METHOD OF TREATING YARNS AND FILAMENTS AND PRODUCTS PRODUCED THEREBY

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This invention relates to a method for improving the physical properties of yarns or filaments of modified acrylonitrile polymers, including homopolymers, copolymers and graft or place polymers, which have been prepared by dry spinning processes. More particularly the present invention relates to a method for increasing the tenacity and elongation and eliminating the hot water shrinkage of such dry spun yarns and filaments which contain a major portion of acrylonitrile. The term modifier or similar term in this specification is employed as the equivalent of the monomers other than acrylonitrile which are present in any particular polymer mentioned herein.

Filaments and yarns of such acrylonitrile compositions made by dry spinning processes are not very satisfactory for use in textile processes since they normally possess tenacities less than one gram per denier, elongations less than 10% and boiling water shrinkage of 10% or greater. In order to achieve their maximum usefulness in the textile field, it is necessary to process these fibers resulting from the dry spinning process in some manner so as to eliminate the boiling water shrinkage and increase the tenacity and elongation.

Hereuntofore various methods have been suggested to improve these physical characteristics of acrylonitrile fibers and filaments. One method proposed is to heat the fibers in a relaxed free-to-shrink condition at a temperature of 80° C. to 300° C. and to maintain the shrunk shaped article under a tension of not more than 0.005 gram per denier which is insufficient to stretch the shrunk article while at a temperature of 80° C. to 300° C. for at least one hour. The heating steps are carried out in the presence of an inert heating medium. It is indicated that the most desirable results are obtained when the heating under tension is extended to three and one-half hours at 150° C. and much longer periods should be employed when the temperature is as low as 80° C.

For commercial production of textile filaments it is, of course, desirable to employ processes which produce the best product in the shortest time commensurate with high quality and, we have invented a process which substantially reduces the time required in the prior art process just described and which results in a yarn having the abovementioned desirable physical characteristics.

There are also prior art processes which heat, stretch and relax acrylonitrile type fibers and yarns at a more rapid rate than one to three hour treatment mentioned above. However, these have the disadvantages that the yarn is subjected to considerable mechanical damage due to stresses applied during stretching, and to abrasion caused by passing the yarn between several pairs of rolls which cause to press and abraid the yarn. An object of the present invention is a method for producing synthetic fibers from such acrylonitrile polymers having improved physical characteristics. A further object of the invention is to produce yarn and filaments from such polymers having an appreciable boiling water shrinkage. A still further object of the invention is to produce such yarns having high strength, high elongation, and low shrinkage in a single continuous operation at relatively high production rates without abrasion of the yarn. Other objects will appear hereinafter.

The invention may be described in connection with the accompanying drawing which schematically discloses apparatus for processing the selected acrylonitrile polymer yarn in accordance with our novel process. Basically as shown in the drawing this apparatus comprises a plurality of rolls over or around which the yarn to be processed is conducted. Two of the rolls 11 and 14 are internally heated and are provided respectively with heated shoes 17 and 18 to assist in maintaining the temperature of the yarn passing over the heated rolls within desired limits. These shoes are mounted concentrically about a portion of the surface of the rolls and out of contact with the adjacent rolls.

An important feature of this apparatus is that the yarn after it is once heated to thermoplasticity never is pressed between pairs of coacting rolls and therefore abrasion and deformation of the yarn due to such processing as employed in the prior art does not occur in the present process.

Another important feature of the present invention is the provision for positive, non-slip, control of the yarn particularly after each heating and during stretching and relaxing. Cooperating rolls 12 and 13 are the essential devices which permit such desirable yarn tension control since the yarn is passed around them several times and they provide a snubbing action between the stretched portion of the yarn leaving heated roll 11 and the relaxing yarn traveling toward heated roll 14.

The operation of our novel process may be further understood by reference to the drawing and the following detailed description. Referring to the drawing, the yarn 8 to be processed is fed from a source, not shown, and passed partly around presser feed rolls 9 and 10 and into heated draft roll 11 where it is heated both by heated draft roll 11 and heated shoe 17, and thence to cooperating rolls 12 and 13 which are skewed in relation to each other in such a way that the yarn is passed around the two several times without tracking itself. These rolls 12 and 13 prevent the yarn from slipping and assure uniform tension on the portion of the yarn leaving hot roll 11 and that portion proceeding to hot roll 14. After leaving roll 12 the yarn is passed around the heated relaxing roll 14 where it is heated by this heated roll 14 and heated shoe 16, and thence to the take up roll 15 and godet roll 16. From godet roll 16, the processed yarn may be wound into a package, not shown. Any suitable means of yarn collection may be employed, such as ring winding or parallel package winding.

In operation, feed roll 10 and heated draft roll 11 always are turned at approximately the same rate, although draft roll 11 may have a slightly faster rate in order to prevent sagging of the yarn between these two rolls. Peripheral speeds of the rolls 12 and 13 are substantially equal, this speed being determined by the degree of draft or stretch to be imparted to the yarn.

Therefore, if the peripheral speed of the draft roll is 50 meters per minute, and it is desired to stretch the yarn to 600% of its original length, then the peripheral speed of the rolls 12 and 13 should be 300 meters per minute. This would be termed a draft factor of six. The yarn stretch takes place in the length shown as A. Heated relaxing roll 14 is rotated at a somewhat lower rate than the rolls 12 and 13 to permit the yarn to relax or shrink as it goes onto this roll. Similarly, the peripheral speed of the takeup roll 15 is still lower to allow for an additional shrinkage as the yarn leaves the heated relaxing roll. Normally, the speeds of the relaxing roll and takeup roll are
adjusted downward until minimum tensions commensurate with good yarn quality are obtained at points B and C thus allowing the yarn to shrink as much as practicable under the prevailing conditions. It is the practice to record the speed ratio between the takeup roll and the rolls 12 and 13 as a relax factor. For instance, if the peripheral speed of the takeup roll is 270 meters per minute, the relax factor would be .90 or a 10% yarn shrinkage. The peripheral speed of the godet roll 16 is equal to or slightly in excess of the peripheral speed of the takeup roll 15. The several rolls are rotated by conventional apparatus, not shown. The hot rolls 11 and 14 may be internally heated by hot oil, water, steam or by electricity as is well understood in this art. The heated shoes 17 and 18 preferably are electrically heated.

The following examples further illustrate our invention:

Example 1

A dry spun acrylonitrile polymer yarn of 642 denier and 60 filaments, having a tenacity of 0.66 gram per denier and an elongation of 6.0% with hot water shrinkage (30 seconds in 100° C. water) in excess of 10%, was drafted and relaxed as follows: Draft input speed (peripheral speed) of feed roll 10 was 20 meters per minute, with a draft factor of 8.5. This was accomplished with a draft roll 11 temperature of 180° C. and a draft shoe 17 temperature of 370° C. The yarn was relaxed with a factor of 0.87, 10% of this taking place going onto the relax roll 14 and 3% coming off the relax roll 14. Relax roll 14 was heated to 210° C. while the temperature of relax shoe 18 was 320° C. Both heated rolls 11 and 14 were in this case 0.500 meter in circumference, and both were heated internally by hot oil. The resulting yarn had a tenacity of 4.00 grams per denier and an elongation of 17.4% with hot water shrinkage of 2.0% and was not deformed since no squeezing pressure is exerted on the yarn.

Example 2

A dry spun acrylonitrile N-methyl methacrylamide graft polymer yarn (18%) modifier of 323 denier and 30 filaments, having a tenacity of 0.72 gram per denier, an elongation of 7.9% and hot water shrinkage in excess of 10%, was drafted and relaxed as follows: Draft input speed was 23 meters per minute, with a draft factor of 7.0. Draft roller 11 and shoe 17 temperatures were 190° and 380° C., respectively. Relax factor was 0.89, 7% of this taking place going onto the relax roll 14 and 4% coming off. Temperatures of relax roll 14 and shoe 18 were 190° C. and 400° C., respectively. Both heated rolls 11 and 14 were 0.500 meter in circumference and, as in Example No. 1, were heated by hot oil. The resulting yarn was undeformed and possessed a tenacity of 3.77 grams per denier, an elongation of 20.2%, and hot water shrinkage of 1.0%.

Example 3

A dry spun acrylonitrile-isopropyl acrylamide graft polymer yarn (25% modifier) of 352 denier and 30 filaments having a tenacity of 0.80 gram per denier and an elongation of 6.4%, with hot water shrinkage in excess of 10%, was drafted and relaxed as follows: Draft input speed was 30 meters per minute, with a draft factor of 5.5. Draft roll and shoe temperatures were 185° C. and 200° C., respectively. The relax factor was 0.82, 8% taking place going onto the relax roll and 10% coming off the relax roll. Relax roll and shoe were heated to 240° and 380° C., respectively. In this case, the heated draft roll was one meter in circumference and the relax roll was 0.469 meter in circumference. Both rolls were electrically heated. The resulting yarn possessed a tenacity of 2.64 grams per denier and an elongation of 26.7% with hot water shrinkage of 1.2%.

No deformation due to roll pressure was found on the yarn.

Example 4

An acrylo-methyl polymer yarn of 510 denier and 30 filaments was dry spun and then subjected to an initial draft of 3.0. This first draft took place at the spinning cabinet prior to the first windup of the yarn, and was accomplished by the use of a heated roll and shoe. The predrafted yarn of 170 denier possessed a tenacity of 1.68 grams per denier and an elongation of 17.6% with hot water shrinkage in excess of 10%.

Next the yarn was given a drafting and relaxing treatment as described in Example 1. Draft input speed was 45 meters per minute, with a draft factor of 2.8. (This second draft multiplied by pre-draft equals total draft of 8.4.) Draft roll and shoe temperatures were 200 and 370° C., respectively. The relax factor was 0.86, 11% of which took place going onto the relax roll and 3% coming off said roll. Relax roll and shoe were heated to 210 and 330° C., respectively. Both heated rolls were 0.500 meter in circumference, and were heated by means of hot oil. The final yarn possessed a tenacity of 4.55 grams per denier, 17.0% elongation, and 0.0% hot water shrinkage and had no physical deformation.

Example 5

An acrylonitrile N-methyl methacrylamide graft polymer yarn (18% modifier) comprised of 60 filaments with a total denier of 840 was dry spun and then (as in Example 4) given a pre-draft of 3.0. The predrafted yarn had a denier of 280 and possessed a tenacity of 2.0 grams per denier and an elongation of 15.4%, with hot water shrinkage in excess of 10%. Final drafting and relaxing treatment was as follows: Draft input speed was 50 meters per minute with a draft factor of 3.0 (thus giving total draft of 9.0). Draft roll and shoe temperatures were 200 and 370° C., respectively. The relax factor was 0.82, 12% taking place going onto the relax roll and 6% coming off said roll. Relax roll and shoe temperatures were 190 and 390° C., respectively. Both heated rolls were 0.500 meter in circumference and were heated internally by means of hot oil. The final yarn possessed a tenacity of 4.26 grams per denier, an elongation of 23.0%, and hot water shrinkage of 0.0% and had no physical deformation.

Example 6

An acrylonitrile-isopropyl acrylamide graft polymer yarn (25% modifier) comprised of 30 filaments with a total denier of 320 was dry spun and prefinished 3.0. The predrafted yarn had a denier of 160, a tenacity of 1.69 grams per denier, an elongation of 10.4%, and hot water shrinkage in excess of 10%. Final drafting and relaxing treatment was as follows: Draft input speed was 70 meters per minute with a draft factor of 3.5 (total draft of 10.5). Draft roll and shoe temperatures were 190 and 330° C., respectively. Relax factor was 0.80, 9% occurs while the yarn progresses toward the relax roll and 11% taking place after the yarn come off the relax roll. Relax roll and shoe were heated to 210° C. and 310° C., respectively. Both heated rolls were 0.500 meter in circumference, and were heated with hot oil. Final yarn had a tenacity of 3.41 grams per denier, an elongation of 23.8%, and hot water shrinkage of 1.8%. No physical deformation of the yarn was caused by the described apparatus.

The temperature of the hot rolls and heating shoes depend on the polymer composition, filament diameter and speed of operation. These temperatures should be closely adjusted below the point at which the yarn will stick to either the heated rolls or itself, and yet hot enough to permit drafting and relaxation of the yarn to take place. In order to obtain optimum properties with our process it is also desirable that the yarn being
processed contain not more than 5% residual solvent and best results are obtained when the yarn has even a lower solvent content.

The advantages of the invention are that it permits the production at high rates of speed of undiformed fibers made from various acrylonitrile polymers, copolymers and graft or place polymers having excellent properties and useful either as continuous filaments, or when suitably cut into staple fiber. The process as is evident from the foregoing examples is rapid in that a given portion of the yarn is exposed to each heating step for only a fraction of a second. The first heating permits the yarn to be stretched to the desired amount but without being overheated so that it does not tend to stick to the apparatus. The second heating after the initial relaxation enables the yarn to relax additionally during the second relaxation step. The maximum improvement in tenacity, elongation and reduction of hot water shrinkage is thereby achieved.

The dry spun fibers mentioned in the foregoing examples may be suitably spun in accordance with the methods described in the copending application entitled "Spinning of Acrylonitrile Polymer Fibers" Ser. No. 328,894 filed of even date, now Patent No. 2,811,409. Solvents such as dimethyl formamide, dimethyl acetamide, diethyl formamide, gamma-butyrolactone, gamma-valerolactone, butyro lactam and sulfone may be employed to form the spinning solution. A 25% by weight of polymer in 75% solvent is suitable for most dry spinning operations. The residual solvent remaining in the yarn is of the order of 5%. The yarn may be treated at 60 yards per minute in our apparatus.

We claim:

1. The continuous method for increasing the tenacity and elongation and eliminating the hot water shrinkage of dry spun yarn of acrylonitrile polymers containing a major proportion of acrylonitrile and an acrylamide selected from the group consisting of isopropyl acrylamide and N-methyl acrylamide which comprises conducting the yarn under predetermined non-stretching tension to a roll heated to a temperature of 180°C, passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 370°C whereby the yarn without being compressed is heated until it becomes stretchable, stretching the heated yarn 550 to 850% after it leaves the heated roll, conducting the yarn to a second roll heated to a temperature of 210°C and passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 320°C whereby the yarn without being compressed is heated until it becomes relaxable, permitting the yarn to relax before and after contact with said second heated roll to an aggregate amount of from 11 to 20%, maintaining uniform tension on the yarn between the stretching and relaxing steps by passing the yarn around two separate non-heated rolls and winding the relaxed portion of the continuous yarn on a support without stretching tension.

2. The continuous method for increasing the tenacity and elongation and eliminating the hot water shrinkage of dry spun yarn of acrylonitrile polymers containing a major proportion of acrylonitrile and isopropyl acrylamide which comprises conducting the yarn under predetermined non-stretching tension to a roll heated to a temperature of 180°C, passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 370°C whereby the yarn without being compressed is heated until it becomes stretchable, stretching the heated yarn 550 to 850% after it leaves the heated roll, conducting the yarn to a second roll heated to a temperature of 210°C and passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 320°C whereby the yarn without being compressed is heated until it becomes relaxable, permitting the yarn to relax before and after contact with said second heated roll to an aggregate amount of 18%, maintaining uniform tension on the yarn between the stretching and relaxing steps by passing the yarn around two separate non-heated rolls and winding the relaxed portion of the continuous yarn on a support without stretching tension.

3. The continuous method for increasing the tenacity and elongation and eliminating the hot water shrinkage of dry spun yarn of acrylonitrile polymers containing a major proportion of acrylonitrile and N-methyl methacrylamide which comprises conducting the yarn under predetermined non-stretching tension to a roll heated to a temperature of 180°C, passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 370°C whereby the yarn without being compressed is heated until it becomes stretchable, stretching the heated yarn 550 to 850% after it leaves the heated roll, conducting the yarn to a second roll heated to a temperature of 210°C and passing the yarn for a fraction of a second between said roll and a shoe spaced therefrom and heated to a temperature of 320°C whereby the yarn without being compressed is heated until it becomes relaxable, permitting the yarn to relax before and after contact with said second heated roll to an aggregate amount of 11%, maintaining uniform tension on the yarn between the stretching and relaxing steps by passing the yarn around two separate non-heated rolls and winding the relaxed portion of the continuous yarn on a support without stretching tension.

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