

1

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**METHOD FOR PREPARING HIGHLY SHRINKABLE
ACRYLONITRILE POLYMER FIBERS**

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This invention relates to the production of highly shrinkable synthetic fibers. More specifically, the present invention relates to the preparation by wet spinning of highly shrinkable acrylonitrile polymer fibers by subjecting them to certain processing treatments during their manufacture.

It may frequently be advantageous and desirable for synthetic fibers to be available having greater shrinkability than that with which they are inherently possessed. Thus, in the preparation of high-bulk yarns, it is beneficial to combine fibers of high shrinkability with others of relatively low shrinkability. When the mixed fibers in the yarn construction (or in cloth or fabric manufactured from such yarn) are shrunk together, the variation of shrinking properties in the fibers produce partial bending and loop formation or "arcinup" in the longer or less shrinkable fibers. This results in a yarn of high bulk and softness. Textile goods of such characteristics are frequently of great desirability for the preparation of such articles as sweaters, comforters, scarfs, etc.

Various means have been employed to prepare fabrics having the foregoing high bulk characteristics. Some of these methods involve such means as subjecting the fibers or filaments to air jets which cause fiber entanglement and general volume increase. Others utilize introducing a false twist in the fibers which is then heat set, or by imposing a crimp into the fiber which is heat set. Some of the means that have been particularly utilized with acrylonitrile polymer fibers is to heat the fibers between a pair of hot plates while simultaneously stretching the fiber until they break or performing the same operation while the fibers are at ambient temperature; or by heating the fibers between a pair of hot plates and stretching the fibers but instead of stretch-breaking the fibers the fibers may be cut or crushed. Still other methods that have been employed or discussed in the art are to introduce certain chemical agents into the fibers which cause the fibers to shrink when exposed to boiling water.

Normal shrinkage of most acrylonitrile polymer fibers when treated with boiling water is about 0–5%. These fibers can be caused to shrink more, however, by imposing certain of the conventional unstabilizing treatments such as those discussed in the foregoing paragraph, e.g. as by giving the fibers a rapid stretch with a simultaneous short heating cycle at about 90–100° C. The more stable of the acrylonitrile polymer fibers generally have a shrinkage of between 12 and 15% when so treated by these conventional treatments. Certain of the acrylonitrile polymers that have been prepared by copolymerizing acrylonitrile with another ethylenically unsaturated monomer may be caused to shrink as much as 16–40% by the conventional unstabilizing treatments mentioned above. These fibers are, however, usually inherently more unstable and are caused to be unstabilized by such a treatment to the point that they tend to continue to shrink after the original bulking shrink in subsequent encounters with hot treatments, for instance, laundering, so that the unstabilizing to increase shrinkability becomes a liability instead of an asset.

It is the chief object and primary concern of the present invention to provide acrylonitrile polymer fibers having significantly increased shrinkability upon exposure to boiling water by an expedient means of building shrinkability into the fibers during their manufacture. It is yet

2

a further object to obtain increased shrinkability without the need to resort to treatments subsequent to the manufacture of the fibers or by altering the fiber composition which may tend to degrade and detract from the fiber physical properties.

These and additional objects and cognate benefits and features are accomplished by and in accordance with the present invention wherein highly shrinkable acrylonitrile polymer fibers are prepared by spinning a solution of a polymer of an ethylenically unsaturated monomeric material containing at least about 80 weight percent acrylonitrile into an aqueous coagulating bath, and then stretching the coagulated filaments to orient the molecule thereof in an aqueous medium at between about 90° and 110° C. at a stretch rate of between about 0.1 and 0.75 feet per second per second, and subsequently irreversibly drying the fiber in a relaxed condition at between about 60° and 90° C.

The wet spinning of acrylonitrile polymer fibers generally involves spinning a solution of the polymer dissolved in a solvent for the polymer into a non-polymer-dissolving liquid causing a polymeric filament to coagulate. The polymer solvent is thus washed or leached out of the coagulated polymer and most often replaced with an inert liquid, frequently water. The filament so formed is usually in a gel state, that is, in a highly swollen condition which may contain as much as 4 to 6 times as much non-polymer-dissolving or inert liquid, e.g. water, as polymer. The gel filament is then ordinarily washed, stretched, and ultimately irreversibly dried to destroy the gel structure.

It is well known in the art that the stretching or orienting of acrylonitrile polymer wet spun fibers is usually carried out at temperatures in the range of 70–110° C., and preferably at 90–100° C. in the presence of moisture. Ordinarily, high stretch ratios are possible only at the higher temperatures if undue filament breakage is to be avoided; and, stretch ratios of about at least 10:1 are normally necessary to produce fibers with a satisfactory combination of physical properties. The total stretch given the fiber has been imparted in one step or stretch pan or in several sequential increments in sequential stretch pans. However, no particular attention has been paid to the rate of stretch that is used in achieving the desired total stretch. The principal interest has been solely in the desired ultimate total stretch that is imparted to the fibers.

The present invention takes advantage of the finding that the rate of stretch of the wet spun fibers has an unexpired influence on increasing the shrinkability of the fibers and when combined with controlled relatively low temperature drying, the resulting fibers have excellently enhanced shrinkability. The fibers prepared according to the present invention can be made to have shrinkages upwards of 20 to 30% when immersed in boiling water. Additionally, the fibers have excellent physical properties coupled with good stability in that continued shrinkage is not encountered or is minimal upon subsequent treatments of the fibers with boiling water.

As indicated, the wet spun fibers are given a slow rate of stretch in a hot aqueous medium which may be water or steam at 90–110° C. but is preferably water at 95–100° C. Other inert constituents may be present in the aqueous medium for any desired purpose such as for enhancing certain fiber properties. In accordance with the definitions of the invention, a fast rate of stretch is defined as one in excess of about 1 foot per second² and a slow rate of stretch is one less than about 0.75 feet per second². The significant increases in shrinkability are accomplished with this invention when a slow rate of stretch of from about 0.75 and preferably from about 0.5 feet per second²

down to about 0.1 feet per second² is employed. Actually, a rate of stretch below 0.1 feet per second² could be employed but for the fact that lower rates of stretch are not commercially attractive due to the slowness of the spinning operation which must necessarily be encountered. Advantageously, and preferably, the rate of stretch that is employed is from between 0.2 and 0.4 feet per second².

It is beneficial when treating the acrylonitrile polymer gel filaments with the slow rate of stretch in the practice of the invention, that a series of stretch pans be employed rather than one single pan. This is principally for convenience in that the length of a single pan that would be required may be inconvenient in usual spinning operations and the control and support of the filaments from one end of the pan to the other may affect uniformity in the product. Therefore, it is convenient and preferable that the stretch be given to the filaments in a series of two or more stretch pans maintained at the same temperature. The rate of stretch, S , is a function of unstretched gel filament velocity, V_0 , final stretched gel fiber velocity, V_t , the number of stretch pans employed, n , of length, l , and the total stretch ratio, R , that is imparted to the fibers. Thus, the rate of stretch can be calculated by the following formulae:

$$S = \Delta V / \text{time of stretch, } t \quad (I)$$

$$V = V_t - V_0 \quad (II)$$

$$V_t = RV_0 \quad (III)$$

$$t = \frac{\text{distance of stretch}}{\text{average velocity}} = \frac{nl}{\frac{RV_0 + V_0}{2}} \quad (IV)$$

$$S = \frac{V_0^2(R^2 - 1)}{2nl} \approx \frac{R^2V_0^2}{2nl} \quad (V)$$

The stretched fibers are dried in a relaxed condition, that is completely unrestrained and free to shrink, at a temperature of between about 60° and 90° C. and preferably between about 70° and 80° C. Beneficially, the heating medium is a hot circulating air, however other means including radiant heaters and other arrangements whereby the fibers can be maintained in a relaxed condition can be employed. Temperatures below 60° C. may be employed to achieve the results of the invention however the rate of drying of the fiber becomes excessively low and is unattractive from an economical processing point of view. When temperatures much in excess of 90° C. are employed in the drying of the fibers, the percent shrinkage of the filaments when exposed to boiling water decreases very rapidly. In contrast, in conventional drying treatments of acrylonitrile polymer aquagel filaments, temperatures of about 120–140° C. are employed. It is also advantageous when drying the fibers that the relative humidity of the air not be so high that the actual temperature of the gel fiber approach the drying-air temperature. Generally, although not critical to the invention, the relative humidity is preferably maintained less than about 50 percent. Depending on the temperature that is used to dry the filaments, the time for drying is ordinarily between about 5 and 30 minutes.

The invention is applicable to treating acrylonitrile polymer fibers which are fabricated from fiber forming acrylonitrile polymers that contain in the polymer molecule at least about 80 weight percent of polymerized acrylonitrile, including homopolymeric acrylonitrile, that are

wet spun in and with systems that are adapted to utilize aqueous coagulating liquids in the spinning operation, such as systems wherein ethylene glycol, dimethylformamide, dimethylsulfoxide, butyrolactone and the like or the various saline polacrylonitrile-dissolving solvents are employed as spinning solution solvents for the polymer and are also present in non-polymer dissolving quantities in the aqueous coagulating liquid used in the spin bath.

The utile, known aqueous saline solvents for the various fiber forming acrylonitrile polymers and polyacrylonitrile include zinc chloride, the various thiocyanates such as calcium and sodium thiocyanate, lithium bromide, salt mixtures of the so-called "lyotropic" series, and others recognized by the art as has been disclosed, among other places, in United States Letters Patents Nos. 2,140,921, 2,425,192, 2,648,592, 2,648,593, 2,648,646, 2,648,648, 2,648,649, and 2,949,435. Advantageously aqueous zinc chloride solutions are used for the purpose.

Exemplary of some of the monomeric material that may be employed with the acrylonitrile in the preparation of the acrylonitrile polymer and copolymer fiber forming systems and treated in accordance with the practice of the present invention include allyl alcohol, vinyl acetate, acrylamide, methacrylamide, methyl acrylate, vinyl pyridine, ethylene sulfonic acid and its alkali metal salts, vinyl benzene sulfonic acid and its salts, 2-sulfoethylmethacrylate and its salts, vinyl lactams such as vinyl caprolactam and vinyl pyrrolidone, etc. and mixtures thereof.

As indicated, after acrylonitrile polymer fibers have been wet spun they are most frequently water washed or washed with an aqueous inert solution to remove any residual polymer solvent from the freshly formed filaments, thus forming an intermediate fiber product often referred to as a gel or aquagel filaments. Thoroughly washed acrylonitrile polymer aquagel fibers, incidentally, are usually found to contain up to about 6 parts by weight of water (including residual extrinsic or exterior water associated therewith) for each part by weight of dry polymer therein. More frequently, washed acrylonitrile aquagel polymer fibers are found to contain from about 3 to 4 parts by weight of water for each part by weight of polymer.

The following examples further illustrate the invention wherein, unless otherwise specified, all parts and percentages are by weight.

Example 1

A polymer solution consisting of about 10.8 percent of a polymer containing in polymerized form about 1.7 percent zinc sulfonethyl methacrylate, about 8.2 percent methyl acrylate and about 90.1 percent acrylonitrile dissolved in an aqueous 60 percent zinc chloride was spun at about 12 f.p.m. into an aqueous about 32 percent zinc chloride coagulation bath at about 30° C. The coagulated filaments were withdrawn from the coagulation bath and water washed essentially completely free of residual zinc chloride. The resulting aquagel filaments were then passed through a boiling water stretch bath and stretched at various rates. The stretched filaments were then irreversibly dried at 70–80° C. in a relaxed condition in a circulating air oven. Samples of the fibers were then immersed in boiling water for about 30 minutes, air dried, and then the resulting shrinkage was determined. The results are set forth in Table I.

TABLE I

Sample	Total Stretch	S. Rate of Stretch (f.p.s.) ²	Drying Temp., ° C.	Fiber Denier	Ultimate Tenacity (g./d.)	Ultimate Extension (Percent)	Boiloff Shrinkage (Percent)
A-----	9X	0.09	80	2.8	2.7	15	26.4
B-----	8.5X	0.10	80	2.8	3.3	33	26.3
C-----	8.5X	0.24	80	3.0	3.0	36	22.4
D-----	11X	0.40	70	2.8	4.6	25	15.7
E-----	12.5X	0.52	70	3.1	4.7	21	15.1
F-----	14X	0.65	70	3.1	4.7	21	15.1

Example 2

The procedure of Example 1 was repeated, with the exception that the fibers were dried at higher temperatures, i.e. 100–130° C. The results are set forth in Table II.

TABLE II

Sample	Total Stretch	S, Rate of Stretch (f.p.s.) ²	Drying Temp., °C.	Fiber Denier	Ultimate Tenacity	Ultimate Extension (Percent)	Boiloff Shrinkage (Percent)
G-----	9X	0.09	100	3.4	2.1	21	19.7
H-----	12.5X	0.52	100	3.0	4.5	21	12.6
I-----	9X	0.09	120	3.0	1.7	20	9.9
J-----	11X	0.40	130	2.9	3.9	25	4.0
K-----	14X	0.65	130	3.0	4.6	24	7.4

Similar excellent highly shrinkable fibers are obtained when other of the acrylonitrile polymers are stretched and dried and when other of the indicated modifications are employed in accordance with the present invention.

It is to be understood that the invention is not to be limited by the foregoing specifically delineated embodiments, but rather, that it is to be construed by the scope of the hereto appended claims.

What is claimed is:

1. A method for preparing highly shrinkable acrylonitrile polymer fibers comprising

(a) spinning a solution of polymer of an ethylenically unsaturated monomeric material containing at least about 80 weight percent acrylonitrile into an aqueous coagulating bath;

(b) stretching the coagulated filaments to orient the molecules thereof in an inert aqueous medium at between about 90° and 110° C. at a stretch rate of between about 0.1 and 0.75 feet per second²; and,

(c) subsequently, irreversibly drying the stretched filaments in a relaxed condition at between about 60° and 90° C.

2. The method of claim 1, wherein said filaments are spun from a solution of an acrylonitrile polymer dissolved in an aqueous zinc chloride solution into a non-polyacrylonitrile-dissolving aqueous solution of zinc chloride.

3. The method of claim 1, wherein said acrylonitrile

polymer is a copolymer of acrylonitrile, sulfoethyl methacrylate, and methyl acrylate.

4. The method of claim 3, wherein said copolymer consists essentially of, in polymerized form, about 90 weight

percent acrylonitrile, about 2 percent sulfoethyl acrylate, and about 8 percent methyl acrylate.

5. The method of claim 3, wherein said sulfoethyl acrylate is zinc sulfoethyl acrylate.

6. The method of claim 1, wherein said inert aqueous medium is essentially water at between about 95° and 100° C.

7. The method of claim 1, wherein said filaments are stretched at a stretch rate of between about 0.2 and 0.4 feet per second².

8. The method of claim 1, wherein said stretched filaments are dried in the presence of circulating air at a temperature between about 60° and 90° C. and the relative humidity of the drying air is not in excess of about 50 percent.

9. The method of claim 1, wherein said stretched filaments are dried at a temperature between about 70° and 80° C.

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