



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D01F 6/86, D01D 5/253	A1	(11) International Publication Number: WO 92/13120 (43) International Publication Date: 6 August 1992 (06.08.92)
(21) International Application Number: PCT/US92/00231 (22) International Filing Date: 23 January 1992 (23.01.92) (30) Priority data: 645,920 25 January 1991 (25.01.91) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: OXFORD, Clarence, Edward ; 806 Harding Avenue, Kinston, NC 28501 (US). SARGEANT, Peter, Barry ; 1703 St. George Place, Kinston, NC 28501 (US). WEIKEL, Robert, James ; 30 Karen Court, New Castle, DE 19720 (US).		(74) Agent: HIGGS, W., Victor; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: IMPROVEMENTS IN POLYESTER FIBERS (57) Abstract Polyester filaments of 0.5 to 3 denier per filament having scalloped-oval cross-section, formed of clear ethylene terephthalate polymers of specified viscosity modified by inclusion of polyethylene oxide, provide fabrics having pleasing luster, greater drapeability, reduced pilling, and low temperature carrier-free dyeing when compared to existing round cross-section 100 % polyester and polyester-rich blended (cotton/wool/rayon/silk) polyester fabrics.		

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TITLE

IMPROVEMENTS IN POLYESTER FIBERS

5 This invention relates to improvements in polyester fibers, and more particularly to a unique combination of special polymer compositions with fiber cross-section/filament deniers that provide desirable fabric properties heretofore unavailable in fabrics produced of conventional 100% polyester and polyester-rich (i.e., at least 50% polyester) blended fabrics, such as are suitable for conventional home washing and drying without loss of attractive appearance.

10 Conventional polyethylene terephthalate (PET) apparel fibers are generally of round cross-section and have many attractive characteristics. These include but are not limited to: good physical properties for processing into fabric and thereafter into wearing apparel good durability after washing/drying by conventional means and good color light fastness. Some complaints, however, have also been reported in the art with regard to some properties of their fabrics/ garments. These include formation of "pills" upon encountering surface abrasion; unattractive appearance: requirement for super atmospheric pressure dyeing conditions; and fabric stiffness/poor drapeability. In contrast, more desirable fabric/garment properties have been provided when so-called "natural fibers", particularly some rayon types, have been used in apparel fabrics. However, rayon fabrics have other important disadvantages, e.g., they do not retain their desirable attributes after repeated subjection to conventional home wash/dry cycles, so preservation of such attributes requires that the fabrics and garments be cleaned by

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professional methods. It has long been desirable to modify conventional polyester fibers, to retain their important advantages, but to impart also some characteristics of new rayon fibers.

5 Some techniques have been suggested to modify polyester polymers (e.g. reduction of polymer viscosity, and incorporation of modifiers, and special treatments) to reduce the tendency of the fabrics to "pill". This has had varying degrees of
10 success with conventional round filament cross-sections. Because use of these modified polymers can lead to undesirable and even excessive spinning discontinuities, however, their use for non-round cross-sections has been more appropriate
15 for high deniers per filament (dpf) that have been unacceptable for usage in apparel.

 Scalloped-oval cross-section fibers produced from conventional polyethylene terephthalate polymers have been used heretofore for specialty
20 areas, e.g. pile fabrics, carpets, paper reinforcement and filters, but the deniers per filament (typically 6 and above) have been higher than what is needed for most apparel applications. Textile deniers of up to 3 dpf have been used, but
25 their pilling performance has inhibited full commercial acceptance.

 Practically all commercial conventional PET apparel fibers of dpf up to about 3 have been delustered, generally with titanium dioxide (TiO_2)
30 pigment, because this has been considered, in practice, desirable to provide fabrics that are more attractive.

 Clear (i.e., un-delustered) polymers have
35 occasionally been used in round cross-section and various deniers per filament for some textile

applications to improve processing, but the resulting fabrics have been considered to have an unattractive luster.

According to the present invention, there is provided a novel combination of selected clear (i.e., without delusterant) modified polymer with selected filament cross-section that provides fabric properties heretofore unattainable with existing polyester polymer/filament cross-section combinations. The polymer modifier is polyethylene oxide (PEO) of molecular weight in the range 200-2000. The viscosities of the polymers are indicated herein, and correspond to the molecular weights of the polymers.

