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(54) Improved high speed process for forming fully drawn polyester yarn.

(57) An improved process is provided for producing fully drawn multifilamentary polyethylene terephthalate yarn via a high speed melt spinning process wherein the multifilamentary material following solidification is passed through a heated conditioning zone wherein substantial crystallisation takes place. Such multifilamentary product is withdrawn from the conditioning zone at a speed in excess of 8000 feet (2438 m) per minute and a conventional drawing step is not required. In accordance with the concept of the present invention it surprisingly has been found that the uniformity of the multifilamentary product is enhanced by the inclusion of a minor substantially uniformly dispersed concentration of particulate silicon dioxide (e.g. fumed silica) in the molten polyethylene terephthalate polymer prior to extrusion and such subsequent processing. In a particularly preferred embodiment the particulate silicon dioxide is substantially uniformly dispersed within the polyethylene terephthalate as a result of its prior admixture with the reactants which were polymerised to form the polyethylene terephthalate.

Croydon Printing Company Ltd.

IMPROVED HIGH SPEED PROCESS FOR FORMING FULLY DRAWN POLYESTER YARN

The invention relates to a process for the production of a highly spin oriented polyethylene terephthalate yarn.

Polyethylene terephthalate multifilamentary yarns have been produced in the prior art under a variety of conditions. For instance, in much of the prior art polyester filaments have been melt extruded, quenched, and taken up at relatively low speeds under relatively low stress conditions. Such filaments must be subsequently drawn in a separate processing step at an elevated temperature in order to produce a fully drawn yarn which possesses tensile properties satisfactory for commercial use (e.g. as textile fibres). In some instances particulate materials including titanium dioxide and silicon dioxide have been included in polyethylene terephthalate fibres and films of the prior art.

More recently it has been disclosed that polyethylene terephthalate fibres possessing fully drawn properties may be prepared in the absence of a conventional drawing step by passing the filaments immediately following quenching through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature and below the melting temperature thereof and withdrawing the same at a relatively high speed. While passing through the conditioning zone substantial crystallisation of the previously solidified filamentary material takes place. Such processing conditions offer the significant advantage of eliminating the time and equipment requirements associated with a subsequent conventional drawing step. See particularly United States Patents 3,946,100, 4,195,161 and 4,246,747. See also Swiss Patent 530,479, German Offenlegungschrift 2,117,659 and Netherland Patent Application 7204536. In some instances in the prior art, particulate material such as titanium dioxide has been included in fibres formed by such high speed spinning. As is known in the prior art, such titanium dioxide particles impart a semi-dull or dull appearance to the resulting filaments.

When forming a fully drawn polyethylene terephthalate multifilamentary yarn product by a high speed spinning process which utilises a conditioning tube, some non-uniformity may be observed upon a careful inspection of the resulting multifilamentary product. Such non-uniformity may manifest itself by random thick filament sections wherein a filament (or filaments) within the multifilamentary yarn has undergone a lesser level of drawing. Upon subsequent dyeing such filaments of increased thickness will tend to absorb a greater quantity of dye and this greater dye absorption may be visually apparent as darker streak areas in fabric which includes such filaments. Also, the overall dye uptake variability as measured by the standard deviation from the mean may be greater than desired. In the prior art it has been observed that such non-uniformity is more apt to occur if the multifilamentary material is of a greater total denier (e.g. a total denier above 40) and/or if titanium dioxide particles are not present in the polyethylene terephthalate polymer at the time of melt spinning.

The present invention provides an improved high speed process for forming a fully drawn polyethylene terephthalate yarn.

It has been found, in a process for the formation of a highly spin oriented polyethylene terephthalate yarn comprising (a) extruding molten fibre-forming polyethylene terephthalate through a plurality of orifices to form a molten multifilamentary material, (b) passing the molten multifilamentary material in the direction of its length through a solidification zone provided with a gaseous atmosphere at a temperature below the glass transition temperature thereof wherein the multifilamentary material is quenched and is transformed to a solid multifilamentary material, (c) passing the resulting multifilamentary material in the direction of its length through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature thereof and below the melting temperature thereof wherein substantial crystallisation of the previously solidified multifilamentary material takes place, and (d) withdrawing the resulting multifilamentary material from the conditioning zone at a speed in excess of 8000 feet (2438 metres) per minute; that improved results are achieved by substantially uniformly dispersing within the fibre-forming polyethylene terephthalate prior to step (a) 0.05 to 1.5 percent by weight of particulate silicon dioxide having a weight average particle size of less than 1 micron which serves to enhance the uniformity of the filaments which compose the resulting multifilamentary material.

