

Description

This invention relates to an improved process for annealing polyester filaments, and is more particularly concerned with an improvement that makes possible products having a novel fine structure and improved balance of filament properties, including dyeability, strength, dimensional heat stability, crimp and low surface cyclic trimer.

Polyester is the synthetic material most used in textile yarns. Such yarns are in the form of either continuous filaments, comprising relatively small numbers of continuous filaments and being of relatively low denier, or of spun yarns that are prepared by some variant of the age-old process of spinning (i.e., twisting together) crimped staple fiber, often comprising blends, and usually on the cotton or wool systems. Polyester staple fiber is generally prepared by cutting or breaking large tows containing many continuous filaments, often of the order of a million or more, such tows being of extremely large total denier. The processing of such tows necessitates techniques that are completely different from those customarily used for continuous filament yarns.

Hitherto, tows of continuous filaments have been prepared from polyester filaments that have been spun at a relatively low speed, to give filaments of relatively low orientation, such as are not suitable for textile purposes, and then drawn to raise the orientation, and thereby increase their strength and so render them suitable for textile purposes. Such a process is disclosed in Vail U.S. Patent No. 3,816,486. The drawing process that has been preferred commercially has involved drawing filaments wet with water. As disclosed also in Vail, if the shrinkage of the resulting product has been undesirably high, this shrinkage can be reduced by annealing. Hitherto, the annealing process that has been preferred commercially has involved the use of heated rolls to heat the filaments, while under controlled tension, to a temperature well in excess of the boiling point of water. This process has required the use of sufficient heat to evaporate all the water from the filaments before it is possible to heat the filaments to the desired annealing temperatures. The annealed filaments are then crimped, e.g., in a stuffer-box crimper, as disclosed in Hitt U.S. Patent No. 2,311,174. The crimped filaments are then dried in relaxed condition.

It has long been desirable to reduce the energy requirements of such a process. Furthermore, although the hot roll annealing process has achieved the desired objective of reducing shrinkage, it has had the undesired effect of reducing the dyeability and, depending on the particular conditions and on the composition of the polymer comprising the filaments, adversely affecting other properties, such as ease of crimping and surface trimer content.

US-A-3 739 056 discloses a process for improving the dyeability of linear, condensation polyester fibers comprising, sequentially, the steps of (a) drawing the fibers at a temperature above their apparent minimum crystallization temperature, (b) relaxing the drawn, crystalline fibers at a temperature greater than the drawing temperature and at least about 180°C, and (c) stabilizing or annealing the fibers by heating them under tension at a temperature greater than the relaxation temperature and less than the fiber softening temperature to further crystallize the fibers. In step (b), the fibers are relaxed as by contact with a hot shoe or by feeding them to a steam jet faster than they are removed and by heating them with the impinging steam. In step (c), the relaxed fibers are annealed as by contact with a hot shoe, by passing them around hot rolls or treating them with heated fluids. Example III illustrates the deleterious effect on dyeability obtained by annealing crystalline-drawn fibers without a relaxation step. Thus, prior art polyester filaments have all had some advantages accompanied by defects that have, hitherto, been considered inevitable. If the filaments have not been annealed, the shrinkage has been undesirably high for many purposes, but the dyeability has been better than that of the annealed filaments.

The combined objectives of high dyeability and high tensile properties remain somewhat irreconcilable in commercial hot-roll-annealing processes. An increase in one of these properties generally must come through some compromise in the other. Similarly opposed interactions are also found when attempting to optimize properties such as low shrinkage, crimpability, and a low amount of surface cyclic trimer. Consequently, considerable incentive remains for discovering a commercially feasible process which can provide an overall better combination of such properties, i.e., one which involves less sacrifice in one or more individual properties to improve another.

An object of this invention is a process for annealing a tow of drawn filaments of poly(ethylene terephthalate) to provide an improved balance of filament properties including strength, dyeability, and shrinkage, and/or crimpability, and/or low surface cyclic trimer deposits. Another object is the improved products made thereby. Still another object of the invention is annealed crimped filaments of poly(ethylene terephthalate) having a novel unexpected combination of fine structure and improved filament properties.

These and other objects are provided by this invention.

According to the present invention, there is provided an improved continuous process for treating a tow of melt-spun polyester filaments, involving the steps of (1) drawing, (2) annealing, (3) crimping and (4) drying, characterized in that the annealing step is effected in a pressurized zone of saturated steam at a pressure of at least 1100 kPa. This pressurized steam-annealing process makes possible the production of crimped polyester filaments having an improved balance of the desired properties to an extent that is believed entirely new. The precise combination of properties that can be obtained will depend on the conditions of preparation and on the specific composition of the polyester.

This invention will be further described with reference to the accompanying Drawings.

FIG. 1 schematically shows an apparatus suitable for the process of the invention.

FIGS. 2—4 are graphs showing X-ray fine structure details of Long-Period Spacing, Apparent Crystallite Size and Percent Crystallinity for steam-annealed filaments of the invention.

FIG. 5 shows graphs plotting tensile properties and surface trimer against relative viscosity.

Referring to FIG. 1, tow 11 is first drawn in a conventional apparatus 10 and then supplied to the annealing zone by rolls 12, 14 aligned with the inlet of steam chamber 20 and advanced through chamber 20 at a controlled length by adjustable-speed puller rolls 22, 24 aligned with the chamber outlet. The tow is then forwarded to crimper 30 and conventionally crimped. From there crimped tow 11' passes to dryer-relaxer oven 40 where the crimped filaments are conventionally dried in a relaxed state. Pressurized steam is supplied to chamber 20 via manifold 21. Condensed water is removed from chamber 20 by condensate outlet 23.

It will be understood from the description of the apparatus that the tension on the filaments during annealing is controlled by rolls outside the steam chamber, and all discussion herein of extension or retraction during annealing or, e.g., in the pressure zone should be understood in this sense. Depending on the particular design of apparatus, the temperature profile along the filaments may affect the location where the filaments tend to retract. So the annealing may take place in more than one step, with different extensions and/or retractions in these steps. Indeed more than one such annealing step may prove desirable in some instances.

We have discovered that saturated steam maintained at a pressure of at least about 150 psig (1100 kPa) can be used to anneal drawn filaments of poly(ethylene terephthalate) while under tension and prior to being crimped with unexpectedly beneficial results. As compared to comparably annealed crimped filaments prepared by hot roll annealing to similar levels of crystallinity and of shrinkage, the steam-annealed crimped filaments have been found to have a superior overall balance of properties which is usually accompanied by an unexpectedly different fine structure.

In the claims herein, and throughout much of the description, the term crimped filament is used generically to embrace not only continuous filaments, generally in the form of a tow, but also staple fiber, and products thereof. It is, however, generally easier to measure the parameters mentioned herein for continuous filaments, rather than for staple fiber.

Accordingly, the preferred process for manufacturing crimped, annealed filaments of poly(ethylene terephthalate) comprises advancing a tow of the filaments, which have been substantially fully drawn, through a pressurized zone of saturated steam maintained at a pressure of at least about 150 psig (1100 kPa) for at least about 0.2 sec., and preferably for a time sufficient to heat substantially all of said filaments up to at least the steam saturation temperature corresponding to the steam pressure, while controlling filament length within the range of from about 5% extension to 10% retraction, withdrawing the tow of filaments from the zone into ambient atmospheric pressure whereupon they become rapidly cooled by vaporization of water to a temperature of about 100°C or less while still under said controlled length, optionally cooling as needed for proper crimping, crimping the cooled filaments, and then drying and relaxing the crimped filaments at a temperature of less than about 125°C, preferably less than 110°C.

After being cooled, the annealed filaments of this invention can be crimped in a conventional manner as in a stuffer-box crimper, as taught for example in U.S.P. 2,311,174 to Hitt, and then dried and relaxed at a temperature of less than about 125°C, since too high a temperature can destroy the benefits of the invention.

The filaments of this invention consist essentially of poly(ethylene terephthalate), that is polymer in which at least about 93% (by weight as used herein) of the repeating radicals consist of the dioxyethylene and terephthaloyl radicals. The remaining radicals, if any, can consist of ionic or neutral (free or ionic dye sites) co-monomer radicals including radicals such as 5-sodium-sulfo-isophthaloyl, dioxydiethylene ether, i.e., the derivative of diethylene glycol (DEG), glutaryl, such as derived from dimethyl glutarate (DMG), and the derivative of poly(ethylene oxide), such as PEO having a molecular weight of 600.

Other remaining radicals can also include those from (including their mixtures) 4—9 carbon straight-chain aliphatic diacids, especially glutaryl and adipyl, and of glycols including diethylene, triethylene and tetraethylene glycol, of 400—4000 molecular weight poly(ethylene glycol), tetramethylene and hexamethylene glycol, poly(butylene glycol) of 400—4000 molecular weight, and copolyethers of ethylene/propylene and ethylene/butylene glycols of 400—4000 molecular weight.

Up to a certain amount of radicals with ionic dye sites, such as 5-sodium-sulfo-isophthaloyl can be included with the neutral radicals. Although all the novel filaments of the invention are characterized by an overall balance of properties that is superior, i.e. improved over comparable hot rolled filaments, the degree and nature of this improvement, that is achieved by the steam-annealing process, varies depending upon the chemical constitution of the particular polyester involved. For textile uses where the relative viscosity is less than 25 and high tensile properties are desired, the improved filaments have a T_7 of at least about 1.5 gpd, a $T + T_7$ of at least about 7 and generally less than about 10 gpd, along with a dry heat shrinkage (196°C) of less than 10%. Such filaments of the invention have a dyeability/orientation balance characterized by a "D" number of less than about 3.8 and greater than about 1.8 and a trimer "T" number that is preferably less than about 20. "D" number and trimer "T" number are as defined hereinafter and are derived from conventionally measured properties.

Preferred filament products of the invention can be grouped according to their intended use. Where strength is of primary concern the filaments are of a polymer containing at least 97% by weight of dioxyethylene and terephthaloyl radicals. Any remaining radicals are preferably selected from the group consisting of glutaryl, oxy-poly(ethylene oxide) and dioxydiethyleneoxide. A small amount of ionic radical (up to about 0.3% 5-sodium-sulfoisophthalate) may be optionally present.

A preferred group of strong filaments is of polymers having at least 97% dioxyethylene and terephthalate radicals, substantially free of ionic dye sites, which in addition to the above balance of properties have a crystalline fine structure within the area HIJK in FIG. 2, or in areas LMNOP or NOPQR of FIG. 3.

When ease of dyeability with disperse dyestuffs is of primary concern, but good tensile properties and low shrinkage remain important, the filaments are of a polymer containing at least about 3% and not more than about 7% by weight of neutral (i.e., substantially free of ionic dye site) organic polyester radicals, particularly those selected from the group consisting of (or derived from) diethylene glycol, glutarate, adipate, and poly(ethylene oxides) having a molecular weight of less than about 4000. Filaments of such copolymers of the invention have the improved balance of properties as defined by a T_7 of at least about 1.1, a $T + T_7$ of at least about 5 and preferably less than about 8 gpd, a dry heat shrinkage (at 196°C) of less than 10%, a "D" number of less than 3.8 and greater than about 1.8, a trimer "T" number preferably of less than about 20 and dye rate (RDDR) of at least 0.12. Such copolymer filaments are preferably annealed while allowing a retraction in filament length (difference in feed and puller roll speeds) within the range of about 3 to 10%. Such filaments include ones having a superior combination of pilling resistance, ease of dyeability, tensile properties and heat stability relative to present commercial copolymer filaments.

Improved ionically-modified cationically dyeable filaments of the invention contain at least 93% dioxyethylene and terephthaloyl radicals, at least 1.3% 5-sodium-sulfo-isophthaloyl radicals and from 0 to about 4% (including DEG impurity) of other neutral radicals as defined above. Such filaments have a T_7 of at least about 1.2 gpd, a $T + T_7$ of at least about 5 gpd and "D" and trimer "T" numbers as for the above polymers.

Preferred 93—97% copolymers and ionic terpolymers have crystalline fine structures within the areas of STUV of FIG. 4 and LMNOP of FIG. 3.

This invention can provide filaments with unexpectedly superior tensile-dye-shrinkage properties, and which usually are combined with improved crimpability and lower surface cyclic trimer content.

The various parameters used herein, and their methods of measurement, are described in the following section. As indicated, it is generally easier to measure these parameters for continuous filaments, rather than for the resulting staple fiber.

Since commercial tows are often extremely large and contain very large numbers of fine filaments, variations between individual filaments and along the same filament inevitably occur, so any property measured on a small segment of a single filament can be misleading. For this reason, it is common commercial practice to make replications, i.e. repeated measurements on different filaments at different locations, to obtain a truer picture of the actual overall properties of filaments in any tow or of staple fiber or yarns therefrom. This should be remembered when considering the properties listed in the Examples, which were not the results of the large numbers of measurements that are characteristic of commercial practice. Thus, scrutiny of small differences between properties in the Examples may not reveal any significant effect in the sense that a difference in process operation was necessarily responsible for this particular difference in properties. We have, however, found that a significant increase in the saturated steam pressure into the pressure range that is according to the process of invention does improve the balance of properties of the resulting filaments, as shown in the comparative tests in the Examples. This is particularly true of the residual shrinkage obtained under otherwise comparable conditions. Thus, although individual shrinkage measurements may vary within a tow by 2 or more % on either side of the mean shrinkage, we have found that the mean shrinkage is significantly reduced as the saturated steam pressure is raised, e.g., from 120 psig to 150 psig. One individual measurement, however, as compared with another individual measurement, may not truly reflect the improvement in the mean values for the tows, as a whole. As the pressure is increased above 150 psig within the pressure range considered, since the mean shrinkage is reduced, other conditions being comparable, it becomes increasingly predictable that any shrinkage measurement will be in the most particularly desired range of 3 to 6%. As indicated elsewhere, depending on the chemical composition of the polyester, there may be a significant improvement in a particular property (the mean value), or a gradual improvement, as the pressure increases above 150 psig. Thus, the dyeability of some copolymers can be measurably improved, as shown in some of the Examples, whereas the dyeability of a homopolymer is not generally improved to the same extent.

Crimp Index and Denier Per Filament (DPF)

The crimped tow is straightened by application of about 0.1 gpd load and 0.5 gm clips 66.6 cm apart are attached to the extended tow. The tow is then cut 11.7 cm beyond each clip to give a sample of 90 cm extended length. The sample is suspended vertically, hanging freely from one of the clips to allow retraction to crimped length. After about 30 seconds, clip-to-clip distance is measured.

$$\text{Crimp index} = \left(\frac{66.6 - L_0}{66.6} \right) \times 100$$

5 where L_0 is clip-to-clip distance in the free-hanging state.

Tow denier is calculated from weight of the 90 cm extended length sample. Average denier per filament is calculated from tow denier and the number of filaments in the tow.

Tensile Properties (T and T_7)

10 Tenacity at break elongation (T), and tenacity at 7% elongation (T_7) are determined from the stress-strain curve in a conventional manner using an "Instron" machine with a sample length of 10 inches (25 cm) and a rate of sample elongation of 60% per minute, at about 75°F (24°C)/65% RH. They are given throughout in gpd units.

Flex Life

15 Flex life is measured by repeatedly bending single filaments, each tensioned to 0.3 gpd, through an angle of 180° over a wire diameter 0.001 inch (0.025 mm). If the denier exceeds 5 dpf, the diameter should be 0.003 inch (.075 mm). Twenty-two filaments are flexed simultaneously. Flex life is defined as number of cycles at the time the eleventh filament fails. This test is repeated, i.e., at least two sets of filaments are tested, and the average number of cycles is taken as the flex life.

DHS — Dry Heat Shrinkage (196°C)

20 Residual shrinkage is preferably and most accurately measured on uncut, crimped dried tow. The ends of a bundle of filaments of about 250 denier are tied to form a loop about 30 cm long. A load of about 0.1 gpd is applied to straighten crimp and loop length is determined to the nearest mm. The loop is coiled and freely suspended with no tension in a 196°C forced air oven for 30 minutes. After cooling, length is remeasured as before.

$$\text{DHS (196°C)} = \left(\frac{L - F}{L} \right) \times 100\%$$

30 where L and F are initial and final loop lengths, respectively.

With cut staple fiber, a single fiber or bundle of about 25 fibers is mounted between a fixed clamp and a moveable clamp attached to a Vernier scale. Sufficient tension is applied to straighten crimp and extended length is measured. The moveable clamp is adjusted to release tension and allow fibers to shrink freely. The assembly is transferred to a 196°C forced air oven for 30 minutes. After cooling, extended fiber length is remeasured and shrinkage calculated as above.

Care to avoid cold drawing of the filaments is essential.

Boil-Off Shrinkage (BOS)

40 Boil-Off Shrinkage (BOS) is measured as in Piazza and Reese (U.S.P. 3,772,872).

Density

45 See the method of Piazza and Reese (U.S.P. 3,772,872) Column 3 or ASTM D1505—63T.

Percent Crystallinity

50 Density is the preferred basis for calculating percent crystallinity for homopolymers. After correcting for any delusterant content, the percent crystallinity is calculated on the basis of an amorphous density of 1.335 gm/cc and a crystalline density of 1.455 gm/cc for 100% homopolymers. However, as the amount of modifier increases, the amorphous and crystalline densities of copolymers can differ significantly from these values conventionally used for homopolymers, so calculation of percent crystallinity on this basis can be misleading. This is especially true when the copolymer contains more than 3% of modifier, but depends on the particular modifier. Percent crystallinity of such copolymers should be calculated from the Crystallinity Index (CI) using the equation:

$$\text{Percent Crystallinity} = 0.676 \times \text{CI}$$

Because large tows can show significant variations in properties, especially from filament to filament, replication of CI measurement is particularly desirable, to avoid obtaining a misleading result.

Melting Point

60 Melting Point is defined as the temperature of the melting endotherm peak measured in a N_2 atmosphere using a Du Pont 1090 Thermal Analyzer with a Du Pont 1910 scanning calorimeter attachment. Sample size was 5 ± 0.2 mg and scanning rate was 20°C per minute.

EP 0 125 112 B1

LPS — Long-Period Spacing

The meridional small-angle X-ray long-period peak was measured using a Kratky Small-Angle X-Ray Camera (made by Anton Paar K.G., Graz-Strassgang, Austria, and sold by Siemens Corp., Iselin, N.J.). The radiation was CuK α (copper K-alpha) emitted by an X-ray tube (Siemens AG Cu 4SK—T) having a 2.5 $\times$ 7 mm focal point and especially designed to be used with the Kratky Camera. The radiation was filtered by a 0.7 mil (18 microns) Ni foil to remove CuK β radiation and detected by a NaI(Tl) scintillation counter employing single-channel pulse-height-analysis set to pass 90% of the CuK α radiation symmetrically. The pulse-height analysis removes the major portion of the continuous radiation emitted by the X-ray tube.

The specimens were prepared by winding uncut, crimped tow on a 2.5 cm square frame with an opening sufficient to pass the X-ray beam. The tow was wound with sufficient tension to yield a uniform thickness of essentially parallel fibers. If the measurement is to be on cut staple fibers, these can be spun into a yarn to maximise fiber parallelization. Care must be taken in yarn preparation to avoid mechanical damage such as cold draw which might change the fiber structure. When working with staple fibers, appropriate control samples, tested both as uncut tow and as a spun staple yarn should be run to determine any correction factors needed to normalize spun yarn data to that of uncut tow.

Specimen thickness after winding was sufficient that transmission of CuK α radiation approached $e^{-1} = 0.368$. This ensures that diffracted intensity will be near the maximum obtainable. About 1 gm of polyester sample will typically give the desired transmission on a 2.5 cm square sample holder.

The wound specimen is mounted in the Kratky camera so that the fibers are vertical (the fiber axis is coincident with the diffraction vector, which bisects the incident and the diffracted beams). The Kratky camera scans in a vertical plane about the horizontal axis described by the intersection of the X-ray beam and the sample.

With the X-ray tube operating at 45 KV and 20 ma and with a beam-defining slit of 120 μ m, the sample is scanned between 0.1° and 2.0° 2 θ in 0.025° steps. Data are digitized for computer analysis and a smoothed curve is constructed using a running fit to a second order polynomial. The instrument background is removed by subtracting, point-by-point, a background scan obtained with no sample multiplied by the observed transmission, T. A correction factor, C, is determined from the transmission, T, as:

$$C = \frac{1.0}{eT \ln(T)}$$

($e = 2.71828$, $\ln(T)$ is the logarithm of T to the base e)

The data are then corrected by multiplying each point by C, which corrects for the amount of sample in the X-ray beam and puts data from every sample on an equivalent basis. If experiments cover an extended period of time, one sample should be retained as a reference and scanned as necessary to monitor any drift in instrumental response.

Long-period spacing, d, is calculated using Bragg's Law, $d = \lambda/2 \sin \theta$, where θ is the angular position of the meridional long-period peak and λ is the wave length of incident radiation (1.54 Å).

Measured long-period spacing sometimes depends on the experimental method. For example, a photographic-film-based procedure can give a slightly different result from the goniometer procedure described above.

Other methods can be calibrated for comparison with the above method by preparing a standard sample as follows.

Spun filaments are prepared from 21 RV polyethylene terephthalate homopolymer containing about one weight percent or less of impurities such as diethylene glycol. Filaments are air quenched and spun at about 1500 ypm (1372 meters/minutes) to 4 dpf. The spun filaments are two-stage drawn in an aqueous environment in a process basically similar to that described by Vail (U.S. 3,816,486) and then annealed at constant length over heated rolls. Draw ratios may differ somewhat from Vail and are selected to ensure uniform draw in the first stage and a final tenacity of about 6.3 gpd. A second stage draw ratio of about 1.15 is suitable. Length retraction of 2 to 4% is allowed in the annealing. Annealing rolls are heated to first dry the filaments and then heat them to an appropriate temperature for about 1.5 seconds. Annealed filaments are water-quenched then stuffer box-crimped and dried in air under zero tension at 120°C for 10 minutes. Filaments are spread into a thin ribbon on the anneal rolls for maximum filament to filament heat treatment uniformity. These filaments have an LPS of 120 Å when tested as described above.

ACS — Crystal Size

Apparent crystallite size (ACS) is measured as described by Blades (U.S. Patent 3,869,429 Col. 12) with some modifications. High intensity X-ray source is a Phillips XRG-3100 with a long, fine focus copper tube. Diffraction is analyzed with a Phillips single axis goniometer equipped with a theta-compensating slit and a quartz monochromator set to exclude copper K β radiation. Diffracted radiation is collected in step scanning mode in 0.025° steps with a 1.5 second per step count time. The digital data so collected are analyzed by a computer and smoothed by a running fit to a second order polynomial. Crystalline polyethylene terephthalate filaments show a clear 010 diffraction peak with a maximum at about 18° and a minimum at

about 20°. The computer is programmed to determine positions of the maximum and minimum from the second derivative of the polynomial, to define the base line as a straight line which begins at the minimum at about 20° and joins the diffractogram tangentially at 10 to 14°, to determine peak width at half height, to correct for the instrumental contribution to line broadening and to calculate ACS as described by Blades.

Crystallinity Index

Crystallinity Index (CI) is determined from the same diffractogram as ACS. The computer is programmed to define a straight base line which joins the diffractogram tangentially at about 11° and 34°. Crystallinity index is defined as

$$\frac{A \times 100}{A - B}$$

$$A - B$$

where A is the intensity of the 18° 010 peak above this base line and B is the intensity of the 20° minimum above this base line.

CI is related to percent crystallinity. It was calibrated by preparing a standard series of hot roll annealed fibers ranging in densities from 1.3766 to 1.3916, after correction for TiO₂ content. Weight percent crystallinity was calculated conventionally assuming amorphous and crystalline densities of 1.335 and 1.455, respectively. Linear regression analysis showed weight percent crystallinity = 0.676 × CI, correlation coefficient was 0.97 and intercept a negligible 0.1.

Relative Viscosity (RV)

Relative Viscosity (RV) is the ratio of the viscosity of a 4.47 weight on weight percent solution of the polymer in hexafluoroisopropanol containing 100 ppm sulfuric acid to the viscosity of the solvent at 25°C.

RDDR

DDR (disperse dye rate) is measured as described by Frankfort and Knox (U.S. Patent 4,195,051, Col. 13). RDDR is calculated from DDR by normalizing to the surface-to-volume ratio of a 1.50 dpf round fiber.

$$RDDR = DDR (DPF/1.50)^{1/2}$$

If the fiber is non-round, additional correction is needed to compensate for its increased surface area. Correction may also be made for denier increase caused by shrinkage in the dye bath (i.e., boil-off shrinkage, or BOS). However, fibers of the invention have low BOS and such correction is usually negligible.

"D" Number

$$"D" = \frac{e^{0.04(T+T_7)} \times (T+T_7)^{-1.06} \times e^{0.26(WMOD)}}{RDDR}$$

where RDDR, WMOD, T and T₇ are as defined herein.

SCT — Surface Cyclic Trimer (Content)

0.5 gm of crimped, dried fibers or tow is accurately weighed and immersed in about 15 ml of spectrograde carbon tetrachloride at about 75°F (24°C) for about 5 minutes. The mixture is stirred periodically. The resulting trimer solution is separated from the fibers using a funnel and the fibers are then washed with about 5 ml additional carbon tetrachloride. Solution and washings are combined and made up to known volume. Trimer concentration is determined by conventional UV spectrophotometry based on absorbance at 2860 Å. Correction for interfering impurities, for example, finish ingredients with absorbance at 2860 Å, may be needed.

A calibrating standard is prepared by purifying a sample containing trimer by repeated recrystallization from methylene chloride to yield pure trimer melting at 325-328°C.

"T" Number (Trimer)

$$"T" \text{ number} = [SCT(\text{ppm}) + 1] \times e^{-0.2(T + T_7)}$$

Trimer level increases with draw ratio and orientation. The word "Trimer" is used generically to cover any low molecular weight polymer on the surface of the filament.

Polymer Compositions

All polymer composition percentages in the Examples are based on analysis of the crimped filaments and refer to polymer components other than ethylene terephthalate units. For diacid comodifiers, unless otherwise specified, "composition" is defined as weight % of ethylene-diacid repeat units. For example, for filaments derived from dimethyl glutarate comonomer (DMG), the polymer composition is defined in terms of weight % ethylene glutarate. For dialcohol modifiers, the composition is specified as grams dialcohol

formed by hydrolysis of 100 gm of copolymer. Unless indicated otherwise, all the polymer compositions in the Examples contained 0.3% by weight of TiO_2 , as delusterant.

