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2,926,065

METHOD OF SHRINKPROOFING ORIENTED, CRYSTALLIZED POLYETHYLENE TEREPHTHALATE YARNS AT ELEVATED TEMPERATURES BY HEAT TENSIONING AND HEAT RELAXING SAID YARNS

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The present invention relates to a method for enhancing the physical properties of threads, yarns and filaments of synthetic polyethylene terephthalate materials. More particularly, the invention relates to a method for treating filaments, yarns or threads of synthetic linear polyethylene terephthalate materials, e.g., those commercially available as "Dacron," to render them stable against shrinkage at elevated temperatures and to improve their tenacity.

The synthetic materials with which this invention is concerned are now well known and are disclosed, for example, in United States Patents Nos. 2,556,295 and 2,578,899, and patents referred to therein.

These synthetic polyethylene terephthalate materials, typically those commercially available as type 5100 Dacron, and type 5500 Dacron, are useful for applications at elevated temperatures, for example in the range 350° F. to 400° F., as they do not show any significant degradation at such temperatures. However, when exposed to such elevated temperatures, these commercially available filaments or yarns (and fabrics made therefrom) undergo serious shrinkage, being reduced in length as much as 20% or more, which undesirable property renders them almost useless for applications at these elevated temperatures in which dimensional stability of the yarn, or of articles fabricated therefrom, is important. When the term "yarn" is used hereinafter it is intended thereby to include filaments, threads and fabrics.

It is known in the art that such undesirable shrinkage can be eliminated by relaxing the yarns, prior to weaving, at the elevated temperature to which it is expected that the fabric will subsequently be exposed, for example at 350° F. While the material then will show substantially no shrinkage at 350° F., this lack of shrinkage has been obtained only at the expense of a large increase in the extensibility of the yarn or fabric. Thus the percentage elongation at rupture which was about 13% before the heat relaxing treatment is, after such treatment, in excess of about 40% and in some instances, in the case of threads, in excess of 60%, with the result that the yarn or articles fabricated therefrom are exceedingly deformable. This stretchiness may be cold-drawn out of the yarn by stress above the yield point, the yarn acquiring a set, but this set will again shrink out upon re-exposure of the yarn to elevated temperature. Thus the stretchiness removed is merely largely reconverted into capacity of the material to shrink when heated. Accordingly, it has been possible heretofore to obtain fabrics of low shrinkage or of low stretch, but not both in the same fabric.

Furthermore, such heat stabilization treatment materially decreases the tenacity of the yarns. For example, a type 5500 Dacron yarn when stabilized by being allowed to retract freely at 350° F. for five minutes, decreased in tenacity from about 4.3 to about 3.3 grams per denier, that is, by about 23%.

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Type 5100 Dacron, and yarns and fabrics thereof, is substantially the same as type 5500, qualitatively, in its behavior in these respects.

The present invention provides a method for heat stabilizing these commercially available polyethylene terephthalate materials (e.g. Dacron) without decreasing their tenacity, but, on the contrary, increasing their tenacity, and without imparting an objectionably high degree of cold-drawable extensibility. In accordance with the invention the yarn of oriented and crystallized (Patents 2,556,295 and 2,578,899) polyethylene terephthalate material is subjected to a treatment involving two operations at elevated temperature and in a critical order. In the first operation, the yarn is heated to a temperature in excess of 340° F., but sufficiently below its melting point to avoid degradation while it is maintained under tension to prevent it from shrinking to the extent it would shrink at this high temperature in the absence of such tension. Preferably the tension is sufficient to stretch the thread, yarn or fabric an amount of the order of less than 50% of its unheated length. Somewhat better results are obtained when this first operation is carried out in two steps, in one of which (preferably the first) the yarn is stretched and in the other is maintained under tension, preferably at least sufficient to hold it at such stretched length, both steps being carried out at the indicated temperature.

Thereafter, in the second operation, the yarn is permitted to shrink or retract freely, substantially without restraint, while it is heated to or above the temperature for which the yarn, or fabric produced therefrom, is to be made stable against shrinkage in subsequent use. For certain fabric uses, useful temperatures are those in the range 340° F. to 400° F. As a practical matter, it will usually be necessary or desirable in this last operation to maintain some slight tension in the yarn to facilitate handling of the material without risk of causing snarls or other mechanical difficulties. It is an essential feature, nevertheless, of the invention that this final relaxation treatment permit the yarn to retract, at the indicated temperature, substantially without restraint. It is also an essential feature that prior to the shrinking or relaxation step the yarn be subjected to the described step or steps of tensioning or stretching at elevated temperature. It is also essential that the polyethylene terephthalate material shall have been, before treatment by our process, oriented and crystallized, for example by the methods disclosed in the patents referred to.

The principles and practice of the invention are further illustrated by the following examples of presently preferred embodiments, but without limiting the invention to the details thereof.

Example 1

A 250 nominal denier (actually 252 denier) type 5500 Dacron yarn, having a tenacity of 4.4 grams per denier, a breaking strength of 1102 grams, a rupture elongation of 13.7% and shrinkage of 21.8% at 350° F., was subjected to a continuous three-stage treatment. In the first stage the yarn was run to a first roll, given six wraps around the roll to prevent slippage, and then passed from the first roll over the highly polished, slightly convex upper surface of a first aluminum plate heated by an 800 watt radiant-strip heater beneath the plate. The plate was 18 inches long. From this plate the yarn passed about a second roll (having six turns thereon to prevent slippage) rotated at a surface speed 1.2 times the surface speed of the first roll, whereby the yarn was stretched 20% during its passage over the plate. The first plate was maintained at a temperature of 450° F. and the yarn in passing thereover approached essentially the temperature of the plate, that is

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450° F. In the second stage, the yarn was passed from the second roll over a second, similar aluminum plate, heated to 425° F., to a third roll (six wraps) rotated at the same surface speed as the second roll, whereby the yarn was held at its stretched length. In the third stage, the yarn was passed from the third roll over a third, similar aluminum plate, heated to 350° F., to a fourth roll. The surface speed of the fourth roll was adjusted to permit the yarn to freely shrink in its passage over the third plate, being just sufficient to take up the yarn without snarls or kinks. The speed of the yarn was such that a given point on the yarn passed across each plate in two seconds. The final yarn product had a breaking strength of 1397 grams, a rupture elongation of 16.2%, a denier of 230 and a tenacity of 6.1 grams per denier. It showed zero shrinkage on re-exposure to 350° F. for twenty-four hours.

Example II

A 250 denier type 5500 Dacron yarn, from the same supply as the yarn of Example I, was subjected to a continuous two-stage treatment in the same apparatus employed in Example I. In the first stage the yarn was run to the first roll as before, and passed from the first roll over the first plate heated to 450° F. From the first plate the yarn passed about the second roll, rotated at a surface speed 1.2 times the surface speed of the first roll, whereby the yarn was stretched 20% while heated to 450° F. during its passage over the first plate. The second hot plate was by-passed and the yarn was run over the third hot plate heated to 350° F. The surface speed of the fourth, or final, roll was adjusted to permit the yarn to freely shrink in its passage over the third plate, being just sufficient to take up the yarn without snarls or kinks. The yarn speed was 15 yards per minute. The final yarn product had a breaking strength of 1268 grams, a rupture elongation of 18.4%, a denier of 232, and a tenacity of 5.5 grams per denier. It showed zero shrinkage on re-exposure to 350° F. for twenty-four hours.

Example III

A sample of 3-ply sewing thread made up of 3 strands of 75 (nominal) denier type 5500 Dacron yarn and having a thread tenacity of 4.3 grams per denier, a denier of 238, breaking strength of 1021 grams, rupture elongation of 27.3% and shrinkage of 14.5% at 350° F. was subjected in the apparatus of Example I, to 34% stretch at 400° F. over hot plate No. 1, held at fixed length while passing over hot plate No. 2, at 400° F., and then freely shrunk at 388° F. over hot plate No. 3. The yarn speed was 15 yards per minute. After this treatment the thread exhibited a tenacity of 6.3 grams per denier, breaking strength of 1282 grams, rupture elongation of 17.8% and denier of 204. Its shrinkage at 350° F. was 0.6%.

Example IV

A sample of 220 nominal denier (actual 225) type 5100 Dacron producer's yarn with about 1/2 turn per inch twist having a tenacity of 5.9 grams per denier, breaking strength of 1338 grams, rupture elongation of 10% and shrinkage of 21% at 350° F. was subjected to the three-stage procedure described in Example I, being stretched 20% at 400° F., held at fixed length at 400° F., and freely shrunk at 388° F. The yarn speed was 15 yards per minute. The product exhibited a tenacity of 6.8 grams per denier, breaking strength of 1377 grams, denier of 202, rupture elongation of 15.3%. Its shrinkage at 350° F. was 1%.

Example V

A sample of type 5100 Dacron yarn from the same supply as that used for Example IV was subjected in the apparatus of Example I to 20% stretch at 400° F. over hot plate No. 1. The yarn was then permitted to freely retract at 350° F. over hot plate No. 3. The yarn speed was 15 yards per minute. The yarn produced by this

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2-stage process then exhibited a tenacity of 6.8 grams per denier, rupture elongation of 21.1%, denier of 213, breaking strength of 1450 grams and 1% shrinkage at 350° F.

Example VI

A different lot of type 5100 nominal 220 (actual 218) denier Dacron producer's yarn having a tenacity of 6.5 grams per denier, rupture elongation of 10%, breaking strength of 1416 grams, and shrinkage of 19.2% at 350° F. was subjected in the apparatus of Example I to a continuous three-step treatment involving first, 20% stretch at 450° F., holding at fixed length at 450° F., then free relaxation at 388° F. The yarn speed was 15 yards per minute. Following this treatment, the yarn exhibited a tenacity of 7.0 grams per denier, breaking strength of 1464 grams, denier of 210, rupture elongation of 15.2% and 0.5% shrinkage at 350° F.

Example VII

A 250 denier type 5500 Dacron yarn from the same supply as the yarn of Example II was treated as in Example II except that the temperature during the 20% stretch was 340° F. After treatment, the yarn showed a breaking strength of 1351 grams, a denier of 252, a tenacity of 5.4 grams per denier, and rupture elongation of 24.5%. Its shrinkage at 350° F. was 0%.

Example VIII

A sample of yarn from the same supply as the yarn of Example VI was processed on the apparatus of Example I, at 40 yards per minute. As it passed over plate No. 1 at 450° F. it was advanced by roll No. 2 at the same speed at which it was supplied by roll No. 1, so that it was held under tension such that it was neither stretched nor allowed to shrink. Over plate No. 2 it was stretched 20% at 450° F. and over plate No. 3 it was allowed to shrink freely at 400° F. The product showed a breaking strength of 1528 grams, a denier of 232, tenacity of 6.6 grams per denier, rupture elongation of 19.2% and shrinkage at 350° F. of 2.8%.

Example IX

A 3-ply sewing thread made up of 3 strands of 250 denier type 5500 Dacron yarn having a thread tenacity of 4.3 grams per denier, a denier of 820, breaking strength of 3490 grams, rupture elongation of 30.1% and shrinkage at 350° F. of 18.4% was treated as in Example III except that the stretch at 400° F. was 50%, instead of 34%. After this treatment the thread showed a tenacity of 6.5 grams per denier, breaking strength of 4065 grams, rupture elongation of 17.8% and denier of 627. Its shrinkage at 350° F. was 1.4%.

Example X

A Dacron yarn from the same supply as the yarn of Example VI was processed on the apparatus of Example I at 15 yards per minute. On Plate No. 1 at 400° F. it was advanced by roll No. 2 at the same speed as it was fed in by roll No. 1 so that the yarn was held against shrinkage but was not stretched. Plate No. 2 was by-passed and the yarn allowed to freely shrink on plate No. 3 at 388° F. The product showed a breaking strength of 1529 grams, a denier of 230, a tenacity of 6.6 grams per denier, a rupture elongation of 15.8% and a shrinkage at 350° F. of 5.7%.

Example XI

A thrown type 5100 Dacron yarn with 5-turns-per-inch twist, having a breaking strength of 1332 grams, denier of 227, tenacity of 5.9 grams per denier, elongation of 12.5%, and shrinkage of 16% at 350° F. was processed on the apparatus of Example I at a speed of 65 yards per minute. On plate No. 1 at 450° F. the yarn was stretched 20%. Now, over plate No. 2, the yarn was allowed to retract partly, although still under

considerable tension. The retraction permitted over hot plate No. 2 at a temperature of 450° F. was accomplished by letting roll No. 3 run at 1.10V₁, while roll No. 2 fed yarn at 1.20V₁ (V₁ being the surface speed of roll No. 1). Finally, the yarn was permitted free relaxation while running over hot plate No. 3 at a temperature of 450° F. The yarn so processed had a breaking strength of 1515 grams, a denier of 208, a tenacity of 7.3 grams per denier, elongation of 14.6%, and shrinkage at 350° F. of 1.8%.

It will be seen from the foregoing examples that the yarns which have been subjected to our process show an increased tenacity which is disproportionately large when compared with the decrease in denier. Also, the absolute ultimate tensile strength of the yarn has been increased materially, an amount in some cases of the order of 30% or more. In each instance the shrinkage upon subsequent heating to the temperature for which the filaments were stabilized is either zero or is greatly reduced from that of the yarn before treatment, and this freedom from shrinkage is gained without sacrifice of other favorable characteristics, particularly without introducing into the yarn an objectionably high capacity to stretch and to acquire a permanent set. This superior temperature stability prevails both in the original unstressed condition of the yarn and after stressing at normal temperatures. Accordingly, it is now possible, for the first time as far as we are aware, to produce polyethylene terephthalate yarns which have both low high-temperature shrinkage and low stretch.

