 2;

FIGURE 2, taken on line 2—2 of FIGURE 1, is a cross-section of a spinneret of this invention showing the routes of polymer in the formation of sheath-core structures;

FIGURE 3 is taken on line 3—3 of FIGURE 2;

FIGURE 4 is taken on line 4—4 of FIGURE 2;

FIGURE 5 is an enlarged section of the bottom portion 10 in the vicinity of the orifice;

FIGURE 6 is a cross-section of a spinneret of this invention showing the flow of polymer in the formation of side-by-side structures;

FIGURE 7 is taken on line 7—7 of FIGURE 6;

FIGURE 8 shows cross-sections of the sheath-core filaments of this invention; and

FIGURE 9 shows cross-sections of the side-by-side filaments of this invention;

FIGURE 10 is a sectional perspective of a fragment of a composite in a crimp form referred to as "alpha crimp";

FIGURE 11 is a sectional perspective of a fragment of a composite in a crimp form referred to as "beta crimp"; and

FIGURE 12 is a diagram of apparatus which can be used in applying a process of this invention in a continuous manner.

Referring first to FIGURE 2 it can be seen that the top component or filter pack 1 of the spinneret has two chamber 2 and 3. Each is fed a different polymer. The chambers are separated by wall 4 and in the bottom of the top portion are a plurality of holes 5 cooperating with outlets below. The chamber 3 and the holes 5 therein cooperate with the grooves or recesses 6 and 23 in the center portion of adapter 7 and feed the polymer melt to the vertical holes 8 or tubes 31. These tubes 31 extend downwardly into the orifices 9 contained in the bottom portion or spinneret face 10. The chamber 2 permits the feeding of polymer downwardly through holes 5 which cooperates with holes 11 in center portion 7 to permit the flow of polymer to grooves or recesses 12 and 29 in the bottom portion 10. The plan views of the top, center and bottom portions may be seen in FIGURES 1, 3, and 4, respectively. As shown, gaskets 25 are provided for sealing purposes, the assembly being held together by means of bolts or by pressure.

As shown in FIGURE 2 and in an enlarged manner in FIGURE 5, polymer 13 coming to the holes 8 or tubes 31 from the chamber 3 constitutes the core feed. As this polymer leaves tube 31 which is surrounded by the melt 14 of polymer coming from chamber 2 and constituting the sheath, bonding occurs so that in the tapered section 30 of orifice 9, polymers 13 and 14 are being extruded simultaneously with polymer 14 completely surrounding the polymer 13. It is to be noted that tube 31 is eccentrically located in the orifice 9. This is done purposely to get the eccentric relation of the polymers, for the more pronounced the eccentricity, the better are the crimp results. As can be seen in FIGURE 8, the filaments thus produced by melt spinning have substantially round, smooth surfaces. Even the core is substantially round and smooth and in all cases the core does not break through the surface. That is, even in such a filament as 15 there is polymer 14 surrounding the core even though the core comes very close to the outer edge at one place.

In the production of eccentric composite filaments such as sheath-core structures, one uses a material 13 and a material 14 which are so related that material 13 has the better tensile recovery properties. If material 14 has a higher shrinkage than material 13, the crimped structure shown in FIGURE 10 wherein the material 14 is located on the inside of the helical coil is obtained. This type of crimp in which the material 14 having the lower tensile recovery properties is located on the inside of the coil is referred to herein as "alpha crimp." Since the material on the inside of the helical coil is the load-bearing constituent of the composite, it is desired to have that material be the material having the better recovery properties. By the process of this invention, it is possible to produce such crimped filaments as are shown in FIGURE 11. In this figure, material 13 is on the inside of the helical coil and has the better tensile recovery properties. This type of crimp shown in FIGURE 11 is referred to herein as "beta crimp." As mentioned above, one method of this invention for producing the desired beta crimp involves the conversion of the alpha crimp type to the beta crimp type. This is referred to herein as "reverse crimp"; in this reversal the material 13 has ben converted so that it is now the material having the higher shrinkage while retaining its better tensile recovery properties.

A relatively low tension applied to the crimped filament results in extension of the coils and finally in straightening of the coils because of the very low crimp modulus. Tensions which are higher than the crimp modulus will extend the straightened composite filament whereby the "shorter" component which forms the inside of the coil bears a relatibely greater part of the total load applied. It follows therefrom that a relatively higher strain is applied to the load-bearing component than to the co-acting component in a tensioned crimped composite filament. When the load-bearing component has the lower tensile recovery properties, which is the case with the combinations of synthetic high polymers proposed herebefore for the preparation of crimped composite filaments, the degree and tightness of the crimp will be reduced after application of relatively high loads, because the load-bearing component does not recover as much as its counterpart. The new composite crimped filaments of this invention do not have this disadvantage because the material with the better tensile recovery properties has been made to be the load-bearing component.