A particularly preferred embodiment of the improved process for the formation of a highly spin oriented polyethylene terephthalate yarn in accordance with the concept of the present invention comprises:

(a) polymerising monomers capable of forming polyethylene terephthalate while in admixture with particulate fumed silica having a nominal particle size of less than 0.1 micron as determined by the BET method to form a fibre-forming polymer having an intrinsic viscosity of 0.5 to 0.8 determined with a solution of 0.1 gram of the polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C.,

(b) extruding the resulting polyethylene terephthalate while in molten form and containing 0.1 to 1.0 percent by weight of the particulate fumed silica introduced in step (a) substantially uniformly dispersed therein through a plurality of orifices to form a molten multifilamentary material,

(c) passing the molten multifilamentary material in the direction of its length through a solidification zone provided with a gaseous atmosphere at a temperature below the glass transition temperature thereof wherein the multifilamentary material is quenched and is transformed to a solid multifilamentary material.

(d) passing the resulting multifilamentary material in the direction of its length through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature thereof and below the melting temperature thereof wherein the substantial crystallisation of the previously solidified multifilamentary material takes place, and

(e) withdrawing the resulting multifilamentary material from the conditioning zone at a speed in excess of 8,000 feet (2438 metres) per minute up to 16,000 feet (4877 metres) per minute,

with the presence of the particulate fumed silica serving to enhance the uniformity of the filaments which compose the resulting multifilamentary material.

The present invention provides a number of surprising advantages, among which are the following:

The present invention provides an improved high speed process for forming a fully drawn polyethylene terephthalate yarn in which the uniformity of the filaments therein is enhanced.

The present invention provides an improved high speed process for forming a fully drawn polyethylene terephthalate yarn wherein each filaments present within the yarn possesses a more constant thickness along its length and is capable of exhibiting less dye uptake variability than commonly observed in the prior art.

The present invention provides an improved high speed process for forming a fully drawn polyethylene terephthalate multifilamentary yarn of enhanced uniformity which is suitable for use in forming yarns having either high or low total denier and with or without the presence of a titanium dioxide delust

The present invention provides an improved high speed process for forming a lustrous multifilamentary polyethylene terephthalate yarn of enhanced uniformity having a total denier of approximately 40 and which lacks the presence of particulate titanium dioxide dispersed therein.

The present invention provides an improved high speed process for forming a multifilamentary polyethylene terephthalate yarn in which the susceptibility of the polymer to thermal and oxidative degradation is diminished.

These and other advantages of this invention will be further apparent from the following additional description of the process of the invention.

The Starting Material

The starting material selected for use in the process of the present invention is principally fibre-forming polyethylene terephthalate which has substantially uniformly dispersed therein a minor concentration of finely divided particulate silicon dioxide which surprisingly has been found to enhance the uniformity of the multifilamentary yarn which is formed under the conditions described herein.

The polymer which is selected for use in the process contains at least 85 mole percent of polyethylene terephthalate and preferably at least 90 mole percent polyethylene terephthalate. Accordingly, the term "polyethylene terephthalate" as used in the present description may optionally include minor amounts of other ester-forming ingredients which may be copolymerised with the dominant polyethylene terephthalate units. Illustrative examples of other ester-forming ingredients which may be copolymerised with the polyethylene terephthalate units include glycols (such as diethylene glycol, tetramethylene glycol and hexamethylene glycol) and dicarboxylic acids (such as hexahydroterephthalic acid, bibenzoic acid, adipic acid, sebacic acid and azelaic acid). In a particularly preferred embodiment of the process the polymer employed is substantially all polyethylene terephthalate.

The polyethylene terephthalate which is selected for use in the improved process of the present invention preferably exhibits an intrinsic viscosity, i.e. I.V., of 0.35 to 1.0, and most preferably 0.5 to 0.8 (e.g. approximately 0.7) determined with a solution of 0.1 gram of the polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C. The I.V. of the melt-spinnable polyethylene terephthalate may be conveniently determined by the equation

$$\lim_{c \to 0} \frac{\ln \eta r}{c}$$

where ηr is the "relative viscosity" obtained by dividing the viscosity of a dilute solution of the polymer by the viscosity of the solvent employed (measured at the same temperature), and c is the polymer concentration of the solution expressed in grams/100 ml. The polyethylene terephthalate when spun into fibres commonly exhibits a glass transition temperature of 75 to 80°C., and a melting point of 250 to 265°C. (e.g. approximately 260°C.) As will be apparent to those skilled in the art, the polymer melting point will be influenced by factors such as polymer modifications, the degree of orientation achieved and so on.

The finely divided silicon dioxide is substantially uniformly dispersed in the polyethylene terephthalate prior to extrusion in a concentration of 0.05 to 1.5 (e.g. 0.1 to 1.0) percent by weight. In a particularly preferred embodiment silicon dioxide is substantially uniformly dispersed in the polyethylene terephthalate in a concentration of 0.1 to 0.4 (e.g. 0.2 to 0.4) percent by weight. Such finely divided silicon dioxide exhibits a weight average particle size of less than 1 micron. Suitable particle size analysers for use when making such particle size determination are available from Micrometrics Instrument Corporation of Norcross, Georgia, and the Leeds and Northrup Corporation of Saint Petersburg, Florida (Microtrac particle size analyser).

The silicon dioxide particles may be obtained from a variety of sources and may be termed fumed silica, colloidal silica, precipitated silica, etc. In a preferred embodiment silicon dioxide particles are selected which have a substantial concentration of available silanol groups present upon their surfaces. A preferred silicon dioxide for use in the process of the present invention is fumed silica having a nominal particle size of less than 0.02 micron as determined by the BET method while assuming that the silicon dioxide particles are spherical in configuration. A representative particularly preferred example of such material is Cab-O-Sil fumed silica, Grade M-5, which is commercially available from the Cabot Corporation of Boston, Massachusetts. (Cab-O-Sil is a Trade Mark). Such particles possess an enormous surface area (e.g. 200 ± $25m^2$/gram), are covered with a substantial concentration of silanol groups and tend to assume a chain-like structure which may be broken up to some degree by shearing prior to use.

The particulate silicon dioxide may be substantially uniformly dispersed within the polyethylene terephthalate prior to the melt spinning thereof by any suitable blending technique commonly employed to introduce particulate materials into a melt-processable polymer. For instance, known melt compounding techniques using single screw extruders, co-rotating twin screw extruders, counter-rotating twin screw extruders or kneaders may be employed, provided the required substantially uniform disperal is achieved. If additional particulate material such as titanium dioxide is present, it too may be introduced by the same technique.

In a preferred embodiment the particulate silicon dioxide is intimately admixed with the reactants or monomers capable of forming polyethylene terephthalate prior to polymerisation and is present with such reactants while they are polymerised in accordance with conventional techniques. For instance, dimethylterephthalate and ethylene glycol may be reacted to form the polyethylene terephthalate. Alternatively, terephthalic acid and ethylene glycol may be the monomers employed during the polymerisation reaction.

Regardless of the manner in which the silicon dioxide particles become blended with the polyethylene terephthalate, it is believed that interaction inherently takes place between the silicon dioxide particles and the polymer which is beneficial during the course of the present process. The nature of this interaction is not fully understood and is considered to be complex and incapable of simple explanation. For instance, such interaction is believed to be more than simple hydrogen bonding, and beneficially alters the structural and spinning behaviour of the polymer when processed as described hereinafter.

It should be understood that the polyethylene terephthalate additionaly may contain various chemical and physical modifiers which are routinely provided in such polymer. For instance, small amounts of monomers may be included which serve as cationic dyeable polymer modifiers and/or other modifiers such as isophthalic acid or 5-sulphoisophthalic acid may be present. Polymer meeting the specified requirements may additionally or alternatively contain minor amounts of materials used in conventional yarns such as stabilisers (e.g. phosphorus-containing stabilisers), delustrants, optical brighteners, polymer modifiers and the like. In a preferred embodiment, when forming a semi-dull or dull multifilamentary product, 0.05 to 1.5 percent by weight of particulate titanium dioxide having a weight average particle size of less than 2 microns additionally are uniformly dipsersed in the polyethylene terephthalate as an additional ingredient.

The Melt Extrusion Step

The extrusion orifices may be selected from among those commonly utilised during the melt extrusion of polyethylene terephthalate by a high speed process to form a fully drawn multifilamentary yarn. The orifices may be provided in a variety of cross-sectional configurations so as to form substantially uniform filaments having different cross-sectional shapes. For instance, the orifices may be round, trilobal, etc. The spinneret selected will commonly have from 6 to 200 holes. Such holes when roundcommonly are 9 to 60 mils (0.229 to 1.52 mm) in diameter (e.g., 9 to 40 mils (0.229 or 1.02 mm))or the equivalent thereof if not round. Spinnerets preferably are selected having 20 to 48 holes.

The molten polyethylene terephthalate having the particulate silicon dioxide substantially uniformly dispersed therein is supplied to the extrusion orifices at a temperature above the melting point of the polyethylene terephthalate. For instance, such polymeric material will commonly be supplied to the extrusion orifices at a temperature of 270 to 310°C., and most preferably at a temperature of 280 to 300°C. (e.g. 282°C.) As the polyethylene terephthalate is extruded through the extrusion orifices, a molten multifilamentary material is formed.

The Solidification Step

Subsequent to extrusion through the extrusion orifices the resulting molten multifilamentary material is passed in the direction of its length through a solidification or quench zone provided with a gaseous atmosphere ata temperature below the glass transition temperature thereof wherein the molten filamentary material is transformed to a solid multifilamentary material. The gaseous atmosphere commonly is provided at a temperature below 75 to 80°C. Within the solidification zone the molten material passes from a melt to a semi-solid consistency, and from the semi-solid consistency to a solid consistency. While present in the solidification zone, the multifilamentary material undergoes substantial orientation while present as a semi-solid. The gaseous atmosphere present within the solidification zone preferably circulates so as to bring about more efficient heat transfer. In a preferred embodiment of the process the gaseous atmosphere of the solidification zone is provided at a temperature of 10 to 40°C., and most preferably at a temperature of 25 to 30°C. The chemical composition of the gaseous atmosphere is not critical to the operation of the process provided the gaseous atmosphere is not unduly reactive with the polyethylene terephthalate. In a particularly preferred embodiment of the process the gaseous atmosphere of the solidification zone is air. Other representative gaseous atmospheres which may be selected for use in the solidification zone include inert gases such as helium, argon, nitrogen, etc.

The gaseous atmosphere of the solidification zone preferably impinges upon the extruded polyethylene terephthalate so as to produce a substantially uniform quench. The uniformity of the quench may be demonstrated through the ability of the multifilamentary product to exhibit no substantial tendency to undergo self-crimping upon the application of heat. A flat multifilamentary yarn accordingly is produced in a preferred embodiment of the process.

The solidification zone is preferably disposed immediately below the extrusion orifices and the extruded polyethylene terephthalate is present while axially suspended therein for a residence time of 0.0008 to 0.4 second, and most preferably for a residence time of 0.033 to 0.14 second. Commonly the solidification zone possesses a length of 1 to 7 feet (0.30 to 2.13 m). A standard cross-flow quench may be employed. Alternatively, a centre flow quench or any other technique capable of bringing about the desired quenching may be utilised.

The Conditioning Step

Immediately following passage through the solidification zone the resulting multifilamentary material is passed in the direction of its length through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature thereof and below the melting temperature thereof wherein substantial crystallisation of the multifilamentary material takes place. As previously indicated, the glass transition temperature of the filaments will typicallybe 75 to 80°C. and the melting point of the polyethylene terephthalate commonly will be 250 to 265°C. (e.g., approximately 260°C.).

The gaseous atmosphere within the conditioning zone commonly is provided at a temperature within the range 90 to 200°C. (e.g. 135 to 220°C.), and the previously solidified multifilamentary material commonly is present therein for a residence time of 0.0001 to 0.8 second (e.g., 0.001 to 0.8 second). The optimum residence time required to produce substantial crystallisation may vary with exact composition of the polyethylene terephthalate involved. Longer residence times may commonly be used without commensurate advantage.

