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3,523,150 MANUFACTURE OF INDUSTRIAL ACRYLIC FIBERS

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ABSTRACT OF THE DISCLOSURE

A method for manufacture of an industrial filament of acrylonitrile having a tenacity of at least about 3 grams per denier, an elongation to break off at least about 15% at a linear take-up rate of at least 800 feet per minute which comprises dry jet-wet spinning a solution of an acrylonitrile polymer, washing the filament to substantially remove the solvent and stretching the filament in hot water to from 2 to 5 times, drying the filament and further stretching it to from 2 to 5 times, by passing the filament in contact with a series of rolls wherein the temperature of the rolls is incrementally elevated from less than 100° C. to from 180° to 200° C. and thereafter passing the hot dried filament to a draw roll to effect said stretch, allowing the stretched fiber to shrink at least about 15 percent in a dry heat relaxation zone and thereafter collecting the filament, said total stretch being at least 9 times the coagulated length. Filament manufactured by the above described process has been found useful for sandbags.

This invention involves a novel process for the manufacture of high tenacity filament of acrylonitrile at unusually high spinning rates. Insofar as the principal object of this process is to produce a synthetic filament of acrylonitrile for industral purposes, as opposed to apparel and carpet fiber end use, the critical features of the instant invention are the combination of steps required to produce filament having high tenacity at unusually high rates of speed.

These objects are accomplished by dry jet-wet spinning a solution of an acrylonitrile polymer from multiple orifices into air or other inert gas for a distance of from ⅛ to 4 inches and then passing the shaped extrudate into a coagulation bath comprising a solvent for the polymer solvent which is a non-solvent for the polymer. The coagulated multifilament bundle or tow is then washed to remove any polymer solvent remaining after which the washed tow is passed to a hot water bath wherein the tow is given an orientation stretch of from 2 to 5 times the coagulated length. This stretch is achieved by passing the tow from the hot water bath to a draw roll having an increased peripheral speed necessary to effect the desired degree of orientation stretch within the above described limits. The stretched tow is thereafter passed to a finish bath wherein lubricant and antistatic agents are applied to the tow to facilitate mechanical handling. After application of finish the tow is in oriented aquagel condition and must according to the instant invention be dried, collapsed and subjected to a plastic stretch of from 2 to 5 times the dried length. This combination of steps is achieved by passing the tow from the finish bath to a series of rolls which dry, collapse and plasticize the

tow prior to passing the tow to a second stage draw roll. The temperature of the series of rolls employed to dry the tow ranges from below about 100° C. up to about 170° C., the temperature being incrementally elevated along the path of the tow. The temperatures up to 170° C. serve not only to dry and collapse the internal void structure of the individual filaments of the tow but also to condition the fiber for subsequent passage over rolls which heat placticize the filament wherein the temperatures lie in the range of from 180° C. to 190° C. The latter elevated temperatures plasticize the tow to the extent that they can be stretched 2 to 5 times their dried length by passage to a draw roll. From the second stage draw roll the tow is passed to a heated zone wherein the positive tension placed on the tow throughout the previous stages of the spinning process is relaxed to the extent that the tow is allowed to shrink at least about 10 percent. Shrinkage of the tow at this stage reduces filament brittleness caused by the unusually high degree of orientation. According to the instant invention the tow emerges from the relaxation stage at greater than 800 feet per minute having a tenacity of at least about 3 and an elongation to break of at least about 15 percent. The tow is cooled on a final godet and collected on bobbins.

As above indicated the unique combination of conditions to which the tow is subjected in combination with dry jet-wet spinning offers highly productive system for manufacturing industrial filaments not available with either wet or dry spinning methods. The fibers so produced are admirably suited for outdoor industrial and military uses, such as sandbags, awnings, and tenting, not only because of their high tenacity and resistance to biological degradation, but also because of the economy brought about through the high output rates of the process according to the instant invention.

