

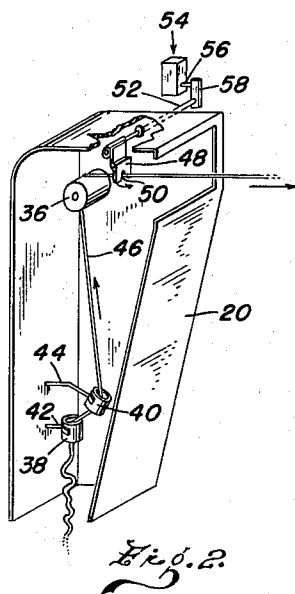
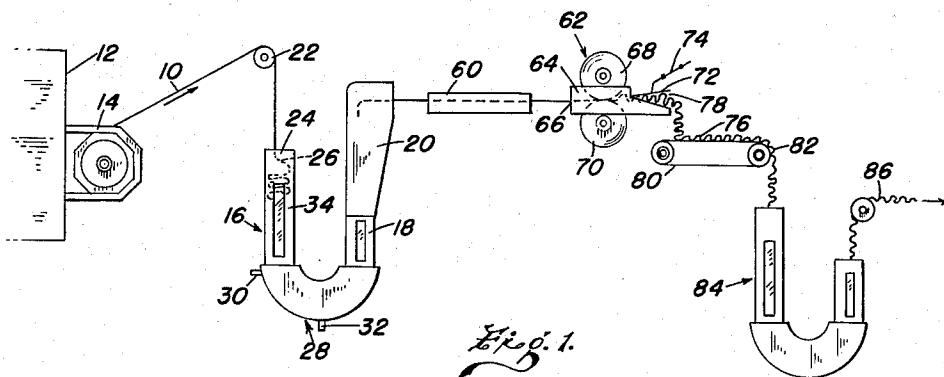
Nov. 22, 1960

M. SONNINO

2,960,752

METHOD FOR PRODUCING A CRIMPED TOW

Filed Nov. 4, 1955



INVENTOR.
MARIO SONNINO,

BY
Harold L. Kauffman
ATTORNEY.

1

2,960,752

METHOD FOR PRODUCING A CRIMPED TOW

Mario Sonnino, Stamford, Conn., assignor to American Cyanamid Company, New York, N.Y., a corporation of Maine

Filed Nov. 4, 1955, Ser. No. 545,043

14 Claims. (Cl. 28—76)

This invention relates broadly to a method and apparatus for producing a crimped tow of filamentary material, more particularly a synthetic filamentary material, and specifically a polyacrylonitrile filamentary material, that is, one which is comprised of a polymer (fiber-forming polymer) of acrylonitrile. The invention is especially concerned with certain new and useful improvements in a continuous method of producing a crimped tow of a polyacrylonitrile filamentary material, advantageously one comprised of a polymer of acrylonitrile containing a major proportion (preferably at least 75%) by weight of acrylonitrile combined in the polymer molecule.

It was suggested prior to my invention that certain vegetable fibers (especially cotton, hemp, jute, ramie and flax) and certain uncrosslinked thermoplastic synthetic fibers (specifically viscose and acetate rayons, nylon, fibers made from condensation products of terephthalic acid and glycol, and fibers made from polyvinylidene chloride) be mechanically crimped while hot and then immediately crimp-set by cooling, while compacted under a substantially constant pressure, in a cooling zone of the same apparatus. Such a method and apparatus for practicing the same are described in, for example, Rainard U.S. Patent No. 2,575,839.

The present invention has, as its primary object, certain new and useful improvements in processing a tow of a polyacrylonitrile filamentary material (oriented polyacrylonitrile filamentary material), and more particularly one comprised of a polymer of acrylonitrile containing a major proportion by weight of acrylonitrile combined in the polymer molecule, whereby a crimped tow having more crimp and greater uniformity of crimp is secured, with less damage to the individual filaments, than was obtainable by prior practices.

Briefly described, the improvement of this invention comprises continuously feeding a hot, wet tow of polyacrylonitrile filamentary material under substantially uniform tension, for example, a substantially uniform low tension of the order of from about 0.005 to about 0.5 gram per denier, preferably from 0.005 to about 0.2 or 0.3 gram per denier, to the feed-in end of a crimping zone. The aforesaid tow, as it is thus fed to the crimping zone, is wet with an aqueous fluid comprising mainly water that is applied after the tow previously had been dried. The wetted tow usually contains water in an amount corresponding to from about 100% to about 700%, by weight, based on the weight of the bone-dry tow. Both the tow and the said aqueous fluid are at a temperature of from about 155° F. to about 205° F., and preferably at a temperature of from about 160° F. to about 195° F., when the wetted tow is fed to the crimping zone. The wetted and heated tow is continuously crimped while it is within the aforesaid temperature range, after which the crimped, hot tow is continuously passed from the crimped zone to a separate cooling zone while it is in a relaxed state. Thereafter the crimped, hot tow is continuously passed, while relaxed, through

2

the aforesaid cooling zone wherein it is cooled to a temperature below 120° F. and preferably to a temperature not higher than about 100° F., e.g., 80°–90° F. The scope of the invention also includes apparatus features.

The novel features of the invention are set forth in the appended claims. The invention itself, however, will be understood most readily from the following detailed description thereof when considered in connection with the accompanying drawing, which is illustrative of the invention, and in which:

Fig. 1 is a somewhat schematic view of apparatus embodying the invention; and

Fig. 2 is a perspective view of a portion of the apparatus indicated in Fig. 1 and with the front side thereof removed so that the working parts thereof will be visible.

It was suggested prior to the present invention (e.g., in Wicker U.S. Patent No. 2,698,970 dated January 11, 1955) that a tow or bundle of polyacrylonitrile fibers or filaments be mechanically crimped or crinkled while in a stretched (oriented), wet-gel state. Such fibers are produced by wet-spinning, for instance as described in Cresswell U.S. Patent No. 2,558,730 dated July 3, 1951. Contrary to this suggested practice of crimping of tow of polyacrylonitrile filaments in gel state, I have found that if the polyacrylonitrile tow to be crimped is dried (or, in general, if the structure of the fiber is collapsed) prior to crimping, it is subject to less damage during crimping than if it is crimped in the wet-gel state. This is apparent by the geometry of the crimp, which is different in the two cases, viz., rounded peaks when the dried polyacrylonitrile tow is crimped as compared with sharp, splintered corners that result when a polyacrylonitrile tow of wet-gel filaments is crimped.

I have also found that if crimping of a tow of polyacrylonitrile filaments is carried out at room temperature (20°–30° C.), the tow is not as receptive to crimping and is subject to greater damage than when crimping is effected at a higher temperature. More particularly, I have found that the higher the crimping temperature, the less the loading at the crimping chamber in producing the same degree of crimp and the higher the tenacity of (that is, the less the damage to) the filaments.

I have further found that the temperature of the tow of polyacrylonitrile filaments, when subjected to crimping, should not exceed an upper limit of about 205° F.; or, for optimum results that upper limit which corresponds approximately to the second order of transition temperature for the particular polyacrylonitrile. Taking as an example a tow of polyacrylonitrile filaments composed of a polymer containing, by weight, about 88% acrylonitrile, about 6% vinyl acetate and about 6% 2-methyl-5-vinylpyridine, the upper temperature limit of crimping, for optimum results, should not exceed about 195° F., which corresponds approximately to the second order of transition temperature of this particular polymer. The criticality of the temperature at which the tow of polyacrylonitrile filaments is crimped is due, for one reason, to the fact that the loading at the crimping chamber that is necessary for crimping, despite the fact that it is relatively low, is sufficient to fuse the filaments together at this point if the temperature is excessive. In such cases the tenacity of the filaments is lowered to a very great extent, and may approach that of unoriented polyacrylonitrile filaments.

The present invention is based on my further discovery that successful crimping of a tow of polyacrylonitrile filaments in a stuffing-box type of tow crimper is contingent, to a great extent, upon feeding the tow under substantially uniform tension to the feed-in side of the crimper and complete relaxation of the tow at the outlet of the crimper. The introduction of the tow under tension to the inlet of the crimper can be effected in various

ways, for example, by the use of suitable guides or feed rolls prior to the crimping-machine rolls. Relaxed delivery of the tow from the crimper can be secured by preventing the tow from being subjected to any tension (even its own weight) until the temperature of the tow has been lowered sufficiently to set the crimp. After crimping the tow as hereinbefore described, it should be cooled or quenched to prevent the crimp from being removed when subjected to the tension of subsequent operations.

Referring to the drawing there is shown somewhat schematically in Fig. 1 apparatus by the use of which the method of the invention can be carried into effect and illustrative thereof. The tow that is processed in practicing the present invention may be one that has been produced either by a dry-spinning or by a wet-spinning method. In the latter case the oriented, gelled tow is commonly first dried. Thus, as shown in Fig. 1, a dried tow 10 of polyacrylonitrile filamentary material (that is, a tow of continuous, oriented filaments comprised of a polymer of acrylonitrile) is led from a dryer 12, which may be of any suitable form, e.g., a tunnel dryer, and through which the tow is passed while supported, in relaxed state, on a moving support or apron 14.

