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PROCESS FOR MELT SPINNING POLYESTERS CONTAINING AN ALKALINE EARTH SULFATE FILLER

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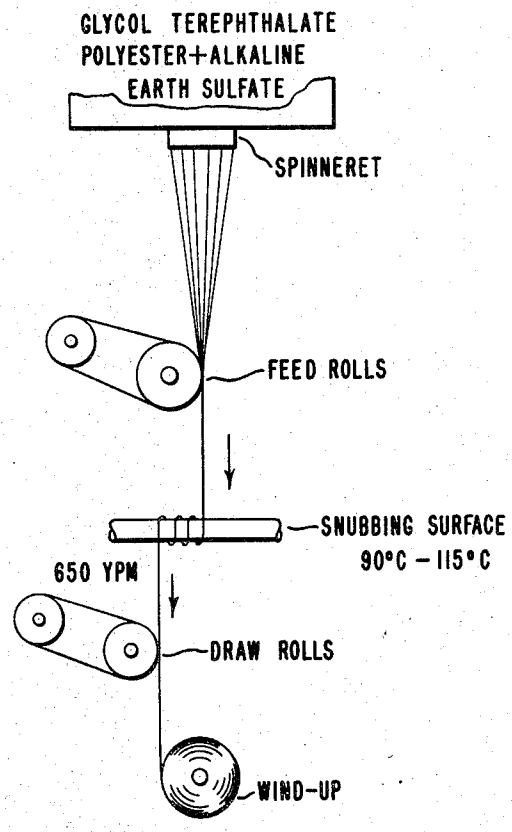

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PROCESS FOR MELT SPINNING POLYESTERS CONTAINING AN ALKALINE EARTH SULFATE FILLER

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10 Claims. (Cl. 18—54)

This invention relates to the rapid production of linear terephthalate polyester yarns, and particularly to the drawing of both delustered and undelustered polyethylene terephthalate yarns at high rates of speed.

The production of highly useful fibers composed of polyethylene terephthalate, including the steps of preparing the polymer, melt-spinning the polymer to form substantially unoriented filaments, and drawing the filaments to a permanent increase in length to yield tenacious oriented filaments, is disclosed in U.S. Patent 2,465,319 to Whinfield and Dickson. For commercial purposes it is desirable to draw at as high a rate of speed as possible, consistent with good quality of yarn. Various expedients have been attempted to increase the rate of drawing, such as drawing the yarn over heated pins and adopting multistage drawing processes. The addition of inert material to the yarn in small quantities (up to 0.05% or 0.1%) is known to decrease the breakage of filaments during drawing as shown in U.S. Patent 2,385,890 to Spanagel.

It has been found that there is a practical limit to the rate of drawing solid, unoriented linear terephthalate polyester yarns above which the drawing begins to proceed in an irregular fashion such that the drawn yarn contains randomly spaced sections of thick, unoriented yarn. In other words, sections of the undrawn yarn simply pass over the draw roll at high speed without becoming oriented. The presence of such unoriented segments in the yarn is highly undesirable, since these segments have greater affinity for dyes than the oriented yarn and show up in dyed fabrics as deeply-dyed flecks. For unmodified polyethylene terephthalate yarns drawn over a heated pin the practical limit of drawing speed has been found to be only about 200 yards per minute. Although this limit can be increased by incorporating various inert materials in the yarn, it has been believed hitherto that the upper practical limit is about 650 yards per minute. Moreover, since these inert additives are usually delusterants for the yarn, it has been possible hitherto to draw at speeds approaching 650 yards per minute only in the case of highly delustered yarns. In drawing undelustered and semi-delustered yarns, the limit for the speed of drawing has been considerably lower.

It is an object of this invention to provide a process for producing undelustered, oriented linear terephthalate polyester yarns from substantially unoriented linear terephthalate polyester yarns at high rates of speed. An additional object of the invention is to provide a process for producing delustered, oriented linear terephthalate polyester yarns from substantially unoriented linear terephthalate polyester yarns at high rates of speed. Other objects will be apparent from the following description and claims.

The foregoing objects are realized by the present invention, in which a molten composition comprising a linear terephthalate polyester and at least about 1% of a finely-divided alkaline earth metal sulfate is melt spun

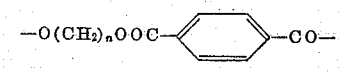
to provide a substantially unoriented filamentous structure; following which said structure is drawn over a snubbing surface heated at from about 90° to about 115° C. at a rate of at least about 650 yards per minute. The product is an undelustered, uniformly oriented yarn. Such yarns are used for a variety of purposes, such as in the preparation of certain fabrics and nets, as stuffing materials, and for other purposes.