It is evident from the foregoing that it is of great importance for evaluating crimped composite filaments to have a reliable method for measuring the crimp retention. A commonly used method is described, e.g., in U.S. 2,287,099. In this test, relatively low loads, equivalent to 0.03 g./denier are applied to the crimped filaments while immersing them for 30 seconds into water of 60° C. These tensions are much lower than the strain usually imposed on the single filaments in normal use of textile products containing these filaments. Therefore, a more stringent test has been developed, which simulates more the actual conditions encountered in practical use of the crimped filaments.

The crimped yarn or filaments are formed into a skein the length of which is measured without applying any tension (*a*, in centimeters). The skein is then loaded with a weight corresponding to 0.01 g./denier and the straightened length of the skein is measured (*b*, in centimeters). The skein is then loaded for 30 seconds with a weight corresponding to 1.0 g./denier. The filaments are allowed to recover, after removal of the load, for 30 seconds and the length of the skein is again measured (*c*, in centimeters).

"side-by-side" structures, is practically eliminated in sheath-core structures. The latter structures therefore permit a much wider application of this principle. Other embodiments include composite filaments which are composed of more than two components. Filaments have been produced in the above examples which consist of about equal parts of the two components. However, sometimes it might be preferred to use a relatively higher amount of one component and a correspondingly lower amount of the other component. Good results can usually be obtained with compositions of at least 20% by weight of one component and 80% by weight of the counterpart up to a ratio of 50% by weight of both components. Those composite filaments containing about equal portions of both components are preferred because of the higher tightness and permanence of the crimp achieved.

Sometimes it might be desirable to spin a bundle of filaments which comprises composite filaments containing the components in various ratios through one and the same spinneret. An example is a bundle of two-component composite filaments which comprises filaments consisting of 20% by weight of the load-bearing component and 80% by weight of the other, a 30%/70% ratio, a 40%/60% ratio and a 50%/50% ratio, respectively. Such filament bundles containing composite filaments with various ratios of components can very conveniently be produced by utilizing the spinneret which is shown in FIGURES 6 and 7. The spinneret shown is composed of two parts. In the upper portion 16 are two chambers 17 and 18 cooperating with holes 19 in the bottom plate of the top portion. These holes permit the feeding of polymer to grooves or recesses 20 in the bottom portion 21 of the spinneret. The polymer coming from hole 19 goes into the recesses 22 immediately below it and is fed to a plurality of recesses 20. Each recess contains and cooperates with a spinneret hole 24. In each spinneret, provision is made for a gasket 25 and conventional means, as by bolting or pressure, can be used to hold the various spinneret elements in place during operation.

However, in the spinneret shown by FIGURES 6 and 7 there is no tube located in the spinneret orifices 24 such as are in the spinneret orifices 9. Thus, in this modification polymer coming from chamber 17 and the other polymer coming from chamber 18 meet at the orifices 24 and are extruded simultaneously to form side-by-side structures. Cross-sections of such structures are shown in FIGURE 9, these structures being designated by reference number 26, the parts being 27 and 28. The apparatus can also be modified to give all composite filaments of the same ratio of components.

The spinning, drawing, and length stabilization of the load-bearing component in the composite filament and the after-treatment for bringing about the crimp were described in the foregoing as a discontinuous procedure wherein each treatment was carried out as a separate processing step. The same outstanding results however can be achieved in a fully continuous process. An apparatus especially useful for the continuous procedure is shown in the schematic drawing of FIGURE 12.

The apparatus comprises a draw pin 32 at which the stretching occurs, a heating medium 33 such as a hot metallic surface, and a draw roll 34. The following Example V is representative of a continuous process for producing the composite filaments having the reversed permanent "beta crimp."

Example V

Following the procedure described in Example I, composite sheath-core poly(ethylene terephthalate)-poly(hexamethylene adipamide) filaments are extruded through a spinneret like that shown in FIGURE 2 having 34 holes. The filaments 35 are attenuated by drawing them from the spinneret at approximately 500 times the speed with which the polymer leaves the spinneret holes. The bundle of filaments is, after cooling, continually drawn over a draw pin 32 which is heated to 85° C. On its path to the draw roll the filament bundle is led over a hot plate 33 which is heated to 140° C. The total draw imposed on the yarn is 3.56. The filaments, the thickness of which corresponds to approximately 2 deniers, are substantially uncrimped but they possess the potential crimp. Subsequent tensionless treatment in boiling water by short immersion developed readily a tight helical crimp. The crimped filaments have on an average approximately 60 crimps per inch and a crimp elongation of 170% and a crimp retention of 90% when measured according to the above-described test with the application of a load of 1 g./denier for 30 seconds. Microscopic inspection of the crimped filaments showed that the filaments have the beta-type crimp wherein the thicker portions of the polyamide skin form the inside of the single coils. Monofilaments are prepared of the components under conditions similar to above. Use of the hot plate following drawing reduces the shrinkage of the polyamide from 9% to about 8% while lowering the shrinkage of the inferior recovering polyester from about 12% to about 4%.