By acrylonitrile polymer is meant polyacrylonitrile, copolymers, and terpolymers of acrylonitrile, and blends of polyacrylonitrile and copolymers of acrylonitrile with other polymerizable mono-olefinic materials, as well as blends of polyacrylonitrile and such copolymers with small amounts of other polymeric materials, such as polystyrene. In general, a polymer made from a monomeric mixture of which acrylonitrile is at least 70 percent by weight of the polymerizable content is useful in the practice of this invention. Besides polyacrylonitrile, useful copolymers are those of 80 or more percent of acrylonitrile and one or more percent of other monoolefinic monomers. Block and graft copolymers of the same general type are within the purview of the invention. Suitable other monomers include vinyl acetate, and other vinyl esters of monocarboxylic acids, vinylidene chloride, vinyl chloride and other vinyl halides, dimethyl fumerate and other dialkyl esters of fumaric acid, dimethyl maleate and other dialkyl esters of maleic acid, methyl acrylate and other alkyl esters of acrylic acid, styrene and other vinyl-substituted aromatic hydrobarbons, methyl methacrylate and other alkyl esters of methacrylic acid, vinyl-substituted heterocyclic nitrogen ring compounds, such as the vinyl imidazoles, etc., the alkyl-substituted vinylpyridines, vinyl chloroacetate, allyl chloroacetate, methallyl chloroacetate, allyl glycidyl ether, methallyl glycidyl ether, allyl glycidyl phthalate, and the corresponding esters of other aliphatic and aromatic dicarboxylic acids, glycidyl acrylate, glycidyl methacrylate, and other mono-olefinic monomers copolymerizable with acrylonitrile.

Many of the more readily available monomers for polymerization with acrylonitrile form copolymers which are not reactive with some dyestuffs and may therefore be impossible or difficult to dye by conventional techniques. Accordingly, these non-dyeable fiber-forming copolymers may be blended with polymers or copolymers which are in themselves more dye-receptive by reason of their physical structure or by reason of the presence of functional groups chemically reactive with the dyestuff, whereby the dyestuff is permanently bonded to the polymer in a manner which lends resistance to removal thereof by the usual laundering and dry cleaning procedures. Suitable blending polymers may be polyvinyl pyridine, polymers of alkyl-substituted vinylpyridine, polymers of other vinyl-substituted N-heterocyclic compounds, the copolymers of the various vinyl-substituted N-heterocyclic compounds and other copolymerizable monomers, particularly acrylonitrile.

Of particular utility are the blends formed of polyacrylonitrile or a copolymer of more than 90 percent acrylonitrile and up to 10 percent vinyl acetate, and a copolymer of vinylpyridine or an alkyl-substituted vinylpyridine and acrylonitrile, the said acrylonitrile being present in substantial proportions to provide heat and solvent resistance, and a substantial proportion of the vinylpyridine or derivatives thereof to render the blend receptive to acid dyestuffs. Of particular utility are the blends of copolymers of 90 to 98 percent acrylonitrile and 10 to 2 percent vinyl acetate and sufficient copolymer of 10 to 70 percent acrylonitrile and 90 to 30 percent vinylpyridine to produce a blended composition with a total of 2 to 10 weight percent vinylpyridine.

The polymers just described may be prepared by any conventional polymerization procedure, such as mass polymerization methods, solution polymerization methods or aqueous emulsion methods. The polymerization is normally catalyzed by known catalysts and is carried out in equipment generally used in the art. However, the prefered practice utilizes suspension polymerization wherein the polymer is prepared in finely divided form for immediate use in the filament-forming operations. The preferred suspension polymerization involves batch procedures, wherein monomers are charged with an aqueous medium containing the necessary catalyst and dispersing agents. A more desirable method involves the semi-continuous procedure in which the polymerization reactor containing the aqueous medium is charged with the desired monomers gradually throughout the course of the reaction. Entirely continuous methods involving the gradual addition of monomers and the continuous withdrawal of polymer can also be employed.

The polymerization is catalyzed by means of a water-soluble peroxy compound, for example, the potassium, ammonium and other water-soluble salts of peroxy acids, sodium peroxide, hydrogen peroxide, sodium perborate, the sodium salts of the other peroxy acids, and other water-soluble compounds containing the peroxy group:

$$(-O-O-)$$

A wide variation in the quantity of peroxy compound is possible. For example, from 0.1 to 3.0 percent by weight of the polymerizable monomer may be used. The so-called redox catalyst system also may be used. Redox agents are generally compounds in a lower valent state which are readily oxidized to the higher valent state under the conditions of reaction. Through the use of this reduction-oxidation system, it is possible to obtain polymerization to a substantial extent at lower temperatures than otherwise would be required. Suitable "redox" agents are sulfur dioxide, the alkali metal and ammonium bisulfites, and sodium formaldehyde sulfoxylate. The catalyst may be charged at the outlet of the reaction, or it may be added continuously or in increments throughout the reaction for the purpose of maintaining a more uniform concentration of catalyst in the reaction mass. The latter method is preferred because it tends to make the resultant polymer more uniform in regard to its chemical and physical properties.

Although the uniform distribution of the reactants throughout the reaction mass can be achieved by vigorous agitation, it is generally desirable to promote the uniform distribution of reagents by using inert wetting agents, or emulsion stabilizers. Suitable reagents for this purpose are the water soluble salts of fatty acids, such as sodium oleate and potassium stearate, mixtures of water-soluble fatty acid salts, such as common soaps prepared by the saponification of animal and vegetable oils, the "amino soaps," such as salts of triethanolamine and dodecylmethylamine, salts of rosin acids and mixtures thereof, the water-soluble salts of half esters of sulfonic acids and long chain aliphatic alcohols, sulfonated hydrocarbons, such as alkyl aryl sulfonates, and any other of a wide variety of wetting agents, which are in general organic compounds containing both hydrophobic and hydrophilic radicals. The quantity of emulsifying agent will depend upon the particular agent selected, the ratio of monomer to be used and the conditions of polymerization. In general, however, from 0.1 to 1.0 weight percent based on the weight of the monomers can be employed.

The emulsion polymerizations are preferably conducted in glass or glass-lined vessels provided with means for agitating the contents therein. Generally, rotary stirring devices are the most effective means of insuring the intimate contact of the reagents, but other methods may be successfully employed, for example, by rocking or rotating the reactors. The polymerization equipment generally used is conventional in the art and the adaptation of a particular type of apparatus to the reaction contemplated is within the province of one skilled in the art.

The optimum methods of polymerization for preparing fiber-forming acrylonitrile polymers involve the use of polymerization regulators to prevent the formation of polymer units of excessive molecular weight. Suitable regulators are the alkyl and aryl mercaptans, carbon tetrachloride, chloroform, dithioglycidol and alcohols. The regulators may be used in amounts varying from 0.001 to two percent, based on the weight of the monomer to be polymerized.

The polymers from which the filaments are produced in accordance with the present invention have specific viscosities within the range of 0.10 to 0.40. The specific viscosity value, as employed herein, is represented by the formula:

$$\eta_{sp} = \frac{\text{Time of flow of polymer solutions in seconds}}{\text{Time of flow of the solvent in seconds}} - 1$$

Viscosity determinations of the polymer solutions and solvent are made by allowing said solutions to flow by gravity at 25° C. through a capillary viscosity tube. In the determinations herein, a polymer solution containing 0.1 gram of the polymer dissolved in 100 ml. of N,N-dimethylformamide was employed. The most effective polymers for the preparation of filaments are those of uniform physical and chemical properties and of relatively high molecular weight.

In general, the spinning solution can be prepared by heating and stirring a mixture of a finely divided acrylonitrile polymer of the type described above with a suitable solvent until the polymer is dissolved. To some extent the selection of the solvent is influenced by the particular polymer chosen. Certain materials such as N,N-dimethylformamide, butyrolactone, dimethyl sulfoxide, N,N-dimethylacetamide and the like are particularly suitable solvents. While ethylene carbonate and the like, concentrated solutions of certain water-soluble inorganic salts, such as zinc chloride, calcium chloride, lithium bromide, cadmium bromide, sodium thiocyanate, etc. may be employed in accordance with the broadest aspects of the invention, such solvents are not preferred for use in produc-

ing the filaments herein where low coagulation temperatures are employed. The percentage of polymer based on the weight of the solution will depend upon the particular polymer and solvent employed, as well as upon the temperature at which the polymer is spun. It is desirable to employ a solution containing a high percentage of polymer for obvious reasons.

An advantage of the present invention is the fact that spinning solutions having much higher temperatures can be employed than ordinarily used in wet spinning. Hence, a greater percentage of polymer in the solution can be used with success. The spinning solution may be maintained prior to and at extrusion at temperatures from about 20 to 180° C. Room temperature is highly satisfactory from an operational standpoint. Ordinarily a solution containing at least 10 percent acrylonitrile polymer is desirable.

Since the viscosity of the acrylonitrile polymer solution varies directly with its temperature, advantage of employing the high spinning temperatures permitted in the instant process may be taken with the result that low extrusion pressures are required for a given percentage of polymer. Normally, the polymer solution temperature for successful wet spinning should be closely correlated with the temperature of the coagulation bath. In order to spin acrylonitrile polymer solution by the conventional wet spinning method, it is necessary to avoid elevated coagulating bath temperatures, since such temperatures substantially reduce the solvent extraction efficiency to a point where it is not possible or feasible to utilize the advantage of spinning a solution containing a high percentage of polymer.

The spinneret used in accordance with the instant invention can be of the type ordinarily used in dry spinning operation. An important variable in any spinning process is the orifice diameter of the spinneret. From practical aspects it is often desirable to employ the largest diameter consistent with good spinning. By increasing the orifice size the filtration of the spinning solution becomes less important and the number of spinneret changes due to clogging thereof is reduced. In the present invention one may employ orifices having relatively large diameters due to the fact that the filaments may be given a considerable attenuation immediately after extrusion of the spinning solution. This in practical terms means a reduction in operating cost. Among other benefits derived by employing a large orifice opening are the higher spinning speeds and the improvement in the physical properties by the attenuation of the filaments that can be attained. Moreover, filament deniers below 1.0 can be spun readily without difficulty whereas 1.2 to 2.0 denier per filament is generally the least that can be spun in the ordinary wet spinning process. Another advantage of the present process is that a wide range of filament denier can be spun from a single spinneret. For example, filament deniers from 0.8 to 22 and higher having satisfactory textile properties may be spun from a single spinnert having an orifice diameter of 0.005 inch. This means that filaments having various deniers may be spun conveniently without shut down being required to change from production of one diameter to another.

The distance that the spinneret is disposed above the coagulating bath may be varied. Ordinarily, the spinneret is positioned so that its face is between ⅛ and 1½ inches above the bath. However, one can increase this distance by taking precaution that adjacent polymer streams do not come in contact with and cohere to each other. For example, a cell through which the streams coaxially pass may be provided to minimize any disturbance thereof. Ordinarily, the gas between the spinneret and the coagulating bath and through which the streams of polymer travel is air, although any other gaseous medium that does not adversely affect the filaments may be used. The temperature of the gas may be regulated; however, the temperature normally present during spinning is satisfactory. For best results the spinning variables should be correlated so that less than one percent of the solvent based on the weight of the solution is exaporated into the gaseous medium from the extruded stream.

Although the reason why the filaments produced by the instant process can be stretched to a much greater extent is not entirely elucidated, it is thought that the extrusion of polymer solution through a spinneret positioned above the surface of the coagulating bath provides a fluid region in each extruded stream of polymer wherein the streams easily yield to a longitudinally applied force without a separation of the mass composing the streams. Therefore, considerable attenuation of the streams of polymer can take place prior to the entry of the streams into the coagulating bath. During their brief passage through the space above the surface of the coagulating bath and below the face of the spinneret only a small amount of the solvent, if any, is removed from the extruded streams of polymer with the result that little or no coagulation takes place when the streams are being attenuated. Because of the high fluidity of the streams of polymer in the zone between the spinneret and coagulating bath, the longitudinal force applied to the coagulating filaments to pull same through and out of the coagulating bath is accepted by the extruded streams of polymer, in the main, in this zone. Apparently, the coagulating filaments as a result are passed through the coagulating bath under a minimum tension; that is, the tension exerted on the coagulating filament would be only that tension required to overcome the viscosity forces within the filaments and drag forces in the coagulating bath. Under these conditions it is believed that isotropic filaments exhibiting only an extremely thin outer skin formation and a reduced susceptibility to skin rupture or fissure to cause undesirable variations in the resulting filaments exist in this zone.

In normal wet spinning a much thicker skin is formed from the very genesis of filament formation; and the longitudinal force necessary to impart even a moderate stretch in the filaments undergoing coagulation can be sufficient to cause ruptures of the filamentary skin. This rupturing also can occur in many instances when the longitudinal force is sufficient only to withdraw the filaments from the coagulating bath. It has been observed that when the skin becomes ruptured during coagulation, an array of voids forms along the line of skin cleavage. Since the longitudinal forces exerted on the filaments in the coagulating bath are minimized in accordance with the present invention, the tendency of the surface of the filaments to crack or rupture accordingly is reduced, resulting in the production of superior filaments.

The coagulating baths suitable for use in the invention normally contain a non-solvent such as water, or a mixture of a solvent and a non-solvent for the acrylonitrile polymer. The solvent used in the coagulating bath is preferably the same as the one used in preparing the polymer solution; however, such need not be the case. Although good spinning can be accomplished while using a coagulating bath composed essentially of water, it is preferred that the bath contain 20 percent to 80 percent solvent. On the basis of available data the temperature range for the coagulating bath is preferred to be from −40 to +80° C. It is preferred that the bath contain high concentrations of solvent at the lower bath temperatures.

The filaments may be given a travel in the coagulating bath, for example, from 2 to 24 inches or more by employment of the two suitable spaced guides and withdrawal rolls. Between the spinneret and the withdrawal rolls, the filaments are subjected to a desired substantial attenuation.

Following the passage through the coagulating bath the filaments are washed substantially free of solvent. While this may preferably be accomplished by spraying water on the filaments travelling around positively driven rolls as the tow leaves the coagulation bath, washing may

be accomplished in the hot water stretch bath hereinafter described or in a separate step after the hot water stretch. Insofar as the object of the washing step is merely to substantially decrease the solvent content of the filament to less than about 1 percent the means employed may be conventional.

Following the coagulation both and the separate washing step, if used, the coagulated tow is given an orientation stretch to increase the strength of the filaments and otherwise improve their physical properties. The second bath may consist simply of water, or it may have the same composition as the coagulating bath but at a greater dilution with water. The temperatures of the second bath may range from between 50° and 100° C., but the preferred range lies between about 90° to 100° C. The type of apparatus used to contain the hot water stretch bath has not been found to be critical so long as the filament is capable of being elevated in temperature to that of the bath. Accordingly, a conventional cascade or a vertical box wherein the tow is passed from the surface of the bath to the bottom, around a guide and back to the surface may be employed. Following the hot water bath the tow is passed to positively driven draw rolls driven at speeds necessary to effect a draw ratio of between 2 and 5. The instant process is designed to produce at high practical speeds and as above indicated the dope is pumped at a rate such that filament can be taken from the coagulation bath at velocities of at least about 100 feet per minute. Accordingly, the provision of a hot water stretch of at least 2 requires that the draw rolls following the hot water stretch take the tow at least 200 feet per minute, and up to 500 feet per minute. The particular draw ratio employed at this stage must be correlated with that employed in the later stretching step such that the total product draw ratio necessary to achieve high tenacities according to this process is at least 9.

Upon completion of the hot water stretch it is customary in this and other processes for the manufacture of synthetic fibers of acrylonitrile polymers to apply an antistatic finish material to the filaments to facilitate mechanical handling and processing. Accordingly, in the preferred embodiments of this invention the tow is passed from the draw roll after the hot water stretch to a bath containing an antistatic material to provide a pick-up of about 1 percent of the lubricant and antistatic material based on the weight of the filament.

Following the finish application the tow is dried, the internal pore structure of the filaments collapsed and the tow is given an additional stretch of from 2 to 5 times its dried length.

In view of the fact that the tow is travelling at a velocity of at least 500 feet per minute when it reaches the drying stage of this process the drying operation becomes particularly critical. That is, the tow must be dried by incrementally elevating the temperatures of the dryer rolls from a point below 100° C. up to about 170° C. and thereafter elevated to a temperature of between 170° to 200° C. The latter range of temperature plasticizes to tow so that it is stretched as it leaves the terminal hot roll and advances to the second stage draw roll, the draw ratio of which lies between 2 and 5. In practice it has been found convenient to employ a multiplicity of rolls wherein the temperature increases are divided into zones. For example, zone 1 having rolls heated to from about 85° to 100° C., zone 2 having rolls heated to from about 100° to about 135° C., zone 3 from about 130° to 160° C., zone 4 from about 155° to about 180° C. and zone 5 from 180° to 190° C. While the use of zone heating above indicated serves to illustrate preferred conditions for drying and plasticizing, other techniques may be employed so long as the critical feature of incremental elevation of temperatures from below 100° C. up to between 180° and 200° C. is observed. Failure to incrementally elevate temperatures results in a tendency for the filament to discolor accompanied by degradation of tensile properties. Other disadvantages found in the use of suddenly raising filament temperatures are that the water in the aquagel filamentary structure tends to flash probably causing an irregular collapsed pore structure. Moreover, it has been noted that antistatic finishes are commonly removed by suddenly subjecting the filament to the extremely high temperatures necessary to plasticize the filament.

On the plastic stretch draw rolls the tow travels at a velocity of at least about 900 feet per minute, the actual speed being the product of the draw ratios times the speed at which the freshly coagulated tow is removed from the coagulation bath. The filaments rapidly cool, they are highly oriented and possess tenacities of greater than 3 grams per denier. The filaments are, however, quite brittle at this stage of the process and must be allowed to relax or shrink to at least about 10 percent. Accordingly, the twice stretched tow is passed from the second stage draw rolls to a continuous dry heat relaxation zone wherein the filaments are heated and the tension heretofore maintained throughout the process is reduced to the extent that the heated tow shrinks at least about 10 percent. Relaxation can be effected by any means which can continuously effect heat transfer from a source of multifilament bundles. Shrinkage temperature for acrylonitrile fibers herein described lie in the range of from 200 to 350° C. One such means known as "hot slot" relaxation involves passing the tow from the stretch godet into the gap between two heated steel plates and then to a final godet. Where the hot slot is employed as a means for effecting relaxation it has been found desirable but not essential to provide incrementally elevated temperatures. For example, the plates may be hotter by 50° C. or more near the center of the plates than at ends.

An alternate means of effecting relaxation uses hot air as a heat transfer medium by passing air under pressure through hot air heaters and into a tube through which the tow is passed between the stretch godet and the final godet. The final godet speed determines the degree of relaxation and takeup. The surface of the final godet should be sufficient to cool the tow before packaging to prevent any restretching of the filaments due to the tension experienced in the packaging operation.

