Dec. 31, 1963 R. A. KASEY, JR 3,116,197

NUBBED FILAMENT AND DYED FABRIC OF SAME

Filed Jan. 19, 1959

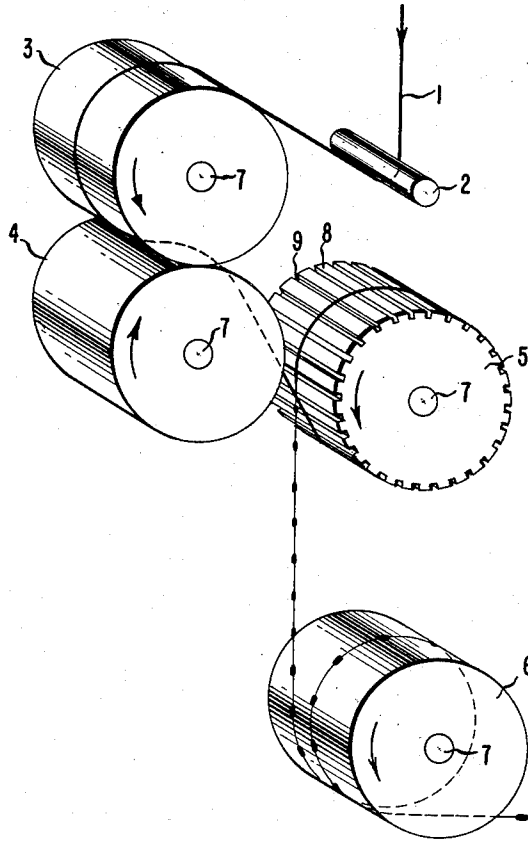


Fig. 1

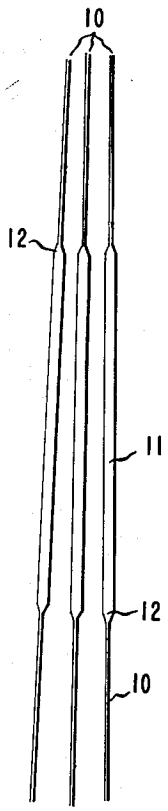


Fig. 2

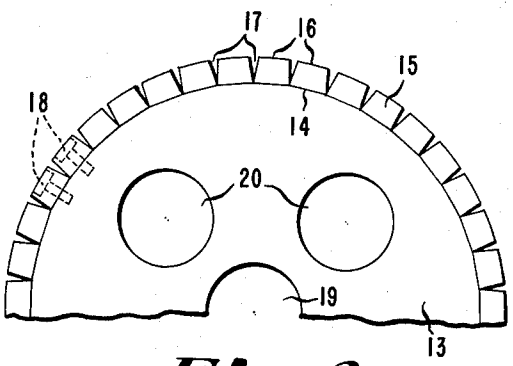


Fig. 3

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3,116,197
NUBBED FILAMENT AND DYED FABRIC OF SAME

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10 Claims. (Cl. 161—170)

This invention relates to the production of novel continuous filaments made from linear condensation polyesters. More specifically, it concerns novel yarns of terephthalate polyesters which exhibit a dry, crepe-like hand when woven or knitted into fabrics and subjected to a mild heat treatment.

This application is a continuation-in-part of my copending application Serial No. 607,499, filed August 31, 1956, and now abandoned.

Polyethylene terephthalate, a well known example of a linear terephthalate polyester, has achieved considerable commercial importance in the form of continuous filament textile yarns owing to its high tenacity, low moisture absorption, resistance to chemical attack, and other desirable properties. However, one characteristic of continuous filament polyethylene terephthalate fabrics which has prevented full acceptance of these fabrics for certain textile uses is their smooth, almost slippery tactile sensation, or "hand." The hand of continuous filament polyethylene terephthalate fabrics prepared from yarns of uniform denier is usually characterized as "cool" and "slick." Fabrics prepared from continuous filament yarns of other linear terephthalate polyesters, such as poly(trans-p-hexahydroxylylene terephthalate), display a similar "cool" and "slick" hand.

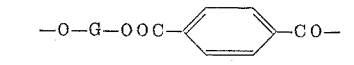
Continuous filament linear terephthalate polyester yarns are usually prepared by extruding the desired number of streams of the molten polymer through a spinneret and winding up the bundle of solidified unoriented filaments into a yarn package, following which the yarn is oriented by drawing it to several times its original length. Preferably the drawing step is facilitated by heating the yarn to about 90–115° C. during the drawing step. Under certain conditions, the drawing step may be carried out in a manner to produce a drawn yarn containing random patches of thick, unoriented yarn, most of the patches being about an inch in length or longer when the amount of unoriented yarn constitutes more than about 1% of the total length of yarn. Continuous filament fabrics prepared from such yarn are found to have a slightly drier hand than fabrics prepared from uniformly oriented yarn, but the hand is still essentially smooth and the fabrics lack the desired crepe-like surface character.

It is an object of this invention to provide novel continuous filament linear terephthalate polyester yarns. A further object is to provide fabrics which have a dry, crepe-like hand from such yarns. Other objects will be apparent from the following description.

These objects are realized by the present invention, which comprehends a continuous filament linear terephthalate polyester yarn characterized by sharply defined alternate smaller and larger denier segments. In a preferred embodiment of the invention, the smaller denier segments are of substantially crystalline structure, and the larger denier segments are substantially amorphous. Woven and knitted fabrics having a desirable dry, crepe-like hand may be prepared from the novel thick-and-thin yarns of this invention. Such fabrics, when dyed, have a novel speckled appearance which is very appealing. The speckled apppearance is especially apparent when the fabrics are not subjected to heat prior to the dyeing step and when a light shade of dye is used.

By "linear terephthalate polyester" is meant a linear

condensation polyester comprising recurring glycol dicarboxylate structural units in which at least about 80% of the recurring structural units are units of the formula



where —G— represents a divalent organic radical containing from 2 to about 18 carbon atoms which is attached to the adjacent oxygen atoms by saturated carbon atoms. Preferably, the radical —G— contains from 2 to about 10 carbon atoms. The terephthalate radical may be the sole dicarboxylate constituent of the recurring structural units, or up to about 25% of the recurring structural units may contain other dicarboxylate radicals, such as the adipate, sebacate, isophthalate, bibenzoate, hexahydroterephthalate, diphenoxyethane-4,4'-dicarboxylate, p,p'-carboxyldibenzoate, and p,p'-sulfonyldibenzoate radicals.

FIGURE 1 is a diagrammatic illustration of apparatus useful in preparing the novel filaments and yarns of this invention;

FIGURE 2 is an illustration of novel linear terephthalate polyester filaments prepared according to the present invention, greatly enlarged; and

FIGURE 3 is an end elevation of the upper half of a roll equipped with vanes which may be used in preparing the novel yarns of this invention.

Referring now to FIGURE 1, substantially amorphous, unoriented linear terephthalate polyester yarn 1 is passed from a source of supply (not shown) under a guide pin 2, between feed rolls 3 and 4, around heated grooved roll 5, and finally around draw roll 6. The rolls rotate on shafts 7 in the direction shown by the arrows, rolls 3, 4, and 5 rotating at the same uniform peripheral speed and roll 6 rotating at a higher peripheral speed, preferably about 2 to 4 times the peripheral speed of rolls 3, 4, and 5. After leaving roll 6, the yarn is wound up in any suitable manner. Rolls 3, 4, and 6 are unheated, while grooved roll 5 is heated to a suitable temperature, usually about 90 to 115° C. Feed rolls 3 and 4 are usually mounted to operate in contact, while roll 5 is slightly separated from the feed roll; however, this arrangement is not critical, and any suitable system which imparts some slight tension to the running yarn ahead of the grooved roll may be used.

The linear terephthalate polyester yarn is passed around the heated grooved roll 5, usually about one full turn, during which time those portions of the yarn which contact the raised areas 8 of the heated roll become heated. The heated portions of the yarns are drawn as they leave the grooved roll because of the tension exerted by draw roll 6, becoming substantially oriented and crystalline; however, portions of the yarn which have passed around the roll above the longitudinal grooves 9 of the roll are unheated and remain substantially undrawn, providing sharply defined sections of the yarn which are still substantially unoriented and substantially amorphous.

FIGURE 2 represents a magnified view (about 100×) of a portion of three filaments from a continuous filament linear terephthalate polyester yarn of this invention, segments 10 being substantially oriented and substantially crystalline and segments 11 of substantially greater diameter being relatively unoriented and relatively amorphous. As shown in the figure, the transistion points 12 between the oriented, crystalline segments and the unoriented, amorphous segments are abrupt. A yarn bundle usually contains from about 10 to about 100 of these filaments, which tend to remain associated together in the same longitudinal relationship prevailing in the drawing step, i.e., the unoriented yarn segments tend to remain grouped together in the yarn bundle, as indicated in the drawing.

Shallow longitudinal grooves 9 may be formed in a solid roll, if desired, by any suitable known means. The

grooves are made approximately the same width as the desired length of the unoriented segments in the yarn to be made with the roll; however, the distance between grooves on the surface of the roll is considerably less than the desired length of the oriented segments of the yarn to be made with the roll, since the oriented segments are formed by drawing the heated portions of yarn as they leave the roll. Usually the separation between grooves is about 30 to 40% of the desired length of the oriented sections, depending on the drawing conditions to be used.

Instead of forming grooves in a solid roll, the grooved roll may be constructed as shown in FIGURE 3. The body 13 of the roll is a right cylinder having a regular polygonal surface 14 of as many sides as the number of grooves desired. Vanes 15 affixed to the body of the roll are substantially rectangular in cross section, having a slightly arcuate surface 16 such that all of the vanes together provide a circular surface interrupted by grooves 17 which constitute the spaces separating the vanes. The vanes are preferably affixed to the body by bolts 18, although other suitable means of attachment may be employed. The roll also has central bore 19 for the shaft and wells 20 into which cartridge heaters or other suitable heating means may be inserted. Alternatively, the roll may be adapted to rotate about and in close contact with a stationary heater block containing suitable heating means.

The novel yarns of this invention are characterized by sharply defined alternate smaller and larger denier segments. The smaller denier segments range in length from about 0.1 to about 1.5 inches, and the larger denier segments range in length from about 0.015 to about 0.15 inch, with the smaller denier segments always being longer than the larger denier segments. Larger denier segments more than about 0.15 inch in length are to be avoided since much of the crepe-like texture and speckled appearance of fabrics prepared from the yarns of this invention is dependent upon substantially unoriented segments which are shorter than about 0.15 inch. Larger denier segments less than about 0.015 inch in length are difficult to obtain in a uniform way, while yarns in which the smaller denier segments are substantially less than about 0.1 inch in length are also difficult to prepare. On the other hand, when the smaller denier segments exceed about 1.5 inches in length, fabric hand becomes progressively more smooth and slick and approaches the fabric hand prepared from uniformly oriented terephthalate yarn.

For convenience in manufacture, the lengths of both the oriented and unoriented segments are usually constant along the length of the filament. However, if desired, the length of either or both may be varied. Fabrics prepared from yarns having oriented and unoriented segments of varying lengths, within the previously defined limits, generally have a hand and appearance similar to fabrics prepared from yarns in which the lengths of each type of segment are constant.

Yarns of this invention are further characterized in that the smaller denier segments are substantially oriented and crystalline, whereas the larger denier segments are substantially unoriented and amorphous. By heating these filaments or yarns, however, they may be converted into structures having even more pronounced intrafilament denier variation but in which both smaller and larger denier segments are substantially crystalline in structure. Heating at a temperature of about 90° C. or above in water, or with dry heat between about 125° C. and about 200° C., is suitable for this purpose. Usually, heating, for about 30 minutes in water at 90° C. will be sufficient to convert substantially amorphous segments of the filament or yarn to a crystalline structure, and at higher temperatures shorter periods of heating are sufficient. At about 200° C. only a few seconds' heating time is necessary. Usually it is desirable to weave or knit the yarn into a fabric prior to heating.

Heating of the novel thick-and-thin yarns of this invention at a temperature between about 90° C. and about 200° C. for from about 30 minutes to about 10 seconds results in non-uniform shrinkage of the yarn, and naturally this shrinkage takes place also if the yarn is in fabric form. The thick or larger denier segments shrink at least 15% more than do the thin or smaller denier segments of the yarn during the heating, and also undergo a corresponding larger increase in denier. For example, if the thin sections shrink 25% during the heat treatment, the thick sections will shrink at least 40%. Actual shrinkage values may be varied over wide limits depending upon the characteristics of the spun yarn, the draw ratio, and the temperature of the vanes of the draw rolls.

Surprisingly, when fabrics prepared from the novel yarns of this invention are subjected to this heat treatment, the hand of the fabric undergoes a marked change from cool and slick to crepe-like.

The thick-and-thin portions of the novel yarn of this invention differ substantially with respect to birefrigence, a measure of the degree of orientation of the yarn. Prior to heat treatment, the thick portions of the yarn are characterized by a birefringence of between about 0.002 and about 0.030, whereas the birefringence of the thin portions is greater than about 0.1. The ratio of the diameter of the thick portions to the thin portions may vary between about 1.3 and about 2.0 prior to heat treatment (shrinkage); after heat treatment, the ratio will vary from about 1.4 to about 2.7.

Fabrics may be prepared by knitting or weaving the yarns of this invention; preferably, the fabrics are prepared before the yarns have been subjected to heat treatment (shrinkage). Fabrics prepared from these yarns and then heat-treated at a temperature above 90° C. in accordance with this invention exhibit a dry crepe-like hand, and, upon dyeing, are characterized by a desirable novel speckled appearance. A fabric having a particularly enhanced speckled appearance is produced when a fabric prepared from yarn of this invention is dyed at a temperature of at least 90° C. prior to any heat treatment of the yarn or fabric above that temperature. Such fabrics also exhibit a dry crepe-like hand.

The following examples are illustrative of novel linear terephthalate polyester yarns provided by the present invention and the process for preparing them.

Example I

Apparatus for drawing yarn is set up as shown in FIGURE 1, the grooved roll being a roll of the type shown in FIGURE 3. The body of the roll, originally a right circular cylindrical aluminum roll 4⅛ inches in diameter and 2 inches wide, is machined to convert the circular surface of the roll into 36 flat sides of equal width. Thirty-six brass vanes extending the width of the roll and having the dimensions of $^{23}/_{64}$ inch (width) x $^{3}/_{16}$ inch (height) are attached to the roll by flat head screws. The surface of the roll is then ground down so that the faces of the vanes comprise a smooth circular surface about 4.5 inches in diameter interrupted by the grooves afforded by the spacings between the vanes, which measure about 0.04 inch in width at the surface of the roll. The outer surfaces of the vanes are then polished and chromium-plated. Means for heating the roll consists of three 50-watt cartridge heaters mounted in a stationary heater block about which the roll rotates, the clearance being $^{1}/_{32}$ inch.

Polyethylene terephthalate polymer, having an intrinsic viscosity of 0.63, is extruded at 275° C. through a spinneret into air, and the yarn is wound up at the rate of 1206 yards per minute. The yarn, comprising 27 filaments having a total undrawn denier of 135, has a birefringence of 0.0090. In drawing the yarn in the apparatus described above, the feed rolls and the grooved roll are operated to give a yarn speed of 141 yards per minute, and the yarn is passed around the draw roll at 375 yards per minute. The grooved roll is maintained at 108° C. The drawn yarn, when examined under magni-

fication, has the novel appearance depicted in FIGURE 2. The thick portions of the yarn are about 0.07 inch in length and have a diameter approximately 1.7 times that of the intervening smaller denier segments, which are about 0.9 inch in length.

A ten-inch length of the drawn yarn is placed under a microscope and the length of each of the thick segments of yarn is measured to the nearest 0.005 inch. The yarn is then placed in boiling water for one minute, after which the yarn is found to have undergone an over-all shrinkage of 15%. The yarn is then placed under a microscope again and the new lengths of the thick segments of yarn are measured. When the original and final lengths of the thick segments are compared, it is found that the thick segments have shrunk 49%. The shrinkage of the thin segments is then calculated by difference as 12.5%.

Analysis of X-ray diffraction patterns of the yarn segments indicates that the thick portions of the filaments are substantially amorphous, while the thin segments are substantially crystalline in character. Thick portions of the filaments exhibit a birefringence of 0.0092, essentially the same as the undrawn yarn, while thin segments have a birefringence of 0.2510, indicating a high degree of orientation. Birefringence, or double refraction, of polyethylene terephthalate filaments is measured by the retardation technique described in "Modern Textile Microscopy," by J. M. Preston (London, 1933) page 270, using a petrographic microscope (such as the Bausch & Lomb Model LB) together with a cap analyzer compensator (Bausch & Lomb Style B).

Yarn prepared as described above is knit into a two-bar jersey tricot fabric (12 inches per rack). Prior to finishing, the fabric has a relatively smooth, slick hand quite similar to a corresponding fabric prepared from conventional polyethylene terephthalate yarn. A striking transformation in the hand of the fabric is achieved, however, by scouring the fabric at the boil for 30 minutes, the scoured fabric having an appealing dry, crepe-like hand. Analysis of X-ray diffraction patterns of the yarn in the scoured fabric indicates that both thick portions and thin portions of the yarn are substantially crystalline.

The fabric is then bleached at 185° F. for 30 minutes with a solution containing 2 grams per liter each of sodium chlorite and nitric acid, followed by dyeing at the boil with ½% (based on fabric weight) of Latyl Brilliant Blue BG dye (listed on page 220 of the 1955 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists, vol. XXXI). The dyed fabric has a novel speckled, pebbly appearance, the color being a medium shade of blue. The finishing treatments are completed with a heat setting step at 430° F. for 30 seconds. The final fabric is characterized both by its dry, crepe-like hand and its novel speckled appearance.

In a similar experiment the tricot fabric is scoured at 60° C., which is insufficient to develop the dry, crepe-like hand. The fabric is then dyed at the boil, which not only develops the dry, crepe-like hand but also provides a greater contrast in the speckled appearance of the fabric than has been achieved previously by scouring the fabric at the boil prior to dyeing.

A two-bar jersey tricot fabric in which the novel polyethylene terephthalate yarn is used in the top bar and 10-filament, 30-denier nylon yarn is used in the bottom bar exhibits a relatively dry, crepe-like hand after heating at 100° C., although the effect is less marked than when the fabric is constructed entirely of the novel polyethylene terephthalate yarn. A filling-face satin fabric woven from the novel polyethylene terephthalate yarn also exhibits an appealing dry, crepe-like hand and has an attractive speckled appearance when dyed.

Polyethylene terephthalate yarn is spun as above described but drawn over a hot pin 1.6 inches in diameter maintained at 100° C. with a rate of feed of 151 yards per minute and a rate of withdrawal of 545 yards per minute. The uniformly drawn yarn is knitted into a two-bar jersey tricot fabric (12 inches per rack). The smooth, slick, cool hand of the fabric is substantially unaltered by scouring at the boil. When bleached and dyed under the same conditions described in Example I, the fabric dyes to a level, uniform shade of blue.

Example II

A roll having a construction similar to that described in Example I is fabricated, except that 72 vanes each 0.16 inch in width are used, the spacings between vanes measuring about 0.04 inch in width at the surface of the roll. Polyethylene terephthalate yarn prepared as described in Example I, comprising 34 filaments having a total undrawn denier of 135, is passed around the grooved roll at 153 yards per minute and around the draw roll at 375 yards per minute. The grooved roll is maintained at 110° C. The thick sections of the yarn, which are about 0.05 inch in length, are about 1.6 times the diameter of the intervening segments, which are about 0.38 inch in length. Tricot fabric prepared, finished and dyed as described in Example I, exhibits a notably dry, crepe-like hand and a highly speckled appearance.

Example III

Undrawn yarn of poly(trans-p-hexahydroxlylene terephthalate) consisting of 27 filaments and having a total denier of 135 is drawn as described in Example I with the exception that the heated grooved roll is maintained at a temperature of 112° C. The drawn yarn, when examined under magnification, has the novel appearance depicted in FIGURE 2. The thick portions of the yarn are about 0.06 inch in length and have a diameter approximately 1.6 times that of the intervening smaller denier segments, which are about 0.9 inch in length.

Yarn prepared as described above is knit into a two-bar jersey tricot fabric. Prior to finishing, the fabric has a relatively smooth, slick hand similar to a corresponding fabric prepared from conventional terephthalate polyester yarns. A striking transformation in the hand of the fabric is observed, however, by scouring the fabric at the boil for 30 minutes, the scoured fabric having an appealing, dry, crepe-like hand.

The fabric is then dyed a light blue color as in Example I and is found to have a novel speckled pebbly appearance.

Example IV

Undrawn yarn of polyethylene terephthalate/5-(sodium sulfo)isophthalate (98/2) consisting of 34 filaments and having a total denier of 135 is drawn as described in Example II with the exception that the heated groove roll is maintained at a temperature of 105° C. When examined under magnification, the drawn yarn is found to have thick sections about 0.05 inch in length and thin sections about 0.4 inch in length. Tricot fabrics prepared from this yarn, finished as in Example I, and dyed at the boil to a medium violet shade with 1,4-diamino-2,3-dichloroanthraquinone, is found to have a remarkably dry crepe-like hand and a highly speckled appearance.

The linear terephthalate polyesters suitable for the purposes of the present invention may be prepared by reacting terephthalic acid or a mixture of terephthalic acid and one or more other dicarboxylic acids with a glycol, $G(OH)_2$, where —G— is a radical as defined above, to form the bis-glycol ester or mixture of esters, followed by polycondensation at elevated temperature and reduced pressure with elimination of excess glycol. In place of the acid or acids, ester-forming derivatives may be used, i.e., derivatives which readily undergo polyesterification with a glycol or derivative thereof. For example, the acid chloride or a lower alkyl ester, such as the dimethyl ester, may be used. Similarly, an ester-

forming derivative of the glycol may be used in place of the glycol; i.e., a derivative of the glycol which readily undergoes polyesterification with dicarboxylic acids or derivatives thereof. For example, a cyclic oxide from which the corresponding glycol can be derived by hydrolysis may be used.