WMOD

- 5 WMOD is the total weight % "foreign" radicals incorporated in the polymer chains. "Foreign" denotes chemical species other than dioxyethylene and terephthaloyl radicals. For example, for a glutarate polymer, the foreign species is $-\text{CO}-(\text{CH}_2)_3-\text{CO}-$. The total weight % includes dioxydiethylene ether (DEG) links usually formed in the polymerization reaction.

10 MDR — PRUD — TDR

These terms are used in the Tables in the Examples and refer to the ratios of roll speeds.

MDR is the machine draw ratio used to make the substantially fully drawn filaments that are fed to the steam-annealing pressurized zone (steam chamber 20 in Fig. 1).

- PRUD is the ratio of the speed of the puller roll (22), after the steam chamber, to the speed of the draw roll (14), before the steam chamber.

TDR is the total draw ratio, i.e. $\text{TDR} = \text{PRUD} \times \text{MDR}$.

- The filaments used in the process of the invention may be drawn by any means known to those skilled in the art. A draw process substantially of the type described by Vail (U.S. Patent 3,816,486) is suitable for the drawn filament supply. First and second stage draw ratios are selected based on polymer composition, spun orientation and desired final tensile properties. Single-stage processes are also suitable. For optimum dyeability, filaments should not be overdrawn. Excessive draw ratios yield no advantage in drawn filament tenacity compared to lower draw ratios. However, it has been found that dye rate is adversely affected when draw ratio is excessive. At any given level of spun orientation, optimum draw ratio depends on polymer composition and relative viscosity. It is known to those skilled in the art that some adjustment can be required to determine optimum draw ratio for any given combination polymer type and spun orientation.

- The drawn filament bundle is advanced to, enters and then leaves the steam chamber through orifices sized and designed to maintain the desired superatmospheric pressure inside the chamber. Filament bundle thickness and shape (e.g., round or ribbon) and chamber residence time are adjusted so that substantially all filaments reach the saturated steam temperature. For tow bundles of about 50,000 denier, circular orifices 0.125 inch (3.2 mm) in diameter and 1.25 inches (32 mm) long are satisfactory. Residence times can be from about 0.2 to about 1 second. A low residence time, such as 0.2 to 0.6 seconds may be preferred when it is desired to minimize surface trimer content, otherwise higher residence times may be preferred.

- Steam can be fed into the chamber substantially uniformly along its length, as from orifices along a manifold along the inside top of the chamber, thus avoiding impingement of the incoming steam directly onto the filaments as is required in steam-jet drawing. The chamber is fitted with a condensate outlet. The steam supply system is sized and fitted with control valves and gauges as appropriate to maintain and measure pressure inside the chamber. As the tow of filaments leaves the chamber, it is rapidly cooled by evaporation of water to about 100°C, or less, at normal atmospheric pressure.

- The tow is then forwarded to a crimper. It is well known that fiber tensile properties, particularly T_f , and crimp frequency and crimp amplitude depend both on temperature of the tow entering the crimper and on temperature inside the crimper. Excessive temperatures can reduce T_f and give undesirably high crimp frequency. Additional cooling of the tow before the crimper may be needed and temperature inside the crimper must be carefully controlled for optimum results. A suitable lubricating finish is generally applied prior to crimping.

In prior commercial hot-roll annealing processes, appreciable energy and time is required to remove residual water from the drawn bundle before annealing occurs. It is a particular advantage of this invention that any such residual water need not be removed.

- The steam pressure in the process of this invention preferably should not exceed about 320 psig (2300 kPa) for the higher melting polymers, corresponding to a saturation temperature of about 220°C. Higher temperatures adversely affect filament properties and create operability problems because of proximity to the filament softening temperature. Copolymers which have a lower softening temperature require a correspondingly lower maximum operating temperature, i.e., a lower steam pressure. It is preferred that the maximum temperature that the filaments reach be that of the condensation temperature corresponding to the steam pressure in the steaming zone. Other than to control flooding, superheating is unnecessary.

To achieve optimum filament dye properties a small amount of let down (retraction), especially with copolymers, of from 3 to 10% in the annealing zone is required. Allowance of greater retractions can lead to operability problems and poorer tensile properties.

- Although it is not fully understood why the steam-annealed filaments prepared by this invention have such an improved combination of properties, it is theorized that it can be attributed to a novel fine structure in which high amorphous orientation and high amorphous chain mobility occur simultaneously. Consistent with this belief, it has been found that the better steam-annealed fibers of this invention have a higher long-period spacing (LPS — the average distance between adjacent crystal centers along the fiber axis) as determined by X-ray, than filaments having similar tensile properties and percent crystallinity but annealed

under comparable conditions with other heating methods such as hot rolls. A high LPS means that anchor points for polymer chains in the amorphous region are widely separated. This perhaps allows for greater amorphous mobility. For example, whereas the LPS is usually less than about 120 Å for highly oriented fibers annealed commercially with heated rolls, fibers annealed with saturated steam to similar levels of crystallinity and of shrinkage generally have an LPS of 125—150 Å.

Highly crystalline, low shrinkage fibers are usually difficult to crimp. This possibly is because some shrinkage in the crimper is needed to develop crimp amplitude. Steam-annealed fibers appear surprising in that, even after crimping, they have a measurable level of low temperature shrinkage, i.e., shrinkage in boiling water (BOS), despite high crystallinity, as indicated by density and low dry shrinkage at 196°C. Both the easy crimpability and the measurable BOS possibly result from the same unusual fine structure feature. It is hypothesized that the intercrystalline regions are relatively free of microcrystals, very small local aggregations of chain segments in a crystalline configuration. Microcrystals would inhibit motion of amorphous chain segments at low temperatures, thereby reducing low temperature shrinkage and making crimping more difficult. However, they would melt at relatively low temperatures and, therefore, not contribute to length stability at high temperatures. Because they reduce amorphous chain mobility, microcrystals could also reduce dyeability.

It is possible that the rapidity with which the filaments are first heated, and then cooled, in the steam-annealing process of the invention, could be of significance in determining the fine structure of the resulting products.

The fine structure of the filaments of the invention and the associated advantages thereof can be most readily detected by measurement of dye rate and filament orientation. Dye rate reflects both mobility and orientation, whereas the sum of the tenacity and T_7 , i.e., $T + T_7$, directly reflects orientation alone. By examining these and other structure-sensitive properties, the effects of the invention can be identified.

The fibers of this invention have an improved combination of properties including improved strength, low dry heat shrinkage to maximize fabric yield after heat-setting, and a high dye rate to reduce dyeing costs. Some filaments of this invention further reflect their improved properties through superior crimp and a lower concentration of surface cyclic trimer. The latter provides improved processability and fewer deposits during processing into yarn.

The improved filaments of the invention can be described by their position in a three-dimensional space described by three coordinates relating to amorphous orientation (namely $T + T_7$), amorphous chain mobility (namely RDDR) and weight percent copolymer modifier (i.e. WMOD). This is why we have used herein the "D" number, which is defined above, as a simple function of the above three parameters, and which is less than about 3.8 for strong, low-shrinkage annealed filaments of the invention.

Steam-annealing by this invention has a particularly unexpected effect on site dye copolymers such as the cationically dyeable polyesters made by including in the polymer chain an aromatic acid monomer containing a sodium sulfonate group, such as 5-sodium-sulfo-isophthalic acid. Whereas the uptake of reactive cationic dyes by such polymers in filaments usually depends upon the number of reactive sites in the fiber, it has been discovered that a terpolymer fiber of the invention containing 1.6 weight % of the site-reactive isophthalate plus a neutral dimethyl glutarate co-monomer gives a higher dye uptake than a conventional fiber containing about 3 weight % of the cationic dye site. This surprising effect can be used to either improve dyeability at an equal modifier level or to maintain dyeability at a reduced modifier level.

The response of dye rate to comonomer content with neutral comonomers also benefits from steam-annealing by this invention. A steam-annealed fiber containing 2.9% ethylene glutarate derived from dimethyl glutarate (DMG) was found to be fully equivalent in dye rate to a known fiber containing 5.7% ethylene glutarate, and to have substantially better tensile properties in addition. In general copolymers show similar improved development of crimp amplitude and reduced levels of surface cyclic trimer as obtained with homopolymers.

On average, the steam-annealed filaments of the invention have about a 1.5% higher dye rate than roll-annealed filaments made from the same base polymer and of similar orientation, crystallinity and shrinkage.

At equal $T + T_7$, steam-annealed homopolymer filaments have less surface cyclic trimer (SCT) than roll-annealed filaments of comparable shrinkage. The trimer level generally increases with draw ratio, i.e., orientation.

Filaments of this invention may be prepared from multifilament tows in textile deniers per filament (dpf), preferably less than 6.0 dpf, as well as in heavier carpet and industrial filament and yarn sizes. The filaments preferably are combined in the form of a heavy tow, such as is greater than about 30,000 denier, and especially greater than about 200,000 denier. The filaments are not restricted to any particular type of filament cross-section and include filaments of cruciform, trilobal, Y-shaped, ribbon, dog bone, scalloped-oval and other non-circular cross-sections, as well as round. The filaments may be used as crimped continuous filaments, yarns, or tows, or as staple fibers of any desired length, including conventional staple lengths of from about 0.75 to about 6 inches (about 20 to 150 mm).

The filaments are crimped to the desired degree depending upon their use. For conventional staple fiber applications the filaments preferably have a crimp index of at least about 20.

The invention is illustrated in the following Examples, which illustrate also the results of comparative workings, some without steam and some using saturated steam at pressures lower than about 150 psig,

i.e., lower than about 1100 kPa, to demonstrate the different results that have been obtained. The use of saturated steam at high pressure according to the invention is believed to be important because this enables the filaments, which are generally present in extremely large numbers, to be heated efficiently and rapidly to the temperature of the saturated steam. When such annealing temperatures are considered, the improvements that can be obtained by raising the pressure of the saturated steam are, with certain polymer compositions, very dramatic in terms of the amount the properties can be changed by a relatively small increase in temperature. This can be seen, for instance, by comparing the results in Example 4.

Example 1

Filaments of poly(ethylene terephthalate) homopolymer (0.5% diethylene glycol impurity, DEG) of about 21RV and having 4.0 dpf, were spun at 1500 ypm (1372 meters/min) and collected. The resulting tow of 31,500 filaments is drawn in two stages using a process substantially of the type as described in U.S. Patent 3,816,486 (Vail) to a drawn dpf of about 1.5. The tow is passed from the last stage draw rolls through a pressurized steam chamber, while maintained under a controlled length, for 0.4 seconds, withdrawn into ambient atmospheric pressure, accompanied by rapid cooling to about 100°C while still at said controlled length. The tow is then passed through a 70°C water-spray with 0.3% finish and then steam-crimped in a conventional manner using a stuffer-box crimper. All crimped fibers were dried at substantially zero tension in a relaxer oven at 90°C unless specified.

The pressurized steam annealing chamber is 15 inches (38 cm) long with an inside diameter of about 1.4 inches (3.6 cm). The tow entrance and exit orifices are 0.125 inch (3.2 mm) diameter and 1.25 inches (3.2 cm) long. Steam enters the chamber horizontally from orifices spaced along sides of a manifold along the inner top of the chamber.

In Table 1A, properties are compared of filaments made under essentially similar conditions except for the pressure of the saturated steam fed to the annealing chamber. Item 1 is a control carried out without steam, and Items 2 and 3 are controls with steam at high pressures that are below 1100 kPa, whereas Items 4 and 5 are carried out according to the invention. A comparison, especially between items 3 and 4, shows a significant reduction in shrinkage, with the tensile properties, dyeability, surface trimer content and crimpability, however, providing a good balance of properties. The difference in fine structure is shown by the significant rise in the long-period spacing for products made according to the process of the invention. This is also shown by comparing the plots in Figs. 2 and 3.

A further comparison of crimped filament properties obtained by varying process conditions can be seen from Table 1B. Item 1 is the same as in Table 1A, having a good combination of properties except for the high shrinkage. Items 2 and 3, prepared under similar conditions except for drying at higher temperatures, show that this method of reducing shrinkage reduces tensile properties and dye rate, and Item 3 also shows a significant and undesired increase in surface trimer. Items 4—7 are all prepared according to the invention using differing draw ratios (MDR) and differing retractions during annealing (PRUD), to show the variety of property combinations that can be obtained by steam-annealing, and all showing a very good balance of orientation and dye-rate. Items 6—7 were prepared from filaments containing 1.0% DEG, and 0.2% TiO₂, of 3.2 dpf, spun at 1900 ypm (1737 meters/min).

As compared with the products of hot roll annealing to comparable levels, the steam-annealed products of the invention generally have a lower surface trimer content, a better crimpability and a higher dye rate.

When another portion of Item 4, Table 1B, was dried at 125°C (instead of 90°C) it had the following properties: DPF 1.45, T 6.6, gpd, T₇ 2.7 gpd, Elongation 14%, DHS (196°C) 6%, SCT 180 ppm, density 1.401 gm/cc, RDDR 0.035, "D" number 4.4 and "T" number 28. When dried at 150°C the properties were: DPF 1.47, T 6.6, gpd, T₇ 2.0 gpd, Elongation 16%, DHS 6%, SCT 565 ppm, density 1.397 gm/cc and RDDR 0.026, "D" number 6.3 and "T" number 101. These higher "D" and "T" numbers demonstrate why it is desirable to maintain the temperature lower during drying.

Further products of the invention are shown in Table 1C, which is included to show fine structure parameters, which are also plotted in Figs. 2 and 3.

The above homopolyester filaments were of relative viscosity within the range 18-22, which is conventional for most apparel purposes. It is well known that use of lower viscosity polymer can provide polyester filaments of lower tensile properties, such as are generally undesirable for many textile purposes. These lower tensile properties are, however, accompanied by a lower flex life, giving a lower pilling tendency in the resulting fabrics. This can be very important, e.g. in certain knit fabrics, and so has sometimes outweighed any disadvantages of lower tensile properties. Accordingly, the tensile properties of the crimped filaments of the invention are affected by the relative viscosity of the polymer used. If lower viscosity polymer is used to make the polyester filaments, the tensile properties of the resulting steam-annealed crimped filaments can be expected to be correspondingly lower than for otherwise similar filaments of conventional viscosity. Thus, for uses when a low pilling tendency is important, a preferred group of filaments is of poly(ethylene terephthalate) having at least 93% dioxyethylene and terephthaloyl radicals, and especially at least 97% of such radicals, and having a relative viscosity of from about 9 to about 14, with a T₇ of greater than about 1.1 gpd, preferably greater than 1.2 gpd, a T + T₇ of greater than about 5 gpd and less than about 8 gpd, a dry heat shrinkage (196°C) of less than about 10%, a "D" number of less than about 3.8 and greater than about 1.8, and a trimer "T" number of less than about 25. As

indicated, the surface trimer content can generally be expected to be higher than for filaments of conventional viscosity. Such dependence on the relative viscosity of the tensile properties ($T + T_7$) and of the surface trimer content ("T" number) is represented graphically as in Fig. 5. These relationships can also be represented mathematically, e.g.—

$$3.31 \geq 3.31 \ln(RV) - (T + T_7) \geq 0.1$$

Because steam-annealing according to the invention provides crimped annealed filaments having an improved balance of properties, this provides a way to improve somewhat the tensile strength of low molecular weight polymers, while improving the dyeability, and also providing filaments of lower flex resistance, i.e. improved pill-resistance, as shown in the following Example.

Example 2

Filaments of poly(ethylene terephthalate) homopolymer (0.7% DEG, and 0.3% TiO_2 with 0.2% tetraethyl silicate added to improve melt viscosity as taught by U.S. Patent 3,335,211 to Mead and Reese) of about 12 RV having 3.8 dpf were spun at 1810 ypm (1655 meters/min) and collected. A combined bundle of 33,400 filaments was drawn in a single stage in the spray zone, but otherwise treated essentially as described in Example 1.

Process conditions and properties of filaments annealed without steam, for comparative purposes, and with steam at the indicated pressures are given in Table 2. The significant improvement achieved by steam-annealing can be noted in the tensile properties, shrinkage, and dye rate, as well as reduced flex life, indicating better pill-resistance.

For the homopolymers containing very little DEG, a high steam pressure of about 150 psig (1100 kPa) or even more is generally used to obtain the desirable low shrinkages, which are preferably not more than 8%. Although such low shrinkage can be obtained by other means, the low shrinkage has not previously been obtained with the desirable balance of properties, as disclosed herein. Similarly, for copolymers containing small amounts of nonionic modifiers, as shown hereinafter, the shrinkage is significantly affected by temperature.

Essentially the same procedures as in Example 1 were used to make the filaments in the following Examples varying the compositions of polymer and the process conditions as discussed and shown in the Tables. Spinning speeds of 1900 ypm (1737 meters/min) were used for some items.

Many of the samples with WMOD exceeding 3.0% were drawn via using single stage equipment similar to that described by Vail (U.S. Patent 3,816,486) but with all the draw taken in the second stage spray zone. Temperature in the draw zone was adjusted for best operability and ranged from 90 to 98°C. It is known to those skilled in the art that experimentation is frequently needed to achieve good draw operability with copolymers.

At least a small amount of letdown (PRUD), about 1 to 2%, in the steam annealing zone is generally desired for optimum properties. A dry heat shrinkage of less than 8% is preferred for filaments to be used in woven fabrics.

Example 3

In Table 3, the properties are compared of crimped filaments prepared from polymers containing higher proportions of dioxy-di(ethylene oxide) obtained by adding diethylene glycol (DEG) to the monomer feed, so that the total content of DEG in the polymer was 2.4% by weight. The filaments comprised polymer of RV 20. A representative crimped sample had a melting point of 249.6°C. Item 1 is a control prepared without steam-annealing, and has a satisfactorily low shrinkage, but also has low tensile properties. The dyeability is superior to that of a homopolymer. The usual reason for modifying the homopolymer is to increase dyeability. Comparison of Items 1 and 2, made under somewhat different draw conditions, shows the improvement in dyeability and tensile properties, and thus the improved balance of properties obtained by steam-annealing (Item 2). Item 2 is also superior to comparable hot roll annealed products in balance of dyeability and tensile properties and in crimp index. Although Items 3 and 4 are both annealed using comparable pressures of saturated steam, the dyeability of Item 4 is inferior to that of Item 3 because Item 4 was overdrawn. Thus, optimum processing conditions can be determined empirically by measuring the properties of the resulting filaments. It should be noted that the tensile properties of Item 4 are superior to those of Item 1.

Example 4

Table 4 shows a comparison of the properties of crimped filaments prepared from a copolymer of poly(ethylene terephthalate), containing about 3% ethylene glutarate (1.8% glutaryl radicals) by adding dimethyl glutarate comonomer (DMG), and 1.2% DEG as impurity, so with total WMOD 2.9%, and 0.2% TiO_2 , spun at 1900 ypm (1737 meters/min) to 3.2 dpf filaments, of about 20 RV, which were drawn, annealed and crimped essentially as described in Example 1. A representative crimped fiber had a melting point of 246.5°C. This comparison shows an improvement in properties that can be obtained by annealing with steam at higher pressures.

Item 3 shows a significantly improved shrinkage of 6% over Item 2 (10%), although the temperature of the saturated steam was only 5° higher (188° instead of 183°), whereas the difference in shrinkage between Items 1 and 2 is smaller (12% to 10%), despite a rise in temperature of 12°. It will be noted also that the LPS

of Item 3 (126 Å) is significantly larger than those of Items 1 and 2 (114 and 115 Å), showing the significant change in fine structure.

Example 5

Table 5 shows the useful properties of crimped filaments obtained by steam-annealing poly(ethylene terephthalate) containing 2.1% of polyethylene oxide of 600 molecular weight, and 1.0% DEG, so with total WMOD 3.0%, and 0.2% TiO₂, spun at 1900 ypm (1737 meters/min) to 3.36 dpf filaments of about 22 RV, which were drawn, annealed and crimped essentially as described in Example 1. A representative crimped sample had a melting point of 253.1°C. The excellent dye rates and low shrinkages can be noted. As compared with hot roll annealed products (comparable levels), the steam-annealed products generally have lower surface trimer levels, better "D" numbers and better crimpability.

Fig. 2 shows relationships between LPS and ACS for items of the invention from the foregoing Examples. Items with ACS and LPS falling below the lines HK and KJ were made at anneal temperatures below 185°C (below 150 psig) and have high residual shrinkages. Further, although high shrinkage fibers usually have relatively high dye rates, those falling outside the area HIJK have the same or a poorer balance of orientation and dye rate than those within the area. This is evident by comparing "D" numbers in the Tables.

Fig. 3 shows relationships between the ratio of ACS to LPS, and weight % crystallinity calculated from density for items containing 1% or less DEG. Best filaments fall within the area LMNOP.

It is hypothesized that steam-anneal fibers of the invention have an unusually high amorphous free volume (which favors dye rate) while also having good tensile properties and low residual shrinkage. It is believed that the parameters in FIGS. 2—4 reflect this good balance of fine structure properties.

Example 6

Table 6 compares the properties of crimped filaments of RV of about 20 from poly(ethylene terephthalate) containing 5.7% ethylene glutarate from DMG comonomer, 3.5% glutaryl radicals and 0.7% DEG (WMOD 4.2%), and 0.2% TiO₂. A representative crimped sample had a melting point of 242°C. There is a surprising improvement in dyeability for the filaments that have been steam-annealed according to the invention over both unannealed filaments (Item 1) and filaments annealed with saturated steam at lower pressures (Item 2). Although Item 2 shows an improvement in tensile properties over the unannealed product (Item 1), the shrinkage is unacceptably high, and the low LPS shows the difference in fine structure from the filaments annealed at the higher pressures according to this invention (Items 3 and 5).

Although Item 4 has low tensile properties, as compared with Items 3 and 5, these tensile properties are comparable to those of Item 1, and yet the dye rate of Item 4 is far superior, showing that the process of steam-annealing according to the invention can lead to useful products outside the product claims.

Example 7

Table 7 shows the useful properties of crimped filaments of poly(ethylene terephthalate) of about 22 RV containing 4.6% polyethylene oxide (PEO) of 600 molecular weight and 0.7 DEG (WMOD 5.2%) and 0.2% TiO₂, spun at 1900 ypm (1737 meters/min) to give filaments which were drawn, annealed and crimped at several draw ratios and annealer retractions. A representative sample of crimped tow melted at 251.9°C. These filaments, containing even more PEO than those in Example 5, show a further improvement in properties, especially dye rate.

Example 8

Table 8 compares the properties of crimped filaments of two cationically dyeable copolymers of poly(ethylene terephthalate) containing the indicated amounts of ethylene sodium sulfoisophthalate, and of DEG, and the WMOD values, and containing 0.2% TiO₂, spun at 1900 ypm (1737 meters/min) prepared in essentially similar manner. A comparison of Items 3 and 4 shows the improvement in tensile properties and dyeability obtained by use of high annealing steam pressures according to the present invention. A representative crimped sample had a melting point of 249.4°C, whereas such a sample of Item 2 had a melting point of 250.2°C. The difference in fine structure is demonstrated by the higher LPS values of the filaments prepared according to the invention. A comparison of these results with those in the following Table will show that the steam annealing of the invention can allow substantial reduction in copolymer content without sacrifice in dyeability.

Example 9

Table 9 shows a comparison of the properties of crimped filaments of cationically-dyeable copolymers of poly(ethylene terephthalate) of RV about 17 containing 3.0% ethylene sulfoisophthalate (2.4% sodium sulfoisophthaloyl radicals) and 2.2% DEG as impurity, (WMOD 4.5%) and 0.2% TiO₂, spun at 1900 ypm (1737 meters/min), prepared in essentially similar manner. A representative crimped sample had a melting point of 247°C. The improvement in dyeability for Item 3 over the unannealed filaments (Item 1) and over the filaments annealed at lower steam pressures (Item 2) is particularly noticeable. Annealing at lower pressures of saturated steam (Item 2) also leads to an increase in shrinkage over the unannealed filaments (Item 1). A particularly good dye rate is obtained with a large retraction during the annealing step, as shown in Item 4, where the retraction was about 12%, although this increase in dyeability may be accompanied by some loss in tensile properties, so letdowns (retractions) of 10% or less are generally preferred. Item 3 has

a good balance of tensile properties and dyeability, and is 70% superior in dye rate over comparable hot-roll annealed filaments.

Example 10

Table 10A compares the properties of crimped filaments of cationically-dyeable copolymers containing 1.6% ethylene sodium sulfoisophthalate (1.3% sodium sulfoisophthaloyl radicals), 2.4% ethylene glutarate (1.4% glutaryl radicals) from DMG, and 1.3% DEG as impurity WMOD 4.0%. A representative crimped sample had a melting point of 246.5°C. The filaments according to the inventions again have improved dyeability. Steam-annealing at lower pressures raises the shrinkage. The difference in fine structure is again shown by the rise in LPS.

The crimped tow of Item 5 is cut to 1.5 inch (38 mm) staple and spun into yarns which are knitted into fabric. The fabric is dyed without carrier at the boil with disperse and with cationic dyes and compared with dyed 2.25 dpf commercial cationically dyeable polyester staple (Type 64 made by E. I. du Pont de Nemours and Company). Filament tensile properties and dye results are shown in Table 10B. It is seen that the dye rate and the dye bath exhaust by the steam-annealed filaments are significantly superior to those of the commercial fiber. It is surprising that higher exhaust is obtained, even with cationic dyes, for the test item of the invention which contained 40% less reactive dye sites than the commercial fiber.

The relationships between LPS and ACS for the items of Examples 6 to 10 are shown in FIG. 4. Items of the invention fall in the area STUV. The criticality of these parameters is evident from the Tables. Items within the area have excellent dye rate/orientation balance and low residual shrinkage.

The criticality of steam pressure is clearly shown by comparison of Table 10A, Items 3 and 4 which were made with comparable draw ratios. Item 4 shows very significant improvements in dye rate/orientation balance as shown by "D" number and in shrinkage.

The LPS coordinates of the area HIJK in FIG. 2 and STUV in FIG. 4 are similar (125 to 150 Å and 124 to 150 Å respectively) but the ACS coordinates for filaments with WMOD 3% are shifted by about 3.5 Å. Presence of comonomer increases ACS significantly but changes LPS only slightly.

In the following Tables, polymer compositions, filament tenacity T , T_7 , and $T + T_7$, were rounded off to one decimal place in the Tables. Small discrepancies (e.g., 0.1 units) between a sum and its components is explained by this rounding off versus calculations from the actual values determined. This applies also to values for machine draw ratio, underdrive in annealing and total draw ratio.