If the dried tow 10 is to be freed of residual shrinkage (assuming that the polyacrylonitrile tow being processed is capable of being further shrunk), this advantageously can be done by the method disclosed (using the apparatus illustrated) and claimed in Cresswell et al. copending application Serial No. 538,618 filed October 5, 1955. Briefly described, this Cresswell et al. method comprises continuously passing a tow of the kind with which this invention is concerned, in a relaxed or free-to-shrink state, through a zone comprised of liquid, e.g., water or other liquid alone or water or other liquid admixed or in contact with a hot gaseous medium, e.g., steam. The temperature of this zone is within the range of from about 99° C. (2105 F.) to about 110° C. (230° F.), and when the zone is composed of water the temperature is generally of the order of from about 99° C. to 100° C. (212° F.). The hot treating-liquid is introduced into the treating zone either continuously or intermittently, as desired or as conditions may require. For example, the liquid may be introduced alternately first from one side of the zone, e.g., at or near the inlet end to the zone, and then from the opposite side. A portion of the tow to be treated is maintained in the treating zone in contact with the hot liquid for a period sufficient to reduce the residual shrinkage to from 0% to not more than about 2% to 3%. To effect this result the contact period is usually at least 5 seconds, e.g., from 5 seconds to 30 minutes or longer. The tow is retained in the treating zone for the required residence time while continuously introducing untreated tow into the inlet end of the treating zone and continuously withdrawing treated tow from the outlet end of said zone.

The tow 10, if it is to be freed of residual shrinkage as described briefly above and more fully in the aforementioned copending Cresswell et al. application Serial No. 538,618 advantageously is first wetted with water by suitable means in order to facilitate subsequent handling, although it is not necessary that this be done. A wetting device (not shown in the drawing of the instant case), if employed, may be of any suitable form, e.g., a spray, trough, tube, wiper, etc.; or it may be of the kind illustrated and described in the aforementioned Cresswell et al. copending application.

From the moving support 14, or from a wetting device, if used, the tow 10 moves continuously to a treating zone for removing residual shrinkage. Such a zone advantageously is provided by means of the J-box 16 having attached to the short leg 18 of the J a section 20. En route to the J-box the tow advantageously is passed through a traverse mechanism (not shown), thence over a fluted lower roll (not shown), an upper roll (not shown)

provided with a pinch roll (not shown), the weight of which is such that the tow is pinched against the surface of the aforesaid upper roll. Such a pinch roll provides traction so that the tow is under tension at least sufficient to move it to the point of contact of the pinch roll upon the surface of the aforesaid upper roll, and is under little or no tension after it leaves that point. From such an arrangement of rolls, if employed (as preferably is done), the tow passes over the fluted feed roll 22, and then falls downwardly in a relaxed, free-to-shrink condition into the inlet end 24 of the J-box 16.

The J-box 16 is preferably provided at its inlet end 24 with spray means on one side and separate spray means on the opposite side. The action of the alternate application of a spray of liquid first from one side of the inlet end of the J-box and then from the opposite side causes the tow to be deposited in the treating zone in the desired configuration, for instance, as indicated at 26 in Fig. 1. In the absence of suitable means, e.g., alternating spraying means such as that herein described, the tow piles up or tends to pile up in a narrow pile directly under the discharge side of the feed roll 22, finally toppling over and causing or tending to cause tangling on the discharge side of the J-box.

The plaited tow is carried downwardly to the middle portion 28 of the J-box which is jacketed. A hot fluid medium, for example, water at 99° C. to 100° C., steam or other hot fluid of the desired temperature, is introduced through the inlet conduit 30 into the jacket and withdrawn through the outlet conduit 32. The water or other liquid introduced into the upper portion of the J-box through the spray means occupies the space, along with the tow, in the middle portion of the J-box. Suitable means (not shown) are provided for draining off excess water from long leg 34 of the J-box, while suitable openings (not shown) in the short leg 18 permit the water which has flowed with and through the mass of tow to escape into a suitable receptacle or conduit (not shown). Inlet conduit 30 provides means for introducing a hot fluid medium, e.g., hot water, steam, oil, etc., to the jacket surrounding the middle portion 28 of the J-box; while outlet conduit 32 provides means for withdrawing the said hot fluid medium. Circulation of this hot fluid medium through the said jacket maintains the temperature of the liquid and tow in the middle portion 28 at the desired point.

In operation, a head of liquid normally builds up in the leg 34 of the J-box, and this liquid head assists in carrying the deposited tow through the middle portion of the J-box. The middle portion of the J-box through which the tow passes is so constructed that there are no sharp corners and hence there are no obstructions to the free movement of the tow through this portion of the box. The tow is retained in contact with the hot liquid in the bottom portion of the J-box 16 for the desired period and which may range from 5 seconds to 30 minutes or more. While the tow is retained in this bottom portion of the J-box, untreated tow is being continuously introduced into the inlet end 24 of the J-box as above described and treated tow is continuously being withdrawn from the outlet end of the J-box at such a rate that the amount of retained tow within the J-box remains substantially constant.

In the foregoing description reference has been made specifically to the use of water at a temperature of from about 99° C. to 100° C. as the liquid that is introduced into the treating zone, e.g., a J-box. As alternative liquids in place of water for shrinking the tow in the treating zone may be used such non-solvent liquids (that is, liquids which do not dissolve or harmfully affect the tow) as ethylene glycol, diethylene glycol, ethylene glycol monoethyl ether, glycerol, propylene glycol and the like. It is desirable that such alternative treating liquids, if employed (either alone or with water or other liquid),

be miscible with water so that they may be readily and economically removed subsequent to the shrinking treatment by washing the tow with water. The use of liquids of the type described above permits the shrinking operation to be carried out at temperatures above 100° C., say 110° C., at atmospheric pressure without distillation of the liquid.

The section 20 attached to the short leg 18 of the J-box 16 contains apparatus, specifically a tow-processing device, which is especially adapted for use in practicing the present invention, although it is not limited thereto. This tow-processing device is claimed in my copending application Serial No. 610,027, filed September 14, 1956 as a division of the instant application.

As shown in Fig. 2, this apparatus includes a guide roll 36 over which the tow passes and a plurality of guides 38 and 40 through which the tow passes en route to the guide roll 36. At least one of the guides 38 and 40 is rigidly held in position. In Fig. 2 both guides are shown as being rigidly held in position by means of the supports 42 and 44. If desired, only the guide 38 may be rigidly held in position while the guide 40 rides freely above the guide 38, in which case it is of sufficient weight that it will subject the upwardly moving, shrunken tow 46 to frictional contact and thereby place the latter under at least some tension. The guides 38 and 40 aid in aligning the filaments of the tow 46 along their longitudinal axis. They are so positioned with respect to each other and to the guide roll 36 that the moving tow 46 is under tension both before and after it leaves the guide roll 36. The tow is drawn by the feed rolls of the crimper against the action of the friction of the free-running guide roll 36, guides 40 and 38, and the weight of the tow.

A notched guide 48 is positioned adjacent to the take-off side of the guide roll 36. The apex of the notch 50 is upward so that a knot-free tow will pass through the notch. The notched guide 48 is suitably mounted on a support 52, e.g., the support 52 can be a pivotal support and the notched guide 48 can be fixedly mounted thereon. The mounting of the guide 48 on the support 52 advantageously is such that, when a knot in the tow contacts the apex of the notch in the notched guide, the resulting movement, specifically upward and backward movement, of the latter will immediately actuate a micro-switch 54 provided with the plunger 56 when the rod 58 attached to the support 52 swings backward and actuates the plunger 56, thus stopping the driven crimping rolls 68 and 70.

From the guide roll 36 the shrunken tow 46 is passed to a conditioning device 60 wherein the tow is contacted with an aqueous fluid comprised mainly or composed solely of water. This aqueous fluid is at a temperature of from about 155° F. to about 205° F. The conditioning device 60 may take the form of spray means; or it may comprise a trough or other receptacle wherein the shrunken tow is continuously passed through a bath of the aqueous fluid; or it may take the form of a receptacle and a series of lower and upper rolls whereby the tow is passed in a serpentine fashion first through the bath of aqueous fluid (that is, over a lower roll immersed in said bath), then upwardly and over an upper roll, and thence downwardly through the bath as before, repeating this operation as many times as may be desired or required in order to provide effective contact between the aqueous fluid and the tow being processed. In this way the tow is brought to the desired elevated temperature at which it is to be fed, under substantially uniform tension, to the feed-in end of the tow crimper 62.

The hot aqueous fluid with which the tow is contacted by device 60 may be hot water alone or it may be an aqueous fluid comprising mainly water and a lesser amount of an effect agent, e.g., an antistatic material containing a low viscosity mineral or other suitable oil; a lubricant; or any other additive that will alter the

properties of the tow or improve its processability either during manufacture or in subsequent textile operations.