The glycol, $G(OH)_2$, from which the polyester is prepared may be any suitable dihydroxy compound containing from 2 to 18 carbon atoms, preferably from 2 to 10 carbon atoms, in which the hydroxyl groups are attached to saturated carbon atoms. Thus, the radical —G— may be of the form $—(C_{n+1}H_{2n+2}Y_{p-1})—$, where n and p are positive integers and Y is a cycloaliphatic group, an aromatic group, an oxy group, or an arylenedioxy group. Examples of suitable glycols where $p=1$ include the polymethylene glycols, such as ethylene glycol, tetramethylene glycol, hexamethylene glycol, and decamethylene glycol as well as the branched chain glycols such as 2,2-dimethyl-1,3-propanediol and 2,2-dimethyl-1,4-butanediol. Suitable glycols in which $p=2$ include trans-p-hexahydroxylene glycol, bis-p-(2-hydroxyethyl)benzene, diethylene glycol, bis-(4-hydroxybutyl) ether, bis-p-(β-hdroxyethoxy)benzene, bis-1,4-(β-hydroxyethoxy)-2,5-dichlorobenzene, bis-4,4′-(β-hydroxyethoxy)diphenyl, 2,6-di(β-hydroxyethoxy)naphthalene, bis-[p-(βhydroxyethoxy) phenyl] ketone, bis-[p-(β-hydroxyethoxy)phenyl] sulfone, and bis[p-(β-hydroxyethoxy)phenyl]difluoromethane. Glycols in which $p=3$ include 4,4′-bis-(β-hydroxyethyl)-biphenyl, 4,4′-bis-(β-hydroxyethyl)dodecahydrobiphenyl, triethylene glycol, and 2,2′-(ethylenedioxybis-[p-phenleneoxy])diethanol. In general, the glycols in which p is greater than 3 are of lesser interest, although certain glycols such as tetraethylene glycol may be used. A preferred class of glycols for use in preparing the terephthalate polyesters are those selected from the series $HO(CH_2)_mOH$ where m is an integer from 2–10. Mixtures of the glycols may be used. If desired small amounts, e.g., up to about 15 weight percent, of a higher glycol such as a polyethylene glycol of high molecular weight may be added.

I claim:

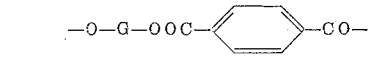
1. A filament of polyethylene terephthalate characterized by sharply defined alternate smaller and larger denier segments, the smaller denier segments ranging in length from about 0.1 to about 1.5 inches, the larger denier segments ranging in length from about 0.015 to about 0.15 inch, and the smaller denier segments being longer than the larger denier segments and of substantially oriented and crystalline structure.

2. A fabric of the filaments of claim 1.

3. The filament of claim 1 in which the ratio of the diameter of the larger denier segments to the diameter of the smaller denier segments is between about 1.3 and about 2.0.

4. The filament of claim 1 in which both smaller and larger denier segments are of substantially crystalline structure.

5. A filament of a linear terephthalate polyester characterized by sharply defined alternate smaller and larger denier segments, the smaller denier segments ranging in length from about 0.1 to about 1.5 inches, the larger denier segments ranging in length from about 0.015 to about 0.15 inch, and the smaller denier segments being longer than the larger denier segments and of substantially oriented and crystalline structure, said polyester being a condensation polymer comprising recurring glycol dicarboxylate structural units in which at least about 80% of the recurring structural units are units of the formula



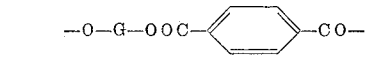
wherein —G— represents a divalent organic radical containing from 2 to about 18 carbon atoms which is attached to the adjacent oxygen atoms by saturated carbon atoms.

6. A fabric of the filaments of claim 5.

7. The filament of claim 5 in which the ratio of the diameter of the larger denier segments to the diameter of the smaller denier segments is between about 1.3 and about 2.0.

8. The filament of claim 5 in which both smaller and larger denier segments are of substantially crystalline structure.

9. A dyed fabric of speckled appearance of filaments of a linear terephthalate polyester characterized by sharply defined substantially crystalline alternate smaller and larger denier segments, with the smaller denier segments being of substantially oriented structure, and wherein the smaller denier segments range in length from about 0.1 to about 1.5 inches, and the larger denier segments range in length from about 0.015 to about 0.15 inch, the polyester being a condensation polymer comprising recurring glycol dicarboxylate structural units in which at least 80% of the recurring structural units are units of the formula



wherein G represents a divalent, organic radical containing from about 2 to about 18 carbons which are attached to the adjacent oxygen atoms by saturated carbon atoms.

10. The filament of claim 5 in which the larger denier segments are substantially unoriented and amorphous.

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