When we use this novel combination of scalloped-oval cross-section with selected clear (un-delustered) polymers (preferably one with enhanced dyeability), a subtle fabric luster can be achieved similar to that of "natural fiber", without loss of the desirable characteristics which make polyester fiber attractive to the industry. This has been most surprising. The pilling performance has also been most surprising, especially in view of the viscosities of the polymers. The art has taught that low viscosity polymer is desired to improve pilling performance.

The fibers of the invention may be made conveniently by melt spinning and drawing un-delustered modified PET filaments of appropriate viscosity, denier per filament, and cross-section, as disclosed herein-after in the Examples. The filaments are generally cut to staple of whatever length is desired for the end-use contemplated, e.g., about 10 to about 100 mm. Deliberately mixed deniers are advantageous, and may be used. It will

be understood that both the terms "filament" and "fiber" are used generically herein. While the primary application discussed here is staple, it is believed that continuous filament applications in the form of yarn or tow would provide similar desirable luster benefits when converted into fabrics, woven or knitted.

The scalloped-oval cross-section of the filaments has been described in the art, such as Gorrafa U.S. Patent No. 3,914,488 and Clark et al U.S. Patent No. 4,707,407, the disclosures of which are hereby specifically incorporated herein by reference, and this art also discloses general details of how filaments of such cross-section may be formed. As indicated herein, an essential element of the present invention, however, is selection of a specific composition of polymer that is spun into such a filament cross-section (known per se for other purposes from different compositions) at a textile denier suitable for the specific purposes and advantages disclosed for the present invention.

Polyethylene terephthalate containing polyethylene glycol has already been disclosed in the art, e.g., by Snyder in U.S. Patent No. 2,744,087 and by DeMartino in U.S. Patent No. 4,666,454, the disclosures of which are hereby incorporated herein by reference. Similarly, the disclosures of Griffing et al U.S. Patent No. 3,018,272, Vail U.S. Patent No. 3,816,486, and Hancock et al. U.S. Patent No. 4,704,329 are hereby incorporated herein by reference to disclose various polymer compositions that may be modified by inclusion of PEO according to the present invention, and various processing techniques for

preparing drawn, annealed and drawn relaxed filaments. A viscosity builder, such as a trifunctional or tetrafunctional monomer, such as tetraethyl silicate, or as used in the Examples, may be advantageously incorporated in the polymer composition in effective amount to enhance spinning performance. Use of such monomers, as chain-branchers, is taught, e.g., by MacLean et al in U.S. Patents No. 4,092,299, and by Mead et al in U.S. Patent No. 3,335,211. Many such prior art polymer compositions, however, contain delusterant, usually titanium dioxide, in contrast to the present invention.

Clear polymer means that the fiber is not delustered, that is, contains essentially no added delustering pigment, generally less than 0.005 percent by weight of delusterant (typically titanium dioxide pigment).

The addition of PEO increases dyeability of the fiber, with larger amounts causing better dyeability. If fiber is made without PEO, it can, however, retain advantages of good luster and drapeability.

A molecular weight of 600 for the PEO was used because it was convenient, but may vary from about 200 to about 2000. The molecular weight must be high enough to be effective, but low enough to be applied practically. Heat can be used to effectively use a higher molecular weight PEO.

As indicated above, each of the elements of the present invention, namely the selected PET polymer(s) and modifier, the selected viscosity, the absence of delusterant, the scalloped-oval filament cross-section, and the apparel deniers, have been used separately for various textile and

industrial end-uses but have not, so far as we know, been used in the present combination, nor for this purpose, and the results are surprising.

5 The invention is further illustrated in the following Examples. The PEO was of molecular weight 600. The relative viscosity of the polyester was measured essentially as described in Hancock et al. U.S. Patent No. 4,704,329, col. 9, lines 6-11, but on a solution obtained by dissolving 0.80 gram
10 fiber in 10.0 milliliters solvent. The DDR (Dye Rate) was measured as described in Frankfort et al. U.S. Patent No. 4,195,051, col. 12 (and in 4,134,882) in comparison with a filament of 1.5 dpf, scalloped-oval cross-section, of similar
15 polymer except that it contained no PEO. The pilling results were from the Random Tumble Pilling Test (RTPT), essentially as described in ASTM D 3512, with ratings at the intervals indicated herein.

