July 4, 1967 E. E. MAGAT ETAL 3,329,557

STATIC RESISTANT FILAMENT AND PROCESS THEREFOR

Filed July 2, 1962 2 Sheets-Sheet 1

FIG. I

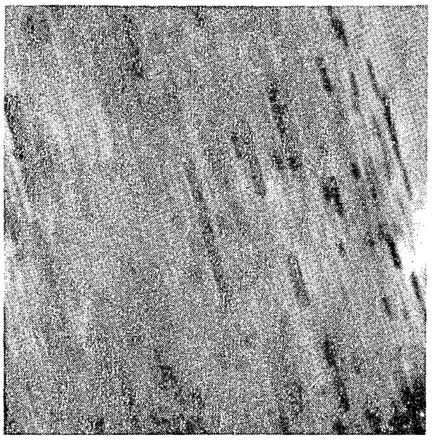

FIG. II

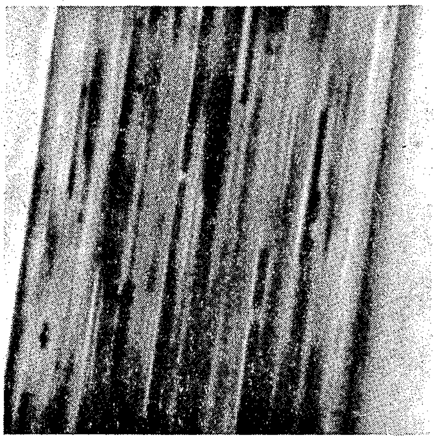

FIG. III

FIG. IV

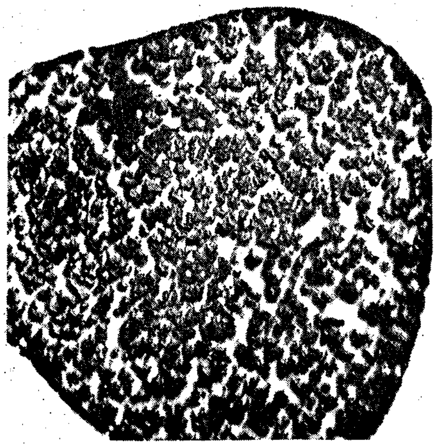

FIG. V

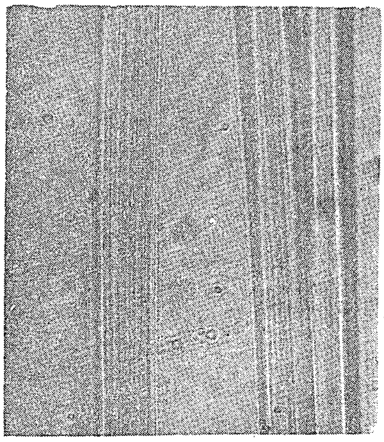

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FIG. VI

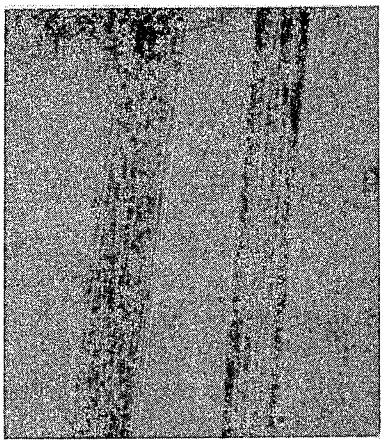

FIG. VII

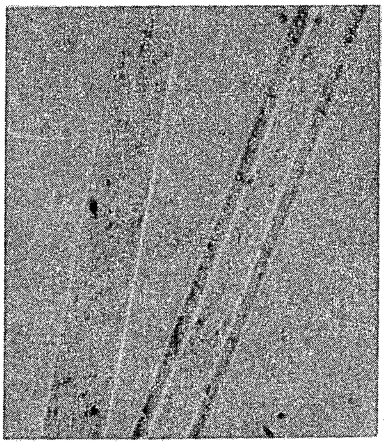

FIG. VIII

FIG. IX

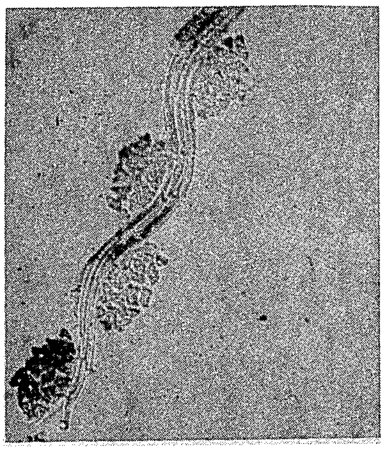

FIG. X

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3,329,557
Patented July 4, 1967