In a preferred embodiment of the invention, a molten composition comprising a linear terephthalate polyester, at least about 1% of a finely divided alkaline earth metal sulfate, and at least about 0.3% of a finely-divided, inert delustering material is melt spun to provide a substantially unoriented filamentous structure; following which said structure is drawn over a snubbing surface heated at from about 90° to about 115° C. at a rate of at least about 650 yards per minute. The product is a delustered, uniformly oriented yarn. Such delustered yarns are highly desired for preparation of fabrics for apparel use as well as for many other uses.

Surprisingly, it has been found that a composition containing a linear terephthalate polyester and at least about 1% alkaline earth metal sulfate can be spun into an unoriented fiber which can be drawn at very high rates of speed, up to 1500 yards per minute or even higher. Moreover, the yarns so produced are undelustered even when 10% or even 15% of the weight of the yarn consists of the alkaline earth metal sulfate. It has also been found that other finely-divided inert materials can be added to the composition to deluster the yarn without interfering with the ability of the composition to be drawn at high rates of speed. However, a linear terephthalate polyester composition containing other common additives, such as titanium dioxide or aluminum oxide, cannot be drawn rapidly if the alkaline earth metal sulfate is not present in a concentration of at least about 1%.

The expression "alkaline earth metal sulfate" is used herein to denote the class of compounds consisting of barium sulfate, calcium sulfate, and strontium sulfate.

By "linear terephthalate polyesters" is meant linear polyesters in which at least 85% of the recurring structural units are units of the formula



wherein n represents an integer within the range of 2 to 10. In a preferred embodiment of the invention, n is equal to 2, that is, the yarns are prepared from polyethylene terephthalate or copolyesters thereof

Reference herein to the "rate" at which yarn is drawn is to the velocity of the yarn after it has been drawn, i.e., to the speed at which the yarn leaves the heated surface over which it is drawn. The speed of the yarn before it has been drawn is less than the speed atfer it has been drawn by a factor equivalent to the draw ratio.

In examining the various yarns for the presence of segments of unoriented filaments, the method employed is to dye fabrics prepared from the yarns with Celanthrene Brilliant Blue FFS dye (C.I. No. 61505). Undrawn segments are readily observed in the dyed fabrics as flecks much deeper in color than the remainder of the fabric.

The luster of the various yarns is determined by preparing a 124-sley, 96-pick filling face satin fabric from the yarn and inserting a sample of the fabric into a slot midway along the length of a 60-inch polished metal tube 3 inches in diameter. A standard microscope lamp is placed at one end of the tube and the amount of light passing through the fabric is determined photometrically (Welch "Densichron" with blue-sensitive photocell).

The photometer readings reported in the examples below may be related to the luster of the yarns as follows:

Numerical Value of Luster	Appearance of Fabric
Below about 35	Somewhat translucent; "bright", undelustered.
About 35 to about 55	Slightly translucent; "semi-dull"; semi-delustered.
Above about 55	Opaque; "dull"; delustered.

The intrinsic viscosity of the polymer, a measure of the degree of polymerization, is determined in dilute solutions of the polymer in Fomal, which comprises 58.8 parts by weight of phenol and 41.2 parts by weight of trichlorophenol.

In the drawing, the single figure represents a diagrammatic arrangement of the apparatus used to carry out the process of the present invention. The legends on the drawing make it self-explanatory.

The following examples are given to illustrate the invention. Examples I, II, V, and VI (in part) show conditions which produce uneven dyeing; whereas Examples III, IV, VI and VII show how this is overcome by the addition of an alkaline earth metal sulfate to the polymer before spinning.

EXAMPLE I

Polyethylene terephthalate, prepared from dimethyl terephthalate and ethylene glycol in accordance with the ester interchange and polymerization procedure described in U.S. Patent 2,465,319 and having an intrinsic viscosity of 0.59, is spun at 285° C. through a 34-hole spinneret at 1206 yards per minute to obtain a 242-denier yarn. A cross-flow cooling chimney, of the type shown in U.S. Patent 2,273,105, is employed, the air flow maintained in the chimney being at the rate of 125 cubic feet per minute.

Samples of the above yarn are withdrawn from feed rolls at the rate of 57 yards per minute, passed twice around a draw pin 1.6 inches in diameter maintained at a temperature in the range 105–110° C., drawn at the rate of 200 yards per minute around a draw roll, and finally wound up on a yarn package. The draw ratio is accordingly 3.5. The yarn has a tenacity of 5.0 grams per denier and an elongation of 24%; it is a bright yarn, having a luster of numerical value 10 as measured by the metthod described above. Examination of samples of dyed fabric reveals that this yarn is substantially free of unoriented yarn segments; however, yarn drawn at the rate of 250 yards per minute at the same draw ratio is found to exhibit numerous dark-dyed defects in the dyed fabric.

EXAMPLE II

The experiment of Example I is repeated, except that 0.1% by weight of titanium dioxide having an average particle size of about 0.3 micron is added to the reaction mixture just prior to polymerization. Yarn spun from this polymer is withdrawn from feed rolls at the rate of 129.5 yards per minute, passed twice around a drawn pin maintained at 105–110° C., and drawn and wound up at the rate of 454 yards per minute. The draw ratio is accordingly 3.5. The yarn has a tenacity of 4.7 grams per denier, an elongation of 24%, and exhibits a luster of numerical value 38 (borderline between bright and semi-dull). Although this yarn is found to be substantially free of unoriented yarn segments, it is found that yarn drawn at the same draw ratio at the rate of about 500 yards per minute and above exhibits numerous segments of unoriented yarn.

The experiment is repeated with polymer containing 0.3% by weight of titanium dioxide. The maximum operable rate of uniform drawing with this yarn is obtained at a withdrawal speed of 155.5 yards per minute and a wind-up speed of 545 yards per minute, the draw ratio being 3.5. The yarn has a tenacity of 4.5 grams per denier and an elongation of 24%; it is a semi-dull yarn, having a luster of numerical value 44. When this yarn is drawn at speeds of 600 yards per minute and higher at the same draw ratio, the yarn is no longer free of unoriented yarn segments.

The experiment is repeated with polymer containing 2.0% by weight of titanium dioxide. The maximum operable rate of drawing obtained with this yarn is achieved at a withdrawal rate of 172.5 yards per minute and a wind-up speed of 604 yards per minute, the draw ratio being 3.5. This yarn has a tenacity of 4.2 grams per denier, an elongation of 24%, and is a dull yarn having a photometrically-obtained luster value of 58. Although this yarn is free of unoriented yarn segments, such segments appear in the yarn when the drawing is conducted at speeds of about 650 yards per minute and higher at the same draw ratio.

EXAMPLE III

The experiment of Example I is repeated, except that 2.0% by weight of barium sulfate having an average particle size of 0.1–2.0 microns is added to the reaction mixture just prior to polymerization. It is found that yarn spun from this polymer can be withdrawn at 257 yards per minute and wound up at 900 yards per minute with no evidence of dark-dyed defects in dyed fabric prepared from the yarn. The draw ratio is 3.5. The yarn is a bright yarn, having a luster of numerical value 10. It has a tenacity of 3.3 grams per denier and an elongation of 22%.

The experiment is repeated using 0.3% by weight of titanium dioxide in addition to 2.0% barium sulfate added prior to polymerization. This yarn also can be drawn at 900 yards per minute at a draw ratio of 3.5 with no evidence of unoriented yarn segments in the drawn yarn. The yarn is semi-dull, having a luster of numerical value of 44, and it has a tenacity of 3.5 grams per denier and an elongation of 22%.

Similarly, yarn containing 2.0% by weight of titanium dioxide as well as 2.0% barium sulfate draws readily at 900 yards per minute at a draw ratio of 3.5 without obtaining unoriented yarn segments in the finished yarn. This yarn has a tenacity of 3.2 grams per denier, an elongation of 24%, and a luster of numerical value 60.

In another series of experiments, polyethylene terephthalate having an intrinsic viscosity of 0.57 and containing 2.0% by weight of barium sulfate having an average particle size of 0.1–2.0 microns is spun under the conditions described in Example I to obtain a 34-filament, 240-denier yarn. In a series of drawing experiments summarized in Table I, samples of the yarn are withdrawn from feed rolls at the indicated rate, passed twice around a draw pin 1.6 inches in diameter maintained at a temperature in the range 102–108° C., drawn at the indicated rate around a draw roll, and finally wound up on a yarn package. The draw ratio is indicated in each case, together with the tenacity and elongation values obtained with each yarn. In each case the yarns are bright, having a luster of numerical value 10 as measured by the method described above. Fabrics prepared from the yarns, when dyed, are found in each case to be free from dark-dyed defects.

Table 1

Speed at Feed Roll (y.p.m.)	Speed at Draw Roll (y.p.m.)	Draw Ratio	Yarn Properties		
			Tenacity (g.p.d.)	Elongation (Percent)	Luster
313	1,100	3.51	4.7	35	10
333	1,100	3.30	4.2	42	10
455	1,500	3.30	4.2	43	10

EXAMPLE IV

The experiment of Example I is repeated, except that

2.0% by weight of calcium sulfate is added to the reaction mixture prior to polymerization. Yarn spun from this polymer under the conditions given in Example I is withdrawn readily at a rate of 257 yards per minute from the feed rolls, passed twice around a draw pin maintained at 105–110° C., drawn at 900 yards per minute around a draw roll, and wound up. The draw ratio is 3.5. The yarn so produced is a bright yarn, as shown by its luster of numerical value 12. The yarn has a tenacity of 3.5 grams per denier and an elongation of 25%. The dyed fabric exhibits no dark-dyed defects.

In another experiment, polyethylene terephthalate having an intrinsic viscosity of 0.56 and containing 2.0% by weight of strontium sulfate and 0.3% by weight of titanium dioxide is spun under the conditions described in Example I to obtain a 34-filament, 259-denier yarn. Samples of the yarn are withdrawn readily at a rate of 250 yards per minute from feed rolls, passed twice around a draw pin maintained at 105–110° C., drawn at 900 yards per minute around a draw roll, and wound up. The draw ratio is 3.6. The yarn so produced is a semi-dull yarn, having a luster of numerical value 44. The yarn has a tenacity of 3.6 grams per denier and an elongation of 26.4%. Fabrics prepared from the yarn, when dyed, exhibit no dark-dyed defects. Similar results are obtained starting with polymer containing 2.0% by weight of strontium sulfate, but no titanium dioxide; except that the luster of the yarns so prepared has a numerical value of only 12.

EXAMPLE V

The experiment of Example I is repeated, except that 1.0% by weight of aluminum oxide and 0.3% by weight of titanium dioxide is added to the reaction mixture prior to polymerization. Yarn spun from this polymer under the conditions given in Example I is withdrawn from the feed rolls at the rate of 172.5 yards per minute, passed twice around a draw pin maintained at 105–110° C., drawn at the rate of 604 yards per minute around the draw roll, and wound up. The draw ratio is 3.5. The yarn has a tenacity of 3.0 grams per denier, an elongation of 23%, and a luster of numerical value 44. The dyed fabrics prepared from this yarn exhibit no unoriented yarn segments; however, when the yarn is drawn at about 650 yards per minute and above at the same draw ratio, dark-dyed defects are observed in the dyed fabrics.

It is essential for the purposes of this invention that at least about 1% alkaline earth metal sulfate be present in the polyethylene terephthalate. Optimum improvement in the rate of drawability of the yarn is achieved when about 1.5% or more of the additive is present. The following example illustrates the drawing performance of yarn containing lower amounts of barium sulfate.

EXAMPLE VI

The experiment of Example I is repeated, except that 0.5% by weight of barium sulfate and 0.3% by weight of titanium dioxide are added to the reaction mixture prior to polymerization. Yarns spun from this polymer under the conditions given in Example I are withdrawn readily at a rate of 186 yards per minute from the feed rolls, passed twice around a draw pin maintained at 105–110° C., drawn at the rate of 650 yards per minute around the draw roll, and wound up. The draw ratio is 3.5. The yarn has a tenacity of 3.5 grams per denier, an elongation of 24%, and a luster of numerical value 39. The dyed fabric is free from dark-dyed defects; however, when the rate of drawing is increased to 750 yards per minute at the same draw ratio, the appearance of dark-dyed defects in the fabric is noted.

The experiment is repeated using 1.0% by weight of barium sulfate in the polymer as well as 0.3% of titanium dioxide. The yarn is withdrawn from the feed rolls at a rate of 214 yards per minute and wound up at 750 yards per minute, the draw ratio being 3.5. The yarn has a tenacity of 3.8 grams per denier, an elongation of 25%, and a luster of numerical value 39. The fabric prepared from this yarn is free of dark-dyed defects. However, such defects appear when the yarn is drawn at the rate of 900 yards per minute.

As indicated by the above example, the minimum concentration of alkaline earth metal sulfate which must be present in the polymer to facilitate rapid drawing is of the order of at least about 1%. The upper limit is less definite. In general, it will be noted that the tenacity of the yarn will be lowered if large amounts of the alkaline earth metal sulfate are present in the polymer. Quantities of up to about 15% of the alkaline earth metal sulfate incorporated into the yarn still facilitate drawing at high speed, although with such a high concentration of filler the tenacity of the yarn is markedly reduced.

