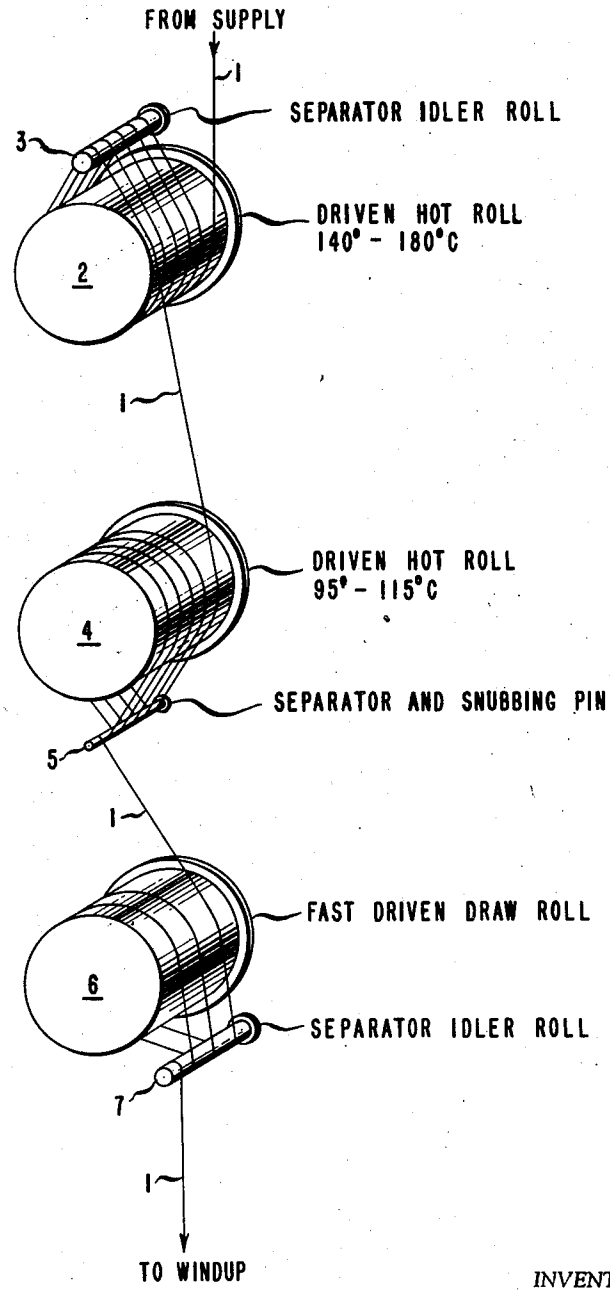
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PROCESS OF TREATING UNDRAWN POLYESTER YARNS AND FILAMENTS

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PROCESS OF TREATING UNDRAWN POLYESTER YARNS AND FILAMENTS

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7 Claims. (Cl. 28—72)

This invention relates to the manufacture of shaped structures comprised of linear superpolymers. More particularly, it relates to a new and improved method for drawing filaments, yarns, thread, and like shaped structures comprised of synthetic linear polyesters.

In the manufacture of synthetic linear polyester yarns and filaments, such as yarns of polyethylene terephthalate disclosed in detail in Whinfield and Dickson U.S. 2,465,319, it is known that the yarn properties such as tenacity and elongation are greatly improved by cold drawing. It is further known that this cold drawing process is facilitated by heating the yarn during the drawing step. The heating operation may be carried out by inserting a hot pin, a hot plate, or hot fluid bath between the feed roll and draw rolls of the drawing apparatus, or by using a heated feed roll. Drawing temperature limitations were recognized by Leben and Little (British Patent 603.840) who taught that difficulties in applying heat and tensions simultaneously are aggravated as the melting points of the filaments are approached and it is, therefore, preferred that the drawing should take place at a yarn temperature considerably less than the melting temperature and preferably less than 140° C. It is also taught that if undrawn yarn is heated without applying drawing tension the yarn becomes brittle and subsequently can be drawn only with great difficulty. The rate of embrittlement increases with the temperature of heating. In contrast, the rate of embrittlement of yarns to which drawing tension has been applied is considerably reduced and, consequently, the art discloses the application of drawing tensions early in the heating step.