The chemical composition of the gaseous atmosphere provided within the conditioning zone is not critical to the operation of the process provided the gaseous atmosphere is not unduly reactive with the multifilamentary material. Static air conveniently may be selected. Other representative gaseous atmospheres which may be employed in the conditioning zone include helium, argon, nitrogen, etc. Band heaters or any other heating means may be provided which will maintain the conditioning zone at the required temperature. The conditioning zone commonly will have a length of 0.5 to 12 feet (0.152 to 3.66 m) and preferably a length of 3 to 12 feet (0.914 to 3.66 m).

As discussed in United States Patent 3,946,100, while present in the conditioning zone, the multifilamentary material is heat treated under constant tension. During this heat treatment, small amounts of thermally induced elongation may occur, but this process is to be differentiated from a conventional draw process because of the constant tension rather than the constant strain criterion. The level of tension on the multifilamentary material in the conditioning zone is important to the development of the desired properties and is primarily influenced by the rate of withdrawal from the conditioning zone. No stress isolation results along the multifilamentary material intermediate the extrusion orifices and the point of withdrawal from the conditioning zone (e.g., the multifilamentary material is axially suspended in absence of external stress isolating devices intermediate the spinneret and the point of withdrawal from the conditioning zone). Should one omit the passage of the multifilamentary material through the conditioning zone, the denier of the product commonly is found to be identical to that obtained while employing a conditioning zone.

As discussed in United States Patent 3,946,100 and 4,195,101, the passage of multfilamentary material through the conditioning zone modifies the internal morphology of the filaments and renders a subsequent conventional hot drawing step unnecessary. Accordingly, the multifilamentary product exhibits properties generally analogous to those of a fully drawn yarn.

The Withdrawal Step

The resulting multifilamentary material is withdrawn from the condtioning zone at a relatively high speed in excess of 8,000 feet (2438 m) per minute. Commonly, withdrawal speeds in excess of 8,000 feet (2438 m) per minute up to 16,000 feet (4877 m) per minute are selected (e.g., 11,000 to 13,000 feet (3353 to 3962 m) per minute). A representative technique for accomplishing the high speed withdrawal is to pass the multifilamentary material to pairs of godet rolls situated at the exit end of the conditioning zone prior to packaging. As will be apparent to those skilled in the art, a substantial drawdown will occur along the spinline while operating under such conditions.

The Improved Multifilamentary Product

It surprisingly has been found that the presence of the particulate silicon dioxide substantially uniformly dispersed within the polyethylene terephthalate prior to melt extrusion beneficially enhances the uniformity of the multifilamentary product formed in accordance with the overall process described herein. Such uniformity enhancement is possible regardless of whether particulate material other than silicon dioxide (e.g., a conventional titanium dioxide delustrant) is present therein.

The multifilamentary product of the present invention is particularly suited for use in textile applications and may be readily woven or knitted. Such multifilamentary polyethylene terephthalate product will commonly consist of

6 to 200 continuous filaments each having a substantially constant denier of 1 to 5.

The enhanced uniformity of the multifilamentary product is evidenced by an inspection of the individual filaments present therein under magnification. It is found that a more constant thickness or diameter along the length of individual filaments is observed. Accordingly, there is a lesser incidence of undesirable thick filament areas which were drawn to a lesser degree. Such thick areas are detrimental since they often tend to absorb dye more readily and can lead to darker streaks in a dyed textile product where they occur. Additionally, the mean deviation in overall dye uptake variability is lessened as a result of the improved process of the present invention. It further has been observed that the susceptibility of the polymer to thermal and oxidative degradation is diminished because of the presence of the silicon dioxide particles.

In a particularly preferred embodiment of the process of the present invention there is formed a lustrous multifilamentary yarn of enhanced uniformity having a total denier of approximately 40 and without having particulate titanium dioxide dispersed therein. In further preferred embodiments a semi-dull multifilamentary yarn of enhanced uniformity having a total denier of 20 to 200 (e.g., 40 to 150) is formed which also includes titanium dioxide particles dispersed therein.

The following Examples are presented as specific illustrations of the claimed invention. The invention is not, of course, limited to the specific details set forth in the Examples.

Example I

To a standard polymerisation charge used to form polyethylene terephthalate comprising dimethylterephthalate and ethylene glycol is added with mixing a quantity of Cab-O-Sil fumed silica, Grade M-5, commercially available from the Cabot Corporation of Boston, Massachusetts. No other solid particles such as titanium dioxide are introduced into the polymerisation vessel. The silicon dioxide particles as purchased possess a nominal particle size of 0.014 micron assuming a spherical configuration as determined by the BET method, and a surface area of 200 ± 25 m^2/gram, and are presheared by milling prior to introduction into the polymerisation vessel. The weight average particle size accordingly is well below 1 micron. The resulting polyethylene terephthalate exhibits an intrinsic viscosity of approximately 0.675 determined with a solution of 0.1 gram of polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C., and the silicon dioxide particles are substantially uniformly dispersed therein in a concentration 0.2 percent by weight.

The spinneret selected for melt extrusion possesses 30 trilobal orifices, each lobe having a maximum width of 0.005 inch (0.127 mm), a length of 0.009 inch (0.229 mm) measured from the centre point, and a depth of 0.018 inch (0.457 mm). Such trilobal orifices are equivalent in size to a 0.013 inch (0.330 mm) round extrusion hole. At a rate of 2.06 lbs./hr., (0.935 kg/hr.), the molten polyethylene terephthalate containing the silicon dioxide particles dispersed therein while at a temperature of 282°C. is extruded through the extrusion orifices to form a molten multifilamentary material. The apparatus arrangement selected generally corresponds to that illustrated in United States Patent 3,946,100.

The molten filamentary material passes downward in the direction of its length through a cross-flow quench zone having a length of approximately 3 feet (0.914 m) which is provided with flowing air at a temperature of approximately 30°C. While present in such quench zone, the molten multifilamentary material is uniformly quenched and is transformed to a solid multifilamentary material.

Situated immediately below the solidification zone is a conditioning zone having a length of approximately 3 feet (0.914 m) through which the multifilamentary material next passes in the direction of its length. The conditioning zone is a cylindrical tube into which heated air is introduced at the bottom. The air is present in the conditioning zone at a temperature above the glass transition temperature of the polyethylene terephthalate and below the melting temperature thereof. At the midpoint of the conditioning zone the temperature is approximately 155°C. Upon being withdrawn from the solidification zone the multifilamentary material is immediately passed through such conditioning zone where it is structurally modified as described in United States Patents 3,946,100 and 4,195,161 and substantial crystallisation takes place.

The resulting multifilamentary material is next withdrawn from the conditioning zone at a rate of approximately 11,500 feet (3505 m) per minute with the aid of godet rolls, has a finish applied thereto, is passed through a pneumatic intermingling jet to improve handleability and is packaged.

The resulting 30 filament multifilamentary yarn has a total denier of approximately 40, possesses a lustrous appearance and exhibits a tenacity of approximately 4.4 grams per denier at room temperature, an elongation of 55 to 60 percent at room temperature and a boiling water shrinkage of approximately 4.5 percent.

It further will be observed that the multifilamentary product exhibits enhanced uniformity when compared to a similarly prepared multifilamentary yarn wherein no silicon dioxide is added to the polyethylene terephthalate prior to melt extrusion. More specifically, the yarn prepared as described above as well as a control yarn may be knitted in a warp knit configuration and dyed with Eastman Blue 210 dye using jet dyeing in accordance with standard dyeing conditions and the uniformity of the dye uptake observed. Over a 100 foot (30.48 m) section of the dyed knitted fabric composed of the multifilamentary yarn formed in accordance with the present invention no streak areas will be observed where non-uniform filaments of increased thickness have adsorbed a greater quantity of the dye. On the contrary, a similarly prepared knitted fabric which lacks silicon dioxide particles dispersed therein will exhibit approximately 50 darkened streak areas where non-uniform filaments of increased thickness have absorbed a greater quantity of the dye.

Additionally, when fabrics are subjected to a load extension test, similar to the Dynafil test, in order to measure short term uptake, the fabric containing filaments formed in accordance with the present invention will exhibit reduced signal variability in grams of standard deviation from the mean. More specifically, the fabric of the present invention will exhibit a value of approximately 3.3, while the control which lacks silicon dioxide will exhibit a greater standard deviation from the mean of approximately 4.

It further is observed, when the multifilamentary yarn of the present invention is subjected to electronic spin resonance or differential scanning calorimetry analysis, that the polyethylene terephthalate of the yarn will have undergone a lesser degree of thermal degradation during melt processing when compared to the control which lacks silicon dioxide.

Example II

Example I is substantially repeated with the exceptions indicated.

To the standard polymerisation charge additionally is added finely divided titanium dioxide having a weight average particle size of approximately 1.06 micron. The titanium dioxide particles are substantially uniformly dispersed in the resulting polyethylene terephthalate in a concentration of 0.3 percent by weight.

The spinneret selected for the melt extrusion possesses 30 round orifices each having a diameter of 0.013 inch (0.330 mm) and a length of 0.018 inch (0.457 mm). The molten polymer containing the silicon dioxide particles dispersed therein is supplied to the spinneret at a rate of 3.6 lbs./hr. (1.63 kg/hr.). The resulting multifilamentary yarn product exhibits a total denier of approximately 70 and a semi-dull appearance.

Over a 100 foot (30.48 m) section of the dyed knitted fabric composed of the multifilamentary yarn formed in accordance with the present invention no streak areas will be observed. On the contrary a similarly prepared knitted fabric which lacks silicon dioxide particles dispersed therein will exhibit approximately 150 darkened streak areas where non-uniform filaments of increased thicknesses have absorbed a greater quantity of dye.

Additionally, when fabrics are subjected to a load extension test in order to measure short term dye uptake, the fabric containing filaments formed in accordance with the present invention will exhibit a reduced signal variability in grams of standard deviation from the mean of approximately 5.0, while the control which lacks silicon dioxide will exhibit a value of approximately 6.2.

Example III

Example I is substantially repeated with the exceptions indicated.

To the standard polymerisation charge additionally is added finely divided titanium dioxide having a weight average particle size of approximately 1.06 micron. The titanium dioxide particles are substantially uniformly dispersed in the resulting polyethylene terephthalate in a concentration of approximately 0.3 percent by weight.

The spinneret selected for the melt extrusion possesses 30 round orifices each having a diameter of 0.013 inch (0.330 mm) and a length of 0.018 inch (0.457 mm). The molten polyethylene terephthalate containing the silicon dioxide particles dispersed therein is supplied to the spinneret at a rate of 6.43 lbs./hr. (2.92 kg/hr.) It will be noted that this extrusion rate is greater than that employed in Example II. The resulting multifilamentary product exhibits a total denier of approximately 125 and a semi-dull appearance.

Over a 100 foot (30.48 m) section of the dyed knitted fabric composed of the multifilamentary yarn formed in accordance with the present invention approximately 5 darkened streak areas will be observed. On the contrary, a similarly prepared knitted fabric which lacks silicon dioxide particles dispersed therein will exhibit approximately 1000 darkened streak areas where non-uniform filaments of increased thickness have absorbed a greater quantity of dye.

Additionally, when fabrics are subjected to a load extension test in order to measure short term dye uptake, the fabric containing filaments formed in accordance with the present invention will exhibit a reduced signal variability in grams of standard deviation from the mean of approximately 12.8, while the control which lacks silicon dioxide will exhibit a value of approximately 15.0.

It is, of course, to be understood that variations and modifications of the embodiments described may be employed without departing from the concept of the invention defined herein.

CLAIMS

1. A process for the formation of a highly spin oriented polyethylene terephthalate yarn comprising (a) extruding molten fibre-forming polyethylene terephthalate through a plurality of orifices to form a molten multifilamentary material, (b) passing said molten multifilamentary material in the direction of its length through a solidification zone provided with a gaseous atmosphere at a temperature below the glass transition temperature thereof wherein said multifilamentary material is quenched and is transformed to a solid multifilamentary material, (c) passing said resulting multifilamentary material in the direction of its length through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature thereof and below the melting temperature thereof wherein substantial crystallisation of said previously solidified multifilamentary material takes place, and (d) withdrawing said resulting multifilamentary material from the conditioning zone at a speed in excess of 8000 feet (2438 m) per minute; characterised in that there is substantially uniformly dispersed within said fibre-forming polyethylene terephthalate prior to step (a) 0.05 to 1.5 percent by weight of particulate silicon dioxide having a weight average particle size of less than 1 micron.

2. A process according to claim 1 wherein the polyethylene terephthalate prior to step (a) has an intrinsic viscosity of 0.35 to 1.0 determined with a solution of 0.1 gram of the polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C.

3. A process according to claim 2 wherein the polyethylene terephthalate exhibits an intrinsic viscosity of approximately 0.7 determined with a solution of 0.1 gram of polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C.

4. A process according to any of claims 1 - 3 wherein the gaseous atmosphere of step (b) is provided at a temperature of 10 to 40°C.

5. A process according to any of claims 1 - 4 wherein the gaseous atmosphere of step (b) is air.

6. A process according to any of claims 1 - 5 wherein the gaseous atmosphere of step (c) is provided at a temperature of 90 to 220°C.

7. A process according to any of claims 1 - 6 wherein the gaseous atmosphere of step (c) is air.

8. A process according to any of claims 1 - 7 wherein in step (d) the resulting multifilamentary material is withdrawn at a speed of 8,000 to 16,000 feet (2438 to 4877 m) per minute.

9. A process according to claim 8 wherein in step (d) the resulting multifilamentary material is withdrawn at a speed of 11,000 to 13,000 feet (3353 to 3962 m) per minute.

10. A process according to any of claims 1 - 9 wherein the multifilamentary material which is withdrawn from step (d) consists of 6 to 200 continuous filaments each having a substantially constant denier within the range of 1 to 5.

11. A process according to any of claims 1 - 10 wherein the particulate silicon dioxide is substantially uniformly dispersed in the polyethylene terephthalate in a concentration of 0.1 to 1.0 percent by weight.

12. A process according to any of claims 1 - 11 wherein the particulate silicon dioxide is substantially uniformly dispersed within the fibre-forming polyethylene terephthalate prior to step (a) as a result of its prior admixture with the reactants which were polymerised to form the polyethylene terephthalate.

13. A process according to any of claims 1 - 12 wherein the polyethylene terephthalate from which the multifilamentary material is extruded is free of solid particulate material other than the silicon dioxide and the resulting filamentary product possesses a lustrous appearance.

14. A process according to any of claims 1 - 12 wherein the polyethylene terephthalate from which the multifilamentary material is extruded additionally contains substantially uniformly dispersed therein 0.05 to 1.5 percent by weight of particulate titanium dioxide having a weight average

particle size of less than 2 microns and the resulting filamentary product possesses a semi-dull or dull appearance.

15. A process according to any of claims 1 - 14 wherein the particulate silicon dioxide possesses a nominal particle size of less than 0.1 micron as determined by the BET method.

16. A process according to any of claims 1 - 15 wherein the particulate silicon dioxide is fumed silica.

17. A process according to any of claims 1 - 16 wherein the polyethylene terephthalate is made by polymerising dimethylterephthalate and ethylene glycol.

18. A process according to any of claims 1 - 16 wherein the polyethylene terephthalate is made by polymerising terephthalic acid and ethylene glycol.

19. An improved process for the formation of a highly spin oriented polyethylene terephthalate yarn according to any of the previous claims comprising:

(1) polymerising monomers capable of forming polyethylene terephthalate while in admixture with particulate fumed silica having a nominal particle size of less than 0.1 micron as determined by the BET method to form a fibre-forming polymer having an intrinsic viscosity of 0.5 to 0.8 determined with a solution of 0.1 gram of the polymer dissolved in 100 ml. of ortho-chlorophenol at 25°C.,

(2) extruding the resulting polyethylene terephthalate while in molten form and containing 0.1 to 1.0 percent by weight of the particulate fumed silica introduced in step (1) substantially uniformly dispersed therein through a plurality of orifices to form a molten multifilamentary material,

(3) passing said molten multifilamentary material in the direction of its length through a solidification zone provided with a gaseous atmosphere at a temperature below the glass

transition temperature thereof wherein the multifilamentary material is quenched and is transformed to a solid multifilamentary material,

(4) passing the resulting multifilamentary material in the direction of its length through a conditioning zone provided with a gaseous atmosphere at a temperature above the glass transition temperature thereof and below the melting temperature thereof wherein substantial crystallisation of the previously solidified miltifilamentary material takes place, and

(5) withdrawing the resulting multifilamentary material from the conditioning zone at a speed of 8,000 to 16,000 feet (2438 to 4877 m) per minute.

20. A process according to claim 19 wherein the particulate fumed silica is substantially uniformly dispersed in the polyethylene terephthalate in a concentration of 0.10 to 0.40 percent by weight.

21. A process according to claim 19 or 20 wherein the particulate fumed silica has a nominal particle size of less than 0.02 micron as determined by the BET method.