EXAMPLE VII

The experiment of Example I is repeated, except that 10% by weight of barium sulfate is added to the reaction mixture prior to polymerization. Yarn spun from this polymer under the conditions given in Example I is withdrawn at a rate of 257 yards per minute from the feed rolls, passed twice around a draw pin maintained at 105–110° C., and wound up at 900 yards per minute The draw ratio is 3.5. The yarn has a tenacity of 2.7 grams per denier, an elongation of 22%, and a luster of numerical value 18.

Finely-divided alkaline earth metal sulfates are preferred. Usually it will be desirable to avoid materials having an average particle size greater than about 2 microns in diameter. Barium sulfate, calcium sulfate, and strontium sulfate having an average particle size of about 100 millimicrons give excellent performance.

In drawing polyethylene terephthalate yarns at high speed in accordance with the invention, the yarn is passed over a heated snubbing surface while the drawing step is taking place. Usually the heated snubbing surface is a draw pin, i.e., a cylinder which may vary in diameter from a fraction of an inch to several inches. However, curved plates or other snubbing surfaces equivalent to a draw pin may be used. The temperature should be at least 90° C., and preferably a temperature in the range 100–110° C. will be employed. Temperatures higher than 115° C. will usually be avoided owing to difficulties in keeping the yarn from sticking on the heated surface.

The draw ratio applied to the yarn will vary depending on the orientation introduced into the yarn during spinning. Yarns spun at speeds up to about 1400 yards per minute are usually substantially unoriented, i.e., having a birefringence no higher than about 0.015. Such yarns will usually be drawn at a draw ratio of the order of about 3.5. If the draw ratio is set at too low a value, segments of the yarn will begin to pass by the draw roll without having become oriented. On the other hand, if too high a draw ratio is applied, the yarn will simply break down; for this reason, it is not possible to eliminate the occurrence of unoriented segments in the yarns drawn under the high-speed conditions stated in Examples I, II, V, and VI by increasing the draw ratio.

Yarns spun at higher spinning speeds may receive a considerable orientation in the spinning step alone. In such cases, the draw ratio required will be correspondingly lower. The present invention is intended to include the spinning of a molten polymer containing at least about 1% by weight of an alkaline earth metal sulfate into any filamentous structure which lacks orientation to a sufficient extent that further orientation is required, followed by drawing the structure at a rate of at least about 650 yards per minute.

Although the invention has been particularly described with respect to the drawing of polyethylene terephthalate yarns, it should be understood that the invention is fully

applicable to the drawing of yarns of modified polyethylene terephthalate or other linear terephthalate polyesters. The preferred polymer is a synthetic linear condensation polyester in which at least about 85% of the recurring structural units are ethylene terephthalate units. Up to 15% of the recurring structural units in the synthetic linear condensation polyester may be units derived from other dicarboxylic acids or other glycols. For example, the polymer may be prepared by reacting ethylene glycol with a mixture of 85 mol percent dimethyl terephthalate and 15 mol percent of diethyl sebacate, dimethyl isophthalate, or sodium 3,5-dicarbomethoxybenzenesulfonate. Similarly, the polymer may be prepared from dimethyl terephthalate and a mixture of 85 mol percent ethylene glycol and 15 mol percent butylene glycol or hexamethylene glycol.

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 producing oriented yarns which comprises melt spinning a composition comprising a linear terephthalate polyester and at least about 1% by weight of a finely-divided alkaline earth metal sulfate to produce filaments and thereafter drawing the said filaments over a snubbing surface heated to a temperature of between about 90° C. and about 115° C. at a rate of at least 650 yards per minute.

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

3. The process of claim 1 in which the alkaline earth metal sulfate is calcium sulfate.

4. The process of claim 1 in which the alkaline earth metal sulfate is barium sulfate.

5. The process of claim 1 in which the alkaline earth metal sulfate is strontium sulfate.

6. The process of claim 1 in which the said sulfate is present in the amount of at least about 1.5%.

7. The process of claim 1 in which the filaments are drawn to a draw ratio of about 3.5.

8. The process of claim 1 in which the average particle size of the sulfate is less than about 2 microns.

9. The process of producing oriented, delustered yarns which comprises melt spinning a composition comprising a linear terephthalate polyester, at least about 1% by weight of a finely-divided alkaline earth metal sulfate, and a finely-divided, inert delustering agent to produce filaments and thereafter drawing the said filaments over a snubbing surface heated to a temperature of between about 90° C. and about 115° C. at a rate of at least 650 yards per minute.

10. The process of claim 9 in which the said composition contains at least about 0.3% of the said delustering agent.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,924,503 February 9, 1960

Cecil E. Reese

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 2, line 7, for "certain" read -- curtain --; line 54, for "atfer" read -- after --; column 3, line 47, for "metthod" read -- method --.

Signed and sealed this 23rd day of August 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents