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WET-SPINNING PROCESS FOR TOUGH, RIBBON-SHAPED, ACRYLONITRILE POLYMER FIBERS

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ABSTRACT OF THE DISCLOSURE

A high-speed wet-spinning process for spinning ribbon-shaped fibers of acrylonitrile polymer, said fibers having an aspect ratio between 2.0 and 3.0, a cover factor of 1.2 to 1.3, and improved abrasion resistance, said process comprising the steps of forming a spinning solution of said acrylonitrile polymer in concentrated aqueous sodium thiocyanate solvent, extruding said spinning solution through rectangular orifices directly into an aqueous coagulating bath containing between 22% and 26% sodium thiocyanate, said bath being maintained below 10° C., and each of said rectangular orifices having a short dimension between 20 microns and 200 microns and a long dimension such that the resultant filament spun therefrom has an aspect ratio between 2.0 and 3.0, pulling the resulting freshly-coagulated filaments away from the rectangular orifices at a linear velocity above about 12 meters per minute, washing said filaments substantially free of sodium thiocyanate stretching said filament 4 to 15 times at a temperature above 65° C., drying said filament, and relaxing said filament at a temperature above 100° C.

This invention relates to a process for wet-spinning acrylonitrile polymer dissolved in concentrated aqueous sodium thiocyanate solvent to form ribbon-shaped fibers or filaments. More particularly, it relates to such a process which produces ribbon-shaped fibers of improved abrasion resistance at high speed for a wet-spinning process.

In recent years, synthetic fiber technology has advanced to the stage wherein its has become recognized that useful properties can be imparted to synthetic fibers by making them of cross-sectional configurations which are other than round, such as of ribbon shape (rectangular or substantially rectangular cross-section). Since round fibers flex equally in all directions whereas ribbon-shaped fibers flex primarily in one direction only (in the direction of the short axis of the cross-section), use of ribbon-shaped fibers gives fabrics made therefrom different appearances and hands from fabrics made of round fibers. Also, fabrics made of ribbon-shaped fibers have better "cover" than corresponding fabrics made of round fibers of equal denier.

The term "cover" is generally used to describe the ability of a fabric to obstruct the passage of light therethrough or to hide what is behind the fabric. It frequently is desirable for fabrics to have a high degree of cover for a given weight of fibers therein. If a round fiber (having a circular cross-section) is viewed against a background, it will hide, shade, or cover a rectangular area equal to the product of the length and diameter thereof. Regardless of how the fiber is rotated about its length, the area covered remains constant. If a ribbon-shaped fiber (having a rectangular or substantially rectangular cross-section whose short dimension is A and whose long dimension is B) is viewed against a background, the area covered is not constant, but is a function of the fiber's orientation around its length. Depending on the angle of view, the area covered by a single ribbon-shaped fiber (the "projection" of the fiber) may be anywhere between the

product on the length and the short side A and the product of the length and the long side B of the cross-section. On the average, for all possible orientations, the covering power of a ribbon-shaped fiber is greater than that of a round fiber of equal cross-sectional area or denier. This increase in covering ability can be quantitatively described by the terms "cover factor" and "cover improvement factor."

The term "cover factor" is defined as the ratio of the average projection of the ribbon-shaped fiber over all angles of tilt or orientation to the average projection of a round fiber of equal cross-sectional area (equal denier if of same density fiber). Expressed mathematically, the cover factor (C.F.) of a ribbon-shaped fiber having an aspect ratio (ratio of the long dimension of the rectangular cross-section to the short dimension) of R_f relative to an equal denier round fiber of same density is:

$$C.F.=\frac{1+R_f}{\sqrt{\pi R_f}}$$

The term "cover improvement factor" is defined as the percentage by which the covering ability of the ribbon-shaped fiber exceeds that of a round fiber of equal cross-sectional area. Expressed mathematically, the cover improvement factor (C.I.F.) is:

$$C.I.F.=100(C.F.-1)$$

In general, synthetic filaments can be produced from polymeric materials by melt-spinning, dry-spinning, or wet-spinning processes. In the "melt-spinning process" for forming synthetic filaments, polymer liquefied by melting is extruded through spinnerette orifices to form an extrudate which is solidified by cooling. Typically, polyamide, polyester, and glass fibers are produced by melt-spinning. In the "dry-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a volatile solvent is extruded through spinnerette orifices to form an extrudate which is solidified by evaporation of the volatile solvent. Typically, cellulose acetate solutions in acetone, acrylonitrile polymer solutions in dimethylformamide, etc. are spun into fibers by dry-spinning. In the "wet-spinning process" for forming synthetic filaments, polymer liquefied by dissolving in a solvent is extruded through spinnerette orifices to form an extrudate which is coagulated by removal of solvent in a liquid coagulating medium. In wet-spinning fibers of some polymers, such as from solutions of acrylonitrile polymers in aqueous nitric acid, aqueous salt, or organic solvents, the solvent is removed by leaching it out of the extrudate in a cold aqueous coagulant. In wet-spinning fibers of other polymers, such as from viscose (aqueous sodium hydroxide solution of cellulose xanthate), the solvent is removed by chemical reaction with an aqueous sulfuric acid coagulant.

The various synthetic filaments of nonround cross-sectional configuration found in the recent prior art were generally made by melt-spinning or dry-spinning processes since, with these processes, it was generally necessary only to replace the spinnerettes having round orifices with other spinnerettes having appropriately shaped orifices. Because of the numerous well-known advantages of wet-spinning processes, it would be highly desirable to be able to spin ribbon-shaped fibers of acrylonitrile polymer by a wet-spinning process. However, when attempts were made to similarly modify wet-spinning processes, particularly ones wherein coagulation was effected by leaching solvent out of the extrudate with a cold aqueous coagulant, acrylonitrile polymer fibers of substantially circular cross-sectional configuration normally were still produced. Perhaps this anomalous result arises because coagulation is a much different process when solvent

has to be leached out of the extrudate as compared to solidification by evaporation of solvent or cooling molten polymer.

Accordingly, it is an object of the present invention to provide a wet-spinning process for spinning ribbon-shaped fibers of acrylonitrile polymer by suitable and minimal modifications to existing wet-spinning processes.

The term "acrylonitrile polymer" as used herein refers to polymers which contain at least 70 percent acrylonitrile and up to 30 percent of an ethylenically unsaturated monomer copolymerizable therewith. Numerous such comonomers are known and several are in commercial use. For the practice of the present invention, any of such comonomers can be utilized provided the resulting acrylonitrile polymer is soluble in an does not react with the concentrated aqueous sodium thiocyanate solvent used in the spinning process.

For wet-spinning acrylonitrile polymers, numerous solvents are known. Illustrative of commercially utilized solvents are concentrated aqueous salt solutions of zinc chloride or sodium thiocyanate, concentrated nitric acid solution, and dimethylacetamide although numerous others can be found in such U.S. Pats. as 2,140,921; 3,124,629; 2,698,646 through 2,698,649; 2,558,730 through 2,558,735; 2,790,700; and many others. To form fibers, solutions of acrylonitrile polymers in such solvents are normally extruded into aqueous coagulants which may be water, dilute aqueous solutions of the same materials which are solvents for acryonitrile polymers when more concentrated or substantially anhydrous, or dilute aqueous solutions containing other materials. A preferred wet-spinning system, and the one to which the present invention is directed, utilizes concentrated aqueous sodium thiocyanate solvent and dilute aqueous sodium thiocyanate coagulant.

When wet-spinning into aqueous coagulants, it has generally been found important to keep the coagulant cold to convert the extrudate into a clear, strong, flexible coagulum which could be dried to form fibers relatively free of porosity. As pointed out in Craig et al., "Characterization of Acrylic Fiber Structure," Textile Research Journal, vol. 32 No. 6, June 1962, pp. 435–448, commercial wet-spinnings of acrylonitrile polymers have long utilized cold aqueous coagulants for this reason.

In such spinning systems, utilizing cold dilute aqueous sodium thiocyanate coagulant, the simple substitution of metal spinnerettes with orifices of rectangular cross-sectional configuration for the metal spinnerettes with circular orifices still yielded round fibers. Thus, until the present invention, it was believed that the highly desirable fibers of ribbon-shaped cross-sectional configuration could not be produced by wet-spinning into such cold aqueous sodium thiocyanate coagulating liquids. Surprisingly, we have found that such fibers can be formed by the process of the present invention.

In application No. 696,495, filed Jan. 9, 1968, assigned to the assignee of the present application, a method is disclosed for making ribbon-shaped fibers in such a spinning system by utilizing spinnerettes of low thermal conductivity, such as of plastic material, and unusually high jet stretch. Unfortunately, ribbon-shaped fibers of acrylonitrile polymer made by such a process do not have as high an abrasion resistance as is desired. Also, this process requires use of unusual spinnerettes made of materials not normally used for such purpose.

Accordingly, it is another object of the present invention to provide a wet-spinning process for spinning ribbon-shaped fibers of acrylonitrile of improved abrasion resistance without the necessity of using plastic spinnerettes while minimally departing from existing wet-spinning processes utilizing concentrated aqueous sodium thiocyanate solvent.

It is a further object of this invention to provide such a process operable at relatively high speed to maximize the productivity of the spinning equipment.

In the practice of the process present invention, a spinning solution of acrylonitrile polymer in concentrated aqueous sodium thiocyanate solvent is extruded directly into a cold (below 10° C.) aqueous coagulating bath containing between 22% and 26% sodium thiocyanate through rectangular orifices each having a short dimension between 20 and 200 microns and a long dimension such that the resultant ribbon-shaped filament spun there-through has an aspect ratio between 2.0 and 3.0. The freshly-formed filaments are pulled from the orifices in the coagulant at a linear velocity above about 12 meters per minute. Thereafter, the filaments are subjected to a previously known processing sequence including washing, stretching 4 to 15 times at above 65° C., drying, and relaxing at above 100° C. This process produces fibers having an aspect ratio between 2.0 and 3.0, a cover factor of 1.2 to 1.3 (a cover improvement factor of 20% to 30%), and improved abrasion resistance. The significance of various of these numerical ranges will be discussed below.

It has been found that when the aqueous coagulant contains more than 26% sodium thiocyanate, the fibers produced are very delustered and make yarns of low strength. If the aqueous coagulant contains less than 22% sodium thiocyanate, it is impossible to spin ribbon-shaped fibers at speeds approaching 12 meters per minute, therefore productivity is prohibitively low. If the coagulant is warmer than 10° C., porous structured fibers result as is well-known. If the fibers have an aspect ratio below 2.0 and a cover factor below 1.2, the fibers are too low in cover improvement factor to be attractive commercially. If the fibers have an aspect ratio above 3.0 and a cover factor above 1.3, the fibers do not have adequate abrasion resistance.

For a more detailed understanding of the present invention, reference may be had to the following examples illustrative of a preferred embodiment thereof. In these examples, all compositions are expressed in weight percentages unless otherwise stated.

EXAMPLE 1

A spinning solution of an acrylonitrile polymer (of 90% acrylonitrile and 10% methyl methacrylate) dissolved in a concentrated aqueous sodium thiocyanate solvent (to give a solution containing 41.2% sodium thiocyanate, 42% water, and 16.8% polymer) was extruded through rectangular orifices measuring 64 microns by 318 microns directly into a cold (—3° C.) aqueous coagulant containing 25% sodium thiocyanate. The freshly-formed filaments were pulled away at a linear velocity of about 40 meters per minute and then treated with 12% aqueous sodium thiocyanate at —1° C. and then stretched to twice their length. These filaments were then washed with water to remove residual sodium thiocyanate and stretched an additional six times (for a total stretch of twelve times) in water at 100° C.

These stretched wet gel filaments were then dried, on a conveyor belt in a humid environment having 127° C. dry bulb temperature and 60° C. wet bulb temperature. The dried fibers were then placed, in a relaxed free-to-shrink condition, in an autoclave at 124° C. and allowed to shrink 31.8% of their stretched undried length. These fibers had a denier per filament of 2.61, an aspect ratio of 2.49, and a cover factor of 1.25. This fiber was lustrous, had good physical properties, and had a cover improvement factor of 25% (it had 25% better covering ability compared with round fibers of equal denier). The resultant fiber was made into 18/1 yarn and tested for abrasion resistance and strength.

Abrasion resistance or toughness is a measure of a fiber's ability to resist abrasive forces on it. One popular test employs a Stoll abrasion apparatus. Various modifications to the apparatus and standard tests are employed in order to obtain meaningful data depending upon the particular characteristics of the test specimen. In general, however, the effect is similar. That is, the yarn is rubbed

over a bar until it breaks or fibrillates and test results are a function of the number of times the yarn is rubbed. When testing yarns, the total denier of the yarn is taken into account and the amount of load placed on the yarn will vary with the denier so that the load per denier is constant. All tests herein were made at 0.115 gram per denier. In the case of nonround fibers, it is also necessary to remove the effect of aspect ratio which alters the number of cycles to failure for reasons other than toughness. To accomplish this, the cycles to break are divided by the aspect ratio. This arises because failure of the yarn in the Stoll abrasion tests occurs either because of fiber pull-out or fiber attrition. When the aspect ratio is low, failure occurs mainly by pull-out of the fibers from the yarn assembly. When the aspect ratio is high, pull-out is minimized but atrition of the fibers is increased due to larger surface area of the fibers in contact with the edge of the bar, and failure occurs mainly by attrition. In this example, the yarn had an average cycle to break of 206 and an aspect ratio of 2.49. The toughness value, therefore, is 206/2.49 or 82.7. Yarn strength is reported as the yarn count times the tensile value (C×S). This yarn had a C×S of 2,493.

EXAMPLE 2

Example 1 was repeated except that the coagulating bath contained 29% sodium thiocyanate. The fiber obtained had an aspect ratio of 2.89 and a cover factor of 1.29. This fiber was very delustered (much duller than the fiber of Example 1). The toughness was barely acceptable at 36.8 but the yarn strength (C×S) of 1,789 was not acceptable.

EXAMPLE 3

A series of fibers was made at nearly the same conditions as Example 1, except that fiber aspect ratios were varied to show the effect on fiber toughness. The table lists the results.

Aspect ratio	Cover factor	Toughness
1.0 (round)	1.0	180
2.38	1.23	43.5
2.51	1.25	49.5
2.58	1.26	43.7
2.89 (Example 2)	1.29	36.8
4.01	1.42	29.9

From this, it can be seen that the toughness decreases with increasing aspect ratio. A compromise, therefore, must be made between acceptable cover and toughness. Toughness factors below about 35 are unacceptable, and, therefore, fibers with aspect ratios greater than about 3.0 must be avoided.

We claim:

1. A high-speed wet-spinning process for spinning ribbon-shaped fibers of acrylonitrile polymer, said fibers having an aspect ratio between 2.0 and 3.0, a cover factor of 1.2 to 1.3, and improved abrasion resistance, said process comprising the steps of:

(a) forming a spinning solution of said acrylonitrile polymer in concentrated aqueous sodium thiocyanate solvent,

(b) extruding said spinning solution through rectangular orifices directly into an aqueous coagulating bath containing between 22% and 26% sodium thiocyanate, said bath being maintained below 10° C., and each of said rectangular orifices having a short dimension between 20 microns and 200 microns and a long dimension such that the resultant filament spun therefrom has an aspect ratio between 2.0 and 3.0,

(c) pulling the resulting freshly-coagulated filaments away from the rectangular orifices at a linear velocity above about 12 meters per minute,

(d) washing said filaments substantially free of sodium thiocyanate,

(e) stretching said filament 4 to 15 times at a temperature above 65° C.,

(f) drying said filaments, and

(g) relaxing said filament at a temperature above 100° C.

2. A process as defined in claim 1 wherein said filaments are treated with an aqueous solution of sodium thiocyanate having a concentration of less than 15% and a temperature below 10° C. prior to washing said filaments substantially free of sodium thiocyanate.

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,801,691 Dated April 2, 1974

Inventor(s) Edmund Brigmanis and Arutun Maranci

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

Column 1, line 6: after ZIP Code "06497", please insert -- , assignors to American Cyanamid Company, Stamford, Conn. --

Signed and sealed this 9th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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