Yarns prepared from polyethylene terephthalate by known processes have gained wide commercial acceptance. However, it is recognized that they are deficient in certain dyeing properties which limit their sales to non-critically dyed end uses. In particular, they are deficient in dye receptivity when dyed by commercial dyeing procedures; also, they are deficient in uniformity of dyeing. This non-uniformity of dyeing is thought to be due to variations in molecular orientation which occur during the spinning operation and which are magnified when the yarn is drawn by presently known processes.

Further, with respect to the general procedure used for preparing yarns from polyesters, it is recognized that the productivity of a yarn manufacturing plant is increased if higher draw ratios are permissible in the drawing operation. Since productivity is limited by the output of the spinning machines, it is obvious that a process which permits the spinning of heavier deniers increases productivity. This fact is of particular importance with reference to some important copolyesters of polyethylene terephthalate which have been found to draw at lower draw ratios than the homopolymer.

The primary object of this invention is to provide an improved and economical method for manufacturing filaments and yarns of synthetic linear polyesters.

Another object is to provide a method of drawing

which produces yarns and filaments of linear polyethylene terephthalates with improved dye receptivity.

Another object is to provide a method of drawing for producing low denier textile filaments with improved dyeing uniformity from linear polyethylene terephthalates.

A further object of this invention is to provide a process for drawing filaments and yarns of polyethylene terephthalates at higher draw ratios. These and other objects will more clearly appear in the detailed description which follows.

These objects are accomplished by a process for drawing synthetic linear condensation polyesters in which the undrawn yarns or filaments are heated to a temperature in the range 140–180° C. at substantially constant length, cooled, and drawn at a temperature in the range of about 95°–115° C.

In a preferred embodiment of the invention the initial heating step is accomplished in a continuous manner by wrapping the yarn around a rotating hot roll, and preferably a hot roll in conjunction with a freely rotating separator roll. The temperature of the rolls may be conveniently controlled thermostatically by electricity. The heating time is important since too short a contact time prevents the filaments from reaching the proper temperature, while excessive heating time permits an increase in crystallization of the polymer which interferes with the drawing process and therefore should be maintained as near 0% as conveniently possible. These conditions are avoided in the process of this invention by limiting the heating time in the first temperature stage of about 140° C. to 180° C. to the preferred time of from about 0.3 to 6 seconds.

As in the initial heating step, the second step of adjusting the temperature of the filaments to 95–115° C. for drawing may be accomplished by the use of a hot fluid, e.g., steam, or other heat transfer means, but preferably is accomplished by the use of a hot roll. Sufficient wraps are taken around the hot roll, with the aid of a separator roll or pin, to permit an exposure time of from 0.1 to 3 seconds.

It is permissible for the filaments to be cooled to a temperature as low as room temperature between the first and second temperature controlling steps in the process of this invention. However, it is obviously more desirable to pass the yarn directly from the first temperature stage of 140–180° C. to the second temperature stage of 95–115° C., thereby eliminating the need for extra heating capacity in the second temperature stage as well as extra yarn handling devices and equipment between the two stages.

In the preferred embodiment of the invention the yarn is passed around a stationary snubbing pin immediately following and within several inches of the second heated roll before proceeding to the draw roll. The function of the stationary snubbing pin is to localize the draw point and thereby further contribute to the uniformity of the product. The snubbing pin, either of ceramic or metallic material, is preferably less than about ½ inch in diameter, and usually from ⅛ to ⅜ inch in diameter. No separate means of heating the pin is required.