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EXAMPLES

Example 1

1-2. A commercial clear PET polymer with essentially no titanium dioxide, but containing 3.9
25 weight percent of polyethylene oxide (PEO) and 0.175 weight percent trimethylol propane, to provide a relative viscosity of 20.5 was utilized. It was melt spun at 290 C and 102 pounds per hour through a spinneret having 1653 capillaries. The
30 capillary orifices were of the general configuration of that shown in Figure 2 of U.S. Patent 4,707,407, with the major axis length being 0.039 inches and the minor axis length being 0.019 inches. The filaments were conveniently collected
35 at 1500 yards per minute on individual bobbins using a commercial wind-up device. Twenty five

bobbins were combined as a creel for a test drawing apparatus having the capability for one (1) and two (2) stages of drawing in saturating liquid spray(s), crimping, and hot air relaxing. The results of these tests are included as Items 1 and 2, respectively, of Table 1.

3. An additional three hundred ninety bobbins were collected under the same conditions and combined as a creel for a commercial drawing machine. They were one-stage drawn, crimped, and relaxed in a hot air dryer. The results of this test are included as Item 3 of Table 1.

4. In like manner a heavier denier was produced at a spinning rate of 50.5 pounds per hour using a spinneret of 360 similar capillaries. Thirty eight bobbins were combined as a creel for the same test drawing machine and the results are included as Item 4 of Table 1.

TABLE 1

Item No.	1	2	3	4
Spun Denier/Filament	3.18	3.18	3.18	7.18
Groove Ratio	1.16	1.16	1.16	1.18
Modification Ratio	1.51	1.51	1.51	1.63
Draw Ratio 1	1.00	2.00	2.50	1.00
Draw Ratio 2	2.38	1.25	0.997	2.86
Crimp Roll %	0.99	0.99	0.91	0.99
Total Draw Ratio	2.36	2.48	2.29	2.83
Relaxer Temp deg C	130	130	130	130
Denier/Filament	1.53	1.52	1.51	3.06
Tenacity	3.2	3.3	3.4	3.8
Elongation %	30.6	27.1	21.3	24.0
Dry Heat Shrinkage %	7.2	5.8	3.7	7.3
Boil off Shrinkage %	2.8	2.0	--	3.6
DDR	320%	323%	263%	225%

Fiber from the Item 3 was cut to 1 1/2" on a standard cutter, baled and processed on commercial textile machinery to a ring spinning frame. The yarn count was 25/1 cc with a 4.0 twist factor. The yarn was woven into a 2 X 1 twill fabric on a standard loom using 112 ends per inch on the warp and 58 picks per inch in the fill. This fabric was dyed atmospherically with disperse dyes without carrier for one hour. Commercial fabric softener was applied. Without further treatment, the fabric was tested on the Random Tumble Pill Test Mechanism. After 10 and 60 minutes tumbling, respectively, the pill ratings were 4.2 and 2.6 (higher pill ratings indicating better resistance to pilling).

Example 2

1. A commercial polymer similar to that used in Example 1 was melt spun at 285C and 68.5 pounds per hour through spinnerets having 1054 capillaries, but otherwise essentially similarly to Example 1, except that the major axis length for the capillary orifice was 0.030 inches. The filaments were conveniently collected at 1500 yards per minute from multiple positions using a commercial device. Nine hundred ends were combined as a creel for a commercial drawing machine. They were one-stage drawn, crimped, and relaxed in a hot air dryer. The results of this test are included as Item 1 of Table 2.

2. In like manner a heavier denier was produced at a spinning rate of 63 pounds per hour using spinneret of 450 capillaries. The capillary had the major axis length of 0.039 inches as in Example 1. Nine hundred eighty four ends were combined as a creel for a commercial drawing

machine. They were one-stage drawn, crimped, and relaxed in a hot air dryer. The results of this test are included as Item 2 of Table 2.

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TABLE 2

Item No.	1	2
Spun Denier/Filament	2.98	6.41
Draw Ratio 1	1.03	1.03
10 Draw Ratio 2	2.46	2.62
Crimp Roll %	0.97	0.97
Total Draw Ratio	2.46	2.62
Relaxer Temp deg C	124	124
Denier/Filament	1.51	3.13
15 Tenacity	3.4	3.1
Elongation %	25.4	25.6
Dry Heat Shrinkage %	2.6	2.7

Example 3

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1. A commercial polymer similar to that used in Example 1, except for having an relative viscosity of 19.8, was melt spun essentially as in Example 2, except at 292C and 96 pounds per hour through spinnerets having 1653 capillaries into
25 filaments that were conveniently collected at 1421 yards per minute . Six hundred thirty ends were combined as a creel for a commercial drawing machine. They were one-stage drawn, crimped, and relaxed in a hot air dryer at 124 C. The results of
30 this test are included as Item 1 of Table 3.

2-3. To evaluate relaxation temperature effect on "pill resistance", material that was spun, drawn, and crimped as Item 1 of Table 3 was not allowed to enter the relaxation dryer. It was
35 taken to a laboratory forced convection, hot-air oven. one sample was exposed to 130 C air for 5

minutes, the other to 160 C air for 5 minutes. These results are reported as Items 2 and 3 of Table 3 respectively.

5 4. To determine if temperature of the relaxation oven had a significant effect on the "pill resistance" of the fiber after drawing, another item was produced with a relaxer temperature of 154 C, other conditions being the same. The results of this test are included as Item 10 4 of Table 3.

Filaments from the above four items were randomly selected from the processed but uncut filament bundle. Individual filaments were tested for flex life by being clamped between two bars 15 having a 0.001 inch radius at the point of nip. A dead weight loading of one gram was applied and then the bars were oscillated in a manner calculated to flex the filaments in opposite directions until rupture occurred. This data is 20 reported in the Table 3 as "flex life". A lower flex life indicates that the resistance to pilling is likely to be better.

Data from Item 3 of Table 1 is reported in Table 3 as "Control".

25 Fiber from the Items 1 and 4 were cut to 1 1/2" on a standard cutter, baled and processed on commercial textile machinery to a ring spinning frame. Yarn counts of 22/1 and 28/1, with a 3.75 twist factor were spun. Each Item yarn was woven 30 into a 2 X 1 twill fabric on a standard loom using 112 ends per inch 28/1 cc in the warp and 58 picks per inch of 22/1 cc in the fill. This fabric was dyed atmospherically with disperse dyes without carrier for one hour. Commercial fabric softener 35 was applied. Without further treatment, the fabric

was tested on the Random Tumble Pill Test Mechanism. After 15 and 120 minutes tumbling, the pill ratings were, respectively, for Item 3.1; 4.5 and 4.4, for Item 3.4: 3.8 and 1.6, and more yarns, prepared from item 3 in Example 1, were similarly woven and tested to give RTP ratings, respectively, of 4.5 and 2.6.

TABLE 3

Item No.	1	2	3	4	Control
Spun Denier/ Filament	3.04	"	"	3.04	3.18
Draw Ratio 1	1.03	"	"	1.03	2.50
Draw Ratio 2	2.46	"	"	2.46	0.997
Crimp Roll %	0.97	"	"	0.97	0.91
Total Draw Ratio	2.46	"	"	2.46	2.29
Relaxer Temp deg C	124	na	na	154	130
Hot air oven deg C	na	135	160	na	na
Denier/Filament	1.41	"	"	1.44	1.51
Tenacity	3.1	"	"	3.2	3.4
Elongation %	31.6	"	"	36.2	21.3
Dry Heat Shrinkage %	3.7	"	"	2.6	3.7
Flex Life, cycles	12599	7824	8848	8890	14310

Example 4

A commercial polymer similar to that used in Example 1 (except for relative viscosity of 19.7), was melt spun at 293 C and 75 pounds per hour through spinnerets having 1054 capillaries, using capillary orifices as in Example 2.1. Four hundred forty eight ends were combined as a creel for a commercial drawing machine. They were one-stage drawn, crimped, and relaxed in a hot air dryer at 142 C. The results of this test are shown in Table 4.

TABLE 4

	Spun Denier/Filament	2.77
	Draw Ratio 1	2.62
	Crimp Roll %	0.96
5	Total Draw Ratio	2.51
	Relaxer Temp C	142
	Denier/Filament	1.61
	Tenacity	3.4
10	Elongation %	35.2
	Dry Heat Shrinkage %	3.2

This product was not cut but was processed as continuous tow on a tow converter.

15 Example 5

Fiber from Example 1, item 3 was blended 50/50 with combed cotton and ring spun into 28/1 cc. It was knit into a 22 cut Jersey fabric on a commercial machine. The fabric was atmospherically dyed and subjected to the standard Random Tumble Pill test method.

For comparison purposes, a commercial 1.5 denier per filament T-107 W (round, 11.5 RV homopolymer) staple fiber was chosen because it is commercially sold as a "pill resistant" product for knit end-uses. This comparison fiber was likewise blended 50/50 with combed cotton and ring spun to 28/1 cc. This yarn was knit on the same knitting machine into a 22 cut jersey, dyed with carrier and subjected to the standard Random Tumble Pill test method.

RTP test results after the indicated test times for the scalloped-oval and round cross-section yarns are in Table 6 below and clearly show the pilling advantage of the scalloped-oval fiber of the invention despite its

higher RV (20.5 vs 11.5), which normally gives more pilling, so the better pilling performance of the higher RV fiber of the invention was extremely surprising.

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TABLE 5

	<u>Test Time</u>	<u>Invention Scalloped-oval</u>	<u>Comparison Round</u>
10	15 minutes	4.5	3.3
	30 minutes	3.3	1.8
	60 minutes	1.5	1.2

CLAIMS:

1. Textile fibers of about 0.5 to about 3 denier per filament, and of scalloped-oval cross-section, consisting essentially of clear ethylene terephthalate polymer of relative viscosity (LRV) in the range about 19 to 21, and containing about 1 to about 8% by weight of polyethylene oxide of molecular weight in the range about 200 to about 2000 .
2. Textile fibers of about 0.5 to about 3 denier per filament, and of scalloped-oval cross-section, consisting essentially of clear ethylene terephthalate polymer of relative viscosity (LRV) in the range about 15.5 to 17.5, containing about 1 to about 3 mol % of 5-(alkali metal sulfo) isophthalate groups in the polymer chain and about 1 to about 8% by weight of polyethylene oxide of molecular weight in the range about 200 to about 2000.
3. Fibers according to Claim 1 or 2, characterized in that they have been crimped and then relaxed at a temperature in the range of about 110-175 C.
4. Fibers according to Claim 1 or 2, characterized in that they have been annealed at a temperature in the range of about 160-230 C.
5. Fibers according to Claim 4, characterized in that they have been crimped and then relaxed at a temperature in the range of about 60-100 C.
6. Textile fibers according to Claim 1 or 2 that are of deliberately mixed denier.
7. Fibers according to Claim 1 or 2, that are staple fibers of cut length about 10 to about 100 mm.

INTERNATIONAL SEARCH REPORT

PCT/US 92/00231

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D01F6/86; D01D5/253		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D01F ; D01D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 125 112 (E.I. DU PONT DE NEMOURS AND CO.) 14 November 1984 see claims & US,A,4 704 329 3 November 1987 cited in the application ---	1-5
Y	US,A,4 634 625 (JOHN S. FRANKLIN) 6 January 1987 see column 5, line 3 - line 14 see column 8, line 11 - line 21; figures ---	1-5
Y	EP,A,0 372 994 (HOECHST CELANESE CORPORATION) 13 June 1990 see claims; examples ---	1,4,7
Y	US,A,3 156 607 (DONALD R. STRACHAN) 10 November 1964 see column 3, line 37 - line 46; figures; example III ---	1,4,7
	--- -/-	
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 APRIL 1992	22 APR 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	TARRIDA TORRELL J.B.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9200231
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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