While we do not wish to be bound by any theory, it is our belief that the mechanism whereby these favorable characteristics are gained by our process is as follows:

The molecular structure of commercial polyethylene terephthalate yarn as delivered by the manufacturer has first been oriented principally in the long axis of the filament in one hot-drawing step, and thereafter the long chain polymer molecules were largely crystallized in a second step.

At this stage, however, the crystal-amorphous texture of the polymer is in a thermally metastable state. At room temperature the kinetic retractive forces are incapable of overcoming the binding effects of larger true crystals and of small localized regions of imperfect or pseudo-crystallization. As the polymer temperature is raised, even to below the minimum crystallization temperature (e.g., about 212° F. for the materials dealt with in the examples), the kinetic forces of the polymer chain become sufficient to tear loose some of the points of weakest internal cohesion, particularly in the smaller imperfectly crystallized domains. The net effect is disorientation and, perforce, retraction in the direction of the long axis of the filament. This effect is even more pronounced at temperatures above the minimum crystallization temperature when the larger true crystals are also somewhat melted out and internal binding is markedly reduced.

Thus, merely free-relaxing commercial yarns at elevated temperatures may result in elimination of subsequent shrinkage at the relaxation temperature, but it accomplishes this at the expense of marked disorientation and decrystallization of the originally imperfectly oriented and crystallized polymer. Subsequent stressing at room temperature of this relaxed material partially reorients the structure, setting up new regions of local pseudo crystallization again capable of holding the molecular network extended and imparting the aforementioned permanent set. This cold-set state is equivalent to the metastable configuration of the original, as-delivered ma-

terial, and will again be upset and create shrinkage on re-exposure to elevated temperatures.

The process of the invention depends on properly redistributing the crystal-amorphous texture under heat and stress. In effect, some of the pseudo or small imperfect crystals set up in the manufacturer's process are allowed to melt out, thus relieving certain otherwise fixed distortions of the polymer chain in the amorphous zone. But this melting out and stress relief is accomplished in our process with yarns restrained to prevent disorientation. By relieving these strains in this fashion without disorientation, the larger more perfect crystallization pattern is encouraged to grow. Yarn in this condition has immediately been improved in tenacity. Now, with this "supercrystallization" accomplished without sacrifice of orientation, if the stress is removed from the yarn at the elevated temperature and free relaxation is permitted, there is a minimum of disorientation and decrystallization. The improvements dependent on this mechanism of heat relaxation are evident in the enhanced tenacity and superior elastic properties of yarns treated by our multi-stage process.

The process of the invention may be performed by the use of hot rolls, heated plates, heated draw pins or heated chambers. Apparatus of this character is well known and readily adjustable and adaptable to our process as described herein. The yarn may be cooled to room temperature after the stretching operation and before the heat-shrinking treatment if desired and thus can be packaged and stored if desirable, to be subsequently heat stabilized at temperatures appropriate to a contemplated end use. Also, as indicated in the examples, the process can be conducted as a continuous process, all of the operations being performed in succession on a traveling yarn.

We claim:

1. The method of treating yarns comprising oriented and crystallized polyethylene terephthalate material to increase their tenacity and reduce their capacity to shrink in use at elevated temperatures, which consists essentially of heating said yarn under chemically non-reactive conditions to a temperature in excess of about 340° F. and below its melting point while maintaining the yarn under a tension from that which is at least sufficient to prevent substantial shrinkage of the same to that which is sufficient to stretch it less than 50% of its unheated length, and thereafter relieving said yarn of substantially all tension and heating the untensioned yarn under chemically non-reactive conditions to an elevated temperature above about 340° F. and below about 450° F. and permitting it while so heated to shrink freely without substantial restraint, whereby the yarn is substantially shrinkproof when thereafter during use it is heated to said elevated temperature.

2. The method of claim 1 wherein said tension is sufficient to stretch the yarn less than 50% of its unheated length.

3. The method as set forth in claim 1 wherein said first heating and tensioning operation is carried out in two steps, in the first step of which the yarn while being heated is stretched and in the second step of which the yarn while being heated is held at a length substantially the same as that to which it had been stretched in the first step.

References Cited in the file of this patent

UNITED STATES PATENTS

2,615,784 McClellan ----- Oct. 28, 1952