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# ACRYLONITRILE CONTAINING TEXTILE HAVING CONTROLLED SHRINKAGE AND PROCESSES FOR FORMING SAME

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This invention relates to acrylonitrile containing polymeric yarn or filaments having high shrinkage characteristics. More particularly, it relates to imparting to the yarn or filaments a high, controlled shrinkage by first shrinking the yarn or filaments in a heated aqueous bath containing alkylene carbonate and then drawing to improve their physical properties whereby subsequent heat treatment after knitting or weaving shrinks the yarn or filaments to substantially their original length.

In the manufacturing of high bulk yarn, pile fabrics, made by weaving or knitting, and the like, where the filaments must undergo a controlled shrinkage to produce various effects such as bulking of the yarn or thickening of the pile it is necessary that the filaments or a part of the filaments used be capable of a high controlled shrinkage after the filaments have been drawn to improve their physical properties. Acrylonitrile containing polymeric yarn or filaments used in the manufacture of bulk yarn or pile fabrics exhibits only limited shrinkage after being drawn. This lack of high filament shrinkage decreases the quality of the bulk yarn, pile fabrics and like material made from the drawn filaments.

Commercial drawing of the filaments is accomplished by heating the filaments to a temperature of 220° F. to 320° F. and then mechanically stretching the filaments while in heated condition. Substantially oriented acrylonitrile containing filaments, such as Orlon 42 (Du Pont), can be effectively drawn up to about 30 percent and when heated in a relaxed state will shrink to their original length. If the filaments are drawn beyond 30 percent, subsequent relaxation and heating will produce only a shrinkage of about 30 percent. Thus, by using conventional methods of drawing and shrinking a 30 percent shrinkage is all that can be achieved regardles of the amount of drawing of the filaments. Where unoriented acrylonitrile containing polymeric filaments such as Orlon L–7 (Du Pont) are drawn, the filaments become brittle and at high point of stretch (less than 30 percent) break thus making it difficult to obtain a high shrinkage.

These and other disadvantages are overcome by first immersing acrylonitrile containing polymeric filaments in a heated aqueous bath containing alkyl carbonates where shrinkage takes place and then drawing the filaments either in the bath or immediately thereafter. Filaments treated by the process of this invention produce filaments having a high, controlled shrinkage which will shrink when heated in a relaxed condition to substantially the degree drawn. Thus, by controlling the degree of drawing, a predetermined controlled shrinkage can be produced.

By the use of the process of this invention, substantially oriented acrylic filaments, such as Orlon Type 42, can be drawn beyond 50 percent and then shrunk to their original length when heat treated in a relaxed condition. Also, unoriented acrylic filaments, such as Orlon L–7, which is difficult to draw under normal conditions because of its brittle structure can be successfully drawn beyond 60 percent with subsequent shrinkage to original length when heated in a relaxed condition.

Typical of the polymeric material which may be treated by the process of this invention are the well-known acrylonitrile type polymeric filaments, both oriented and unoriented, which include those containing at least 50 percent by weight acrylonitrile units in the polymer chain;



for example, polyacrylonitrile and its copolymers and interpolymers of acrylonitrile with other polymerizable monomers. These monomers include, among others, vinyl acetate, vinyl chloride, acrylic and methacrylic acids or derivatives and homologues thereof, styrene, methyl vinyl ketone, vinyl pyridines, such as 2-vinyl, 4-vinyl, 5-ethyl-2-vinyl or 2-methyl-5-vinyl pyridine and isobutylene or other similar polymerizable hydrocarbons.

Exemplary of alkylene carbonates used in the bath of this invention are the alkylene carbonates having 3 to 5 carbon atoms. Among the more important of these carbonates are ethylene carbonate, propylene carbonate, trimethylene carbonate, tetramethylene carbonate, 2,3-butylene carbonate, glycerine carbonate, and the like, ethylene and propylene carbonate being preferred.

In carrying out the process of this invention the acrylonitrile containing filaments are passed through a heated aqueous bath containing the alkylene carbonate. The filaments are quickly heated to the temperature of the bath which effects rapid penetration of the alkylene carbonate from the liquid. The penetration is deep and uniform, which is evidenced by the fact that a small amount of residual treating liquid remains imbedded in the filament even after thorough washing and drying. It is believed that the small residual amount of alkylene carbonate in the filaments aids in the realignment of the molecules of the filaments as they are being drawn so that there is the greatest possible degree of elasticity within the filament structure to allow for the increased drawing strength. The substantially uninhibited realignment of the molecules produced by the presence of the small amount of alkyleen carbonate allows for a high degree of shrinkage of the filaments after drawing is accomplished.

The treating bath is prepared by the inclusion in water of from about 2 to 20 percent by volume of an alkylene carbonate containing 3 to 5 carbon atoms. It has been found that as the alkylene carbonate concentration in the aqueous bath is increased the degree to which the filaments can be drawn after initial shrinkage in the bath is increased. Excellent results have been obtained for filament tow when the alkylene carbonate concentration is from 6 to 10 percent by volume.

Advantageously, the temperature of the bath may be maintained between 80° C. and its boiling point. Very good results are obtainable when the bath temperature is at the boiling point. The bath can be maintained at a pH of from 2 to 8. Excellent results have been obtained when the bath is about neutral. If a low pH is desired, organic or inorganic acids can be included in the bath to provide the desired pH.

The filaments can be drawn after shrinkage in the aqueous alkylene carbonate bath or they can be drawn after removal from the bath. Also, the filaments can be passed through a washing bath to remove from the surface presence of alkylene carbonate before the drawing is accomplished. The washing bath may include a hydrolyzation agent for hydrolyzing the alkylene carbonate on the surface of the filaments. The filaments can be exposed in the aqueous alkylene carbonate bath from 2 to 20 seconds which allows for a rapid and economical continuous process for inducing into the filament structure a high degree of controlled shrinkage.

Where the filaments are drawn after passing through the aqueous alkylene carbonate bath they may be maintained at a drawing temperature sufficient to impart plasticity to the filament so that the filaments will not break during the drawing operation. It has been found that acrylic filaments of the Orlon type maintained at a temperature between 140° F. to 170° F. have the desired plasticity for such a drawing operation. This plasticity, coupled with the elasticity provided by the residual alkylene carbonate in the filament structure is believed to pro-

vide the high degree of uniform drawing without breakage or fracture of the filament, such as is evidenced in the drawing of Orlon L–7 as heretofore described.

The process can be carried out with the filament tow in a relaxed state being first passed through the aqueous alkylene carbonate bath where the filaments are initially shrunk. The shrunken filaments are then passed through a wash to remove excess bath liquid from the surface of the filaments. The filaments are then drawn while in a heated bath maintained at a temperature of from 140° to 150° F. by passing the filaments over two sets of spaced rolls with the second set of rolls operating at an increased speed. The differential in speed between the two sets of rolls can be set so that the desired percentage of elongation is introduced into the filaments. Advantageously, the drawing can take place in the treating bath immediately after the initial shrinkage of the filaments and the filaments washed and dried while under tension, the produced filament having therein a predetermined shrinkage ratio.

The filaments processed in accordance with this invention possess new and different physical characteristics as is apparent from the high degree of controlled shrinkage exhibited when the filaments are heated under relaxed tension. It is believed that the realignment of the molecules due to the high degree of drawing and the residual alkylene carbonate in the filament structure produces the new and improved physical characteristics.

The invention will be more clearly understood by reference to the following examples which are given for purposes of illustration and are not to be construed in any sense as limitative of the invention.

*Example I*

A sample of raw Orlon tow (type 42) 10 inches in length was immersed under relaxed tension in a bath containing 440 cc. of water and 60 cc. of propylene carbonate. The tow was removed from the bath after 10 seconds and heated to a temperature of 160° F. and drawn to 15.4 inches and dried under tension. The tow in a relaxed state was then shrunk to 10 inches in boiling water. Upon examination the tow exhibited excellent properties and the sample showed a shrinkage of 34.5 percent.

*Example II*

Orlon tow was treated as set forth in Example 1 by immersing it in an aqueous bath containing 435 cc. of water and 65 cc. of propylene carbonate with the following results:

| | | |
|---|---|---|
| Original length | inches | 9.8 |
| After drawing | do | 14.8 |
| After treatment in boiling water | do | 9.0 |
| Shrinkage | percent | 39 |

*Example III*

Orlon tow was treated as set forth in Example I by immersing it in an aqueous bath containing 430 cc. of water and 70 cc. of propylene carbonate with the following results:

| | | |
|---|---|---|
| Original length | inches | 10.0 |
| After drawing | do | 16.0 |
| After treatment in boiling water | do | 9.0 |
| Shrinkage | percent | 43 |

*Example IV*

Orlon tow was treated as set forth in Example I by immersing it in an aqueous bath containing 425 cc. of water and 75 cc. of propylene carbonate with the following results:

| | | |
|---|---|---|
| Original length | inches | 9.25 |
| After drawing | do | 14.5 |
| After treatment in boiling water | do | 7.5 |
| Shrinkage | percent | 48 |

*Example V*

The treating bath, as described in Example I, was used except that ethylene carbonate was included in the bath. The tow exhibited the same percentage shrinkage.

*Example VI*

Tow was treated under the same conditions as described in Example I except that glycerine carbonate was used. The tow exhibited the same percentage shrinkage.

It is to be noted that Orlon type 42 (oriented) when treated by the process of this invention tends to shrink slightly below its original length after drawing.

*Example VII*

Orlon tow (type L–7) was processed as described in Example I except that 475 cc. of water and 25 cc. of propylene carbonate was used with the following results:

| | | |
|---|---|---|
| Original length | inches | 10 |
| After drawing | do | 20 |
| After treatment in boiling water | do | 10 |
| Shrinkage | percent | 50 |

*Example VIII*

Orlon tow (type L–7) was processed as described in Example I except that 465 cc. of water and 35 cc. of propylene carbonate was used with the following results:

| | | |
|---|---|---|
| Original length | inches | 10 |
| After drawing | do | 24 |
| After treatment in boiling water | do | 10 |
| Shrinkage | percent | 58 |

*Example IX*

A sample of Orlon tow (type L–7) was processed as described in Example I except that 490 cc. of water and 10 cc. of propylene carbonate was used with the following results:

| | | |
|---|---|---|
| Original length | inches | 10 |
| After drawing | do | 17 |
| After treatment in boiling water | do | 10 |
| Shrinkage | percent | 38 |

It will be noted that the Orlon type L–7 (unoriented) shrunk to approximately its original length after drawing when heat treated.

*Example X*

As set forth in Examples VII through IX, tow (L–7) was processed with ethylene and glycerine carbonate being used in place of propylene carbonate with the same final results.

Several tests were conducted in which acetic acid and phosphoric acid was used to maintain the pH of the bath below 7. The results of these tests show that the tow treated in a bath at low pH had high shrinkage as set forth in the foregoing examples.

It will be appreciated that the process set forth above produces filaments capable of a controlled amount of shrinkage. It has been found that the shrinkage is dependent on the concentration of the alkylene carbonate in the bath as well as the percentage of draw induced into the filament. Thus by varying the percentage of draw and the concentration of the alkylene carbonate filaments having predetermined precentage shrinkage characteristics can be obtained.

What is claimed is:

1. A process for inducing controlled shrinkage in polymeric filaments containing at least 50 percent by weight of acrylonitrile, after formation and during heat processing of the yarn after stretching, which comprises immersing said filaments in a heated aqueous bath maintained at a temperature above 80° C. for a period of from 5 to 20 seconds, said bath containing essentially as its sole additive from 2 to about 20 percent by volume of an alkylene carbonate having from 3 to 5 carbon

atoms, and stretching said filaments from about 30 to 70 percent of their original length.

2. The process of claim 1 in which the temperature of said bath is at its boiling point.

3. The process of claim 1 in which the filaments are stretched under heated conditions after removal from said alkylene carbonate bath.

4. The process of claim 1 in which said stretched filaments in the form of textile are heated to shrink the filaments to substantially their original length.

5. A process for inducing controlled shrinkage in polymeric filaments containing at least 50 percent by weight of acrylonitrile, after formation and during heat processing of the yarn after stretching, which comprises immersing the filaments in a heated aqueous bath at a temperature above 80° C. for a period of from 5 to 20 seconds, said bath having esssentially as its sole additive from 2 to about 20 percent by volume of propylene carbonate and maintained at a pH of from 2 to about 8, and stretching said filaments from about 30 to 70 percent of their original length.

6. A process for inducing controlled shrinkage in polymeric filaments containing at least 50 percent by weight of acrylonitrile, after formation and during heat processing of the yarn after stretching, which comprises immersing the filaments in a heated aqueous bath at a temperature above 80° C. for a period of from 5 to 20 seconds, said bath having essentially as its sole additive from 2 to about 20 percent by volume of glycerine carbonate and maintained at a pH of from 2 to about 8, and stretching said filaments from about 30 to 70 percent of their original length.




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