United States Patent

[11] 3,624,196

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[21] Appl. No. **1,548**
[22] Filed **Jan. 8, 1971**
[45] Patented **Nov. 30, 1971**

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[54] **STABILIZATION OF ACRYLONITRILE FIBERS TO HOT-WET CREEP**
7 Claims, No Drawings

[52] **U.S. Cl.** **264/234,** 8/149.3, 264/182, 264/345

[51] **Int. Cl.** **B29c 25/00,** D01f 7/00

[50] **Field of Search** 264/182, 210, 346, 345, 234, 235; 28/72.12, 72.17; 8/149.3

[56] **References Cited**

UNITED STATES PATENTS

2,920,934	1/1960	Schaefer et al.	264/184
3,447,998	1/1969	Fitzgerald et al.	264/210 Z
3,463,846	8/1969	Nakagawa et al.	264/182

FOREIGN PATENTS

43/22,358	9/1968	Japan	264/182
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ABSTRACT: A process is provided for improving the dimensional stability under hot-wet conditions of fibers prepared from acrylonitrile polymers containing at least 95 percent acrylonitrile wherein spun fibers after orienting and drying are heated with wet steam under pressure to a temperature below the temperature where they shrink until the tendency to creep under hot-wet conditions is reduced.

STABILIZATION OF ACRYLONITRILE FIBERS TO HOT-WET CREEP

This invention relates generally to fibers prepared from acrylonitrile polymers and, more particularly, to a method of improving the dimensional stability of such fibers under hot-wet conditions.

Various processes for preparing fibers from acrylonitrile homopolymers, copolymers, terpolymers and the like have been proposed. Such processes involve dissolving the polymer in a suitable solvent therefor and spinning fibers therefrom by extruding the solution through a spinnerette into a coagulating bath. One such process is disclosed by Cresswell in U.S. Pat. No. 2,588,730. In accordance with the Cresswell process, a water coagulable solution of the polymer is extruded into an aqueous coagulant maintained at a temperature of not more than about +10° C.

One disadvantage of fibers prepared heretofore from acrylonitrile polymers is lack of dimensional stability under hot-wet conditions. Fabrics prepared from such fibers tend to shrink or elongate when they are dyed, washed or steam pressed. The tendency of fibers to shrink has been more or less eliminated by preshrinking the fibers with steam under pressure after the fibers have been oriented by stretching. For example, the process disclosed in U.S. Pat. No. 2,920,934 not only reduces fibrillation but also reduces shrinkage of the resulting fiber. In accordance with that process, fibers prepared from polymers containing at least 70 percent acrylonitrile are subjected to wet steam in an autoclave under a pressure of 30 to 60 p.s.i.g. and a temperature where fibers of such polymer composition shrink. As most apparent from table 1, column 8 of the patent, the elongation of the annealed shrunken fibers is greater than that of an unannealed fiber of the same composition.

Another process for improving the quality of filaments prepared from polymers containing acrylonitrile by treating the filaments with steam is disclosed in U.S. Pat. No. 3,101,245. That process combines a drying step under controlled humidity with a subsequent steam treatment. The filaments are subjected while relaxed to steam at a temperature between 105° C. and 160° C. under conditions where they shrink. The elongation of the fiber increases as is indicated in the patent. While the processes of U.S. Pat. Nos. 2,920,934 and 3,101,245 produce a fiber having improved dyeability, reduced tendency to shrink and reduced fibrillation, such fibers have the disadvantage of elongating under hot-wet conditions and are consequently undesirable for making fabrics which are piece dyed, washed or steam pressed.

It is, therefore, an object of this invention to provide an improved process for post treating extruded filaments prepared by spinning a solution of a polymer containing acrylonitrile. Another object of the invention is to provide a process for improving the dimensional stability of a fiber prepared from a polymer containing acrylonitrile by a wet-spinning process. Still another object of the invention is to provide a method for making acrylonitrile fibers adapted to be used for making fabrics which are to be exposed to hot-wet conditions such as washing in water or steam pressing. A still further object of the invention is to provide a fiber produced by spinning a solution of a polymer containing acrylonitrile which has good flexibility combined with improved dimensional stability under hot-wet conditions.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speaking, by providing a process wherein stretch oriented, relaxed and dried filaments are spun from a solution of a polymer containing at least about 95 percent acrylonitrile and are subjected to wet steam under pressure but at a temperature below that at which the filament will shrink. It has been found that fibers spun from a solution of a polymer containing at least about 95 percent by weight acrylonitrile and heated with wet steam under pressure to a temperature above about 120° C. but below a temperature where they will shrink have less tendency to elongate under hot-wet conditions than similar but untreated fibers. Furthermore, the flexibility of the fiber is not deleteriously affected by the steam treating step provided the composition of the polymer from which the fiber is spun contains at least 95 percent acrylonitrile and the maximum temperature reached by the fiber while subjected to steam is below the point where it will shrink while it is in a relaxed or tensionless state. The maximum steam temperature permissible will vary from one polymer composition to another depending upon the temperature where shrinkage begins. For example, an oriented, dried fiber having the composition of about 90 parts acrylonitrile and 10 parts methyl methacrylate will shrink when heated with wet steam at 125° C. However, a fiber spun from a homopolymer of acrylonitrile can be heated with steam up to about 160° C. without appreciable shrinkage while one spun from a copolymer of about 5 percent methyl methacrylate and about 95 percent acrylonitrile should not be heated above about 150° C. As a general rule for all polymer compositions contemplated by the invention, the fiber is heated above about 100° C. and the preferred process contemplates heating the fiber with steam under pressure to a temperature of between about 120° C. and 150° C.

Generally speaking, in preparing the fiber having improved dimensional stability under hot-wet conditions provided by this invention, a homopolymer or copolymer containing at least about 95 percent by weight acrylonitrile is dissolved in a suitable solvent therefor, extruded into an aqueous coagulating bath to form gel filaments, and the filaments are then washed substantially free from solvent, oriented, dried, and heated with steam under pressure in the relaxed state while avoiding a temperature where the fibers will shrink to any appreciable extent. Stretching the gel filaments prior to washing and again after washing to orient the polymer molecules improves the strength of the fibers. Preferably, the filaments are stretched in air prior to washing free from solvent and are stretched again after washing and before drying. The second stretching process is preferably conducted in water at about 80° C. or higher. Usually, the fibers are stretched to only two to four times their unstretched length in air and are then stretched to 10 or more times their original unstretched length in hot water. Surprisingly, it has been found that although no shrinkage or visible change occurs in the fiber when it is heated with steam as provided herein, the dimensional stability under hot-wet conditions is improved as evidenced by a decrease in the tendency of the fiber to creep when exposed to hot water. For some yet unexplainable reason, decrease in creep has not been obtained when fibers spun from polymers containing less than about 95 percent acrylonitrile are treated by the heat treatment process of this invention.

The stability of fibers under hot-wet conditions can be determined by subjecting them to a "creep test." The creep test is a standard test used by the industry and differs from other static strength tests by taking into account the element of time. In making such a test, the fibers to be tested are mounted on clamps in the form of a loop from 5 to 10 cm. long. A load of 0.1 g. per denier of the fiber is suspended from the lower end of the loop. The loaded fiber is placed in water at 90° C. and the length thereof is measured after 1 minute and again after 10 minutes in the water. The change in length or creep after 1 minute is known as E_1. The change in length after 10 minutes exposure to the water is known as E_{10}. Delta creep is E_{10} minus E_1 or the change in length between the first minute and 10th minute exposure.

The process provided by this invention reduces the tendency to creep of fibers produced by spinning any polymer, copolymer, terpolymer or the like containing at least about 95 percent by weight acrylonitrile so any of the various wet-spinning processes can be used to prepare the gel filament. A preferred process is that disclosed by Cresswell in U.S. 2,558,730 but any of the other wet-spinning processes known to the art can be used, if desired. The fibers resulting from wet spinning, stretch orienting and washing may be dried by any suitable process including the one disclosed by Robertson et

al. in U.S. Pat. No. 2,984,912. The fibers may be relaxed prior to drying by shrinking with steam or they may be relaxed after drying. Relaxing or shrinking of the fibers imparts greater flexibility thereto. Since very high temperatures are required to relax fibers having a composition of greater than 95 percent acrylonitrile after drying, it is more practical and preferred to relax them prior to drying. Temperatures of about 70° C. and higher are used when relaxing or shrinking fibers before drying. The fibers should not be stretched during treatment with steam as provided herein in order to avoid subsequent shrinkage under hot-wet conditions.

As indicated hereinbefore, the polymer from which the fibers are produced may be a homopolymer of acrylonitrile or any other polymer containing at least 95 percent by weight acrylonitrile and another monomer or two or more monomers which are polymerizable with acrylonitrile. Any suitable ethenoid monomer containing a CH_2=C=group which is polymerizable with acrylonitrile may be used and is contemplated in an amount of up to about 5 percent by weight in the polymer. Some specific examples of suitable monomers are methyl methacrylate, methyl acrylate, vinyl acetate and the like. Other suitable monomers and polymers are disclosed in U.S. Pat. No. 2,883,260 and elsewhere in the art.

In preparing the solution to be extruded in making the fibers, the polymer may be first dissolved in a suitable solvent to form a spin dope or the polymer may be prepared by polymerizing monomer or monomers in the solvent to be used in the spin dope. Any suitable water soluble solvent for the polymer may be used such as, for example, dimethyl acetamide, dimethyl formamide, ethylene carbonate, the metal thiocyanates disclosed in Cresswell U.S. Pat. No. 2,588,730 and the like. The filaments may be extruded into any suitable aqueous bath such as, for example, those disclosed in the aforesaid Cresswell patent.

In the following examples, all parts are by weight unless otherwise indicated.

EXAMPLE I

A spinning solution is prepared by dissolving about 11.2 parts polyacrylonitrile homopolymer in about 88.8 parts of a 50 percent aqueous solution of sodium thiocyanate. The spinning solution is extruded through a spinnerette submerged in an aqueous coagulating bath containing about 14 percent sodium thiocyanate at a temperature of about 0° C. The resulting filaments are removed from the coagulating bath, stretched in air to about twice their unstretched length and washed with water at room temperature until substantially all solvent has been removed. The filaments are next stretched in water at about 98° C. to about five times their washed length or, in other words, to about 10 times their length prior to stretching in air. Skeins of the stretched aqua-gel filaments are immersed in water at about 85° C. and allowed to relax for about 10 minutes at about 85° C. The skeins are removed after the water has cooled to room temperature (about 20° C.). The filaments relax about 19 percent of their fully stretched length. The skeins are now conditioned in an oven having an atmosphere of about 127° C. dry bulb and about 60° C. wet bulb and left until dry. The filaments relax an additional 37 percent of their wet fully stretched length to a final dry denier of about 3.

A series of samples of fibers thus produced are treated in an autoclave under steam pressure for periods of 20 minutes at the temperatures indicated in table I. The results which are obtained in the creep test described hereinbefore on the steam treated samples and on an untreated sample are recorded in table I.

TABLE I

Steam temp., ° C.	Percent shrinkage	Elongation		Percent creep		
		Straight	Loop	E_1	E_{10}	$E_{10}-E_1$
No treatment	0	47.0	21.1	17.4	26.3	8.9
120	0	42.1	18.4	6.4	8.4	2.0
130	0	40.4	13.9	7.7	9.9	2.2
140	0	42.7	12.0	5.2	6.8	1.6
150	0	39.0	12.9	6.2	8.6	2.4
160	0	33.6	13.4	4.5	7.2	2.7

EXAMPLE 2

Fibers are produced in accordance with the process described in example I except a copolymer having the composition of about 95.7 percent polyacrylonitrile and about 4.3 percent methyl acrylate is substituted for the homopolymer of example I.

The extruded gel filaments are stretched in air to 2.5 times their unstretched length. The filaments are then stretched in water at about 98° C. to about 5.6 times their length after stretching in air or to about 14 times their length prior to stretching in air. The denier is about 1.9. Skeins of the filaments are gel-relaxed in water at about 98° C. for about 10 minutes and shrink about 26 percent of their stretched length. The relaxed fibers are dried at about 127° C. dry bulb temperature and about 60° C. wet bulb where they relax to a total of 37 percent of the stretched length and a denier of about 2.8 per filament.

The filaments are steam treated as described in example I and measured for creep and elongation. The results are recorded in table II.

TABLE II

Steam temp., ° C.	Percent shrinkage	Elongation		Percent creep		
		Straight	Loop	E_1	E_{10}	$E_{10}-E_1$
No treatment	0	49.9	26.9	20.9	20.9	9.1
120	0	44.3	28.5	11.2	14.5	3.3
130	0	48.1	26.7	12.7	15.4	2.7
140	0	40.9	29.5	13.0	16.8	3.8
150	3.0	43.5	30.7	15.8	21.3	5.5
160	14.0	65.2	51.6	26.4	63.0	36.6

Comparison of the results of table II shows that the delta creep of samples which have been heated to 120°–140° C. with steam is greatly improved over that of the untreated sample. Furthermore, the fiber does not shrink. However, the fibers prepared from the copolymer of acrylonitrile and methyl acrylate began to show shrinkage at 150° C. and the shrinkage is more evident at 160° C. The stability of fibers heated to 160° C. is adversely affected as shown by the elongation and creep.

EXAMPLE 3

The process of example I is repeated except the 10 minute relaxation step in water is omitted. The dried fiber is heated with steam to 127° C. The hot-wet creep is as follows:

TABLE III

Fiber	E_1	E_{10}	Δ
Dried only	26.2	30	3.8
Dried only	26.6	30	3.4
Steamed at 127° C.	6.1	7.8	1.7
Steamed at 127° C.	8.1	9.1	1.0

It is to be noted that significant improvement in creep is obtained by heating the fiber with steam to a temperature where it does not shrink even when the gel relaxation step is omitted.

The term "polymer of acrylonitrile" is used in the claims to mean any polymer containing at least about 95 percent by weight acrylonitrile and not more than about 5 percent of one or more other ethenoid monomer containing a CH_2=C=radical which is copolymerizable with acrylonitrile.

Although the invention has been described in detail for the purpose of illustration, such detail is solely for that purpose and it is to be understood that variations can be made by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

I claim:

1. A process for improving the dimensional stability of acrylonitrile polymer fibers under hot-wet conditions which comprises (a) wet spinning an acrylonitrile polymer containing at least about 95 percent of acrylonitrile by a process which includes the steps of extruding, coagulating, stretching, washing, and drying the fibers so spun and (b) heating the thus dried fibers while in a substantially tensionless state in the presence of wet steam under pressure to a temperature above 100° C. but below the temperature where substantial shrinkage of said fiber occurs.

2. A process as defined in claim 1 wherein said acrylonitrile polymer is a homopolymer of acrylonitrile and wherein said fiber is heated to between 100° C. and about 160° C. with the steam.

3. A process as defined in claim 1 wherein said acrylonitrile polymer contains up to about 5 percent of another ethylenically unsaturated comonomer copolymerizable with acrylonitrile and wherein said fiber is heated to between 100° C. and about 150° C. with the steam.

4. A process as defined in claim 3 wherein said acrylonitrile polymer contains about 95 percent acrylonitrile and about 5 percent methyl methacrylate.

5. In a process for wet spinning acrylonitrile polymer fibers which includes the steps of extruding, coagulating, washing, stretching, and drying the fibers so spun, the improvement comprising (a) using in said wet-spinning process an acrylonitrile polymer containing at least about 95 percent of acrylonitrile and (b) heating such fibers subsequent to drying and while in a substantially tensionless state in the presence of wet steam under pressure to a temperature above 100° C. but below the temperature where substantial shrinkage of said fibers occurs, thereby reducing the tendency of said fibers to creep under hot-wet conditions.

6. A process as defined in claim 5 wherein said acrylonitrile polymer is a homopolymer of acrylonitrile and wherein said fibers are heated to between 100° C. and about 160° C. with the steam.

7. A process as defined in claim 5 wherein said acrylonitrile polymer contains up to about 5 percent of another ethylenically unsaturated comonomer copolymerizable with acrylonitrile and wherein said fiber is heated to between 100° C. and about 150° C. with the steam.

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