21

EP 0 125 112 B1

TABLE 1A
Homopolymer (0.5—1% DEG)

Item No.	1	2	3	4	5
<i>Process</i>					
MDR	2.92	2.91	2.90	2.91	2.91
PRUD	0.99	0.99	0.99	0.99	0.99
TDR	2.89	2.88	2.88	2.88	2.88
Press. (kPa)	—	440	760	1130	1480
Temp. (°C)	—	148	168	185	198
<i>Properties</i>					
DPF	1.55	1.52	1.50	1.49	1.45
T (gpd)	5.1	5.7	6.2	6.2	6.7
T ₇ (gpd)	2.0	2.3	3.4	3.1	3.7
Elongation (%)	24	21	21	19	19
T + T ₇ (gpd)	7.1	8.0	9.6	9.3	10.4
BOS (%)	7.4	2.4	3.1	1.3	2.2
DHS (196°C) (%)	14	11	11	7	8
Density (g/cc)	1.368	1.37	1.386	1.390	1.392
RDDR	0.052	0.049	0.042	0.046	0.043
Crimp Index	32	37	31	30	27.5
SCT (ppm)	0	1	11	47	52
Cryst. Index (%)	20	31	45	60	—
ACS (Å)	49	53	51	57	—
LPS (Å)	—	95	95	127	—
"D" Number	3.6	3.5	3.6	3.4	3.3
"T" Number	<1	<1	2	7	7
Weight % Crystal	—	30	42	46	—
ACS/LPS Ratio	—	.55	.53	.45	—

All except 1 steam-annealed, and all dried at 90°C.

TABLE 1B
Homopolymer (0.5—1% DEG)

Item No.	1	2	3	4	5	6	7
<i>Process</i>							
MDR	2.92	2.92	2.92	3.04	2.76	2.52	2.52
PRUD	0.99	0.99	0.99	0.96	0.93	0.97	0.93
TDR	2.89	2.89	2.89	2.93	2.58	2.45	2.34
Press. (kPa)	—	—	—	1480	1480	1480	1480
Temp. (°C)	—	—	—	198	198	198	198
Drier (°C)	90	125	135	90	90	90	90
<i>Properties</i>							
DPF	1.55	1.65	1.68	1.43	1.57	1.40	1.43
T (gpd)	5.1	5.2	5.0	6.5	6.0	5.7	5.6
T ₇ (gpd)	2.0	1.2	1.2	3.4	2.5	3.0	2.0
Elongation (%)	24	28	33	14	26	19	22
T + T ₇ (gpd)	7.1	6.4	6.2	9.9	8.5	8.7	7.6
BOS (%)	7.4	0.9	0.5	1.6	1.5	2	2
DHS (196°C) (%)	14	7	5	7	5	6	3
Density (g/cc)	1.368	1.385	1.384	1.393	1.396	1.392	1.398
RDDR	0.052	0.046	0.034	0.042	0.062	0.049	0.065
Crimp Index	32	30	28	29	20	27	28
SCT (ppm)	0	60	200	116	55	35	25
Cryst. Index (%)	20	—	49	75	—	72	73
ACS (Å)	49	—	54	68	—	64	69
LPS (Å)	—	—	100	138	—	131	134
"D" Number	3.6	4.4	6.2	3.5	2.6	3.6	3.0
"T" Number	<1	17	58	16	10	6	5
Weight % Crystal	—	—	41	48	—	48	53
ACS/LPS Ratio	—	—	.54	.49	—	.49	.51

EP 0 125 112 B1

TABLE 1C
Homopolymer (0.5—1% DEG)

Item No.	1	2	3	4	5
<i>Process</i>					
MDR	2.75	2.92	3.10	2.94	2.74
PRUD	0.96	0.94	0.90	0.90	0.90
TDR	2.65	2.74	2.79	2.64	2.47
Anneal Press. kPa	1510	1440	1480	1510	1550
Anneal Temp. (°C)	199	197	198	199	202
DPF	1.59	1.54	1.46	1.54	1.65
T	5.6	6.3	6.8	6.0	5.7
T ₇ (gpd)	2.9	2.8	2.3	2.0	1.7
T + T ₇ (gpd)	8.5	9.1	9.1	8.0	7.4
DHS (196°C) (%)	6	6	5	3	3
"D" Number	2.9	2.9	3.0	2.7	2.1
"T" Number	11	13	11	8	6
RDDR	0.057	0.055	0.053	0.064	0.085
SCT	61	76	65	38	24
Density (g/cc)*	1.3942	1.3921	1.3965	1.3968	1.3995
Cryst. Index (%)	70	72	73	77	79
ACS (Å)	66.5	64	67	71	74
LPS (Å)	140	134	138	137	146
Weight % Crystal	49	47.5	51	51	54
ACS/LPS Ratio	.475	.475	.485	.52	.51

TABLE 2
Homopolymer (0.7% DEG)—12RV

Item No.	1	2	3
<i>Process</i>			
MDR	3.08	3.08	3.09
PRUD	0.99	0.95	0.95
TDR	3.05	2.93	2.93
Press. (kPa)	—	1340	1510
Temp. (°C)	—	193	199
Drier (°C)	110	80	80
<i>Properties</i>			
DPF	1.60	1.55	1.56
T (gpd)	3.4	4.5	4.2
T ₇ (gpd)	1.7	2.5	2.5
Elongation (%)	32	18	21
DHS (196°C)	7.5	3	3
Density (g/cc)	1.370	1.395	1.395
RDDR	0.056	0.075	0.088
Crimp Index	32	24	23
SCT (ppm)	—	49	86
Cryst. Index (%)	37	75	72
ACS (Å)	55	65	65
LPS (Å)	94	130	137
"D" Number	4.7	2.8	2.4
"T" Number	—	13	23
Flex Life	9611	5198	6324
Weight % Crystal	29	50	50
ACS/LPS Ratio	.59	.50	.47

TABLE 3
Copolymer Containing Added DEG, WMOD 2.35%

Item No.	1	2	3	4
<i>Process</i>				
MDR	3.19	3.08	2.84	3.19
PRUD	0.98	0.94	0.99	0.99
TDR	3.14	2.90	2.82	3.15
Press. (kPa)	—	1440	1480	1480
Temp. (°C)	—	197	198	198
Drier (°C)	130	90	90	90
<i>Properties</i>				
RV	20	20	20	20
DPF	1.61	1.47	1.56	1.41
T (gpd)	5.4	6.6	5.6	6.6
T ₇ (gpd)	1.2	2.9	2.6	2.6
Elongation (%)	31	19	24	17
Crimp Index	—	28	32	32
DHS (196°C) (%)	7	6	9	7
Density (g/cc)	—	1.394	1.387	1.388
SCT (ppm)	—	46	—	73
RDDR	0.054	0.075	.073	.057
T + T ₇ (gpd)	6.6	9.4	8.3	9.2
"D" Number	5.9	3.3	3.7	4.3
"T" Number	—	7	<13*	12
Cryst. Index	—	—	75	73
ACS (Å)	—	—	70	69
LPS (Å)	—	—	136	132
Weight % Crystal	—	—	50	49
ACS/LPS Ratio	—	—	.51	.52

*estimated

TABLE 4
Copolymer From DMG and DEG, WMOD 2.9%

Item No.	1	2	3
<i>Process</i>			
Press. (kPa)	790	1070	1200
Temp. (°C)	170	183	188
<i>Properties</i>			
T ₇ (gpd)	1.8	2.6	2.2
T + T ₇ (gpd)	6.8	7.9	7.1
DHS (196°C)	12	10	6
RDDR	.087	.094	.11
"D" Number	4.1	3.4	3.2
"T" Number	4	—	—
Density (g/cc)	1.384	1.385	1.392
Cryst. Index (%)	65	76	68
ACS (Å)	58	67	62
LPS (Å)	114	115	126
Weight % Crystal	44	51	46
ACS/LPS Ratio	.51	.58	.49

TABLE 5
Copolymer Containing PEO (2.1%) and DEG (1%), WMOD (3.0%)

Item No.	1	2	3	4
<i>Process</i>				
Press. (kPa)	1480	1480	1200	1200
Temp. (°C)	198	198	188	188
<i>Properties</i>				
T ₇ (gpd)	2.3	2.2	2.3	2.5
T + T ₇ (gpd)	7.9	7.4	7.6	8.0
DHS (196°C)	ca 3	4	8	8
RDDR	.12	.13	.12	.11
"D" Number	2.6	2.7	2.9	2.9
"T" Number	5	8	—	3
Density (g/cc)	1.388	1.388	1.377	1.388
Cryst. Index (%)	72	67	63	70
ACS (Å)	66	63	61	65
LPS (Å)	132	132	126	127
Weight % Crystal	49	45	42	47
ACS/LPS Ratio	.50	.48	.49	.51

TABLE 6
Copolymer From DMG and DEG, WMOD 4.2%

Item No.	1	2	3	4	5
<i>Process</i>					
MDR	2.39	2.39	2.59	2.31	2.49
PRD	0.98	0.97	0.90	0.90	0.94
TDR	2.34	2.32	2.33	2.08	2.34
Press. (kPa)	—	760	1410	1380	1440
Temp. (°C)	—	168	196	194	197
Drier (°C)	140	90	90	90	90
<i>Properties</i>					
DPF	1.78	1.51	1.47	1.66	1.44
Tenacity (gpd)	3.5	3.9	4.1	3.6	4.7
T ₇ (gpd)	0.9	2.0	1.1	1.0	1.6
Elongation (%)	49	39	26	37	28
Crimp Index	35	26	24	21	26
DHS (196°C)	7	12	6	6	6
Density (g/cc)	1.384	1.387	1.396	1.391	1.39
SCRT (ppm)	—	—	35	28	30
RDDR	0.15	0.16	0.22	0.26	0.21
T + T ₇ (gpd)	4.5	5.9	5.2	4.6	6.2
Cryst. Index (%)	—	70	81	—	76
ACS (Å)	—	65	76	—	70
LPS (Å)	—	111	131	—	130
"D" Number	4.8	3.6	2.9	2.7	2.5
"T" Number	—	—	12	11	9
Weight% Crystal	—	47	55	—	51
ACS/LPS Ratio	—	.58	.58	—	.54

TABLE 7
Copolymer Containing PEO and DEG, WMOD 5.2%

Item No.	1	2	3	4
<i>Process</i>				
Press. (kPa)	1200	1480	1480	1340
Temp. (°C)	188	197	197	193
<i>Properties</i>				
T ₇ (gpd)	1.2	1.4	1.5	1.6
T + T ₇ (gpd)	5.7	6.3	6.7	6.7
DHS (196°C)(%)	4	3	5	8
RDDR	.27	.27	.22	.21
"D" Number	2.7	2.5	2.9	3.1
"T" Number	8	2	4	3
Density (g/cc)	1.384	1.389	1.390	1.389
Cryst. Index (%)	79	83	80	71
ACS (Å)	72	77	73	65
LPS (Å)	131	138	131	126
Weight% Crystal	53	56	54	48
ACS/LPS Ratio	.55	.56	.56	.51

TABLE 8
Copolymers containing NaSO₃I and DEG, WMOD as shown

Item No.	1	2	3	4
<i>Composition</i>				
NaSO ₃ I	1.8	1.8	2.4	2.4
DEG	1.7	1.7	1.7	1.7
WMOD	3.1	3.1	3.6	3.6
<i>Process</i>				
MDR	2.18	2.11	2.19	2.27
PRUD	0.97	0.90	0.97	0.94
TDR	2.11	1.89	2.12	2.14
Pres. (kPa)	1270	1410	790	1440
Temp. (°C)	191	196	170	197
<i>Properties</i>				
RV	18	18	17	17
DPF	1.71	1.77	1.74	1.62
T ₇ (gpd)	2.2	1.1	1.0	1.9
T + T ₇ (gpd)	6.4	4.9	4.9	6.5
Crimp Index	34	20	34	32
DHS (196°C)(%)	7	1.5	8	7
RDDR	.11	.19	.12	.15
"D" Number	3.6	2.6	4.6	2.9
"T" Number	—	<1	—	<1
Density (g/cc)	1.39	1.396	1.390	1.396
Cryst. Index (%)	—	—	53	77
ACS (Å)	—	—	53	67
LPS (Å)	—	—	114	130
Weight% Crystal	—	—	36	52
ACS/LPS Ratio	—	—	.47	.51

TABLE 9
Copolymer Containing NaSO₃I and DEG, WMOD 4.5%

Item No.	1	2	3	4	5
<i>Process Conditions</i>					
MDR	2.18	2.28	2.27	2.36	2.12
PRUD	0.99	0.96	0.94	0.88	0.94
TDR	2.17	2.18	2.14	2.07	1.99
Press. (kPa)	—	760	1440	1550	1440
Temp. (°C)	—	168	197	200	197
Drier (°C)	140	90	90	90	90
<i>Fiber Properties</i>					
DPF	1.79	1.60	1.58	1.62	1.72
Tenacity (gpd)	3.9	4.4	4.3	4.2	3.9
T ₇ (gpd)	1.0	1.9	2.2	1.1	1.5
Elongation (%)	33	17	18	20	22
Crimp Index	36	27	31	28	28
DHS (196°C)	5	8	4	3	5
Density (g/cc)	1.391	1.386	1.395	1.400	1.401
SCT (ppm)	—	—	0	0	0
RDDR	0.14	0.14	0.17	0.22	0.20
T + T ₇ (gpd)	4.9	6.3	6.5	5.2	5.4
"D" Number	5.0	4.0	3.2	3.0	3.2
"T" Number	—	—	<1	<1	<1
Cryst. Index (%)	—	—	—	—	80
ACS (Å)	—	—	—	—	75
LPS (Å)	—	—	—	—	136
Weight% Crystal	—	—	—	—	54
ACS/LPS Ratio	—	—	—	—	.55

EP 0 125 112 B1

TABLE 10A
Copolymer Containing NaSO₃I, DMG and DEG, WMOD 4.0%

32

Item No.	1	2	3	4	5	6
<i>Process</i>						
MDR	2.94	2.94	2.79	2.79	2.8	2.7
PRUD	0.96	0.96	0.96	0.96	0.92	0.92
TDR	2.82	2.82	2.68	2.68	2.60	2.47
Press. (kPa)	—	1130	790	1130	1480	1410
Temp. (°C)	—	186	170	186	198	196
Drier (°C)	135	80	90	90	90	90
<i>Properties</i>						
DPF	2.42	2.18	2.25	2.25	2.35	2.46
T ₇ (gpd)	1.1	2.1	1.9	1.9	1.2	1.2
T + T ₇ (gpd)	5.3	6.8	6.3	6.1	5.2	5.0
Crimp Index	19	31	31	27	28	27
DHS (196°C)	7	7	11	6	3	4
RDDR	.10	.14	.12	.18	.24	.26
"D" Number	5.7	3.3	4.2	2.9	2.5	2.3
"T" Number	—	—	1	—	12	1
Density (g/cc)	1.388	1.396	1.389	1.395	1.3975	1.3976
Cryst. Index (%)	—	—	70	74	82	69
ACS (Å)	—	—	64	66	78	70
LPS (Å)	—	—	117	125	136	139
Weight% Crystal	—	—	47	50	56	47
ACS/LPS Ratio	—	—	.55	.53	.58	.50

EP 0 125 112 B1

TABLE 10B

	Composition%	Steam	T-64
5	NaSO ₃ -I	1.6	(2.8)*
	DMG	2.35	—
10	DEG	1.33	(1.9)
	WMOD	4.0	(4.1)
	<i>Fiber Properties</i>		
15	DPF	2.35	2.25
	T (gpd)	3.9	3.4
20	T ₇ (gpd)	1.2	1.1
	Elongation(%)	28	28
	DHS (196°C)(%)	3	ca 5
25	T + T ₇ (gpd)	5.2	4.5
	RDDR	0.24	0.11
30	"D" Number	2.5	(6.2)
	<i>% Dye Bath Exhaust 60 Min. at Boil:</i>		
35	Disperse Dye	95	90
	Cationic Dye	82	66
	Yarn Strength (GM)	440	410
40	Yarn DHS (196°C)(%)	2	5

* Based on nominal composition.

Claims

1. A continuous process for treating a tow of melt-spun polyester filaments, involving the steps of (1) drawing, (2) annealing, (3) crimping and (4) drying, characterized in that the annealing step is effected in a pressurized zone of saturated steam at a pressure of at least 1100 kPa.
2. A process according to Claim 1, characterized in that, between the drawing and crimping steps, the length of the tow is controlled within the range of from about 5% extension to about 10% retraction.
3. A process according to Claim 2, wherein the length of the tow is controlled to permit about 3 to 10% retraction.
4. A process according to any one of the preceding claims, characterized in that the drawn filaments are subjected to the pressurized zone of saturated steam for at least about 0.2 seconds.
5. A process according to any one of the preceding claims, characterized in that the drawn filaments are subjected to the pressurized zone of saturated steam for a time sufficient to heat substantially all of the filaments up to at least the steam saturation temperature corresponding to the steam pressure.
6. A process according to any one of the preceding claims, wherein the drawn filaments are subjected to the pressurized zone of saturated steam for less than about 1 second.
7. A process according to any one of the DP-3630-A(EC) preceding claims, wherein the drawn filaments are subjected to the pressurized zone of saturated steam for about 0.2—0.6 seconds.
8. A process according to any one of the preceding claims, characterized in that the annealing takes place in more than one step.
9. A process according to any one of the preceding claims, characterized in that the filaments are sprayed with an aqueous solution of a lubricating finish between the annealing and crimping steps.

EP 0 125 112 B1

TABLE 10B

	Composition%	Steam	T—64
5	NaSO ₃ —I	1.6	(2.8)*
	DMG	2.35	—
10	DEG	1.33	(1.9)
	WMOD	4.0	(4.1)
	<i>Fiber Properties</i>		
15	DPF	2.35	2.25
	T (gpd)	3.9	3.4
20	T ₇ (gpd)	1.2	1.1
	Elongation(%)	28	28
	DHS (196°C)(%)	3	ca 5
25	T + T ₇ (gpd)	5.2	4.5
	RDDR	0.24	0.11
30	"D" Number	2.5	(6.2)
	<i>% Dye Bath Exhaust 60 Min. at Boil:</i>		
35	Disperse Dye	95	90
	Cationic Dye	82	66
	Yarn Strength (GM)	440	410
40	Yarn DHS (196°C)(%)	2	5

* Based on nominal composition.

Claims

1. A continuous process for treating a tow of melt-spun polyester filaments, involving the steps of (1) drawing, (2) annealing, (3) crimping and (4) drying, characterized in that the annealing step is effected in a pressurized zone of saturated steam at a pressure of at least 1100 kPa.

2. A process according to Claim 1, characterized in that, between the drawing and crimping steps, the length of the tow is controlled within the range of from about 5% extension to about 10% retraction.

3. A process according to Claim 2, wherein the length of the tow is controlled to permit about 3 to 10% retraction.

4. A process according to any one of the preceding claims, characterized in that the drawn filaments are subjected to the pressurized zone of saturated steam for at least about 0.2 seconds.

5. A process according to any one of the preceding claims, characterized in that the drawn filaments are subjected to the pressurized zone of saturated steam for a time sufficient to heat substantially all of the filaments up to at least the steam saturation temperature corresponding to the steam pressure.

6. A process according to any one of the preceding claims, wherein the drawn filaments are subjected to the pressurized zone of saturated steam for less than about 1 second.

7. A process according to any one of the DP—3630—A(EC) preceding claims, wherein the drawn filaments are subjected to the pressurized zone of saturated steam for about 0.2—0.6 seconds.

8. A process according to any one of the preceding claims, characterized in that the annealing takes place in more than one step.

9. A process according to any one of the preceding claims, characterized in that the filaments are sprayed with an aqueous solution of a lubricating finish between the annealing and crimping steps.





10. A process according to any one of the preceding claims, characterized in that the filaments are dried in a relaxed condition at a temperature of less than about 125°C.

11. A process according to Claim 10, characterized in that the filaments are dried at a temperature of less than about 110°C.

5 12. A process according to claims 1, 2, 4 and 10, characterized in that the tow is withdrawn from the pressurized zone into ambient atmospheric pressure whereupon the filaments are rapidly cooled by vaporization of water while they are still under said controlled length.

13. A process according to Claim 12, characterized in that the filaments are cooled further before crimping.

10 14. A process according to any one of the preceding claims, characterized in that the polyester filaments consist essentially entirely of dioxyethylene and terephthaloyl radicals with dioxydiethylene oxide as impurity.

15. A process according to any one of Claims 1—13, characterized in that the polyester is a copolymer containing at least 93% by weight of dioxyethylene and terephthaloyl radicals and is substantially free of units with ionic dye sites.

16. A process according to Claim 15, wherein the other comonomer radicals are one or more of glutaryl, oxy-poly(ethylene oxide) of less than 4000 molecular weight, adipyl, and dioxydiethylene oxide.

17. A process according to Claim 15 or 16, characterized in that the polyester contains at least 97% by weight of dioxyethylene and terephthaloyl radicals.

20 18. A process according to any one of Claims 11—13, characterized in that the polyester contains at least 93% by weight of dioxyethylene and terephthaloyl radicals, at least 1.3% of aromatic radicals containing an anionic dye site and up to about 4% of neutral organic radicals.

19. A process according to Claim 18, characterized in that the aromatic radicals containing an anionic dye site are 5-sodium sulfonate isophthaloyl radicals.

25 20. A crimped filament of poly(ethylene terephthalate) having a relative viscosity of less than about 25 and comprised of at least about 97% by weight of dioxyethylene and terephthaloyl radical repeating units, the filament having an improved balance of dyeability and tensile properties comprising a T_7 of at least about 1.5 gpd and a $(T + T_7)$ of at least about 7 gpd and less than about 10 gpd, wherein T_7 is tenacity at 7% elongation and T is tenacity at break elongation, a dry heat shrinkage at 196°C of less than about 10%, and a dyeability/orientation relationship characterized by a "D" number of less than about 3.8 and greater than about 1.8, wherein the "D" number =

$$e^{0.04(T+T_7)} \times (T+T_7)^{-1.06} \times e^{0.28(WMOD)}$$

35 $RDDR$

wherein WMOD is the total wt.% of radicals other than dioxyethylene and terephthaloyl radicals in the polymer chains and

40
$$RDDR = DDR (DPF/1.50)^{1/2}$$

wherein DDR is measured as described in US—A—4 195 051 and DPF = denier per filament.

21. A crimped filament of poly(ethylene terephthalate) having a relative viscosity of less than about 25 and comprised of at least about 93% by weight of dioxyethylene and terephthaloyl radical repeating units and containing at least about 3% of other neutral radicals but no more than about 0.3% radicals with ionic dye sites, the filament having an improved balance of dyeability and tensile properties comprising a T_7 of at least about 1.1 gpd and a $(T + T_7)$ of at least about 5 gpd and less than about 7 gpd, wherein T_7 is tenacity at 7% elongation and T is tenacity at break elongation, a dry heat shrinkage at 196°C of less than about 10%, a "D" number of less than about 3.8 and greater than about 1.8, and an RDDR of at least about 0.12, wherein the "D" number and RDDR are as defined in Claim 20.

22. A crimped filament of poly(ethylene terephthalate) having a relative viscosity of less than about 25 and comprised of at least about 93% by weight of dioxyethylene and terephthaloyl radical repeating units and containing at least about 1.3% of aromatic radicals containing an ionic dye site and up to about 4% of neutral organic radicals, the filament having an improved balance of dyeability and tensile properties comprising a T_7 of at least about 1.2 gpd and a $(T + T_7)$ of at least about 5 gpd and less than about 7 gpd, wherein T_7 is tenacity at 7% elongation and T is tenacity at break elongation, a dry heat shrinkage at 196°C of less than about 10%, and a "D" number of less than about 3.8 and greater than about 1.8, wherein the "D" number is as defined in Claim 20.

23. A filament according to any one of Claims 20 to 22 having a relative viscosity within the range of about 16 to about 20.

24. A filament according to any one of Claims 20 to 22 having a relative viscosity within the range of about 9 to about 14.

25. A crimped filament of poly(ethylene terephthalate) having a relative viscosity of from about 9 to about 14 and comprised of at least about 93% dioxyethylene and terephthaloyl radical repeating units, the filament having an improved balance of dyeability and tensile properties comprising a T_7 of at least about



1.1 gpd and a $(T + T_7)$ of at least about 5 gpd and less than about 8 gpd, wherein T_7 is tenacity at 7% elongation and T is tenacity at break elongation, a dye heat shrinkage at 196°C of less than about 10%, and a "D" number of less than about 3.8 and greater than about 1.8, wherein the "D" number is as defined in Claim 20.

26. A filament according to Claim 20 or Claim 25 which contains no more than about 0.3% radicals containing ionic dye sites.

27. A filament according to Claim 26 substantially free of ionic dye sites.

28. A filament according to Claim 22 or any one of Claims 25 to 27 having at least about 97% dioxyethylene and terephthaloyl radical repeating units.

29. A filament according to Claim 20 or Claim 25 in which the polyester consists essentially entirely of dioxyethylene and terephthaloyl radicals, with dioxydiethylene oxide as impurity.

30. A filament according to any one of Claims 20 to 22 or any one of Claims 25 to 28 wherein neutral radicals are present and are one or more of glutaryl, adipyl, dioxydiethylene ether, or oxy-poly(ethylene oxide) having a molecular weight of less than 4000.

31. A filament according to Claim 21 or Claim 25 containing from about 3 to about 4% glutaryl radicals and about 1% dioxyethylene ether radicals.

32. A filament according to Claim 22 containing about 3% glutaryl radicals and about 1% dioxyethylene ether radicals.

33. A filament according to Claim 20, Claim 21 or Claim 25 wherein radicals containing an ionic dye site are present and are 5-sodium sulfonate isophthaloyl radicals.

34. A filament according to Claim 22 wherein the aromatic radicals containing an ionic dye site are 5-sodium sulfonate isophthaloyl radicals.

35. A filament according to any one of Claims 20 to 24 having a surface cyclic trimer content as defined by a "T" number of less than about 20, wherein the "T" number =

$$[SCT(\text{ppm}) + 1] \times e^{-0.2(T + T_7)}$$

wherein SCT = surface cyclic trimer.

36. A filament according to Claim 25 having a surface cyclic trimer content as defined by a "T" number of less than about 25, wherein the "T" number is as defined in Claim 35.

37. A filament according to Claim 21 or Claim 25 wherein the T_7 is at least about 1.2 gpd.

38. A filament according to Claim 20, Claim 25 or Claim 29 having an X-ray crystalline fine structure characterized by a long period spacing/crystallite size relationship within the area HIJK of FIG. 2.

39. A filament according to Claim 21, Claim 22 or Claim 25 wherein the long period spacing and apparent crystallite size are such as to be within the area of STUV of FIG. 4.

40. A filament according to any one of Claims 20 to 39 having an apparent crystallite size/long period spacing ratio and weight percent crystallinity such as are within the area LMNOP of FIG. 3.

41. A filament according to Claim 40 having an apparent crystallite size/long period spacing ratio and weight percent crystallinity such as to be within the area NOPQR of FIG. 3.

42. A filament according to any one of Claims 20 to 41 having a dry heat shrinkage at 196°C of less than about 8%.

43. A filament according to Claim 42 having a dry heat shrinkage at 196°C of about 3% or more.

44. A filament according to Claim 42 or Claim 43 having a dry heat shrinkage at 196°C of less than about 6%.

45. A bundle of filaments according to any one of Claims 20 to 44 having a Crimp Index of at least about 20, wherein Crimp Index =

$$\frac{(66.6 - L_c)}{66.6} \times 100$$

and wherein for the measurement of L_c , the crimped tow is straightened by application of about 0.1 gpd load and 0.5 g clips 66.6 cm apart are attached to the extended tow, the tow is then cut 11.7 cm beyond each clip to give a sample of 90 cm extended length, the sample is suspended vertically, hanging freely from one of the clips to allow retraction to crimped length, and after about 30 seconds, the clip-to-clip distance in the free-hanging state (L_c) is measured.

Patentansprüche

1. Kontinuierliches Verfahren zur Behandlung eines Kabels aus schmelzversponnenen Polyester-filamenten, welches die Schritte des (1) Verstreckens, (2) Wärmebehandelns, (3) Kräuseln und (4) Trocknens beinhaltet, dadurch gekennzeichnet, daß der Thermofixierungsschritt in einer Druckzone aus gesättigtem Dampf bei einem Druck von wenigstens 1100 kPa bewirkt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß zwischen dem Verstreckungs- und dem



Kräuselungsschritt die Länge des Kabels innerhalb eines Bereiches von etwa 5% Ausdehnung bis etwa 10% Schrumpfung gesteuert wird.

3. Verfahren nach Anspruch 2, worin die Länge des Kabels so gesteuert wird, daß sich etwa 3 bis 10% Schrumpfung ergibt.

5 4. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die verstreckten Filamente der Druckzone aus gesättigtem Dampf wenigstens etwa 0,2 Sekunden ausgesetzt werden.

5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die verstreckten Filamente der Druckzone aus gesättigtem Dampf über eine Zeit ausgesetzt werden, die ausreicht, im wesentlichen alle Filamente auf wenigstens die Dampfsättigungstemperatur entsprechend dem Dampfdruck aufzuheizen.

10 6. Verfahren nach einem der vorstehenden Ansprüche, worin die verstreckten Filamente der Druckzone aus gesättigtem Dampf weniger als etwa eine Sekunde ausgesetzt werden.

7. Verfahren nach einem der vorstehenden Ansprüche, worin die verstreckten Filamente der Druckzone aus gesättigtem Dampf etwa 0,2 bis 0,6 Sekunden ausgesetzt werden.

15 8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Wärmebehandlung in mehr als einem Schritt stattfindet.

9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Filamente zwischen dem Wärmebehandlungs- und dem Kräuselungsschritt mit einer wässrigen Lösung einer Schmelzappretur besprüht werden.

20 10. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Filamente in entspanntem Zustand bei einer Temperatur von weniger als etwa 125°C getrocknet werden.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß die Filamente bei einer Temperatur von weniger als etwa 110°C getrocknet werden.

25 12. Verfahren nach den Ansprüchen 1, 2, 4 und 10, dadurch gekennzeichnet, daß das Kabel aus der Druckzone in atmosphärischen Umgebungsdruck abgezogen wird, worauf die Filamente schnell durch Verdampfung von Wasser abgekühlt werden, während sie sich noch im Zustand der gesteuerten Länge befinden.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß die Filamente vor dem Kräuseln weiter abgekühlt werden.

30 14. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Polyesterfilamente im wesentlichen vollständig aus Dioxyethylen- und Terephthaloylresten mit Dioxydiethylenoxid als Verunreinigung bestehen.

35 15. Verfahren nach einem der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß der Polyester ein wenigstens 93 Gew.-% Dioxyethylen- und Terephthaloylreste enthaltendes Copolymer ist und im wesentlichen frei von Einheiten mit ionischen Färbestellen ist.

16. Verfahren nach Anspruch 15, worin die anderen Comonomerreste ein oder mehrere aus Glutaryl, Oxy-poly(ethylenoxid) mit einem Molekulargewicht von weniger als 4000, Adipyl und Dioxydiethylenoxid sind.

40 17. Verfahren nach Anspruch 15 oder 16, dadurch gekennzeichnet, daß der Polyester wenigstens 97 Gew.-% Dioxyethylen- und Terephthaloylreste enthält.

18. Verfahren nach einem der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß der Polyester wenigstens 93 Gew.-% Dioxyethylen- und Terephthaloylreste, wenigstens 1,3% aromatische Reste, die eine anionische Färbestelle enthalten, und bis zu etwa 4% neutrale organische Reste enthält.

45 19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß die aromatischen Reste, die eine anionische Färbestelle enthalten, 5-Natriumsulfonatisophthaloylreste sind.

20. Gekräuselteres Filament aus Poly(ethylterephthalat) mit einer relativen Viskosität von weniger als etwa 25 und enthaltend wenigstens etwa 97 Gew.-% Dioxyethylen- und Terephthaloylrestwiederholungseinheiten, wobei das Filament eine verbesserte Balance der Färbbarkeits- und Zugeigenschaften unter Einschuß eines T_7 von wenigstens etwa 1,5 gpd und eines $(T + T_7)$ von wenigstens etwa 7 gpd und weniger als etwa 10 gpd, worin T_7 die Festigkeit bei 7% Dehnung und T die Festigkeit bei Bruchdehnung ist, eines Trockenhitzeschrumpfs bei 196°C von weniger als etwa 10% und eines Färbbarkeits/Orientierungs-Verhältnisses, das durch eine "D"-Zahl von weniger als etwa 3,8 und mehr als etwa 1,8 gekennzeichnet ist, worin die "D"-Zahl =

$$e^{0,04(T + T_7)} \times (T + T_7)^{-1,06} \times e^{0,025(WMOD)}$$

RDDR

worin WMOD der gesamte Gewichtsprozentanteil der von Dioxyethylen- und Terephthaloylresten verschiedenen Reste in der Polymerkette ist und

$$RDDR = DDR (DPF/1,50)^{1/2}$$

worin DDR gemessen wird, wie in der US—A—4 195 051 beschrieben, und DPF = Denier per Filament ist.

21. Gekräuselteres Filament aus Poly(ethylterephthalat), das eine relative Viskosität von weniger als etwa 25 aufweist und aus wenigstens etwa 93 Gew.-% Dioxyethylen- und Terephthaloylrestwieder-



holungseinheiten zusammengesetzt ist und wenigstens etwa 3% andere neutrale Reste aufweist, jedoch nicht mehr als etwa 0,3% Reste mit ionischen Färbestellen, wobei das Filament eine verbesserte Balance der Farbe- und Zugeigenschaften unter Einschluß eines T_7 von wenigstens etwa 1,1 gpd und eines $(T + T_7)$ von wenigstens etwa 5 gpd und weniger als etwa 7 gpd, worin T_7 die Festigkeit bei 7% Dehnung ist und T die Festigkeit bei Bruchdehnung ist, eines Trockenhitzeschrumpfs bei 196°C von weniger als etwa 10%, einer "D"-Zahl von weniger als etwa 3,8 und mehr als etwa 1,8 und eines RDDR von wenigstens etwa 0,12, worin die "D"-Zahl und der RDDR wie in Anspruch 20 definiert sind, aufweist.

22. Gekräuselter Filament aus Poly(ethylterephthalat), das eine relative Viskosität von weniger als etwa 25 aufweist und aus wenigstens etwa 93 Gew.-% Dioxyethylen- und Terephthaloylrestwiederholungseinheiten besteht und wenigstens etwa 1,3% aromatische Reste enthält, die eine ionische Färbestelle enthalten, sowie bis zu 4% neutrale organische Reste, wobei das Filament eine verbesserte Balance der Farbe- und Zugeigenschaften unter Einschluß eines T_7 von wenigstens etwa 1,2 gpd und eines $(T + T_7)$ von wenigstens etwa 5 gpd und weniger als etwa 7 gpd, worin T_7 die Festigkeit bei 7% Dehnung und T die Festigkeit bei Bruchdehnung ist, eines Trockenhitzeschrumpfs bei 196°C von weniger als etwa 10% und einer "D"-Zahl von weniger als etwa 3,8 und mehr als etwa 1,8, worin die "D"-Zahl wie in Anspruch 20 definiert ist, aufweist.

23. Filament nach einem der Ansprüche 20 bis 22 mit einer relativen Viskosität im Bereich von etwa 16 bis etwa 20.

24. Filament nach einem der Ansprüche 20 bis 22 mit einer relativen Viskosität im Bereich von etwa 9 bis etwa 14.

25. Gekräuselter Filament aus Poly(ethylterephthalat), das eine relative Viskosität von etwa 9 bis etwa 14 aufweist und wenigstens etwa 93% Dioxyethylen- und Terephthaloylrestwiederholungseinheiten umfaßt, wobei das Filament eine verbesserte Balance der Farbe- und Zugeigenschaften unter Einschluß eines T_7 von wenigstens etwa 1,1 gpd und eines $(T + T_7)$ von wenigstens etwa 5 gpd und weniger als etwa 8 gpd, worin T_7 die Festigkeit bei 7% Dehnung und T die Festigkeit bei der Bruchdehnung ist, eines Trockenhitzeschrumpfs bei 196°C von weniger als etwa 10% und einer "D"-Zahl von weniger als etwa 3,8 und mehr als etwa 1,8, worin die "D"-Zahl wie in Anspruch 20 definiert ist, aufweist.

26. Filament nach Anspruch 20 oder Anspruch 25, das nicht mehr als etwa 0,3% ionische Färbestellen enthaltende Reste enthält.

27. Filament nach Anspruch 26, das im wesentlichen frei von ionischen Färbestellen ist.

28. Filament nach Anspruch 22 oder einem der Ansprüche 25 bis 27 mit wenigstens etwa 27% Dioxyethylen- und Terephthaloylrestwiederholungseinheiten.

29. Filament nach Anspruch 20 oder Anspruch 25, worin der Polyester im wesentlichen vollständig aus Dioxyethylen- und Terephthaloylresten mit Dioxydiethylenoxid als Verunreinigung besteht.

30. Filament nach einem der Ansprüche 20 bis 22 oder einem der Ansprüche 25 bis 28, worin neutrale Reste vorhanden sind und eines oder mehrere aus Glutaryl, Adipyl, Dioxydiethylenether oder Oxy-poly(ethylenoxid) mit einem Molekulargewicht von weniger als 4000 sind.

31. Filament nach Anspruch 21 oder Anspruch 25, das etwa 3 bis etwa 4% Glutarylreste und etwa 1% Dioxyethylenetherreste enthält.

32. Filament nach Anspruch 22, das etwa 3% Glutarylreste und etwa 1% Dioxyethylenetherreste enthält.

33. Filament nach Anspruch 20, Anspruch 21 oder Anspruch 25, worin eine ionische Färbestelle enthaltende Reste vorhanden sind und 5-Natriumsulfonatisophthaloylreste sind.

34. Filament nach Anspruch 22, worin die eine ionische Färbestelle enthaltenden aromatischen Reste 5-Natriumsulfonatisophthaloylreste sind.

35. Filament nach einem der Ansprüche 20 bis 24 mit einem durch eine "T"-Zahl von weniger als etwa 20 definierten oberflächlichen cyclischen Trimergehalt, worin die "T"-Zahl =

$$[SCT(\text{ppm}) + 1] \times e^{-0,2(T + T_7)}$$

worin SCT = oberflächliches cyclisches Trimer.

36. Filament nach Anspruch 25 mit einem durch eine "T"-Zahl von weniger als etwa 25 definierten oberflächlichen cyclischen Trimergehalt, worin die "T"-Zahl wie in Anspruch 35 definiert ist.

37. Filament nach Anspruch 21 oder Anspruch 25, worin der T_7 wenigstens etwa 1,2 gpd ist.

38. Filament nach Anspruch 20, Anspruch 25 oder Anspruch 29 mit einer kristallinen Röntgen-Feinstruktur, die durch ein Verhältnis des langperiodischen Abstands zur Kristallitgröße im Bereich HIJK in Fig. 2 gekennzeichnet ist.

39. Filament nach Anspruch 21, Anspruch 22 oder Anspruch 25, worin der langperiodische Abstand und die scheinbare Kristallitgröße so sind, daß sie innerhalb der Fläche STUV von Fig. 4 liegen.

40. Filament nach einem der Ansprüche 20 bis 39 mit einem Verhältnis von scheinbarer Kristallitgröße zu langperiodischem Abstand sowie einer gewichtsprozentualen Kristallinität innerhalb der Fläche LMNOP von Fig. 3.

41. Filament nach Anspruch 40 mit einem Verhältnis der scheinbaren Kristallitgröße zum langperiodischen Abstand und einer gewichtsprozentualen Kristallinität innerhalb der Fläche NOPQR von Fig. 3.



42. Filament nach einem der Ansprüche 20 bis 41 mit einem Trockenhitzeschrumpf bei 196°C von weniger als etwa 8%.

43. Filament nach Anspruch 42 mit einem Trockenhitzeschrumpf bei 196°C von etwa 3% oder mehr.

44. Filament nach Anspruch 42 oder Anspruch 43 mit einem Trockenhitzeschrumpf bei 196°C von weniger als 6%.

45. Filamentbündel nach einem der Ansprüche 20 bis 44 mit einem Kräuselindex von wenigstens etwa 20, worin der Kräuselindex =

$$\frac{(66,6 - L_0)}{66,6} \times 100$$

und worin zur Messung von L_0 das gekräuselte Kabel durch Anwendung einer Belastung von etwa 0,1 gpd gestreckt wird und Clips von 0,5 g im Abstand von 66,6 cm an dem gestreckten Kabel befestigt werden, das Kabel dann 11,7 cm jenseits jeden Clips unter Erhalt einer Probe von 90 cm gestreckter Länge abgeschnitten wird, die Probe vertikal aufgehängt wird und von einem der Clips frei herabhängt, um die Zusammenziehung auf die gekräuselte Länge zu ermöglichen, und nach etwa 30 Sekunden der Abstand Clip zu Clip in freihängendem Zustand (L_0) gemessen wird.

Revendications

1. Un procédé continu pour traiter un câble de filaments de polyester filés à l'état fondu, comportant les étapes de (1) étirage, (2) recuit, (3) frisage et (4) séchage, caractérisé en ce que l'étape de recuit est effectuée dans une zone sous pression de vapeur d'eau saturée à une pression d'au moins 1100 kPa.

2. Un procédé selon la revendication 1, caractérisé en ce que, entre les étapes d'étirage et de frisage, la longueur du câble est réglée dans l'intervalle d'environ 5% d'allongement à environ 10% de rétraction.

3. Un procédé selon la revendication 2, dans lequel la longueur du câble est réglée de façon à permettre environ 3 à 10% de rétraction.

4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les filaments étirés sont soumis à la zone sous pression de vapeur d'eau saturée pendant au moins environ 0,2 seconde.

5. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les filaments étirés sont soumis à la zone sous pression de vapeur d'eau saturée pendant une durée suffisante pour chauffer sensiblement tous les filaments au moins jusqu'à la température de saturation de la vapeur d'eau correspondant à la pression de vapeur.

6. Un procédé selon l'une quelconque des revendications précédentes, dans lequel les filaments étirés sont soumis à la zone sous pression de vapeur d'eau saturée pendant moins d'environ 1 seconde.

7. Un procédé selon l'une quelconque des revendications précédentes, dans lequel les filaments étirés sont soumis à la zone sous pression de vapeur d'eau saturée pendant environ 0,2 à 0,6 seconde.

8. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le recuit a lieu en plus d'une étape.

9. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les filaments reçoivent une pulvérisation d'une solution aqueuse d'un apprêt lubrifiant entre les étapes de recuit et de frisage.

10. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les filaments sont séchés dans un état relaxé à une température inférieure à 125°C environ.

11. Un procédé selon la revendication 10, caractérisé en ce que les filaments sont séchés à une température inférieure à 110°C environ.

12. Un procédé selon les revendications 1, 2, 4 et 10, caractérisé en ce que le câble est retiré de la zone sous pression pour être mis à la pression atmosphérique ambiante, de façon que les filaments soient rapidement refroidis par vaporisation d'eau tandis qu'ils se trouvent encore sous ladite longueur réglée.

13. Un procédé selon la revendication 12, caractérisé en ce que les filaments sont refroidis davantage avant le frisage.

14. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les filaments de polyester sont essentiellement entièrement constitués de radicaux dioxyéthylène et téréphtaloyle avec du dioxy(oxyde de diéthylène) comme impureté.

15. Un procédé selon l'une quelconque des revendications 1 à 13, caractérisé en ce que le polyester est un copolymère contenant au moins 93% en poids de radicaux dioxyéthylène et téréphtaloyle et il est sensiblement dépourvu de motifs ayant des sites ioniques pour colorants.

16. Un procédé selon la revendication 15, dans lequel les autres radicaux de comonomères sont l'un ou plusieurs des radicaux glutaryle, oxy-poly(oxyde d'éthylène) d'un poids moléculaire inférieur à 4000, adipyle et dioxy(oxyde de diéthylène).

17. Un procédé selon la revendication 15 ou 16, caractérisé en ce que le polyester contient au moins 97% en poids de radicaux dioxyéthylène et téréphtaloyle.

18. Un procédé selon l'une quelconque des revendications 1 à 13, caractérisé en ce que le polyester contient au moins 93% en poids de radicaux dioxyéthylène et téréphtaloyle, au moins 1,3% de radicaux



aromatiques contenant un site anionique pour colorants et jusqu'à 4% environ de radicaux organiques neutres.

19. Un procédé selon la revendication 18, caractérisé en ce que les radicaux aromatiques contenant un site anionique pour colorants sont des radicaux 5-(sulfonate de sodium)isophtaloylo.

- 5 20. Un filament frisé de poly(téréphtalate d'éthylène) ayant une viscosité relative inférieure à 25 environ et constitué d'au moins environ 97% en poids de motifs récurrents de radicaux dioxyéthylène et téréphtaloylo, le filament ayant un équilibre amélioré d'aptitude à la teinture et de propriétés en traction comprenant une T_7 d'au moins environ 1,5 gpd et une $(T + T_7)$ d'au moins environ 7 gpd et inférieure à 10 gpd environ, où T_7 est la ténacité à 7% d'allongement et T est la ténacité à l'allongement de rupture, un
10 retrait à la chaleur sèche à 196°C inférieur à 10% environ, et une relation d'aptitude à la teinture/orientation caractérisée par un indice "D" inférieur à environ 3,8 et supérieur à environ 1,8, où l'indice "D" =

$$\frac{e^{0,04(T + T_7)} \times (T + T_7)^{-1,08} \times e^{0,025(PMAD)}}{RDDR}$$

15

RDDR

où PMAD est le % en poids total de radicaux autres que les radicaux dioxyéthylène et téréphtaloylo dans les chaînes polymères et

20

$$RDDR = DDR (DPF/1,50)^{1/2}$$

où DDR est mesuré comme décrit dans US—A—4 195 051 et DPF = denier par filament.

21. Un filament frisé de poly(téréphtalate d'éthylène) ayant une viscosité relativement inférieure à 25 environ et constitué d'au moins environ 93% en poids de motifs récurrents de radicaux dioxyéthylène et téréphtaloylo et contenant au moins environ 3% d'autres radicaux neutres mais ne contenant pas plus
25 d'environ 0,3% de radicaux ayant des sites ioniques pour colorants, le filament ayant un équilibre amélioré d'aptitude à la teinture et de propriétés en traction comprenant une T_7 d'au moins environ 1,1 gpd et une $(T + T_7)$ d'au moins environ 5 gpd et inférieure à 7 gpd environ, où T_7 est la ténacité à 7% d'allongement et T est la ténacité à l'allongement de rupture, un retrait à la chaleur sèche à 196°C inférieur à 10% environ, un
30 indice "D" inférieur à 3,8 environ et supérieur à 1,8 environ, et un RDDR d'au moins environ 0,12, où l'indice "D" et RDDR sont tels que définis dans la revendication 20.

22. Un filament frisé de poly(téréphtalate d'éthylène) ayant une viscosité relative inférieure à 25 environ et constitué d'au moins environ 93% en poids de motifs récurrents de radicaux dioxyéthylène et téréphtaloylo et contenant au moins environ 1,3% de radicaux aromatiques ayant un site ionique pour
35 colorants et jusqu'à 4% environ de radicaux organiques neutres, le filament ayant un équilibre amélioré d'aptitude à la teinture et de propriétés en traction comprenant une T_7 d'au moins environ 1,2 gpd et une $(T + T_7)$ d'au moins environ 5 gpd et inférieure à 7 gpd environ, où T_7 est la ténacité à 7% d'allongement et T est la ténacité à l'allongement de rupture, un retrait à la chaleur sèche à 196°C inférieur à 10% environ, et un indice "D" inférieur à 3,8 environ et supérieur à 1,8 environ, où l'indice "D" est tel que défini dans la
40 revendication 20.

23. Un filament selon l'une quelconque des revendications 20 à 22, ayant une viscosité relative située dans l'intervalle d'environ 16 à environ 20.

24. Un filament selon l'une quelconque des revendications 20 à 22, ayant une viscosité relative située dans l'intervalle d'environ 9 à environ 14.

- 45 25. Un filament frisé de poly(téréphtalate d'éthylène) ayant une viscosité relative d'environ 9 à environ 14 et constitué d'au moins environ 93% de motifs récurrents de radicaux dioxyéthylène et téréphtaloylo, le filament ayant un équilibre amélioré d'aptitude à la teinture et de propriétés en traction comprenant une T_7 d'au moins environ 1,1 gpd et une $(T + T_7)$ d'au moins environ 5 gpd et inférieure à 8 gpd environ, où T_7 est la ténacité à 7% d'allongement et T est la ténacité à l'allongement de rupture, un retrait à la chaleur sèche à
50 196°C inférieur à 10% environ, et un indice "D" inférieur à 3,8 environ et supérieur à 1,8 environ, où l'indice "D" est tel que défini dans la revendication 20.

26. Un filament selon la revendication 20 ou la revendication 25, qui ne contient pas plus d'environ 0,3% de radicaux contenant des sites ioniques pour colorants.

27. Un filament selon la revendication 26, sensiblement dépourvu de sites ioniques pour colorants.

- 55 28. Un filament selon la revendication 22 ou l'une quelconque des revendications 25 à 27, ayant au moins environ 97% de motifs récurrents de radicaux dioxyéthylène et téréphtaloylo.

29. Un filament selon la revendication 20 ou la revendication 25, dans lequel le polyester est essentiellement entièrement constitué de radicaux dioxyéthylène et téréphtaloylo, avec du dioxy(oxyde de diéthylène) comme impureté.

- 60 30. Un filament selon l'une quelconque des revendications 20 à 22 ou l'une quelconque des revendications 25 à 28, dans lequel des radicaux neutres sont présents et sont l'un ou plusieurs des radicaux glutaryle, adipyle, dioxy(oxyde de diéthylène) ou oxy-poly(oxyde d'éthylène) ayant un poids moléculaire inférieur à 4000.

31. Un filament selon la revendication 21 ou la revendication 25, contenant environ 3 à environ 4% de
65 radicaux glutaryle et environ 1% de radicaux dioxy(oxyde de diéthylène).



32. Un filament selon la revendication 22, contenant environ 3% de radicaux glutaryle et environ 1% de radicaux dioxy(oxyde de diéthylène).

33. Un filament selon la revendication 20, la revendication 21 ou la revendication 25, dans lequel des radicaux contenant un site ionique pour colorants sont présents et sont des radicaux 5-(sulfonate de sodium)isophtaloyle.

34. Un filament selon la revendication 22, dans lequel les radicaux contenant un site ionique pour colorants sont des radicaux 5-(sulfonate de sodium)isophtaloyle.

35. Un filament selon l'une quelconque des revendications 20 à 24, ayant une teneur en trimère cyclique de surface, telle que définie par un indice "T", inférieure à 20 environ, ou l'indice "T" =

$$[TCS(ppm) + 1] \times e^{-0,2(T + T_7)}$$

où TCS = trimère cyclique de surface.

36. Un filament selon la revendication 25, ayant une teneur en trimère cyclique de surface, telle que défini par un indice "T", inférieure à 25 environ, où l'indice "T" est tel que défini dans la revendication 35.

37. Un filament selon la revendication 21 ou la revendication 25, dans lequel la T_7 est d'au moins environ 1,2 gpd.

38. Un filament selon la revendication 20, la revendication 25 ou la revendication 29, ayant une structure fine cristalline aux rayons X caractérisée par une relation de distance de longue période/taille des cristallites se situant à l'intérieur de la région HIJK de la Figure 2.

39. Un filament selon la revendication 21, la revendication 22 ou la revendication 25, dans lequel la distance de longue période et la taille apparente des cristallites sont telles qu'elles se situent à l'intérieur de la région STUV de la Figure 4.

40. Un filament selon l'une quelconque des revendications 20 à 39, ayant un rapport taille apparente des cristallites/distance de longue période et un pourcentage en poids de cristallinité tels qu'ils se situent à l'intérieur de la région LMNOP de la Figure 3.

41. Un filament selon la revendication 40, ayant un rapport taille apparente des cristallites/distance de longue période et un pourcentage en poids de cristallinité tels qu'ils se situent à l'intérieur de la région NOPQR de la Figure 3.

42. Un filament selon l'une quelconque des revendications 20 à 41, ayant un retrait à la chaleur sèche à 196°C inférieur à 8% environ.

43. Un filament selon la revendication 42, ayant un retrait à la chaleur sèche à 196°C d'environ 3% ou plus.

44. Un filament selon la revendication 42 ou la revendication 43, ayant un retrait à la chaleur sèche à 196°C inférieur à 6% environ.

45. Un faisceau de filaments selon l'une quelconque des revendications 20 à 44, ayant un Indice de Frisure d'au moins environ 20, où l'Indice de Frisure =

$$\frac{(66,6 - L_p)}{66,6} \times 100$$

et où, pour la mesure de L_p , le câble frisé est redressé par application d'une charge d'environ 0,1 gpd et des pinces de 0,5 g sont attachées au câble étendu avec un écartement de 66,6 cm, le câble est ensuite coupé à 11,7 cm au-delà de chaque pince pour former un échantillon d'une longueur étendue de 90 cm, l'échantillon est suspendu verticalement, en pendant librement de l'une des pinches de façon à permettre une rétraction à la longueur d'état frisé, et, après environ 30 secondes, la distance entre pinches à l'état pendant librement (L_p) est mesurée.