In carrying out the process of this invention in the preferred manner in which hot rolls are used at the two temperature controlling stages it is permissible to operate at yarn windup speeds of 200 to 900 yards per minute. It is understood that the contact times on the hot rolls may be brought within desired limits by adjusting the size of the rolls and the number of wraps taken around the rolls.

The draw ratio applied to the filaments will vary depending upon the specific composition of the polymer, the character of the product desired, and the temperature of

the filaments entering the draw zone. In general, a draw ratio between about 3 and about 5 is ordinarily used.

The invention will be more readily understood by reference to the accompanying drawing in which the single figure is a diagrammatic plan view of the arrangement of the various rolls. In the figure, **1** represents a bundle of filaments which travel from a supply, not shown, around a driven roll **2** and an idler roll **3**. The yarn is passed around the two rolls to form about from 4 to 15 wraps as shown. It is then led over and around driven roll **4** and pin **5** which is a combination separator and snubbing pin for about 2 to 10 wraps as shown in the drawing. Roll **2** is heated to about 140° C. to 180° C. and roll **4** is heated to a temperature of about 95° C. to 115° C. These may be heated by any convenient means. After leaving the snubbing pin **5**, the yarn passes over the driven draw roll **6** and around idler roll **7** to a windup. The surface of roll **6** travels from about 3 to 5 times faster than that of hot roll **4** to accomplish drawing and its peripheral speed will be in proportion to the degree of drawing desired. Draw roll **6** is not usually heated. Fewer wraps around rolls **6** and **7** are necessary, and for most practical purposes 3 wraps are normally sufficient.

The following examples will serve to illustrate the invention although they are not intended to be limitative.

Example I

A copolyester is prepared in accordance with the general procedure described in U.S. Patent 2,465,319 to Whinfield and Dickson, in which dimethyl terephthalate (0.988 mol.) and sodium 3,5-di-(carbomethoxy)benzenesulphonate (0.012 mol.), and ethylene glycol (about 2.1 mols.) are heated together in the presence of a catalyst until the evolution of methanol ceases, following which the mixture is heated at an elevated temperature and reduced pressure with evolution of glycol until a copolyester having an intrinsic viscosity of 0.48 is attained. This copolyester is melt spun at 295° C. through a spinneret having 34 orifices, each 0.009 inch in diameter, and the yarn is wound up at a speed of 1,200 yards per minute. The yarn has a denier as spun of 240, a birefringence of 0.0094, and a crystallinity level of about 0% (substantially amorphous). This undrawn yarn is passed through suitable guides to a pair of rolls one of which is driven (surface speed: 110.7 y.p.m.) and heated to 144° C., and the other being a freely rotating separator roll with its axis canted to the axis of the driven roll. The diameter of the driven roll is 3 inches; that of the separator roll, ⅝ inch. Eleven wraps are taken around this first pair of rolls to bring the yarn up to temperature. The yarn then passes to and around (5 wraps) a second driven roll 3 inches in diameter having substantially the same surface speed as the first driven roll but being heated to only 100° C. Separation of wraps is obtained by the use of a separator pin 3/16 inch in diameter one end of which also serves as a snubbing pin. The thus cooled yarn then passes around the end of the 3/16 inch snubbing pin (one wrap), where drawing occurs, and proceeds to a third driven roll (unheated) which has a surface speed 4.1 times that of the second driven roll, or 454 yards per minute. Several wraps are made around the third roll to prevent slippage and the yarn then passes to a yarn takeup device. The resulting yarn has a tenacity of 3.0 grams per denier, a break elongation of 20%, and a shrinkage in boiling water of 12.4%.

Samples of this yarn, when dyed in the same dye bath with yarns prepared by a similar process except for the preheating step (but drawn to the same elongation, and thus the same degree of orientation), are found to be from 5 to 10 shades darker. The term "shade" is defined as the last discernible color difference between two samples are rated by an experienced observer.

Similar results are obtained when the second hot roll is operated at 95° C. or 115° C.; however, when the roll is operated at a temperature appreciably above or below 95° C. or 115° C. a product of lower quality is obtained.

The process of this example operated without the preheating step required the lower draw ratio of 3.26 to give tenacity and elongation properties equivalent to those obtained with the preheating step.

Example II

A copolyester of polyethylene terephthalate containing 2 mol percent sodium 3,5-di-(carbomethoxy) benzenesulfonate and having an intrinsic viscosity of 0.50 is spun at 295° C. through a spinneret having 34 orifices, each 0.009 inch in diameter, and the yarn is wound up at a speed of 1200 yards per minute. The yarn is found to have a denier as spun of 245, a birefringence of 0.0095 and a crystallinity level of about 0%. This undrawn yarn is passed through suitable guides to a roll 3 inches in diameter driven at 108 yards per minute and heated to 160° C. Eleven wraps are taken around this roll in order for the yarn to attain the proper temperature. Wraps are separated by means of a freely rotating separator roll. The yarn then passes to and around (5 wraps) a second driven roll 3 inches in diameter having substantially the same surface speed as the first driven roll and heated to 100° C. The yarn, having been cooled to the proper temperature for drawing, then passes around a ¼ inch diameter snubbing pin, where drawing occurs, and then to a third driven cold roll which has a surface speed 4.2 times that of the second driven roll. Several wraps are made around the third roll to prevent slippage and the yarn then passes to a yarn takeup device. The resulting yarn has a tenacity of 2.6 grams per denier, an elongation of 31.5%, and a shrinkage in boiling water of 13.1%. Samples of this yarn subjected to a dyeing operation are found to achieve a considerably deeper dye depth and a more uniform appearance than similar yarns drawn without the preheating step (but drawn to the same measured elongation value).

The process of this example operated without the preheating step required the lower draw ratio of 3.26 to give tenacity and elongation properties equivalent to those obtained with the preheating step.

Substantially equivalent results to those described in this example are obtained when the number of wraps on the first hot roll is about 4 to 15. In like manner, substantially equivalent results are obtained when the number of wraps on the second hot roll is about 2 to 10.

Example III

Polyethylene terephthalate having an intrinsic viscosity of 0.58 is spun at 295° C. through a spinneret having 34 orifices, each 0.009 inch in diameter, and the yarn is wound up at a speed of 1,200 yards per minute. The yarn is found to have a denier as spun of 240, a birefringence of 0.0079, and a crystallinity level of about 0%. This undrawn yarn is passed through suitable guides to a metal roll 3 inches in diameter which is driven at a surface speed of 106.4 yards per minute and heated to 140° C. Eleven wraps are taken around this hot roll with the aid of a freely rotating separator roll. The yarn is then passed to and around a second driven roll having a diameter of 3 inches and rotating at substantially the same surface speed as the first driven roll but being heated to only 100° C. Five wraps are made around this second heated roll with separation of wraps being obtained by the use of a 3/16 inch diameter combination separator and subbing pin. The yarn, now cooled to the proper temperature for drawing, passes to and around one end of the same 3/16 inch in diameter pin which acts as a snubber, where drawing occurs, and proceeds to a cold driven roll which has a surface speed 4.27 times that of the preceding driven rolls, i.e., 454 yards per minute. Several wraps are made around the third driven roll to prevent

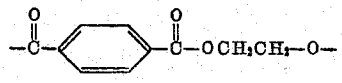
slippage and the yarn then passes to a yarn take up device. The resultant yarn has a tenacity of 3.5 g.p.d., an elongation of 27%, and a shrinkage in boiling water of 10.6%.

Samples of this yarn, when dyed in the same dye bath with yarns prepared by a similar process except for the preheating step (but drawn to the same elongation, and thus the same degree of orientation), are found to be several shades darker. Further, when the dyeing rates of such yarns are measured and compared, the yarn of this example is found to dye at a rate at least 10% faster than the comparison yarn.

The process of this example operated without the preheating step required the lower draw ratio of 3.49 to give tenacity and elongation properties equivalent to those obtained with the preheating step.

A result equivalent to that produced by this invention is not obtained by heating the yarn to a temperature of 140° C. to 180° C. followed by snubbing on a draw pin. Such a process has been found to be inoperable at windup speeds above 200 y.p.m. because of the low strength of undrawn polyethylene terephthalate filaments at high temperature. In addition to frequent breaks in the threadline, the resulting product is characterized by a great degree of non-uniformity because of intermittent sticking of the yarn to the hot roll and to the draw pin.

Although the invention has been particularly described with respect to the drawing of filaments of polyethylene terephthalate and polyethylene terephthalate copolymers containing small residues of sodium 3,5-di(carbomethoxy)benzenesulfonate, it is understood that the invention is fully applicable to the drawing of filaments of other modified polyethylene terephthalates in which at least 90% of the recurring structural units are



i.e., polyethylene terephthalate copolymers containing residues of other dicarboxylic acids or other glycols in significant quantities. For example, in some preferred modifications the polyethylene terephthalate copolymer may contain recurring polyester linking units comprised of aliphatic acids selected from the series

$$HOOC(CH_2)_nCOOH$$

where "*n*" is zero or an integer from 1 to 8, isophthalic acid, phthalic acid, naphthalic acids, bibenzoic acids, polyalkylene glycols, or aliphatic glycols having the formula $HO(CH_2)_nOH$ where "*n*" is an integer from 2 to 10. The invention may be applied to filaments of such polyesters whether produced by wet spinning, dry spinning or melt spinning. It is further to be understood that filaments containing such modifications of the polyester in whole or part may be used directly in the examples in place of the polyester used therein to illustrate the invention.

The use of the present invention permits drawing polyester filaments at higher draw ratios which in turn permits the spinning of heavier denier filaments and thereby materially increases the productivity of a yarn manufacturing plant.

The uniformity of the orientation-sensitive physical properties of the yarns and filaments of synthetic linear condensation polyesters drawn according to this invention do not depend upon the uniformity of orientation obtained during the spinning process but only on the drawing process. Therefore, special measures and equipment for maintaining uniformity of orientation in the spinning process may be eliminated.

Yarns of synthetic linear condensation polyesters drawn according to the present invention are found to accept dyestuffs much more readily than similar yarns drawn by other commercial processes to the same break elongation (same orientation) and tenacity level. This is surprising since it would be expected that yarns spun from the same polymer and drawn to the same orientation would accept dyestuffs with equal facility.

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. The process of treating undrawn synthetic linear polyester yarns and filaments which comprises heating the same without significant elongation to a temperature of about 140° C. to 180° C. for a period of from about 0.3 second to about 6 seconds while the yarn is in a low state of crystallinity and thereafter drawing the said yarn or filaments heated to a temperature of from about 95° C. to 115° C.

2. The process of claim 1 in which the yarn or filaments are heated in the second step for a time from about 0.1 second to 3 seconds.

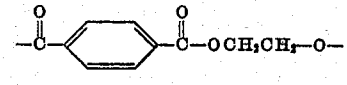
3. The process of claim 1 in which the yarn leaves the second heating treatment at a windup speed of from 200 to 900 y.p.m.

4. The process of claim 1 in which the draw ratio is between about 3 and 5 times.

5. The process of claim 1 in which the crystallinity of the undrawn yarn is substantially zero.

6. The process of claim 1 in which the polyester is polyethylene terephthalate.

7. The process of claim 1 in which the polyester contains at least 90% of the recurring structural units



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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,942,325 June 28, 1960

Floyd E. Spellman, Jr.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 73, for "last" read -- least --; line 74, after "samples" insert -- when said samples --.

Signed and sealed this 6th day of December 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents