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3,193,603

PRODUCTION OF ACRYLIC FIBERS BY SPINNING INTO A HIGH SOLVENT, LOW TEMPERATURE SPIN BATH

Alvah L. Rowe, Jr., and Thomas B. Truscott, Decatur, Ala., assignors to Monsanto Company, a corporation of Delaware

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This invention is concerned with improving textile properties of wet-spun thermoplastic fibers by changes in normal or conventional spinning conditions. More specifically, this invention is concerned with a method of improving the textile properties of wet-spun acrylic fibers processed into fabrics.

With the introduction to commercial use of synthetic fibers, a number of problems have arisen which had not occurred when natural fibers were used. While these synthetic fibers have many excellent properties, some of which are vastly superior to the properties of natural occurring fibers, there are a number of properties which are not equal to those of natural occurring fibers, such as static electrical charges, dyeability, resistance to light degradation, discolored fibers due to the spinning methods and many others. A serious problem which occurs with acrylic fibers during their textile processing is that of a tendency for the filaments to break. This is particularly true when the acrylic yarns are being knitted or processed on conventional wool machinery. This has resulted in a large accumulation of fly which results in having to stop the knitting process, partially disassembling the knitting machines and cleaning them due to this increase in fly accumulation which obviously increases the cost of producing articles on conventional wool or natural fibers conventional machinery in a textile process.

An object of this invention is to provide a method for producing synthetic fibers which retain good textile properties.

Another object of this invention is to provide a method for the production of acrylic fibers which retain good textile properties.

Another object of this invention is to provide a method for the production of acrylic fibers which possess a minimum filament breakage during textile processing.

Another object of this invention is to provide a method for the production of acrylic fibers in which there is no excessive fly buildup during processing of these fibers in conventional knitting machinery.

Other objects and advantages of this invention will become apparent from the hereinafter detailed description.

The objects of this invention are generally accomplished by spinning the fibers into a spin bath of high solvent and low temperature when compared to the conventional wet spin bath. In addition, the jet stretch is lower than in the conventional wet spin method for acrylonitrile based fibers.

More specifically, the polymers are spun into a wet spin bath in which the solvent, based upon the total weight of the spin bath, may vary from 50 percent to 75 percent, with the preferred depending upon the specific polymer composition as described hereinafter. This solvent in the spin bath is normally the same solvent in which the polymer is dissolved prior to spinning. The water portion of the spin bath will comprise the remainder. In addition, this spin bath is maintained within a temperature range of from 0° C. to 40° C. with the preferred temperature being 30° C.-32° C. Under the normal wet spinning method for acrylic fibers, there is a jet stretch ratio of 0.7 to 2.0; however, in the process of the present invention this jet stretch ratio may vary from

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0.1 to 0.75 with the preferred jet stretch ratio being 0.5 to 0.07. This jet stretch is the ratio of the linear rate of withdrawal of fibers from the spin bath of the linear rate of extrusion of dope into the spin bath. Further, under the normal wet spinning method for acrylic fibers, there is a cascade stretch ratio of 4 to 6, which is a hot wet stretch; however, in the process of the present invention this cascade stretch ratio may vary from 5 to 10 with the preferred cascade stretch ratio being 7. The method of this invention is applicable primarily to the spinning of small denier fibers varying from one-half denier per filament to 8 denier per filament.

While this application has been generally directed to synthetic fibers, it is especially useful in the wet spinning of fibers composed of acrylic polymers. The polymeric materials of the acrylic fibers may be polyacrylonitrile, copolymers, including binary and ternary polymers containing at least 80 percent by weight of acrylonitrile in the polymer molecule or a blend comprising polyacrylonitrile or copolymers comprising acrylonitrile with from 2 to 50 percent of another polymeric material, a blend having an overall polymerized acrylonitrile content of at least 80 percent by weight. While the preferred polymers employed in the instant invention are those containing at least 80 percent of acrylonitrile, generally recognized as the fiber forming acrylonitrile polymers, it will be understood that the invention is likewise applicable to polymers containing less than 80 percent acrylonitrile. The acrylonitrile polymers containing less than 80 percent are useful in forming additional fibers in the modacrylic range, film, coating compositions, lacquers, etc.

For example, the polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing



linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers, including acrylic, alpha-chloroacrylic and meta-acrylic acid; the acrylates, such as methacrylate, ethylmethacrylate, butylmethacrylate, methoxy methylmethacrylate, beta-chloroethylmethacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1 chloro-1-bromo-ethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloroacrylamide; or monoalkyl substitution products thereof; methylvinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic esters; N-vinylcarbazole; vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethylcitrate, diethylmesaconate, styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridine, for example 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, etc.; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles such as 2-, 4-, and 5 methyl-1-vinylimidazole, and other



containing polymerizable materials.

The polymer may be a ternary or higher interpolymer, for example products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, and preferably the ternary polymer comprises acrylonitrile, methacrylonitrile, and 2-vinylpyri-

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dine. The ternary polymer preferably contains from 80 to 98 percent of acrylonitrile, from 1 to 10 percent of vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another substance such as methacrylonitrile or vinyl chloride.

The polymer may also be a blend of a polyacrylonitrile or of a binary interpolymer of from 80 to 99 percent acrylonitrile and from 1 to 20 percent of at least one other



containing substance with from 2 to 50 percent of the weight of the blend of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 percent to 90 percent of at least one other



containing polymerizable monomer. Preferably, when the polymeric material comprises a blend, it will be a blend of a copolymer of 90 to 98 percent acrylonitrile and from 2 percent to 10 percent of another monolefinic monomer, such as vinyl acetate, with a sufficient amount of a copolymer of from 10 percent to 70 percent acrylonitrile and from 30 percent to 90 percent of a vinyl-substituted tertiary heterocyclic amine, such as vinylpyridine or 1-vinylimidazole, to give a dyeable blend having an overall vinyl-substituted tertiary heterocyclic amine content of from 2 percent to 10 percent based on the weight of the blend.

The following examples are cited to illustrate the invention. They are not intended to limit it in any way. Unless otherwise noted, percentages as expressed in the examples indicate percent by weight.

Example 1

A 3 denier per filament fiber composed of 94 percent acrylonitrile and 6 percent vinyl acetate was dissolved in a dimethylacetamide solvent, representing a 25.5 percent solid dope. This composition was spun into a coagulating bath comprising 56 to 58 percent of a dimethylacetamide solvent and 44 to 42 percent water at a temperature of 44 to 45° C. and a jet stretch of 0.96. The fibers were then subjected to a cascade stretch of 5.5. The fibers were then dried, crimped, subjected to steam under pressure and then recripped. The fibers were then stretched and random broken on a Turbo stapler under conventional conditions for commercial acrylic fibers. These fibers were then worsted processed into yarn and knitted on an Interlock knitting machine. The amount of fly collected on this machine was 1.059 grains per pound of yarn used on this knitting machine. Thus the fly of this fiber spun under normal conditions is much larger than the fly of the subsequent examples which were spun under the conditions of the process of this invention.

Example 2

The exact process of Example 1 was repeated with the same fiber composition except the temperature of the spin bath was 30–32° C., solvent was 65 percent to 67 percent of the spin bath with water comprising the remainder. The jet stretch was 0.75 and the cascade stretch was 7.0. After knitting this yarn on an Interlock knitting machine it was found that there was only 0.315 grain per pound of yarn used by the knitting machine.

Example 3

The exact procedure was followed in Example 1 except for the following. The temperature of the spin bath was 30–32° C., the solvent of the spin bath was 65 percent to 67 percent with the remainder being water, the jet stretch was 0.75 and the cascade stretch was 7.0. The fly which accumulated on the knitting machine amounted to 0.447 grain per pound of yarn.

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Example 4

The exact procedure of Example 1 was repeated except for the following. The temperature of the spin bath was 30–32° C., the concentration of the solvent in the spin bath was 65 percent to 67 percent with the remainder of the spin bath being water, the jet stretch was 0.52 and the cascade stretch was 7.0. The fly which accumulated on the knitting machine was 0.378 grain per pound of yarn.

Example 5

The exact procedure of Example 1 was repeated except for the following. The temperature of the spin bath was 30–31° C., the concentration of the solvent in the spin bath was 63 percent to 65 percent with the remainder being water, jet stretch was 0.75 and the cascade stretch was 7.0. The fly which accumulated on the spinning machine was 0.437 grain per pound of yarn knitted.

Thus was the wet spinning method of this invention, small denier per filament acrylonitrile fibers are produced in which there is retained good wear and textile properties, especially the reduction of fly accumulation on knitting machines during the knitting process. This of course points out that filament breakage during the various textile processes is held to a minimum and there is no increase in the cost of processing these yarns due to machinery clogging, etc.

It is understood that changes in variations may be made in the present invention by one skilled in the art without departing from the spirit and scope thereof as defined in the appended claims.

We claim:

1. A method for the production of an acrylic fiber composed of 94 percent acrylonitrile and 6 percent vinyl acetate of a denier from 0.5 to 8 denier per filament comprising spinning a solution of said polymer into a spin bath composed of 65 percent of an organic solvent, said solvent being chemically identical to the solvent of said solution, and 35 percent water with the spin bath held at a temperature of 32° C. with a jet stretch of 0.5 and a cascade stretch of 7.0.

2. A method for the production of an acrylic fiber composed of a blend of two copolymers, 88 percent of the first copolymer being 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of a second copolymer being 50 percent acrylonitrile and 50 percent methyl vinylpyridine of a denier from 0.5 to 8 denier per filament, comprising spinning a solution of said blend into a spin bath composed of 63 percent to 67 percent of an organic solvent, said solvent being chemically identical to the solvent of said solution, water comprising the remainder of the spin bath, at a temperature of 30° C.–32° C. with the jet stretch of 0.5 and a cascade stretch of 7.0.

3. A method for the production of synthetic linear acrylonitrile fibers of 0.5 to 8 denier per filament with improved textile properties comprising spinning a solution containing said polymer into a spin bath composed of from 50 to 75 percent of an organic solvent, said solvent being chemically identical to the solvent of said solution, with the temperature of the spin bath varying from 0 to 36° C. and with a jet stretch of from 0.1 to 0.75 and a cascade stretch being between 5 and 10.

4. The method of claim 3 in which the fiber is a fiber composed of at least 80 percent acrylonitrile and up to 20 percent of another monoolefinic monomer copolymerizable therewith, within a range of 0.5 to 8 denier per filament, the solvent in the spin bath being 65 percent to 67 percent, water comprising the remainder, the temperature of the spin bath being between 0° C. and 32° C., the jet stretch being 0.5 to 0.55, the cascade stretch being 7.0.

5. A method for the production of acrylic fiber composed of a blend of 2 copolymers, 88 percent of the first copolymer being 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of a second copolymer being 50 percent acrylonitrile and 50 percent methyl vinyl pyri-

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dine, of a denier from 0.5 to 8 denier per filament comprising spinning a solution, said solvent being dimethylacetamide, of said blend into a spin bath composed of 63 percent to 67 percent dimethylacetamide, water comprising the remainder of the spin bath, at a temperature of 30 degrees C. to 32 degrees C., with the jet-stretch of 0.5 and a cascade stretch of 7.0.

6. The method as claimed in claim 5 wherein the dimethylacetamide solvent is a dimethylformamide solvent.

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ALEXANDER H. BRODMERKEL, *Primary Examiner.*

WILLIAM J. STEPHENSON, *Examiner.*

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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Alvah L. Rowe, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 2, for "0.07" read -- 0.7 --.

Signed and sealed this 25th day of January 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents