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# PROCESS FOR THE MANUFACTURE OF POLYESTER SYNTHETIC FIBERS

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## ABSTRACT OF THE DISCLOSURE

A process for producing terephthalate polyester filaments of improved dye affinities and excellent creep resistance comprising drawing undrawn terephthalate polyester filaments having a birefringence of 0.0050–0.0250 at a relatively low draw ratio at a temperature of from 55° to 95° C. with heating of the drawn filaments at a temperature of from 100° to 220° C. while allowing shrinkage. The heat-treated yarn is thereafter redrawn at a temperature of not less than about 160° C. to not less than about 1.16 times the length of the heat-treated yarn to thereby produce a polyester synthetic fiber having improved dyeability and yarn characteristics. The draw ratio ranges from the minimum draw ratio of the undrawn yarn to a draw ratio about 0.5 higher than such minimum.

This invention relates to a process for the manufacture of polyester synthetic fiber, and more particularly to a synthetic fiber composed of terephthalate polyester which has an improved dyeability.

In order to improve its mechanical properties, a polyester synthetic fiber is generally heated to a temperature above its second order transition temperature, drawn 3.5–5.5×, and thereafter heat-treated. As a result, the degree of orientation and crystallinity of the fiber becomes high, and its interior structure is so compact as to make it difficult for the dyestuff molecules to enter. Consequently, the dyeability is worsened. In an attempt to overcome this difficulty, there have hitherto been proposed such remedies as the copolymerization of a third component with the polyester synthetic polymer or the heat-treatment of the fiber at high temperature in chemicals. However, in the former, the thermal resistance of the fiber is lowered, and the latter treatment involves a defect of high cost, and marked degradation of the fiber.

It has now been found that by employing a process which comprises drawing an undrawn filament composed of terephthalate polyester and having a relatively high birefringence (i.e., birefringence in the range of 0.0050–0.0250) at a temperature of 40–95° C. at a relatively low ratio (i.e., draw ratio ranging from the minimum draw ratio of the said undrawn filament to a draw ratio slightly higher than this), and thereafter heating the drawn filament at a temperature of 100–220° C. under a state of shrinkage, there can be prepared a polyester synthetic fiber having excellent affinity for disperse dyestuffs.

By the term "terephthalate polyester" used in the specification and claims is meant a polymeric polyester derived from a dihydric alcohol component and a bibasic acid component at least 85 mol percent of which is a terephthalic acid. As the dihydric alcohol component, ethylene glycol is preferably used, but there may also be used



other dihydric alcohols such as polylene glycol, 1,4-butane-diol and other alkylene glycols, or 1,4-dihydroxymethyl cyclohexane. A portion of the acid component accounting for up to 15 mol percent may be bibasic acids other than terephthalic acid such as isophthalic acid, parahydroxy benzoic acid, vanillic acid and adipic acid. Furthermore, the terephthalate polyester may contain, as a branching agent, benzene 1,3,5-tricarboxylic acid 5 oxydimethyl isophthalate in substitution of part of the bibasic acid component, and a polyhydric alcohol such as pentaerithritol, glycerine nad sorbitol in place of part of the dihydric alcohol. Such branching agent can usually be used in the amount up to about 1.0 mol percent of the acid or alcohol component. These terephthalate polyesters and method for their manufacture are well known.

It is necessary that the starting undrawn filament of this invention should have a birefringence of at least 0.0050, and preferably at least 0.0080, which is higher than those of ordinary undrawn filaments. When an undrawn filament having a birefringence lower than 0.0050 is subjected to the drawing and heat-treating operations of this invention, a desired improvement in dyeability cannot be achieved. It is also difficult to manufacture a product having excellent dyeability from an undrawn filament having excess birefringence (more than 0.0250). Thus, we have found that the birefringence of the starting undrawn filament of the process of this invention should be in the range of 0.0050–0.0250, and preferably in the range of 0.0080–0.020.

The birefringence of the undrawn filament depends upon spinning conditions in the manufacture of undrawn filaments, particularly upon the spinning speed, cooling rate of the thread line, the spinneret temperature and the types of the polymers (especially, degree of branching and polymerization). Among these conditions, the spinning speed and the cooling rate are particularly dominant. Generally speaking, a high spinning speed and cooling rate result in a higher birefringence. For instance, the birefringence of the undrawn filament prepared by the steps of melting polyethylene terephthalate chip having an intrinsic viscosity of 0–60 and extruding the molten polyethylene terephthalate from a spinneret having 0.35 mm. x 50 holes into the air at room temperature at a spinneret temperature of 275° C. varies among 0.0096, 0.0148 and 0.0215 depending upon 1500 mm./min., 2000 m./min. and 2500 m/min, respectively Also, the birefringence of an undrawn filament obtained by extruding a polyethylene terephthalate adipate copolymer chip (3 mol percent adipate) having an intrinsic viscosity of 0.64 from a spinneret having 0.24 mm.$\phi$ x 35 holes at a spinneret temperature of 265° C. through a quenching chimney with a length of 20 cm. provided therebelow, into which the air at room temperature is sent at right angle to the filament, and taking up the extruded filament at the rate of 1500 m./min. varies from 0.0126 to 0.0194 depending upon the linear velocity of the air of 25 m./min. and 55 m./min., respectively.

In accordance with the process of this invention, the undrawn filament having a relatively high birefringence as specified above is drawn at a temperature of 40–95° C. at a draw ratio ranging from its minimum draw ratio to a ratio slightly higher than this.

The minimum draw ratio means a minimum of the draw ratios at which no filaments remain substantially undrawn. As to a certain specific undrawn filament, its minimum draw ratio is decided according to the follow-

ing procedures. Namely, a given tow of an undrawn filament is drawn and taken up at a rate of 100 m./min., and maintained at 145° C. for 15 minutes while allowing a free shrinkage. This is thereafter cut into staple fibers of 3 cm. length. The staple fibers are then dyed for 5 minutes at a bath ratio of 1:100 in a dispersion containing 4% O.W.F. of Dispersol Fast Scarlet B–150F (C.I. 11110) and 0.5 g./litre of sodium dodecylsulfate. The dyed staple fibers are dried and observed under a magnifying glass to count the number of the fibers (undrawn filaments) dyed especially in deep color. When this number exceeds 200 among 100,000 filaments, the draw ratio used is regarded as being lower than the minimum draw ratio. When an undrawn filament of polyethylene terephthalate having a birefringence of 0.0081 is tested in a water bath of 80° C. using various draw ratios, the following results are obtained.

| Draw ratio: | Number of undrawn filaments in 100,000 draw filaments |
|---|---|
| 1.70 | 3520 |
| 1.80 | 1830 |
| 1.90 | 135 |
| 1.95 | 82 |
| 2.00 | 35 |

According to this series of tests, the minimum draw ratio of the said undrawn filaments determined in a water bath of 80° is 1.90. The minimum draw ratio depends upon the birefringence of the given undrawn filaments and the types of the polymers, particularly upon its degree of branching. Generally speaking, the higher the birefringence is and the higher the degree of the branching of the polymer is, the lower the minimum draw ratio becomes. The determination of the minimum draw ratio is hardly affected by the dyeing conditions in the above tests. A simplified method of determining the minimum draw ratio is to examine a sample of tow which is drawn and heated for 15 minutes at 145° C. while allowing a free shrinkage. When the sample is not substantially stuck together, the empoyed draw ratio can be regarded as not being lower than the minimum draw ratio.

The draw ratio to be used in the process of this invention should be in the range from the minimum draw ratio to a ratio slightly higher than this. At a draw ratio lower than the minimum draw ratio, the obtained product contains an undrawn portion. When the draw ratio is excessive, a desired effect of the improvement of the dyeability cannot be achieved. We have found that it is possible to use a draw ratio higher than the minimum draw ratio by about 0.5 and preferably by 0.3.

The draw temperature may be in the range of 40–95° C. In general, when the temperature is too low, drawing cannot be effected smoothly, and when the temperature is too high, a desired effect of the improvement of dyeability cannot be achieved. The preferable range of the draw temperature is 60–70° C.

The drawing as above mentioned can be effected either by using a gaseous or liquid medium, or by contact heating by means of a hot plate. The draw rate is not an important requirement and can be selected within the range of 10–500 m./min., and particularly 20–150 m./min.

The drawn filament, so obtained, is heated, under a shrinkable state at a temperature of 100–220° C., and preferably 130–180° C. When the temperature is too low, the shrinkage and setting are not fully achieved and when it is too high, the fibers are stuck together. This is not desirable. The heat treatment is carried out under a state of a free or limited shrinkage. In this treatment, the fibers are subjected to about 5–60% of shrinkage. As a matter of course, the heat treatment may be effected by using either gas or liquid medium, or by contact heating.

The polyester fiber to be manufactured by the process of this invention may be cut into staple fibers prior to, or after, the said heat treatment. Furthermore, it is possible to subject the tow drawn and heated in accordance



with the process of this invention to an additional drawing. We have found that this additional drawing gives rise to the improvement of the strength and elongation of the obtained product, and does not give substantial damage to the excellent dyeability once obtained. This is extremely surprising.

The polyethylene terephthalate fiber obtained in accordance with the process of this invention can be dyed in deep colours without the reliance of a special dyeing technique. The obtained dyeings exhibit more excellent fastness to washing as compared with the ordinary polyethylene terephthalate dyed in the same degree of deep colour by means of a special dyeing method such as high temperature dyeing or carrier dyeing. This is an unexpected fact.

The polyethylene terephthalate fiber whose dyeability is improved by heat treatment under shrinkage at high temperature as more than 220° C. has a poor elastic recovery. On the contrary, the product in accordance with the process of this invention is as superior as the ordinary polyethylene terephthalate fiber with respect to its elastic recovery.

Furthermore, the polyethylene terephthalate fiber obtained in accordance with the process of this invention has a very low creep strain (strain which results by application of a specific load for a prolonged time) and a low residual strain after creep recovery (residual strain when the said load is taken off to recover the creep). When comparison is made among the ordinary polyethylene terephthalate fiber, the polyethylene terephthalate fiber obtained in accordance with the process of this invention and polyethylene terephthalate isophthalate fiber, the said creep strain and residual strain after creep recovery are the minimum for the fibers of this invention and the maximum for the isophthalate modified fiber. The difference between these becomes increasingly remarkable as the temperature at determination becomes higher from room temperature, 50° C. to 70° C. This shows that the fiber obtained in accordance with the process of this invention has a very excellent dimensional stability against the changes in stress, temperature and time.

Also, the fabrics woven from the staple fibers obtained in accordance with the process of this invention have improved resistance to pilling.

The following examples are intended for the explanation of this invention, in which the dye absorptions are the values determined with respect to Dispersol Fast Scarlet B–150F (C.I., 11110) in accordance with JIS (Japanese Industrial Standard). In this method of determination, the sample is dyed at a bath ratio of 1:100 in a dispersion containing 4% O.W.F. of the dyestuff and 0.5 g./litre sodium dodecylsulfate for 90 minutes at 100° C. Using a residual liquor after the removal of the sample, the degree of light absorption (wave length 500 mμ) is determined by means of a photocolouring meter, and expressed in terms of ratio to the value prior to the dyeing.

## EXAMPLE 1

An undrawn filament of polyethylene terephthalate having a birefringence of 0.0081 was drawn in a hot water bath of 65° and 80° C. at a ratio of 2.0× and 3.6×, and taken up at a speed of 100 m./min. It was thereafter heated at 145° C. for 15 minutes under a state of free shrinkage. The obtained fibers had the properties shown below.

| Draw temperature, ° C. | Draw ratio | Dye absorption (JIS percent) | Tenacity, g./d. | Elongation, percent |
|---|---|---|---|---|
| 65 | 2.0 | 89 | 2.8 | 120 |
| 65 | 3.6 | 55 | 5.0 | 50 |
| 80 | 2.0 | 82 | 3.0 | 110 |
| 80 | 3.6 | 53 | 5.8 | 39 |

The minimum draw ratio in this example was 1.9.

EXAMPLE 2

An undrawn filament of polyethylene terephthalate having a birefringence of 0.1860 was drawn 1.5× on a hot pin having a surface temperature of 70° C. and passed successively on a metal plate of 180° C. at a rate of 10 m./min. while causing 20% shrinkage, and thereafter drawn 1.3× on a metal plate of 160° C. The resulting filament showed a dye absorption of 89.6%, a tenacity of 2.44 g./d. and an elongation of 55.3%.

The minimum draw ratio in this example was 1.45.

EXAMPLE 3

An undrawn filament of polyethylene terephthalate having a birefringence of 0.0120 was drawn 2.1× at a draw bath temperature of 45° C. at a rate of 40 m./min., and heated at 150° C. for 20 minutes under a state of free shrinkage. The resulting fiber had a dye absorption of 92%.

The minimum draw ratio in this example was 1.80.

EXAMPLE 4

A polyethylene terephthalate chip having intrinsic viscosity of 0.64 determined in o-chlorophenol of 35° C. was extruded from a spinneret having orifices of 0.24 mm.$\phi$ x 35 holes and having a temperature of 270° C., and thereafter taken up at a rate of 1500 m./min. At this time a quenching chimney with a size of 20 cm. in length and 15 cm. in inside diameter was provided below the orifices and the air at room temperature was blown inwardly at right angle to the filament at a linear speed of 25 m./min. for quenching the filament. There was obtained a 6 denier per filament undrawn yarn having a birefringence of 0.0132. This yarn was drawn on a hot pin of 80° C. at a ratio of 1.9, 2.2 and 2.5× respectively and then wound up at a rate of 40 m./min. The drawn yarn was then immediately heated on a metal plate of 140° C. while causing 10% shrinkage and successively drawn 1.2× on a metal plate of 210° C. The obtained yarn had the following properties.

| Draw ratio | Dye absorption, percent | Tenacity, g./d. | Elongation, percent | Shrinkage in boiling water, percent |
|---|---|---|---|---|
| 1.9 | 89 | 2.98 | 42.3 | 1.3 |
| 2.2 | 82 | 3.30 | 36.1 | 1.6 |
| 2.5 | 57 | 4.92 | 32.5 | 3.1 |

The minimum draw ratio in this example was 1.75.

EXAMPLE 5

The same procedures as in Example 4 were repeated except that there were used polyethylene terephthalate chips having an intrinsic viscosity of 0.55, a take-up rate of 2,200 m./min. and the air of 10° C. There was obtained undrawn filament having a birefringence of 0.0239. This yarn was drawn 1.5X on a hot pin of 90° C. and thereafter wound at a rate of 40 m./min., and successively shrunk 20% on a metal plate of 180° C. The minimum draw ratio under this condition was 1.32. This shrunken yarn is successively drawn 1.3× at a temperature of 200° C. and 230° C. The properties of the thus obtained yarns in comparison with the shrunken yarn not treated further are shown in the following table.

| Re-drawing temperature, (°C.) | Re-draw ratio | Dye absorption, percent | Tenacity, g./d. | Elongation, percent | Shrinkage in boiling water, percent |
|---|---|---|---|---|---|
| | | 88.3 | 2.75 | 49.5 | 0.6 |
| 200 | 1.3 | 86.3 | 3.21 | 30.4 | 2.1 |
| 230 | 1.3 | 87.1 | 3.27 | 33.6 | 1.8 |

EXAMPLE 6

Polyethylene terephthalate isophthalate chip containing 9 mol percent of isophthalic acid as acid component (having an intrinsic viscosity of 0.67 and a softening point of 241° C.) was extruded from a spinneret of 255° C. into the air at room temperature and then taken up at a rate of 1700 m./min. There was obtained a 5 denier per filament undrawn yarn having a birefringence of 0.0123. This yarn was drawn 1.95× on a hot pin of 55° C. and wound up at a rate of 45 m./min. It was then shrunk 20% on a metal plate of 130° C. and successively drawn 1.25× at 180° C. The obtained fiber had a dye absorption of 92%, a tenacity of 3.15 g./d. and an elongation of 34.8%. The minimum draw ratio in this example was 1.75×. The fiber obtained by drawing the same undrawn yarn 3.75× and heating it at 140° C. for 15 minutes had a dye absorption of 75%, a tenacity of 4.65 g./d. and an elongation of 53.4%.

EXAMPLE 7

Polyethylene terephthalate chip having an intrinsic viscosity of 0.62 and containing pentaerithritol in 0.4 mol percent based on the recurring unit of said polyester was extruded from a spinneret of 280° C. and taken up at a rate of 1,000 m./min. The other procedures were the same as in Example 4. There was obtained an undrawn yarn having a birefringence of 0.0067. This yarn was drawn 1.75× on a hot pin of 80° C. and successively shrunk 10% on a metal plate having a surface temperature of 180° C., and further drawn 1.16× at 240° C. The minimum draw ratio in this example was 1.50×. The obtained fiber had a dye absorption of 91%,a tenacity of 1.91 g./d. and an elongation of 24.3%.

The fiber obtained by drawing the said undrawn filament 1.75× at 80° C. and thereafter heating it under a state of free shrinkage at 145° C. for 20 minutes showed a dye absorption of 92%, a tenacity of 1.13 g./d. and an elongation of 60%.

EXAMPLE 8

Polyethylene terephthalate chip having an intrinsic viscosity of 0.65 was extruded from a spinneret having orifices of 0.24 mm.$\phi$ x 48 holes and having a temperature of 275° C. into the air at room temperature, and thereafter taken up at a rate of 750 m./min. There was obtained a 6.0 denier per filament undrawn yarn having a birefringence of 0.0024. This yarn was drawn 3.45× in a bath of 90° C. and heated under a state of free shrinkage for 20 minutes at 145° C. The resulting fiber had a dye absorption of 58%, a tenacity of 4.35 g./d. and an elongation of 56.5%. The minimum draw ratio under this condition was 3.25.

EXAMPLE 9

The same chip as used in Example 8 was spun at a rate of 2,500 m./min. Using the same quenching chimney as in Example 4, the filaments are quenched by air which was blown at a linear speed of 85 m./min. There was obtained a 6.0 denier per filament undrawn yarn having a birefringence of 0.0289. This yarn was drawn 1.10× in a bath of 85° C., and heated under a state of free shrinkage for 20 minutes at 145° C. The resulting fiber had a dye absorption of 65%, a tenacity of 5.25 g./d. and an elongation of 26.8%. The minimum draw ratio under this condition was 1.10×.

EXAMPLE 10

The fiber of Example 4 obtained by drawing 2.2× and the fiber obtained in Example 8 were dyed for 90 minutes at 105° C. and 125° C., respectively. Both of the dyed fibers showed a dye absorption of 88–89%. These dyed fibers were treated for 60 minutes in a boiling water at a bath ratio of 1:500. The degree of light absorption of the residual liquor was determined by means of a photocolouring meter (wave length being 500 m$\mu$) and the

dye desorption was calculated. It was found that the former fiber had a dye desorption of 8.5% and the latter, 19.5%.

Both fibers were subjected creep for 4 hours by exerting to a load of 1 g./d., and their strains and the residual strains after removal of the load in 4 hours were determined at a temperature of 20, 50, 70 and 100° C. The results are shown below.

| | Example 4 | | Example 8 | |
|---|---|---|---|---|
| Temperature (° C.) at determination | Creep strain, percent | Residual strain, percent | Creep strain, percent | Residual strain, percent |
| 20 | 3.0 | 1.3 | 3.2 | 1.4 |
| 50 | 3.6 | 1.7 | 4.7 | 1.9 |
| 70 | 3.7 | 1.7 | 5.8 | 3.6 |
| 100 | 4.8 | 2.0 | 8.8 | 6.1 |

Both fibers were spun to make spun yarns having 30 counts and number of twists of 550 turn/m. From these, plain fabrics having a warp density of 45 cm. and a weft density of 48 cm. were prepared. These fabrics were subjected to a pilling test on a ICI type pilling tester. It was found that the pilling resistance of the fabric obtained from the fiber of Example 4 was Grade 4.5, and that of the fabric obtained from the fiber of Example 8 was Grade 1.5.

We claim:

**1.** Process for the manufacture of polyester synthetic fibers having improved dyeability and yarn characteristics which comprises the steps of (1) drawing and undrawn yarn composed of terephthalate polyester and having a birefringence of 0.0050–0.0250, at a temperature of 55–95° C. to about 1.5–2.2 times its original length and at a draw ratio ranging from the minimum draw ratio of said undrawn yarn to a draw ratio about 0.5 higher than this; (2) heat-treating the said yarn under a shrinkage of about 5–60% at a temperature of 100–220° C.; and (3) thereafter re-drawing said heat-treated yarn at a temperature of not less than about 160° C. to not less than about 1.16 times the length of said heat-treated yarn.

**2.** The process in accordance with claim **1** wherein the undrawn yarn has a birefringence of 0.0080–0.0200.

**3.** The process in accordance with claim **1** wherein the undrawn yarn is drawn at a temperature of 60–70° C.

**4.** The process in accordance with claim **1** wherein the undrawn yarn is drawn at a draw ratio ranging from the minimum draw ratio of the said undrawn yarn to a ratio about 0.3 higher than this.

**5.** The process in accordance with claim **1** wherein the drawn yarn is heat treated at a temperature of 130–180° C.

**6.** The process in accordance with claim **1** wherein the terephthalate polyester is polyethylene terephthalate.

**7.** The process of claim **1** wherein the heat-treated yarns are re-drawn at a temperature of from 160 to 240° C.

**8.** The process of claim **1** wherein the re-drawing is conducted so that the heat-treated yarn is drawn from about 1.16 to 1.3 times its length.

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