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[54] **WET-SPINNING PROCESS FOR "DOG-BONE" SHAPED ACRYLONITRILE POLYMER FIBERS**

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[58] **Field of Search** ..... 264/177 F, 182; 161/177, 178

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[57] **ABSTRACT**

In a wet-spinning process for spinning acrylonitrile polymer fibers from a spinning solution of said polymer in a concentrated aqueous sodium thiocyanate solvent, said process comprising extruding said spinning solution through orifices directly into a cold aqueous coagulating bath to form filaments, pulling the freshly-coagulated filaments away from the orifices, followed by washing, stretching, drying, and relaxing said filaments; the improvement comprising forming such fibers having dog-bone or dumbbell cross-sectional configuration by use of the following conditions; said spinning solution contains 9 percent to 13 percent by weight of acrylonitrile polymer dissolved therein; said aqueous coagulating bath contains 22 percent to 28 percent by weight of sodium thiocyanate dissolved therein; said rectangular orifices each have a long dimension between about 450 and about 700 microns and a short dimension such that the resulting filament spun therefrom has an aspect ratio between 3.0 and 4.0; and said pulling, washing, and stretching steps are operated at a denier-speed product per filament of between 75 and 850 denier-meters per minute.

2 Claims, No Drawings

WET-SPINNING PROCESS FOR "DOG-BONE" SHAPED ACRYLONITRILE POLYMER FIBERS

This invention relates to a process for wet-spinning acrylonitrile polymer dissolved in concentrated aqueous sodium thiocyanate solvent to form fibers or filaments having a "dog-bone" or "dumbbell" cross-sectional configuration utilizing spinnerettes with rectangular orifices.

In recent years, synthetic fiber technology has advanced to the stage wherein it 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 dog-bone or dumbbell cross-sectional configuration (such as is typical of Vinyon or Orlon). Since round fibers flex equally in all directions whereas dog-bone or dumbbell shaped fibers flex primarily in one direction only (in the direction of the short axis of the cross-section), use of such fibers gives fabrics made therefrom different appearances and hands from fabrics made of round fibers. Also, fabrics made of such shaped fibers have better "cover" than corresponding fabrics made of round fibers of equal denier.

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 liquified 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 liquified 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 non-round 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 dog-bone or dumbbell 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 dog-bone or dumbbell 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 and 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. Patents as U.S. Pat. Nos. 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 acrylonitrile 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, pages 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 dog-bone or dumbbell 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 Ser. No. 696,495, filed Jan. 9, 1968, assigned to the assignee of the present application, a method is disclosed for making 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, only ribbon-shaped fibers of acrylonitrile polymer were made by such a pro-

cess when rectangular orifices were used. 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 dog-bone or dumbbell shaped fibers of acrylonitrile polymer without the necessity of using plastic spinnerettes while using rectangular orifices and minimally departing from existing wet-spinning processes utilizing concentrated aqueous sodium thiocyanate solvent.

A known wet-spinning process for making acrylonitrile polymer fibers generally comprises forming a spinning solution of the acrylonitrile polymer in a concentrated aqueous sodium thiocyanate solvent, extruding the spinning solution through orifices directly into a cold (below 10°C.) aqueous coagulating bath to form filaments, pulling the freshly-coagulated filaments away from the orifices, followed by washing, stretching, drying, and relaxing the filaments. These latter steps may be performed in various orders, e.g., relaxation may precede or follow drying; part of the stretching may precede washing or all the stretching may be after washing; etc., and may be performed by various means, e.g., stretching may be in air or in hot water; relaxation may be in steam or hot air; drying may be over heated rolls or in controlled humidity hot air; etc., as is well-known in the art. The present invention is based upon the discovery of certain conditions under which this known wet-spinning process can be made to yield acrylonitrile polymer fibers of dog-bone or dumbbell cross-sectional configuration instead of the round fibers normally obtained.

In accordance with the present invention, dog-bone or dumbbell shaped fibers are obtained from rectangular orifices in this wet-spinning process when (a) the spinning solution contains 9 percent to 13 percent by weight of acrylonitrile polymer dissolved therein, (b) the cold (below 10°C.) aqueous coagulating bath contains 22 percent to 28 percent by weight of sodium thiocyanate, (c) the rectangular orifices each have a long dimension between about 450 and about 700 microns and a short dimension such that the resulting filament spun therefrom has an aspect ratio (ratio of the long dimension of the fiber cross-section to the short dimension) between 3.0 and 4.0, and (d) the pulling, washing, and stretching steps are operated at a denier-speed product per filament (product of filament denier, on a bone-dry basis, times the linear speed in meters per minute through these processing steps) of between 75 and 850 denier-meters per minute.

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 hot (40°C.) spinning solution of an acrylonitrile polymer (of 90 percent acrylonitrile and 10 percent methyl methacrylate) dissolved in a concentrated aqueous sodium thiocyanate solvent (to give a solution containing 40.5 percent sodium thiocyanate, 48.3 percent water, and 11.2 percent polymer) was extruded through a metal spinnerette having 100 rectangular orifices, each measuring 75 microns by 500 microns directly into a cold (−4°C.) aqueous coagulant containing 26 percent sodium thiocyanate. The freshly-formed filaments were pulled away by pullaway rolls rotating at a peripheral speed of 8.3 meters per minute. These filaments were then stretched 2X in air by a draw roll rotating at a peripheral speed of 16.6 meters per minute, washed with water, stretched an additional 6X in water at about 100°C. in two stages to a speed of 100 meters per minute. The denier of these filaments after the total 12X stretch was 1.6 which gave a denier-speed product per filament of 160 denier-meters per minute. The aspect ratio of these filaments was 3.5 and they were of dog-bone or dumbbell cross-sectional configuration. Thereafter, these filaments can be dried and relaxed in any conventional manner.

EXAMPLE 2

Example 1 was repeated substituting a spinnerette having 20 rectangular orifices, each measuring 90 microns by 600 microns, keeping all other conditions the same as specified in Example 1. These filaments, spun at a denier-speed product per filament of 160 denier-meters per minute, had an aspect ratio of 4.0 and were of dog-bone or dumbbell cross-sectional configuration.

EXAMPLE 3

Example 1 was again repeated substituting a spinnerette having 20 rectangular orifices, each measuring 90 microns by 450 microns, keeping all other conditions the same as specified in Example 1. These filaments, spun at a denier-speed product per filament of 160 denier-meters per minute, had an aspect ratio of 2.0 and did not have the desired dog-bone or dumb-bell cross-sectional configuration.

EXAMPLE 4A

Example 1 was again repeated using the spinnerette there described but using as the coagulating bath a cold (−4°C.) aqueous solution containing 24 percent sodium thiocyanate. These filaments had an aspect ratio of 2.5 and did not have the desired dog-bone or dumbbell cross sectional configuration. Increasing the length of the long dimension of the rectangular orifice and/or reducing the denier-speed product of the process can serve to raise the aspect ratio of the filaments produced until the aspect ratio is between 3.0 and 4.0 in order to obtain dog-bone or dumbbell cross-sectional configurations with this coagulant concentration.

EXAMPLE 4B

Example 1 was again repeated but using a 28 percent aqueous solution of sodium thiocyanate at −4°C. as the coagulating bath. These filaments had an aspect ratio of 4.2 and did not have the desired dog-bone or dumbbell cross-sectional configuration. Reducing the length of the long dimension of the rectangular orifice and/or increasing the denier-speed product of the process can serve to lower the aspect ratio of the filaments produced until the aspect ratio is between 3.0 and 4.0 in order to obtain dog-bone or dumbbell cross-sectional configurations with this coagulant concentration.

EXAMPLE 5

Examples 1, 2, and 3 were again repeated (using, respectively, the three spinnerettes there described) using cold 26 percent aqueous sodium thiocyanate coagulant except that the pullaway rolls, draw rolls, etc. were all operated at twice the peripheral speeds there given to produce filaments, after the total 12X stretch,

of 1.2 denier, giving a denier-speed product per filament for each run of 240 denier-meters per minute. Using the spinnerette of Example 1, the filaments had an aspect ratio of 2.3 and did not have the desired dog-bone or dumbbell cross-sectional configuration. Using the spinnerette of Example 2, the filaments had an aspect ratio of 3.2 and were of dog-bone or dumbbell cross-sectional configuration. Using the spinnerette of Example 3, the filaments had an aspect ratio of 1.5 and did not have the desired dog-bone or dumbbell cross-sectional configuration. Using the spinnerettes of Examples 1 and 3, increasing the coagulant concentration and reducing the denier-speed product of the process can serve to raise the aspect ratio of the filaments produced until the aspect ratio is between 3.0 and 4.0 in order to obtain dog-bone or dumbbell cross-sectional configurations.

I claim:

1. In a wet-spinning process for spinning acrylonitrile polymer fibers from a spinning solution of said polymer in a concentrated aqueous sodium thiocyanate solvent, said process comprising extruding said spinning solution through orifices directly into a cold aqueous coagulating bath to form filaments, pulling the freshly-coagulated filaments away from the orifices, followed by washing, stretching, drying, and relaxing said filaments; the improvement comprising forming such fibers having dog-bone or dumbbell cross-sectional configuration by use of the following conditions:

a. said spinning solution contains 9 percent to 13 percent by weight of acrylonitrile polymer dissolved therein;

b. said aqueous coagulating bath contains 22 percent to 28 percent by weight of sodium thiocyanate dissolved therein;

c. said rectangular orifices each have a long dimension between about 450 and about 700 microns and a short dimension such that the resulting filament spun therefrom has an aspect ratio between 3.0 and 4.0; and

d. said pulling, washing, and stretching steps are operated at a denier-speed product per filament of between 75 and 850 denier-meters per minute.

2. A process as defined in claim **1** wherein said coagulating bath is maintained at a temperature below 10°C.

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