The tow crimper 62 advantageously is of the "nip-rolls and stuffing-box" type, or, for brevity, sometimes designated merely as "stuffing-box" type. A preferred type of tow crimper for use in practicing the present invention is disclosed and claimed in my copending application Serial No. 545,023, filed concurrently with the present application, and which has now matured into Patent No. 2,846,729, dated August 12, 1958. The hot, wet tow from the conditioning device 60 enters an extension of the stuffing box 64 of the crimper at the feed-in end 66, and then passes between the top crimping roll 68 and the bottom crimping roll 70. In the preferred tow crimper, and as is more fully described in my aforementioned copending application, the stuffing-box body is extended toward the feed-in end in order to confine the tow at the nip of the crimping rolls and to form a feed trumpet. The confinement at the nip of the rolls prevents the sides of the tow from being differently crimped than that of the middle of the tow. The extension of the stuffing box on the feed side of the crimper further serves to provide rigid support for the stuffing box proper, the length of which is kept to a minimum in order to obtain maximum uniformity of crimp. The gate 72 permits the discharge of the crimped tow, while the loading rod 74 attached to said gate provides the proper load for crimping the particular tow to the desired degree.

The crimped, hot tow 76 is discharged continuously from the discharge end 78 of the tow crimper. The temperature of the tow at this point ranges from about 150° F. to about 200° F. and, more particularly, from about 165° F. to about 195° F. It contains, for example, from about 50% to about 150% or 200% by weight of water, based on the weight of the bone-dry tow. The crimp in the tow is set by continuously passing the hot tow, while in a relaxed state (preferably while in a supported, relaxed state), to a cooling zone wherein the temperature of the tow is reduced to below 120° F., and preferably to a temperature not higher than about 100° F., e.g., 80°-90° F. By cooling or quenching the hot-crimped tow in a separate cooling zone while in a relaxed state in accordance with my invention, there is greater assurance of obtaining a more uniform product since there is less chance for physical damage to the crimped tow. A uniform product is a matter of considerable practical importance, not only from the standpoint of dye uniformity but also from the standpoint of uniformity in mill processing and in end uses.

Any suitable means may be employed in cooling or quenching the hot, crimped tow, while it is in a relaxed state, in order to set the crimp therein. For example, it could be exposed to blasts of cold air or other gas sufficient to cool the tow quickly and to set the crimp; or it could be continuously passed through water or other cooling fluid, or sprayed with such fluids, while it is in a relaxed state; or it could be brought to or near room temperature by conveying it through air at room temperature for a considerable distance while it is in a relaxed state on a continuously moving support, such as a belt or apron. A particularly suitable method for quenching the hot, crimped tow is that disclosed and claimed in the copending application of William N. Sellers, Serial No. 544,847, filed concurrently herewith, and which has now matured into Patent No. 2,874,446, dated February 24, 1959.

As is described in the aforementioned copending Sellers application, a tow of a polyacrylonitrile filamentary material is passed directly from a tow crimper, wherein it has been hot-crimped mechanically, to a quenching zone in which cooled gas (e.g., cooled air, nitrogen, flue gas, etc.) is circulated. The tow-quenching apparatus or so-called "tow quencher," as with the other means mentioned hereinbefore, is separate and distinct from the

crimping apparatus, as a consequence of which the hot-crimped tow is readily available for inspection prior to setting of the crimp therein and the practical advantages of which will be immediately apparent to those skilled in the art. The hot tow in relaxed state is supported on a moving support, e.g., a continuously moving apron or screen formed of metal or other suitable material. This support is preferably porous, e.g., by being provided with orifices or slots, or by the use of wire screening, so as to facilitate the passage of the cooled gas through the thusly supported tow. The supported, relaxed tow is passed continuously through the quenching zone. The temperature of the quenching zone and the time the tow is present therein are correlated so that the tow is at a temperature below 120° F., and preferably not higher than about 100° F., when it leaves the said zone.

In the embodiment of the invention illustrated in Fig. 1, the crimped, hot tow 76 is shown as being continuously discharged from the tow crimper to the feed-in end of a continuously moving support or conveyor 80, e.g., a belt or apron, which carries the tow, while relaxed, to the take-off end 82 of said conveyor. The conveyor 80 advantageously may be positioned so that it is at about the same level (or only slightly below the same level) as the discharge end of the tow crimper, so as to obviate or minimize crimp damage of the hot, wet tow while falling any substantial distance upon the conveyor 80.

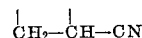
From the take-off end 82 of the conveyor the tow is continuously passed, as illustrated in Fig. 1, to a suitable cooling device, e.g., a J-box 84, which contains a relatively cold aqueous fluid, e.g., cold water (for instance, at 15°-30° C. as charged to the J-box), thereby cooling or quenching the tow to a temperature within the range hereinbefore mentioned. Cold water or other aqueous fluid can be introduced into, and withdrawn from, this J-box (and also to and from the jacket thereof) in the same manner fully described hereinbefore and in the aforementioned Cresswell et al. copending application with respect to the introduction of hot water to and from J-box 16. When this method of quenching the tow is employed, the water that is taken up by the crimp-set tow 86 (thereby forming a substantially saturated tow) is removed by passing the tow through a squeeze roll or other suitable device to press out a maximum amount of the entrained water. Thereafter it can be cut into staple lengths, e.g., by means of centrifugal cutters, and thence dried, opened and baled for shipment; or, alternatively, it can be dried in the form of tow, and the dried tow then plaited into a suitable container for shipment as tow.

Various modifications obviously can be made in the method and apparatus described hereinbefore and illustrated in the accompanying drawing. Thus, the tow used in practicing the present invention may be one produced either by a dry-spinning or by a wet-spinning method; in the latter case the oriented, gelled tow is commonly first dried in a suitable dryer. Such drying means may take the form of, for example, an apron dryer or the obvious equivalent thereof and whereby the tow is dried in a gaseous atmosphere, for instance, an atmosphere of air. Tow produced by a dry-spinning process may be processed as herein described, for example, after the freshly spun tow has been washed to remove residual solvent, oriented by stretching and the wet material then dried, if necessary, in a gaseous atmosphere.

When so-called "bulk" yarns are to be produced and wherein the residual shrinkage is desirable, then the J-box 16 (employed in reducing residual shrinkage to from 0% to about 3%) may be by-passed; or the tow may be passed therethrough without contacting it with any liquid whatsoever. If J-box 16 is by-passed, as in, for example, the production of bulk yarns, then suitable tensioning

means (e.g., a guide roll and a pinch roll, and between which the tow is passed) are provided a short distance before the tow is led through the conditioning device 60.

The polyacrylonitrile used in forming the tow of filamentary material (oriented continuous filaments) may be comprised of, for example, a homopolymer of acrylonitrile; or of a copolymer of, by weight, about 95% acrylonitrile and about 5% methyl acrylate; or of a ternary polymer of, by weight, about 88% acrylonitrile, about 6% of vinyl acetate and about 6% of a vinylpyridine, e.g., 2-methyl-5-vinylpyridine. Other acrylonitrile copolymers (thermoplastic acrylonitrile copolymers) of which the tow may be composed or comprised are acrylonitrile copolymers containing in the polymer molecules an average of, for example, at least about 35%, preferably at least about 75%, by weight of combined acrylonitrile. Taking as an example the expression "an acrylonitrile polymer containing in the polymer molecules an average of at least about 35% by weight of combined acrylonitrile," this means herein a polymerization product (homopolymer, copolymer or graft polymer or mixtures thereof) containing in the molecules thereof an average of at least about 35% by weight of the acrylonitrile unit, which is considered to be present in the individual polymer molecule as the group



or, otherwise state, at least about 35% by weight of the reactant substance converted into and forming the polymerization product is acrylonitrile. The expression "an acrylonitrile polymer containing in the polymer molecules an average of at least about 75% by weight of combined acrylonitrile" has a similar meaning herein.

Illustrative examples of monomers which may be copolymerized with acrylonitrile to yield a polymerization product containing in the polymer molecules an average of at least about 35%, preferably at least about 75%, by weight of combined acrylonitrile are compounds containing a single $\text{CH}_2=\text{C}<$ grouping, for instance, the vinyl esters and especially the vinyl esters of saturated aliphatic monocarboxylic acids, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinyl halides, e.g., the vinyl chlorides, bromides and fluorides; allyl-type alcohols, e.g., allyl alcohol, methallyl alcohol, ethallyl alcohol, etc.; allyl, methallyl and other unsaturated monohydric alcohol esters of monobasic acids, e.g., allyl and methallyl acetates, laurates, cyanides, etc.; acrylic and alkacrylic acids (e.g., methacrylic, ethacrylic, etc.) and esters and amides of such acids (e.g., methyl, ethyl, propyl, butyl, etc., acrylates and methacrylates, acrylamide, methacrylamide, N-methyl, -ethyl, -propyl, -butyl, etc., acrylamides and methacrylamides, etc.); methacrylonitrile, ethacrylonitrile and other hydrocarbon-substituted acrylonitriles; unsaturated aliphatic hydrocarbons containing a single $\text{CH}_2=\text{C}<$ grouping, e.g., isobutylene, etc.; and numerous other vinyl, acrylic and other compounds containing a single $\text{CH}_2=\text{C}<$ grouping which are copolymerizable with acrylonitrile to yield thermoplastic copolymers. Alkyl esters of alpha, beta-unsaturated polycarboxylic acids also may be copolymerized with acrylonitrile to form copolymers, e.g., the dimethyl, -ethyl, -propyl, -butyl, etc., esters of maleic, fumaric, citraconic, etc., acids.

Ordinarily, the molecular weight (average molecular weight) of the polyacrylonitriles (homopolymeric or copolymeric acrylonitriles) used in making the tow of filaments is within the range of 25,000 or 30,000 to 200,000 300,000 or higher, and advantageously is of the order of 50,000 to 100,000, e.g., about 70,000-80,000, as calculated from a viscosity measurement of the said polymerization product in dimethyl formamide using the Staudinger equation (reference: U.S. Patent No. 2,404,713).

The tow of polyacrylonitrile filamentary material may be produced from an acrylonitrile polymerization product

by any suitable method and using any suitable apparatus, but advantageously is produced as is described in, for example, the copending application of Mario Sonnino, Serial No. 536,479 filed September 26, 1955, now Patent No. 2,849,751, dated September 2, 1958.

In my copending divisional application Serial No. 5,074, filed January 27, 1960, claims are made to certain apparatus features in addition to those made in my copending divisional application Serial No. 610,027, filed September 14, 1956.

I claim:

1. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material, the improvement which comprises continuously feeding a tow of polyacrylonitrile filamentary material under substantially uniform tension to the feed-in end of a crimping zone, said tow, as thusly fed, being wet with an aqueous fluid comprising mainly water that was applied after the tow previously had been dried, the water content of the wetted tow being not less than about 100%, by weight, based on the weight of the bone-dry tow, and both the tow and the said aqueous fluid being at a temperature of from about 155° F. to about 205° F.; continuously crimping the thusly heated tow wet with the said aqueous fluid while it is within the said temperature range; continuously passing the crimped, hot tow from the crimping zone, while it is in a relaxed state, to a separate cooling zone containing a cold, fluid medium; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 120° F.

2. The improvement as in claim 1 wherein the tow which is processed is a tow of wet-spun filamentary material comprised of a polymer of acrylonitrile containing a major proportion by weight of acrylonitrile combined in the polymer molecule.

3. The improvement as in claim 2 wherein the polymer of acrylonitrile of which the tow is comprised contains at least 75% by weight of acrylonitrile combined in the polymer molecule.

4. The improvement as claim 1 wherein both the tow and the said aqueous fluid are at a temperature of from about 160° F. to about 195° F. immediately prior to and during crimping, and the crimped, hot, relaxed tow is cooled to a temperature not higher than about 100° F.

5. The improvement as in claim 1 wherein the tow of polyacrylonitrile filamentary material is fed to the feed-in end of the crimping zone under a substantially uniform tension within the range of from about 0.005 to about 0.3 gram per denier.

6. The improvement as in claim 1 wherein the aqueous fluid with which the tow is wetted consists of water in an amount corresponding to from about 100% to about 700% by weight, based on the weight of the bone-dry tow.

7. The improvement as in claim 1 wherein the tow that is fed to the feed-in end of the crimping zone has a residual shrinkage of from 0% to about 3%.

8. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material, the improvement which comprises continuously feeding a tow of polyacrylonitrile filamentary material under substantially uniform tension to the bite of a pair of conveying feed rolls of a tow crimper of the stuffing-box type, said tow, as thusly fed, being wet with an aqueous fluid comprising mainly water that was applied after the tow previously had been dried, the water content of the wetted tow being not less than about 100%, by weight, based on the weight of the bone-dry tow, and both the tow and the said aqueous fluid being at a temperature of from about 155° F. to about 205° F.; continuously crimping the thusly heated tow wet with the said aqueous fluid, after it issues from between the bite of the said pair of conveying feed rolls and while it is within the said temperature

range, by passing it through the crimping zone of said crimper; continuously passing the crimped, hot tow from the said crimping zone, while it is in a relaxed state, to a separate cooling zone containing a cold, aqueous, fluid medium; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 120° F.

9. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material, the improvement which comprises continuously contacting, while under tension, a tow of wet-spun and subsequently dried filamentary material with an aqueous fluid comprising mainly water and which is at a temperature of from about 160° F. to about 195° F., said tow being comprised of a polymer of acrylonitrile containing at least 75% by weight of acrylonitrile combined in the polymer molecule; continuously feeding the wetted tow under a substantially uniform tension to the feed-in end of a crimping zone, said tow, as thusly fed, containing from about 100% to about 700% by weight of water, based on the weight of the bone-dry tow, and being at a temperature of from about 160° F. to about 195° F.; continuously conveying the crimped, hot tow from the crimping zone, while it is in a supported, relaxed state, to a separate cooling zone containing a cold, aqueous, fluid medium; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 100° F., thereby setting the crimp.

10. The improvement as in claim 9 wherein the residual shrinkage of the tow is reduced to from 0% to about 3% before being contacted with the aqueous fluid comprising mainly water.

11. The improvement as in claim 9 wherein contacting of the tow, while under tension, with an aqueous fluid comprising mainly water and which is at a temperature of from about 160° F. to about 195° F. includes immersion in a bath of said aqueous fluid within said temperature range.

12. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material, the improvement which comprises continuously removing residual shrinkage from a tow of polyacrylonitrile filamentary material; continuously guiding the shrunken tow whereby alignment of the filaments of the tow along their longitudinal axis is aided and, concurrently with said guiding of the tow, tensioning it as it continuously moves toward a point at which it changes its direction of movement, the moving tow being under tension both before and after it leaves said point; continuously feeding the tow under substantially uniform tension to the bite of a pair of conveying feed rolls of a tow crimper of the stuffing-box type, said tow, as thusly fed, containing from about 100% to about 700% by weight of water, based on the weight of the bone-dry tow, and being at a temperature of from about 155° F. to about 205° F.; continuously crimping the thusly heated tow wet with the said water, while it is within the said temperature range and after it issues from between the bite of the said pair of conveying feed rolls, by passing it through the crimping zone of said crimper; continuously passing the crimped, hot tow from the crimping zone to a separate cooling zone while it is in a relaxed state; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 120° F.

13. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material comprised of a polymer of acrylonitrile, the improvement which comprises continuously removing residual shrinkage from a tow of said polyacrylonitrile filamentary material which is capable of being further shrunk by continuously passing said tow in a relaxed state through a zone comprised of liquid, the temperature of which is within the range of from about 210° F. to about 230° F.; introducing liquid

11

at said temperature into said zone; maintaining a portion of said tow in said zone for a period of at least 5 seconds while continuously introducing untreated tow into the inlet end of said zone and continuously withdrawing treated tow from the outlet end of said zone; continuously contacting the resulting tow, while under tension, by a treatment which includes immersing the said tow in a bath of aqueous fluid comprising mainly water and which is at a temperature of from about 155° F. to about 205° F.; continuously feeding the wetted tow under a substantially uniform tension to the feed-in end of a crimping zone, said tow, as thusly fed, containing not less than about 100% by weight of water, based on the weight of the bone-dry tow, and being at a temperature of from about 155° F. to about 205° F.; continuously conveying the crimped, hot tow from the crimping zone to a separate cooling zone while it is in a supported, relaxed state; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 100° F., thereby setting the crimp.

14. In a continuous method of producing a crimped tow of polyacrylonitrile filamentary material comprised of a polymer of acrylonitrile containing at least 75% by weight of acrylonitrile combined in the polymer molecule, the improvement which comprises continuously removing residual shrinkage from a tow of said polyacrylonitrile filamentary material which is capable of being further shrunk by continuously passing said tow in a relaxed state through a zone comprised of liquid, the temperature of which is within the range of from about 210° F. to about 230° F.; introducing liquid at said temperature into said zone; maintaining a portion of said tow in said zone for a period of at least 5 seconds while continuously introducing untreated tow into the inlet end of said zone and continuously withdrawing treated tow from the outlet end of said zone; continuously subjecting the thusly shrunken tow to tensioning means adapted to

12

align the filaments of the tow along their longitudinal axis; continuously contacting the resulting tow, while under tension, by a treatment which includes immersing the said tow in a bath of aqueous fluid comprising mainly water and which is at a temperature of from about 160° F. to about 195° F.; continuously feeding the wetted tow under a substantially uniform tension to the feed-in end of a crimping zone of a stuffing-box type of crimper in which the tow is crimped, said tow, as thusly fed, containing from about 100% to about 700% by weight of water, based on the weight of the bone-dry tow, and being at a temperature of from about 160° F. to about 195° F.; continuously conveying the crimped, hot tow from the crimping zone to a separate cooling zone while it is in a supported, relaxed state; and continuously passing the crimped, hot tow, while relaxed, through said cooling zone wherein it is cooled to a temperature below 100° F., thereby setting the crimp.

References Cited in the file of this patent

UNITED STATES PATENTS

2,267,718	Campbell et al.	Dec. 30, 1941
2,294,957	Caldwell	Sept. 8, 1942
2,446,647	Frankwich	Aug. 10, 1948
2,556,011	Swayze et al.	June 5, 1951
2,575,781	Barach	Nov. 20, 1951
2,575,838	Rainard	Nov. 20, 1951
2,669,001	Keen	Feb. 16, 1954
2,686,339	Holt	Aug. 17, 1954
2,690,607	Moos	Oct. 5, 1954
2,696,034	Schwarz	Dec. 7, 1954
2,697,023	Martin	Dec. 14, 1954
2,733,122	Herele et al.	Jan. 31, 1956
2,734,251	Rainard et al.	Feb. 14, 1956
2,805,464	Bolmeyer et al.	Sept. 10, 1957
2,818,630	Le Boeuf	Jan. 7, 1958