Similar composite filaments produced according to the foregoing method however omitting the length stabilization on the hot plate had a crimp elongation of only 70% and a crimp retention of only 40% when measured by the test used above.

Example VI

Poly(2-methyl-hexamethylene terephthalamide) of inherent viscosity 0.69 as measured in m-cresol and the poly(hexamethylene adipamide) of Example I are cospun as core and sheath respectively to make composite fibers as in Example I. The composite fibers are drawn 3.6 times their original length over a pin heated to 83° C. Upon boiling the drawn yarn in water, the fibers helically crimp wherein the major proportion of the poly(2-methylhexamethylene terephthalamide) core is on the inner side of the helical coils. Monofilaments spun from the same polymers under similar conditions have shrinkages of 13 and 9% respectively.

When the as-spun filaments produced above are drawn 3.6× over a pin heated to 80° C. and thereafter over a hot plate heated to 150° C., the filaments crimp in the beta configuration upon shrinking in boiling water. The thicker part of the poly(hexamethylene adipamide) sheath is on the inner side of the helical coils. Monofilaments of the two component polymers spun and drawn under the same conditions display shrinkages of 5.3 and 8% and have tensile recovery at 3% elongation of 73 and 86% respectively after the boil-off.

Suitable components for producing the permanently crimpable composite fibers by the process which includes the length stabilizing step can be found in all groups of synthetic fiber-forming materials. Because of their commercial availability, ease of processing and excellent properties, the condensation polymers and copolymers, e.g., polyamides, polysulfonamides and polyesters and particularly those that can be readily melt spun are preferred for application in this method. Suitable polymers can be found for instance among the fiber-forming polyamides and polyesters which are described, e.g. in U.S. Patents 2,071,250; 2,071,253; 2,130,523; 2,130,948; 2,190,770 and 2,465,319.

Suitable polyamides for use in this invention are those synthetic linear polyamides which are prepared from polymerizable monoamino monocarboxylic acids or their amide-forming derivatives, or from suitable diamine and suitable dicarboxylic acids or from amide-forming derivatives of these compounds. The —R— group of the intercarbonamide linkages —$C(R)_2$— may be hydrogen, halogen, monovalent organic radical, alkylene or the like. Typical of such polyamides are those formed from a diamine and a diacid containing the repeating unit:

—X—Z—Y—Z—

The crimp permanence is calculated by the following equation:

$$\text{Percent crimp permanence} = 100\left(\frac{\frac{b}{c}}{\frac{b}{a}-1}\right)$$

In the examples parts and percentages are by weight.

Example I

Poly(ethylene terephthalate) flakes having an intrinsic viscosity of 0.67 in a solvent mixture of 58.8 parts by weight phenol and 41.2% by weight of trichlorophenol and poly(hexamethylene adipamide) flakes having an intrinsic viscosity of 1.02 in m-cresol are melted separately and extruded at 285° C. through a multi-hole spinneret assembly shown in FIGURE 2. The extruded filament is air quenched. The polyester melt is extruded through the inner tube of the spinneret and the polyamide through the outer space surrounding the tubes, thus forming a sheath-core filament. FIGURE 8 shows a cross-section of a bundle of the eccentric sheath-core filaments thus obtained. This drawing, based on a microphotograph, shows clearly the eccentric position of the polyester cores in the polyamide sheaths over the cross-section of the single filaments forming the fiber bundle.

The eccentric sheath-core filaments are attenuated by pulling them as they are spun away from the spinneret holes with a speed which is about 100 times as high as the speed of the extruded melt. After spinning and cooling, they are drawn over a pin at room temperature to 3.3 times their original length. About 100 yards of the stretched filaments were tightly wound on a bobbin, and the bobbin was heated for 30 minutes in an electric oven, the temperature of which was 115° C. The cooled filaments were then unwound from the bobbin and showed upon inspection no distinct crimp. However, they possess a potential crimp which can be developed immediately after the heat treatment or at any time after the fiber is processed into woven textile materials or into knitted goods or after cutting the fibers into staple lengths.

Example II

A part of the continuous filament of Example I containing the potential crimp was skeined and hung in boiling water for one minute without applying any tension to the filaments. A very tight helical crimp developed instantly. The filaments contained on an average 50 crimps per inch. Microscopic inspection of the filaments showed that the core of poly(ethylene terephthalate) was positioned in the outer portion of the single coil and the thicker parts of the polyamide skin were situated on the inside of the single coil. Therefore, the filaments contained the "beta crimp."

Example III

Part of the eccentric sheath-core composite filament yarn of Example I was plyed and twisted to a yarn containing 56 filaments with a total denier of 180. The twist was 0.5 turn per inch. This yarn was knit into tubing which when flattened to double thickness measured 3⅝" wide. A piece of this tubing 12 inches long was placed in boiling water containing 0.5% "Duponol" for 30 seconds. The fabric was then rinsed, centrifuged and dried in the open air. The dry fabric was found to measure 3⅜" wide and 5⅜" long. The bulk and covering power of the fabric were correspondingly increased. Moderate tension caused stretching of the fabric beyond the original dimensions but the shrunken form returned almost completely upon release of such tensions. This good shape retention of the boiled-off knit fabric is attributed to the good crimp retention of the crimped fibers composing the fabric.

If the spun and drawn filaments of Example I are given the shrinkage treatment of Examples II or III without applying first the length stabilization treatment of Example I, highly crimped filaments are obtained. However, microscopic inspection of the cross-section of these crimped filaments shows that the cores consisting of the polyester are positioned on the inner portion of the coils and the thicker portions of the polyamide skin are on the outside of the coils. These fibers therefore possess the "alpha crimp" and do not possess the crimp retention of the "beta" type of this invention.

Example IV

Poly(ethylene terephthalate) flakes having an intrinsic viscosity of 0.67 in a solvent mixture comprising 58.8 parts by weight phenol and 41.2 parts by weight trichlorophenol and polyethylene, having an inherent viscosity (0.5% concentration) of 0.88 in tetralin measured at 125° C., were melted separately and extruded at 296° C. through a spinneret as shown in FIGURE 2. The polyethylene melt was extruded through the inner tube of the spinneret and the polyester through the outer space surrounding the tubes, thus forming a sheath-core filament.

After spinning and winding, the quenched sheath-core filaments were passed through a water bath at 30° C. to a roll heated to 65° C. and then to an unheated roll rotating at a higher speed whereby the yarn was stretched 2.6 times its original length.

A part of this continuous filament yarn was skeined and hung in boiling water for 1 minute without applying any tension to the filaments, whereupon the yarn crimped spontaneously. Microscopic examination of the crimped filaments showed that the heavy part of the polyester skin was situated on the inside of the single filament coil, which corresponds to the "alpha crimp" described above. These "alpha crimped" filaments showed a crimp retentivity of less than 25% when measured according to the new method described above.

Another portion of the freshly spun yarn was wound tightly on a bobbin and immersed in acetone at room tmperature for one minute. This yarn was then skeined and hung in boiling water, tension free, for one minute. Crimp developed readily. Crimp retentivity was found to be higher than 90% when measured according to the new method described above. Microscopic inspection of the crimped filaments showed that the crimp was the beta type.

In the foregoing examples the filaments were spun through the spinneret shown in FIGURE 2 which was found to be especially suited and economical to be used for obtaining a random eccentric sheath-core structure in the single filaments. However, the invention is not limited to the application of this specific spinneret. Any other form of a spinneret which permits production of a composite filament which contains at least two components in an eccentric relationship over the full length of the filament can be used. There are no restrictions with respect to which component forms the core and which component forms the sheath in the sheath-core structures of this invention. Though it is generally preferred to choose the component with the higher tensile recovery properties to form the sheath, other considerations like solubility, spinning technique, appearance and hand, and physical properties may make the reverse order desirable. The invention is further not limited to the eccentric sheath-core filaments. Any other form of a composite filament which contains the components in an eccentric relationship over the cross-section of the single filament may be utilized instead of the sheath-core structure shown in the examples. So for instance, the components can also be spun in the so-called "side-by-side" relationship wherein the components are combined at only part of their surface and both components take part of the surface of the composite filament. However, the "sheath-core" structures are preferred in this invention because the problem of coherence, which exists with many polymer combinations, particularly on drawing the

wherein —Y— represents divalent aliphatic, alkaryl (such as xylylene), cycloaliphatic or aromatic groups; —Z— represents the

linkage and —X— represents divalent aliphatic, cycloaliphatic or alkaryl groups. Polyhexamethylene adipamide, caproamide (i.e., "66" and "6" nylons) and polyhexamethylene terephthalamide are illustrative of such polymers.

Another class of suitable polyamides containing other than aromatic intracarbonamide repeating units are those prepared from piperazine, such as those from piperazine and adipic acid, piperazine and terephthalic acid, and the like. Copolyamides, condensation copolymers wherein the amide linkage is the predominant linkage and polyamide mixtures are also useful. To form the structures of the present invention, such polyamides must be of high molecular weight.

Particularly suitable polyamides include polyhexamethylene adipamide, poly(epsilon-aminocaproamide), poly(p-xylylene azalamide), poly(m-xylylene adipamide).

The preferred polyesters to be used in this invention are those wherein at least about 75% of the recurring structural units of the polyester are glycol terephthalate structural units. These should be fiber-forming and have a relative viscosity of at least about 12. Such polymers may be represented in a more general way by the formula $HO—G—(OOC—A—COO—G)_y—OH$ 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 number suffiicent that the polymer is of fiber-forming molecular weight; at least about 75% of the —A— radicals being terephthalate 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-sulfonyibibenzoate radicals, derived from the corresponding dicarboxylic acids or ester-forming derivatives thereof. Suitable glycols include ethylene glycol, 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. The glycols may be used alone or in mixtures, e.g., ethylene glycol plus up to about 25 mol percent of the above-mentioned glycols.

Fiber-forming polysulfonamides can be produced by reacting at an interface between two immiscible phases organic sulfonic acid halides, e.g., dichlorides, which form or are contained in one phase, with primary or secondary organic diamines which form or are contained in the other phase, whereby preferably one of the phases is dispersed in the other while the reaction takes place. Such a method is described, for instance, in U.S. Patent 2,667,468.

Another group of condensation polymers which can be used in this invention, comprises the polymers which contain sulfonamide groups as well as carbonamide groups. These polymers are conveniently produced by the same method as described above, however, substituting the disulfonic acid halides by the corresponding organic monocarboxylic, sulfonic acid dihalides.

The above-described interfacial polymerization methods may also be used for producing the polyamides, when organic dicarboxylic acid halides are used instead of the sulfonic acid halides. When dicarboxylic acid halides are reacted with glycols in the above reactions, the fiber-forming polyesters are obtained. Other groups of polymers useful as components in the filaments of the present invention can be found among the polyurethanes or polyureas which may be made either by conventional methods or by the above-described interfacial methods as well as among the polyvinyl compounds including such polymers as polyethylene, polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, and similar polymers. Copolymers may also be used. Numerous monomers, including ethylenically unsaturated sulfonic acids as the methallyl sulfonic acids and others disclosed in U.S. Patents 2,527,-300 and 2,601,256, can be copolymerized with acrylonitrile as disclosed in Jacobson U.S. 2,436,926 and in Arnold U.S. 2,456,360 using the techniques of U.S. Patents 2,628,223 and 2,546,238 to produce copolymers useful herein.

The new higher melting, higher density forms of polyhydrocarbons as polyethylene and polypropylene having a decreased amount of chain branching and/or isotatic structures are particularly suitable in this invention.

In addition to the polymers and copolymers discussed above, polymers can be used that have been grafted with another monomer, e.g., N-vinyl pyrollidone on 66 nylon as disclosed in Belgian Patent 572,577 granted April 30, 1959. It is evident from the foregoing description that the compounds are operative in the method comprising the length stabilization step only when the materials are combined in the composite filaments in such a way that the "normally load-bearing" component which is the component with the higher shrinkage can be length stabilized under conditions which do not substantially reduce the residual shrinkage of the other component so that a differential in shrinkage of at least 2% and preferably 5% or more is achieved. Actually, after the length stabilizing treatment, the "normally load-bearing" component has a lower shrinkage than the other component and reversal of crimp results. The physical properties and particularly those properties as residual shrinkage, tensile recovery, or permanent set by extension among others of the fiber-forming polymers are well known and can easily be determined. Therefore, by comparing the physical property data of the desired components, the operability of any given combination according to the present invention can easily be determined by following the teachings given herein.

The fiber-forming high polymeric materials can be length stabilized by crystallizing the polymer under conditions wherein no shrinkage can occur. In other words the crystallization is effected under conditions of tension which equals the forces developed in the filaments during the treatment. Crystallization or length stabilization respectively of many of the fiber-forming high polymeric materials can therefore be accomplished preferably by a heat treatment of the taut filaments. The temperature applied should generally be higher than the apparent minimum crystallization temperature of the "normally load-bearing" component which is well known or can easily be determined for each polymer. A convenient method for determining the apparent minimum crystallization temperature (T_i) is described, e.g., in U.S. 2,578,899. Preferably, however, the apparent minimum crystallization temperature is determined by X-ray diffraction measurements on samples of cold drawn filaments which have been subjected to taut heat treatment at progressively increasing temperatures. Filament exposures are suitably made 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). The degree of crystallinity may be judged by direct examination of the diffraction pattern or from radical densitometer traces along the equator of the X-ray diagram. Such a trace will show two distinct peaks for fibers having a well developed crystalline structure whereas with an amorphous structure or with very low degrees of crystallinity the peaks cannot be resolved. The apparent minimum crystallization temperature by

this method is the minimum temperature of heat treatment at which a definite crystalline structure is detectable from direct examination of the X-ray diagram or at which two distinct peaks are observable in the densitometer trace.

The X-ray diffraction technique for determining the apparent minimum crystallization temperature is preferred since it is a direct method and is subject to fewer errors than indirect methods such as the "change in density" method described above. For a given type of polymer the apparent minimum crystallization temperature will vary to some extent depending on the molecular weight of the polymer and upon other factors such as orientation, etc.

To achieve the results of the present invention, namely, length stabilizing one component and not affecting to a substantial extent the residual shrinkage of the other component, a temperature may be chosen which is lower than the apparent minimum crystallization temperature of the counterpart. However, depending on the nature of the other component or components in the combination and the length of time of exposing the composite filaments to the taut heat treatment, a higher or lower temperature can be chosen to achieve optimum results and the tightest possible crimp.

For instance, the other component may have a lower crystallization temperature than the "normally load-bearing" component but have a substantially higher shrinkage after crystallization than does the "normally load-bearing" component after crystallization. In this case both components will be crystallized after the heat treatment but the "normally load-bearing" component having the lower tensile recovery properties will be on the outside of the crimp helix.

The temperature range for the taut heat treatment may vary in wide limits and may be up to about 100° C. or more above T_i of the "normally load-bearing" component. Usually, however, best results are obtained when applying a temperature in the range of 5° C. to 70° C. above T_i of the "normally load-bearing" component. The lower temperatures in this range are applied when the composite filaments are exposed to the taut heat treatment for longer periods of time, e.g., for 30 to 60 minutes, while the higher temperature range is applied with shorter heat treatments, e.g., of some minutes or seconds or less. The temperature of the heat treatment should in any event, however, be lower than the softening or melting temperature of the lower melting component in the composite filament. For a given combination with a given set of processing conditions, however, the temperature of the taut heat treatment is very critical and usually should be kept in a range of plus or minus 10° to plus or minus 15° of its optimum temperature in order to achieve maximum results. In the continuous process shown in Example V the temperature of 140° C. at the hot plate should be maintained within the limits of approximately plus or minus 10° C. in order to produce a yarn with maximum crimp retention and crimp tightness. If optimum properties are not desired, the temperature of the hot plate could be varied in limits of about plus or minus 15 to 20° C. Even though the temperature of the draw pin is not as critical as the temperature of the hot plate, it should not vary more than approximately 30° C. and preferably 15° C. from the temperature of 85° C. used in the foregoing example. As already pointed out with varying spinning and processing conditions and with different combinations of materials, the optimum temperatures may vary in wide limits.

It is known that only elevated temperatures bring about crystallization and length stabilization of a given polymer but also other special conditions under which the material is treated. Thus, for instance, the presence of plasticizers has a great effect on the temperatures necessary to achieve crystallization and reduction of residual shrinkage. This can be utilized in the present invention by adding a plasticizer to the "normally load-bearing" component. This can be an organic plasticizer as commonly used in polymer applications which may be subsequently removed. Water may take the function of a plasticizer especially when the two polymers differ in their ability to absorb moisture.

On the other hand, for instance, when poly(hexamethylene adipamide) and poly(ethylene terephthalate) are used in a combination wherein the polyamide forms at least part of the outer skin of the composite filament, it is advantageous to remove most of the moisture from the polyamide before or while applying the taut heating step of this invention. The reverse situation may be true with other combinations. By varying these conditions, as well as the lengths of time of the heat treatment and/or the temperature of the treatment, the tightness of crimp and crimp permanence can be varied. In order to obtain a crimp as tight as possible, optimum conditions for the stabilizing treatment are generally observed.

With some combinations of high polymeric materials it is not possible to avoid fully the reduction of residual shrinkage of the co-acting compound or compounds in the composite filaments when the length stabilization is brought about by heating to a temperature higher than the apparent minimum crystallization temperature of the normally load-bearing component. This is true, for instance, when the "normally-load-bearing" component has a higher apparent crystallization temperature than its counterpart. In these instances and also for other reasons, sometimes other methods might be preferred for crystallizing or length stabilizing the normally load-bearing component. A very convenient method comprises the exposure of the composite filament, while in taut condition, to the action of certain polar organic liquids which are latent solvents for the amorphous regions of the load-bearing component and which therefore promote crystallization of the normally load-bearing component but do not affect the other component or components substantially. A suitable liquid will be chosen depending on the specific combination of polymeric materials. In a combination of polyethylene and poly(ethylene terephthalate), for instance, acetone has proven to be an excellent material to promote crystallization of the poly(ethylene terephthalate). Other suitable polar liquids are, for instance, chloroform, methylene chloride, tetrachloroethane, phenol, m-cresol among others. In those liquids having too great swelling action, dilution with water or other less active liquids may be necessary. Temperatures and other conditions of the liquid treatment may be varied in wide limits with various combinations of polymers to achieve every desired result with respect to the tightness, permanence and appearanec of the "beta crimped" filaments. Example IV above shows the preparation of a composite filament from polyethylene and poly(ethylene terephthalate), using a liquid treatment for length stabilization.

The conditions applied for drawing the spun multicomponent filaments of this invention may vary in wide limits. Instead of using a pin as mentioned in Example I, other convenient means for drawing the filaments may be applied, for instance, rolls being driven at different speeds. Also, the temperatures at which the filaments are drawn may vary in wide limits and depend mostly upon the properties of the single materials forming the composite filament and of the final desired results. As is the case in the production of conventional unitary filaments, the preferred drawing temperatures for the composite filaments of this invention may vary between room temperature or slightly elevated temperatures and temperatures of about 100° C. up to relatively high temperatures which may be in some cases as high as about 70° C. below the melting point of the lower melting material. Since in the present invention combinations of at least two different materials are employed, the specific drawing characteristic of each material used should be considered in order to obtain best results. Drawing temperatures which are lower than the apparent minimum crystallization temper-

ature (T_i) of the "normally load-bearing" component may be employed where a separate plasticizing step is provided. However, if desired the drawing and taut heat treatment may be combined to achieve the desired stabilization of the "normally load-bearing" component.

The composite filaments have been prdouced in the examples by the melt spinning technique. Naturally, also any other spinning method like "plasticized melt" spinning, dry spinning, wet spinning, can be employed successfully. In some instances, particularly when the melting behavior or the solubility of the components in a combination would not permit spinning the components by similar methods, a combination of dissimilar methods is indicated. Thus, for instance, one component, preferably the component forming the sheath can be spun as a solution in a high boiling solvent or as a plasticized melt, while the core-forming component is extruded as the molten polymer. Similar combinations of spinning methods can be used for spinning "side-by-side" structures. In these instances, the solvents or plasticizers may be wholly or partially removed subsequently, preferably by washing them out by the help of low boiling solvents.

In the method involving length stabilization, as shown in Example I, the composite filaments are substantially uncrimped after the application of the length stabilization treatment but contain, however, a "potential crimp." The crimp can be developed in these filaments very readily by a suitable after-treatment. The filaments containing the "potential crimp" can be processed as any ordinary uncrimped continuous filaments or staple fibers to worsted or knitted goods. The crimp can then be imposed on the filaments at any time by a suitable relaxing or shrinkage treatment. This shrinkage treatment was performed in the foregoing examples by exposing the composite filament containing the potential crimp to boiling or hot water. Good results, however, may also be obtained, for instance, by the application of moist heat or steam, which of these after-treatments for bringing about the crimp are chosen depends mostly on the properties of the components forming the composite filaments and on the final properties which are desired in the crimped filaments. In general, the temperature applied in the crimping procedure should be higher than the apparent second-order transition temperatures (T_g) of the polymers forming the composite filament in order to achieve the favorable results of the invention. The apparent second-order transition temperature (T_g) of a polymer is defined as the temperature at which a discontinuity occurs in the curve of a first derivative thermodynamic quantity with temperature. A convenient method for measuring this temperature is shown in U.S. Patent No. 2,578,899. Since water acts as a plasticizer in many polymers, thus lowering the apparent second-order transition temperature (T_g), this should also be considered in measuring T_g and in selecting the appropriate crimping method and temperature. Other factors influencing the optimum condition for crimping the composite filaments of this invention are, for instance, the spinning, drawing and length stabilizing conditions used and also other factors, for instance, whether the composite filament is processed as continuous filament or as staple or as a woven or knitted textile fabric. Therefore, by varying the after-treating conditions for bringing about the crimp, also the properties and appearance of the crimped filaments can be varied to a great extent in any desired way.

In general, the composite filaments are drawn from about 2 times to about 8 times their original lengths. Prior to drawing the filaments are attenuated; that is, they are slenderized by pulling the freshly extruded filaments away from the orifice at a rate faster than the extrusion rate. The drawing or orientation step is in addition to attenuation, but also has a slenderizing effect. The extent of drawing will, of course, also depend somewhat upon the nature of the particular polymers used in the composite filament and upon the type of eccentric relationship between those polymers in the composite filament.

In the hot relaxing treatment of this invention used to develop the crimp, the medium may be any inert atmosphere capable of being heated to a temperature of about 100° C. Thus, the filaments may be heated in air, nitrogen, hot or boiling water, carbon dioxide or any gaseous or liquid media inert to the polymers in the composite filaments. The temperature used is generally in the neighborhood of 100° C., but it may be lower or higher. In general, any temperature above about 50° C., but below the melting point of the lowest melting polymeric constituent in the composite fiber, may be used. With certain combinations of polymers, however, there may be a tendency for the shrinkage characteristics to change as the temperature is increased and at relatively high temperatures the crimp may be reversed. For this reason, a temperature in the range of about 50° C. to about 150° C. is preferred.

The length of time that the composite filaments are subjected to the hot, relaxing treatment is not critical, because the crimp develops immediately and spontaneously. Thus, the time may be very short, as, for example, a matter of seconds, although it may be desired in some cases to continue the length of treatment for a longer period of time such as 30 minutes, or even for several hours.

Further, the spinnerets described herein may be simplified in certain respects. To illustrate, the tube 31 in the spinneret shown in FIGURE 2 may be dispensed with, for hole 8 in the adapter is eccentrically located above and in respect to orifice 9, and the jetting of polymer 13 into the melt of polymer 14 and the polymer flow thereafter leads to a sheath-core structure. Also, the provision of recesses 23 of relatively large area in conjunction with channels 6 of smaller area, as shown in the spinneret assembly given in FIGURE 2, results in the formation of ridges between the channels. These ridges can be removed both in the adapter or spinneret plate. That is, one very large recess is provided, the orifices being appropriately placed, and the polymer fed under pressure flows to the various orifices.

The crimped two-component filaments of this invention show a tight permanent crimp. The crimp obtainable in this invention corresponds usually to more than 10 crimps per inch and up to 300 crimps per inch. The crimp permanence is 50% up to 100% when measured and calculated by the test described above, and those composite filaments having a crimp permanence of about 80% or more are preferred.

It is well known that, in many applications of the continuous or staple-length crimped filaments in textile materials, sometimes relatively high tensions are applied to the fabrics and thus to the single filaments in daily use of these materials. Therefore, high crimp retention, also under high tensions, which is necessary for dimensional stability of the worsted or knitted goods from these crimped filaments is very important for practical application of the crimped filaments.

The characteristic of the new crimped filaments containing the "beta crimp" to retain the original high crimp also after the application of high tensions or high loads to the filaments makes them especially usful for many textile applications where bulky highly crimped filaments are desired and where high crimp retention under high stress is of great importance. This applies also to the crimped filaments which are cut to staple length and which are usually spun into yarns and processed according to known textile processing methods to knitted or woven goods. The new staple filaments of this invention can be crimped before they are further processed or in any state of processing, for instance, after they are spun into yarns or after the woven or knitted goods are made from these yarns. Another important application comprises the processing of the continuous filaments into

bulky fabrics which again can be carried out with the continuous filaments in the crimped or uncrimped state. In the latter case, the crimp can be developed after weaving or knitting the yarns obtained therefrom or in any stage of the processing. Very interesting applications of the continuous yarns are, for instance, the preparation of worsted fabrics which may be woven from the uncrimped yarns containing the potential crimp and which are crimped after weaving and finishing. These worsted fabrics have an appearance and hand very similar to those obtained from staple yarns. However, they do not possess the disadvantages in processing and use of these fabrics. Another very important application of the fibers of this invention comprises the use in carpets and other heavy textile goods where again the fibers containing the potential crimp can be knitted or woven and the crimp is developed in the finished goods.

This application is a continuation-in-part of copending application Serial No. 856,572, filed December 1, 1959.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process for preparing improved helically crimped composite filaments having a component of higher tensile recovery properties located at the inner portion of the helical coils, said process comprising the steps of

(1) simultaneously extruding a plurality of different synthetic fiber-forming polymeric materials through an orifice to form a unitary filament in which said different materials extend as distinct filamentary components along the length of the filament in adhering relationship, one of said components having for a predetermined degree of orientation higher shrinkage and lower tensile recovery properties than the remainder of said components,

(2) stretching said filament to provide said predetermined degree of orientation in said components,

(3) stabilizing the length of said higher shrinkage component by selectively crystallizing it while holding said filament under tension,

(4) releasing the tension on said filament and thereafter heating said filament in an unrestrained condition at an elevated temperature above the second order transition temperature but below the melting temperature of all of said components whereby said filament develops a helically coiled configuration.

2. The process of claim 1 in which said one component is a polyethylene terephthalate component and said other different component is polyhexamethylene adipamide.

3. The process of claim 2 wherein said elevated temperature is between about 50° C. and about 150° C.

4. A process for preparing improved composite filaments which are readily crimpable to form helically crimped filaments having a component of highest tensile recovery properties positioned at the inner portions of the helical coils of the crimped filament which comprises

(1) simultaneously extruding a plurality of different synthetic fiber-forming polymeric materials through an orifice to form a unitary filament in which said different materials extend as distinct filamentary components along the length of the filament in adhering relationship, one of said components having for a predetermined degree of orientation higher shrinkage and lower tensile recovery properties than the remainder of said components,

(2) stretching said filament to provide said predetermined degree of orientation in said components, and

(3) stabilizing the length of said higher shrinkage component by selectively crystallizing it while holding said filament under tension.

5. The process of claim 4 in which said one component is a polyethylene terephthalate component and said other different component is polyhexamethylene adipamide.

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