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MODIFICATION OF CRIMP OF COMPOSITE ACRYLIC FIBERS

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This invention is concerned with processing of composite fibers prepared from acrylonitrile polymers. More specifically, it is concerned with the treatment of fibers from acrylonitrile polymers whereby unusual crimp and shrinkage properties are developed.

Among the fiber properties of importance to the aesthetics of textile fabrics, both crimp and shrinkage are highly significant. For a given type of fiber the crimp frequency, that is the number of crimps per inch of fiber length, is of importance in determining both the appearance and the handle of the fabric. This is particularly true when the crimp is of such nature as to be retained by the fiber after it has been put into fabric form.

Shrinkage is of particular importance in the attainment of good fabric cover. With a fiber having a high level of shrinkage, fabrics can be prepared of both the woven and knit type, having a greater degree of tightness and form stability than attainable in the absence of any reasonable amount of fiber shrinkage. Mixed shrinkage yarns, that is to say yarns composed of blended fibers in which some fibers in the blend are of a low order of shrinkage and other fibers are of a high level of shrinkage, have proven to be of high commercial value in the preparation of highly bulked yarns. A high level of fiber shrinkage has also been found to be of importance in the preparation of pile fabrics that simulate natural furs. Multiheight fabrics can be prepared by utilizing fibers of different shrinkage levels in the pile of these fabrics, shearing the pile to constant height, and then giving the fabric a boil-off or similar treatment to bring about the shrinkage of the various fibers.

One object of this invention is to provide a process for the preparation of spirally crimped acrylic fibers having a high crimp frequency level. It is another object of the invention to provide a process for the preparation of acrylic fibers with latent high-frequency spiral crimp and a high shrinkage level. It is yet another object to provide a process for the preparation of acrylic fibers of high-crimp frequency in such form that they may readily be converted to yarn of good quality. Other objects will appear hereinafter.

The process of the invention is applied to composite fibers in which each filament has two separate and distinct acrylic polymeric species arranged as side-by-side sections or components throughout its length. The choice of polymers is such that a fiber is produced which has a spiral crimp similar to that of wool fibers along with the ability to change its crimp configuration with exposure to various finishing treatments. The spiral shape of the crimp, the ease of the development of this crimp by finishing treatments after it has been straightened out to any degree by textile processing, and the renewability at any time thereafter, such as during use, combine to make fibers of this type extremely valuable for the preparation of fine textile fabrics.

The frequency of crimp of composite fibers, however, depends primarily on the polymeric composition used for each of the sections of the fiber. For example, it has been found that excellent fibers can be made utilizing as one component an acrylic polymer having a content of sulfonic acid groups substantially greater than those possessed by the acrylic polymer used as the other component. Increasing the differential increases the crimp frequency of the fiber. This difference, however, is frequently limited by other considerations. It is impractical to use a polymer having too many sulfonic acid groups because of the resulting difficulty in obtaining uniform dyeability of the two-component fiber and because the high-sulfonate polymers are difficult to isolate after their preparation. Furthermore, this method is quite limiting in that it requires separate polymer systems for each slight variation in product crimp frequency.

The present invention is applicable to composite filaments which are characterized in that at least one of the acrylic components contains at least 50 milliequivalents of an ionizable group per kilogram of polymer. It is preferred that one component in addition to containing at least 50 milliequivalents, contains a substantial excess of ionizable groups over the other component where both components contain such groups. Such ionizable groups are readily obtained by copolymerizing acrylonitrile for example with monomers containing acid groups such as carboxylic, sulfonic or phosphonic in either the salt or free acid form. The following sulfonated, polymerizable monomers and their salts are eminently suited for use in making such polymers: p-styrenesulfonic acid, methallyl sulfonic acid, allyl sulfonic acid and ethylenesulfonic acid. It will be obvious to those skilled in the art that the required ionizable groups can be incorporated into a polymeric component by the blending of two or more polymers. The polymers should preferably be compatible.

The combination of polyacrylonitrile (the homopolymer) of inherent viscosity 1.5 to 2.5 and a copolymer containing at least 95% acrylonitrile and from 1–5% of an acidic modified monomer (95–350 milliequivalents of acidity per kilogram of polymer) of inherent viscosity 1.0 to 2.5 is preferred. Even more preferred is the use of polyacrylonitrile and a copolymer of acrylonitrile containing sulfonic acid groups in the amount of 200–300 milliequivalents of acidity per kilogram of polymer. This preferred combination affords a product which has a medium level of crimped intensity (10–18 crimps per inch of extended length) and is eminently suitable for processing in accordance with the present invention.

Thus the present invention is applicable only to those acrylic fibers which are crimped due to the presence of two side-by-side polymeric components within each fiber. With such fibers, in an oriented form due to prior stretching up to about 4×, frequency of crimp may be readily modified by the process of the invention. In accordance with the invention such fibers are stretched between about 1.1× and 2.5×, preferably between about 1.15× and 2.25× and under the influence of dry heat. The temperature of the stretching operation is preferably determined by the operability of the equipment to give the desired stretch ratio. Temperatures between about 50° F. and about 400° F. may be used to advantage. If the maximum amount of sliver shrinkage is desired, the maximum temperature under which the stretching operation may be carried out successfully, should be utilized. Further increase in both crimp frequency and sliver shrinkage may be obtained by operating with moist tow or by injecting steam at the point of stretching.

In this range of temperature and stretch, a variety of products of different reproducible crimp frequencies between about 10 crimps per inch and about 30 crimps per inch can be obtained. Varying degrees of shrinkage between about 20% and about 55% are also developed in this process. The upper level of shrinkage obtainable with the process is considerably higher than any hitherto reported for such products.

The hot-stretch treatment may be followed by a

stretch-breaking operation. During the stretch-breaking operation a wide range in break ratios may be used in order to cause variation in the length distribution of the staple fibers produced. For example, the break ratio may be between 2.5× and 4×.

The invention will be better understood on the basis of the following examples, which are meant to be illustrative and are not intended to limit the invention in any way.

Example I

The starting material for this example was a 470,000-denier tow of stretched acrylic fibers which were prepared as follows:

A copolymer of acrylonitrile and sodium styrenesulfonate having an inherent viscosity of 1.5 and containing 204 milliequivalents of acid groups per kilogram of dry polymer was made from the monomers using the technique of U. S. Patents 2,628,223 and 2,546,238 (i.e., continuous polymerization in water with $K_2S_2O_8$ catalyst, sodium metabisulfite activator and Na_2CO_3 for stopping the polymerization at the desired point), the monomers being fed to the reactor at relative rates of 97.0 and 3.0 respectively. Composite filaments of polyacrylonitrile with an intrinsic viscosity of 2.0 containing 26 milliequivalents of acid groups per kilogram of polymer and the acrylonitrile-sodium styrenesulfonate copolymer were spun side-by-side from 22% solutions in dimethylformamide through a spinneret having 140 orifices .0047 inch in diameter. The spun yarn was drawn 400%, the original spun denier having been adjusted so that the final filament denier was 6.0. This material had a crimp frequency of 11–12 crimps per inch and a shrinkage of about 3%. This tow was then stretched 1.31× between a pair of parallel plates in contact with the tow surface, each plate measuring 14 inches in the direction of yarn travel and 10 inches in the direction perpendicular to the yarn travel. The temperature of the plates was 280° F., and the input speed of the tow was 23 yards per minute. The tow was then subjected to the stretch-breaking treatment described in U.S. Patent 2,419,320, of J. L. Lohrke. The fibers in the resulting sliver had essentially no crimp. Individual fiber shrinkage in boiling water was 21%. Shrinkage of the sliver itself was found to be 25% in steam at 10 p.s.i. pressure.

A portion of the sliver was subjected alternately to vacuum and the action of steam at 10 pounds pressure for a period of 16 to 20 minutes. In this operation an initial two-minute period of vacuum was followed by a like period of steaming, followed by a second two minutes of vacuum, then 6 minutes of steam pressure and, finally, 4 minutes of vacuum. At the end of this treatment the individual fibers showed no shrinkage in boiling water, and had an average crimp frequency of 14 crimps per inch. This sliver was converted to yarn on conventional drafting and spinning machinery. The yarn could be knit or woven into desirable fabrics.

A second sample of the sliver was converted to yarns by drafting and spinning without the intermediate steam-setting operation. By proper control of knitting and weaving conditions, loose fabrics were prepared from this yarn which upon treatment with boiling water shrank to fabrics showing good cover and pleasing aesthetics. The good cover of these fabrics was due to the development of the crimp during the final boiling water treatment.

Example II

Example I was repeated in all details except that a stretch ratio of 1.58× was used in the stretching operation by which the original stretched tow was restretched between heated plates. The sliver produced by the second stretching followed by stretch-breaking had a shrinkage of 29%. Individual fibers from this sliver showed a 22% shrinkage. When the sliver was set with steam as in the previous example, the filaments showed an average crimp frequency of 18 crimps per inch. This crimp frequency was raised to 19 crimps per inch by subsequent boil-off.

Yarns were prepared from this sliver and were used for preparing both knit and woven fabrics.

In other experiments a stretch ratio of 1.88× and a stretch ratio of 2.25× were used. Both sliver and fiber shrinkage were found to increase with increasing stretch ratio, the values for the 1.88× stretch being 40.0% for sliver shrinkage and 31.4% for fiber shrinkage. Crimp frequency also increased with the increasing draw ratio, the frequency after steam setting and water boil-off being 20.5 crimps per inch for the 1.88× product and 22.0 crimps per inch for the 2.25× product.

Increased crimp frequency was found to give increased cover in fabrics prepared from the various samples. The handle of the fabric also changed with increasing crimp frequency, becoming more wool-like as the frequency increased. Thus, by changes in crimp frequency readily brought about in the same starting fiber, a wide range of fabric properties was made available.

Example III

The starting material for this example was identical with that used in Example I except that the tow contained twice as many filaments, and the individual filament denier was 3.0. This tow was stretched 2.25× at 325° F. and was then stretch-broken as in previous examples. The product obtained showed 52% shrinkage, as compared to an original tow shrinkage of only 3.9%. Whereas the original tow had a crimp frequency of 13 crimps per inch, this value was doubled to 26 crimps per inch, as measured on the stretched and broken sliver after steam treatment as described in the previous examples. In spite of the high crimp frequency after this setting operation, the set sliver was readily transformed into yarn by drafting and spinning operations.

The type of equipment used in the stretching process is not critical, but the Turbo Stapler, manufactured by the Turbo Machine Company of Lansdale, Pennsylvania, is particularly useful. On this equipment the original stretched tow of two-component fibers may be readily stretched and then stretch-broken to produce directly a sliver which may be steam-set if desired and may be converted to weaving or knitting yarns by the usual drafting and spinning operations, whether steam-set or not. The steam-setting operation may readily be carried out on the Turbo Fiber Setter, manufactured by the same company.

As indicated previously, the sliver product after stretch breaking may be converted directly to weaving or knitting yarns by the usual drafting and spinning operations. Yarns produced in this way will, of course, have a high level of shrinkage and fabrics produced from them must be constructed in loose fashion because of the shrinkage which will occur during after treatment. Maximum crimp development will occur when this procedure is followed. Alternatively, the sliver may be set with steam, which brings about a good degree of shrinkage and develops fiber crimp. Setting temperatures between 220° F. and 260° F. have been found to be quite useful. The higher the temperature used in this operation, the greater will be the amount of shrinkage that takes place and the higher the crimp frequency of the resulting product. When steam setting is carried out before yarn production tighter fabric construction must be used because the degree of shrinkage of the yarns will be considerably lower, being for the most part brought about by the redevelopment of any crimp straightened out during the textile processing to that point. Regardless of whether or not the fibers have been steam-set prior to fabric preparation, the crimp frequency of the fiber in the fabric after finishing operations have been carried out will reach nearly the same level, which level is determined by the stretch ratio and to a lesser extent the other variables utilized in the after-stretching operation which is

brought about in accord with the present invention.

The process of this invention is useful in producing in simple fashion a variety of products varying in shrinkage and in potential crimp frequency, all from the same starting material. The different products produced are of value in a variety of woven and knit fabrics and in pile fabrics. Ultimate uses are woven and knit sportshirts, dress goods, blouses, sweaters, slacks, suitings, childrens playsuits, home furnishings particularly in the field of blankets, draperies, and upholstery fabrics, pile fabrics of all types, especially including those with more than one pile height, and the like.

In these and other uses, the products of this invention, particularly when blended with each other and with other fibers, lead to unusual bulk, cover, elasticity, and compressional resilience.

What is claimed is:

A process for producing improved spirally crimped composite acrylic filaments of uniform dyeability and from about 20–30 crimps per inch of extended length, said process comprising the steps of first, simultaneously spinning together through the same spinneret orifice at least two differing acrylic polymeric fiber-forming materials to form unitary filaments in which said materials exist as adherent substantially distinct and separate components in side-by-side relationship along the length of

the filaments, one of said materials essentially comprised of an acrylic polymer having a content of sulfonic acid groups substantially greater, by at least 50 milliequivalents of ionizable groups per kilogram of polymer, than those possessed by the acrylic polymeric material of which the other component is formed; second, initially drawing the filaments a uniform amount not exceeding 4×; third, in a separate step additionally drawing the filaments between 1.1× and 2.5× in an atmosphere of live steam at a temperature between about 200° F. and 400° F; fourth, subjecting the filaments to a stretch-breaking treatment; and fifth, subjecting the filaments in an unrestrained condition alternately to a vacuum and the action of steam at a pressure of about 10 pounds per square inch over a period of about 16 to about 20 minutes after said stretch-breaking treatment to completely develop the crimp.

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