EXAMPLE I

In one embodiment of the above described process a polymer of acrylonitrile and vinyl acetate (93.3/6.7) having a specific viscosity of 0.15 was dissolved in dimethylacetamide to form a polymer solution or dope having 25 percent solids. The dope was filtered and pumped to a spinnerette having a 100 nine mil. orifice at a rate of 108.5 cc. per minute. The dope was heated at the face of the spinnerette to 75° C. and extruded into air at ambient temperature for a distance of ⅜" and into a coagulation bath composed of dimethylacetamide and water (60/40 by weight) held at 25° C. The filament was immersed in the coagulation bath for a length of 24 inches and drawn out of the bath onto a godet at a velocity of 133.3 feet per minute. The freshly coagulated tow was wrapped around the godet several times to prevent slippage and to provide adequate washing by water sprayed onto the godet from a shower suspended above. The tow was then passed through a hot water (96–99° C.) cascade for an immersion distance of 36 inches and onto a draw godet at a velocity of 500 feet per minute to provide a hot water stretch of 3.75. From the hot water stretch godet the tow was immersed in a finish bath containing a 3% aqueous disposition of an antistatic agent and then to the first drier godet. Drying was accomplished by passing the tow over a series of electrically heated rolls wherein roll temperatures were incrementally elevated along the path of the tow from 80° C. to about 190° C. to result not only in drying and col-

lapsing the filament, but in plasticizing the filaments as well. The heat plasticized tow was passed from the terminal heating rolls to the second stage stretch godet at 1200 feet per minute to provide an additional 2.4× stretch, the total stretch being 9.0×. Following the plastic stretch godet the tow was passed between heated steel plates and on to the final godet at 1020 feet per minute. The gap between the two steel plates was set at 0.025", and the plates were heated to 300° C. The reduced speed to the final godet was set to allow a shrinkage of 15 percent to occur as the tow passed between the heated plates, from the final godet the tow was packaged in a conventional manner.

The filament spun as above was sampled and determined to have average properties as indicated:

Denier—742/100
Tenacity—3.41 grams per denier
Elongation—16.3 percent
Knot tenacity—2.24 grams per denier
Knot elongation—10.5 percent.

EXAMPLE II

In an embodiment similar to that described in Example I a copolymer of acrylonitrile and vinyl acetate (93.3/6.7) having a specific viscosity of 0.24 was used to prepare a spinning solution comprising 19 percent by weight of the polymer in dimethylacetamide. The dope was extruded at 90° C. at a rate of 131.5 cc. per minute into air for 3/8" and into a dimethylacetamide and water (60/40) coagulation bath held at 25° C. The coagulated tow was withdrawn on the first godet at 116.7 feet per minute, washed and withdrawn from the hot water cascade at 350 feet per minute to provide a hot water stretch of 3.0. The tow was given an antistatic finish application, dried and heat plasticized through incremental temperature elevation as in Example I and passed to the second stage stretch godet at 1190 feet per minute to provide a plastic stretch of 3.4, the total orientation stretch being 10.2. The tow was thereafter relaxed 15 percent between hot plates and packaged at 1012 feet per minute. Filament samples possessed averaged properties indicated.

Denier—694/100
Tenacity—488 grams/denier
Elongation—16.8 percent
Knot tenacity—3.21 grams/denier
Knot elongation—11.0 percent.

EXAMPLE III

Fabric woven filament manufactured according to the process of this invention was made into sandbags and were exposed alongside those made from cotton and jute for three months in the Tennessee River at Decatur, Ala. Results of Instron tensile tests shown in Table I made on the fabric before and after exposure indicate that the acrylic fiber of this invention was vastly superior for this end use to cotton and jute.

TABLE I

Sand Bag Fabric	Test Conditions	Before Exposure: Breaking Strength (pounds)	Before Exposure: Elongation at Break (percent)	After Exposure: Breaking Strength (pounds)	After Exposure: Elongation at Break (percent)	Tensile Strength Retained (percent
Acrylic Industrial Fiber of this Invention.	Wet	198	15	197	15	99
	Dry	222	17	201	14	90
Jute	Wet	97	8	24	7	25
	Dry	118	7	26	6	22
Cotton	Wet	Destroyed				
	Dry					

EXAMPLES IV–VI

Different polymers were dissolved in solvent and processed into continuous filament according to the process of this invention under the conditions below in Table II.

TABLE II

	Polymer Composition: 87.5% 88% AN/VA+12.5% PVC (96/6) Plus 12% AN/MVP* (50/50)	88% AN/VA+12% AN/MVP (94/6) (50/50)	AN/VA/VBr** (90/6.7/3.3)
η_{sp} and Percent Solids in DMAc.	0.24–19%	0.24–19%	0.5–25%.
Pump Rate, cc./min	104	112.7	88.2.
Dope Temp., ° C. at Jet	90	90	75.
Jet Size	110 hole—1 mil	100—9 mil	100 hole—9 mil.
Coagulation Bath	60% DMAc 40% H_2O, 40° C	60% DMAc+40% H_2O), 30° C	60%DMAc+40% H_2O, 25° C.
1st Godet, f.p.m	111	100 (washed with H_2O at 25° C.)	3.4×, Hot Water Stretch.	100(washed with H_2O at 25° C.).	5.25×, Hot Water Stretch.
Cascade	H_2O at 96–99° C	H_2O at 96–99° C		H_2O at 96–99° C	
2nd Godet, f.p.m	500	340	3.0×, Plastic Stretch.	525	2.0×, Plastic Stretch.
3rd Godet	1,000	1,020		1,050	
Relaxation	Hot Slot, 20% Shrinkage	15% Shrinkage—Hot Slot	Hot Air Tube—15% Shrinkage.
Final Godet, f.p.m	800	867	893.
Total Stretch	9.0×	10.2×	10.5×.
Denier	733/100	697/100	697/100.
Tenacity (g.p.d.)	3.85	3.89	17.5.
Elongation (percent)	24.2	17.6	17.5.
Knot Tenacity (g.p.d.)	2.35	2.69	2.63.
Knot Elongation (percent)	14.0	11.6	10.5.

*MVP=Methyl Vinyl Pyridine.
**VBr=Vinyl Bromide.

I claim:

1. A method for the manufacture of an industrial filament of an acrylonitrile polymer having a tenacity of at least 3 grams per denier and an elongation at break of at least 15 percent at linear take-up speeds of at least 800 feet per minute which comprises extruding a solution of a polymer of acrylonitrile into an inert gaseous medium for a distance of from 1/8 to 4 inches to form a filamentary shaped polymer solution and then passing the thus formed filamentary shaped solution into a coagu-

lation bath; passing the filament from the coagulation bath to a first godet and into a hot water bath at 90° to 100° C. for a distance sufficient to elevate the temperature of the filament to the temperature of the bath and then passing the filament to a first stretch godet having a peripheral speed of from 2 to 5 times the peripheral speed of said first godet to stretch the filament from 2 to 5 times the coagulated length; applying an antistatic finish to said filament and thereafter passing the filament over a series of rolls wherein the temperature is incrementally elevated from temperatures below about 100° C. up to about 170° C. to dry and collapse the filamentary structure and thereafter elevating the temperature of the rolls to from 180° to 200° C. and passing the filament from rolls in the latter temperatures range to a second stretch godet having a peripheral speed of from 2 to 5 times the speed of said first stretch godet to further stretch the filament to from 2 to 5 times; thereafter passing said filament to a heat relaxation zone wherein the filament is allowed to shrink at least about 10 percent of its length, with the proviso that the total stretch imparted to the filament in by said first and second stretch rolls is at least 9 times the length of the coagulated filament.

2. The method of claim 1 wherein the first stretch lies between 3 and 4 times the coagulated length and the further stretch lies between about 3 and 4 times the length of the filament after the first stretch.

3. The method of claim 1 wherein the coagulated filament is washed with water on said first godet.

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264—182, 203

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,523,150 August 4, 1970

Richard E. Vigneault

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 9, "placticize" should read -- plasticize --. Column 7, line 7, "both" should read -- bath --. Column 10, line 7, "488" should read -- 4.88 --. Columns 9 and 10, TABLE II, first column, line 4 thereof, "110-hole- 1 mil" should read -- 100 hole-mil --; same TABLE II, third column, line 14 thereof, "17.5%" should read -- 3.96 --.

Signed and sealed this 16th day of March 1971.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents