United States Patent Office 3,180,913 Patented Apr. 27, 1965

3,180,913

METHOD FOR PRODUCING HIGH SHRINKAGE FIBERS

John D. Veitch and Byrd T. Thompson, Decatur, Ala., assignors, by mesne assignments, to Monsanto Company, a corporation of Delaware

No Drawing. Filed Mar. 19, 1962, Ser. No. 180,805
5 Claims. (Cl. 264—290)

This invention is concerned with a method of producing high shrinkage synthetic linear fibers. More particularly, this invention is concerned with a method of producing high shrinkage acrylic fibers in which at least 80 percent of the fibers is acrylonitrile.

The fibers produced by the process of this invention possess a number of uses, primarily among them being for the use as the short hair in artificial furs when they are combined with a relatively non-shrinking fiber which will form the guard hair or high level pile portion of the fabric. In addition, when the high shrinkage fibers produced by the process of this invention are platted with relatively non-shrinkage fibers and then this yarn is treated with wet heat, there is an excellent bulking effect. Further, if a raised pattern on a piece of fabric is desired, the raised area will be composed of relatively non-shrinking fibers and the low section will be composed of the fibers produced by the process of this invention. Also, the fibers produced by the process of this invention may be used in producing non-bonded felt as no binder is necessary in that the shrinkage of this fiber will pull or bind the materials together into a felt.

The object of this invention is to provide a method for producing synthetic linear fibers which shrink upon treatment by heat. Another object of this invention is to provide a method for producing high shrinkage acrylic fibers which shrink upon treatment by heat. Another object of this invention is to provide a method for producing high shrinkage acrylic fibers composed of at least 80 percent acrylonitrile which shrink upon treatment with heat. Another object of this invention is to provide a method for producing high shrinkage acrylonitrile fibers which shrink upon treatment with wet or dry heat. Other objects of this invention will hereinafter become apparent in the following detailed description and appended claims.

Generally the objects of this invention are accomplished by first reducing the stretch ratio in the conventional stretching step subsequent to the spinning of the acrylic fiber. This results in low molecular orientation of the thus produced fiber. The fiber is then subjected to steam under pressure. After this step the fiber is stretched in a hot water bath under controlled temperature. The tow is then removed from the hot water bath, cooled, crimped wet, dried, cut to staple and is then ready to be blended with relatively non-shrinkage fiber tow for whatever end use is desired.

More particularly, the objects of this invention are accomplished by spinning the acrylic fibers in a conventional spin bath, then passing the fibers through boiling water during which the fibers are stretched in a ratio of 1.5 to 2.5 with the preferred ratio being 1.8, giving a low molecular orientation to the polymer. The fibers are then passed through a finish bath to add whatever finishes or additives are desired and then generally the fibers or tow are dried and crimped, both conventional operations. the fibers or tow are then subjected to steam under pressure varying from 35 p.s.i.g. to 55 p.s.i.g. with the preferred being around 45 p.s.i.g. until all the fibers have been contacted by the steam. The tow, after the pressure and steam treatment, is stretched by a ratio of at least 1.7, but no more than 3.0 in a hot water bath at a temperature of 70° C. to 95° C., the preferred temperature being 85° C. The stretched tow is cooled

under tension, crimped and dried at a temperature of below 70° C. and then cut into staple. The staple is then processed through the conventional textile industry steps into yarns etc. When these yarns are exposed to boiling water, they shrink 37 percent to 50 percent of their original length. The degree of shrinkage depending upon the specific conventional spinning and stretching conditions used in preparing the fibers. These same fibers will shrink from 32 percent to around 45 percent of their original length when exposed to dry heat of 145° C. to 155° C. The time the tow remains in the hot second stretch zone is not of importance. It remains there only as long as it takes for the fiber to reach the required temperature. In addition, the method of this invention may be used to produce high shrinkage fibers of many different denier, the desired denier depending upon the end product required. The shrinkage produced in the fibers manufactured by the process of this invention is considerably greater than typical commercial synthetic fibers upon treatment with heat.

The polymeric materials, which may be employed in the practice of the present invention are polyacrylonitrile, copolymers including binary and ternary polymers containing at least 80 percent by weight of arcylonitrile in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising acrylonitrile with from 2 to 50 percent of another polymeric material, the 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 acrylonitrile are useful in forming films, coating compositions, molding operation and lacquers.

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 the >C=C< linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers, include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene; 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 diethylcitraconate, diethylmesaconate, styrene, vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, etc.; 1-vinylimidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, and other >C=C< 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-vinylpyridine. The ternary polymer preferably contain from 80 to 98 percent

of acrylonitrile, from 1 to 10 percent of a 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 >C=C< 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 to 90 percent of at least one other >C=C< 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 to 10 percent of another mono-olefinic monomer, such as vinyl acetate, which is not receptive to dyestuff, with a sufficient amount of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 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 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

Polymer composed of 94 percent acrylonitrile and 6 percent vinyl acetate was dissolved in a conventional solvent and spun into an aqueous spin bath. The spun filaments or fibers were then passed over rolls and then into a water bath at 100° C. The filaments or fibers were stretched during their passage through said bath 1.94 times their original length. In addition, the fibers were dried over drying rolls heated with 30 p.s.i.g. steam. They were then exposed to steam under 45 p.s.i.g. pressure until all fibers were fully contacted by the steam. The fibers were then stretched 1.83 times their original length in a hot water bath at 87° C., removed from the bath and cooled while still under tension. The fibers were wet crimped and dried at a temperature of 40° C. Tow, as produced above was placed in a boiling water bath and it was determined that the fibers had a boiling water shrinkage of 38 percent by comparing the original length of fiber to the length of the fiber after the boiling water step. Another sample of tow, produced as above, was exposed to dry heat in a hot air oven at a temperature of 145° C. for a period of 6 minutes. It was determined that the fiber under these conditions had a dry heat shrinkage of 34 percent.

Example 2

The exact process of Example 1 was repeated except the initial stretch ratio was 1.06 and the second stretch was at a ratio of 1.67 at a temperature of 85° C. The boiling water shrinkage was determined to be 38 percent. Another sample of the tow, produced as above, was exposed to dry heat in a hot air oven at a temperature of 145° C. for a period of 6 minutes. It was determined that the fiber under these conditions had a dry heat shrinkage of 32 percent.

Example 3

The exact process of Example 2 was repeated except the second stretch ratio was 2.0 and the temperature of the hot water was 86° C. The boiling water shrinkage was determined to be 44 percent. Another sample of the tow, produced as above, was exposed to dry heat in a hot air oven at a temperature of 149° C. for a period of 6 minutes. It was determined that the fiber under these conditions had a dry heat shrinkage of 40 percent.

Example 4

The exact process of Example 1 was repeated except the second stretch water temperature was approximately 85° C. and the stretch ratio was 2.0. The boiling water shrinkage was determined to be 39.6 percent.

Example 5

Polymer composed of a blend of one copolymer in the amount of 98.5 percent which comprises 94 percent acrylonitrile and 6 percent vinyl acetate and 1.5 percent of cellulose acetate was dissolved in a conventional solvent and spun into an aqueous spin bath. Spun filaments or fibers were then passed over rolls and then into a hot water bath at a low boil. The filaments or fibers were stretched during their passage through said hot water bath 1.6 times their original length. In addition, the fibers were dried over drying rolls with 30 p.s.i.g. of steam. They were then exposed to steam under 47 p.s.i.g. pressure until all fibers were fully contacted by the steam. The fibers were then stretched 1.9 times their original length in a second hot water bath at 85° C., removed from the bath and cooled while under tension. The fibers were then crimped and dried at a temperature of 145° F. for 10 minutes. A fiber, as produced above was exposed to hot air in an oven at 300° F. for approximately 6 minutes, and then cooled. Upon measuring the original length of the fiber against the length of the fiber after it had been exposed to dry heat, it was found that there was a shrinkage of 40 percent.

Thus with the process of this invention high shrinkage fibers are produced which, when combined with relatively low shrinkage fiber, and subjected to wet heat, will result in high shrinkage producing beautiful and commercially acceptable bulked fabrics, raised pattern fabrics etc. For two level pile fabrics or artificial furs, dry heat is preferred for developing the shrinkage and the preferred dry heat shrinkage being in the range of 35 percent and up.

It is understood that changes and 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 appending claims.

We claim:

1. A method for producing high shrinkage acrylic fibers composed of at least 80 percent acrylonitrile and up to 20 percent of another copolymerizable mono-olefinic monomer comprising subjecting said fibers in the freshly spun state to a first low ratio stretch in the range of 1.5 to 2.5 in boiling water, subjecting said stretched fibers to steam under pressure in a range of 35 p.s.i.g. to 55 p.s.i.g., then subjecting said fibers to a second low ratio stretch in the range of 1.7 to 3.0 in a hot water bath at a temperature of between 70° C., and 95° C., then cooling said fibers under tension and then drying said fibers at a temperature of below 70° C.

2. A method for producing high shrinkage acrylic fibers composed of 94 percent acrylonitrile and 6 percent vinyl acetate comprising subjecting said fibers in the freshly spun state to a first low ratio stretch in the range of 1.5 to 2.5 in boiling water, subjecting said stretched fibers to steam under pressure in a range of 35 p.s.i.g. to 55 p.s.i.g., then subjecting said fibers to a second low ratio stretch in the range of 1.7 to 3.0 in a hot water bath at a temperature of between 70° C. and 95° C., then cooling said fibers under tension and then drying said fibers at a temperature of below 70° C.

3. The method of claim 2 in which the first low ratio stretch is 1.9, the steam is under 45 p.s.i.g. pressure, the second low ratio stretch is 1.8 and the hot water bath is at a temperature of 87° C.

4. A method of producing high shrinkage acrylic fibers composed of a blend of 88 percent of one copolymer of 94 percent acrylonitrile and 6 percent vinyl acetate and 12 percent of another copolymer of 50 percent acrylonitrile and 50 percent methyl vinyl pyridine comprising subjecting said fibers in the freshly spun state to a first low ratio stretch in the range of 1.5 to 2.5 in boiling water, subjecting said stretched fibers to steam under pressure in a range of 35 p.s.i.g. to 55 p.s.i.g., then subjecting said

fibers to a second low ratio stretch in the range of 1.7 to 3.0 in a hot water bath at a temperature of between 70° C. and 95° C., then cooling said fibers under tension and then drying said fibers at a temperature of below 70° C.

5. The method of claim 4 in which the first low ratio cascade stretch is 1.9, the steam is under 45 p.s.i.g. pressure, the second low ratio stretch is 2.0 and the hot water bath is at a temperature of 85° C.

References Cited by the Examiner

UNITED STATES PATENTS

2,681,265	6/54	Hoxie	18—54
3,099,517	7/63	Hurley et al.	18—48

ALEXANDER H. BRODMERKEL, *Primary Examiner.*