3,329,557

STATIC RESISTANT FILAMENT AND PROCESS THEREFOR

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Filed July 2, 1962, Ser. No. 207,117
18 Claims. (Cl. 161—172)

This application is a continuation-in-part of U.S. Ser. No. 569,976, filed Mar. 7, 1956, which is a continuation-in-part of United States Ser. No. 499,754, filed Apr. 6, 1955, now abandoned.

This invention relates to product and process. More specifically it concerns a novel oriented synthetic melt-spun filament having a low static propensity due to the presence in the filament of a dispersed phase of high molecular weight poly(alkylene ether). The invention also concerns a process for adhering the poly(alkylene ether) dispersed phase to the continuous phase and the product formed thereby.

It is an object of this invention to provide an oriented synthetic melt-spun filament which is substantially antistatic.

Another object is to provide a filament as described above which also possesses a high covering power.

A further object is to provide a filament as described above having a dispersed phase of high molecular weight poly(alkylene ether) chemically adhered to the polymeric filamentous matrix and a process for its production.

Another object is to provide a woven fabric from yarn of the filament as described above, which fabric is lustrous and opaque, having a high degree of silk-like resilience.

These and other objects will become apparent in the course of the following specification and claims.

In accordance with the present invention, at least about 2% by weight of a high molecular weight poly(alkylene ether) is uniformly dispersed in a melt-spinnable synthetic polymer, which is then melt-spun and drawn to provide a textile filament. The poly(alkylene ether) is distributed through the filament structure in the form of microscopic elongated particles which are oriented with their longest dimension parallel to the major axis of the filament, giving the fiber a striated appearance. The filament in this form is highly anti-static. The filament may thereafter be subjected to bombardment by high energy particle radiation to produce adherence between the polymer and the poly(alkylene ether), thereby increasing the wickability of the scoured fiber, and the level and durability of its antistatic properties. However, where an antistatic fiber of maximum covering power and luster is desired a major proportion of the poly(alkylene ether) is extracted by aqueous boil-off before irradiation. This technique leaves sufficient residue of the polyether to provide static protection whether or not the filament is subsequently irradiated. Removal of the polyether leaves microscopic voids in the filament, greatly increasing its opacity and covering power while retaining its normal surface luster. As will be explained in greater detail hereinafter, it is essential for purposes of the present invention that the poly(alkylene ether) be of a relatively high molecular weight and be substantially inert to the polymer of the substrate filament under melt spinning conditions.

The invention will be more readily understood by reference to the illustrations. FIGURES I and II are photomicrographs at a magnification of about 3000 times of a longitudinal section of a filament of the present invention, as described more in detail hereinafter. In axial section, FIGURE I shows the yarn in an undrawn condition whereas FIGURE II is the same yarn in a drawn condition. FIGURES III and IV are electron photomicrographs at a magnification of about 8000 times of a filament produced in accordance with the present invention and as described more in detail hereinafter, the view in FIGURE III being a longitudinal section and FIGURE IV being a cross section. FIGURES V, VI and VII are photomicrographs, at a magnification of about 700 times of a longitudinal section of a filament in the greige and scoured conditions (FIGURES V and VI each containing 15% of the poly(alkylene ether) of high molecular weight, i.e. about 20,000) and in the greige condition (FIGURE VII, containing 10% of a low molecular weight poly(alkylene ether), i.e. about 9,000). FIGURES VIII, IX and X are photomicrographs of fabric cross sections, FIGURES VIII and IX demonstrating the appearance of the greige and scoured fabrics of the present invention, FIGURE X being a control of conventional nylon polymer.

In the practice of the present invention, the poly(alkylene ether) may be coated upon a polymeric substrate which is later shaped. If the monomer from which the polymer is to be prepared and the modifying agent are non-reactive under polymerizing conditions, then the poly(alkylene ether) can be mixed with the monomer before polymerization. After polymerizing the polymeric matrix with the poly(alkylene ether) modifier incorporated (but not adhered thereto) may then be exposed to high energy particle irradiation after extruding as a filament, or after drawing, whereby adherence is induced.

The poly(alkylene ether) may be added to the polymeric material in the melt, the polymer extruded into filaments with exposure to particle irradiation when desired, either before or after drawing and either before or after extraction. Since large doses of radiation may introduce cross-links in the polymer which increase the difficulty of subsequent shaping steps, it will usually be preferable to irradiate the filament in the drawn state. Particle radiation is especially suitable in this regard, due to penetration which is adequate for bundles of filaments, combined with a high dose rate whereby reasonable throughput rate is obtained.

The drawn filaments may be converted into a fabric which is highly wickable and which exhibits antistatic properties. The fabric may be water-extracted by using a conventional boil-off, usually in the presence of soap, a synthetic detergent, an alkaline scouring agent, or similar composition. Depending on the radiation dose, and the amount and type of poly(alkylene ether) used, the fabric may develop varying degrees of opacity during the water-extraction step. Alternatively, a yarn prepared from the extruded filaments may be extracted prior to fabric preparation. In this latter procedure, the benefit of fiber swelling upon fabric geometry is not obtained.

Melt blending the poly(alkylene ether) with the fiber-forming hydrophobic polymer is a particularly useful method when poly(alkylene ethers) having end groups which must be kept from reacting with the hydrophobic polymer components, e.g., during polymerization, are utilized. Preferably, the poly(alkylene ether) and the fiber-forming polymer blend then are spun substantially immediately from the melt to form fibers. Subsequent irradiation may be employed in combination with the processing steps previously described.

Proper distribution of the poly(alkylene ether) as a separate phase in the fiber is essential to obtain an antistatic product. It is clear that elongated particles of the polyether phase constitutes the major electrical conductor in the fiber. Surprisingly, there has been no evidence of any conductive network connecting these particles when polyamides are the hydrophobic polymer. As shown in FIGURES I and II, the polyether particles appear to be distributed in polyamide filamentary substrates as discontinuous rods. It is believed that the static charge is dissipated by conduction through the substrate polymer itself, from one polyether "rod" to the next. Due to the high resistivity of the polyamide, the electrical paths through the polyamide must be kept short as possible, and also of maximum cross-section perpendicular to the direction of current flow. This is attained in the fiber because of the large number (and close spacing) of conductive particles in the fiber cross-section, combined with a large overlap between consecutive adjacent particles. The large overlap provides maximum current carrying area in the high-resistance areas of the current path.

In contrast, as shown in FIGURES III and IV, the polyether particles distributed in polyester filaments appear more like fibrils than rods, when examined at high magnification, even though they have some superficial similarity at low magnification. There is some evidence of a network, which may be conductive, connecting these particles.

It has been observed that fibers having the proper distribution of the poly(alkylene ether) particles to give optimum conductivity are also characterized by having fluid-like molecular motion at room temperature, as identified by nuclear magnetic resonance (NMR) techniques. The NMR spectogram typical of nylon shows a broad absorption "hump" corresponding to a restricted type of molecular motion, on which is superimposed a barely visible very narrow peak, corresponding to rapid proton motion. The narrow peak is greatly enhanced on adding the poly(alkylene ether). The ratio of the height of these peaks (called "NMR peak ratio") is a measure of the relative amount of rapid proton motion, which is a type of fluid-like mobility. This "peak ratio" correlates well with the conductivity of the fibers of this invention for both polyamides and polyesters, as shown in some of the examples. It is therefore a method of characterizing the filament structure which gives electrical conductivity. The NMR peak ratio therefore is useful to sum up the effect of polyether distribution and concentration. By the term "melt-spinnable synthetic polymer" is intended any synthetic, linear condensation or addition polymer which can be extruded into filaments from the melt, without substantial polymer degradation.

By a "synthetic condensation polymer" is meant a polymer which can be formed by polymerization with elimination of small molecules such as HCl, H_2O, NaCl, NH_3 and the like as well as those polymers which on chemical degradation (e.g. by hydrolysis) yield monomeric end products differing in composition from the structural units. Among such polymers may be mentioned polyamides, polyoxymethylenes, polyureas, polyurethanes, polyesters, polysulfonamides, and the like and copolymers of such materials. By a "synthetic addition polymer" is intended a polymer which can be formed by vinyl polymerization, i.e., polymerization which proceeds by combination of an unsaturated monomer with itself or with other unsaturated monomers by the linkage at the olefinic bonds. The backbone chain of such polymers is, therefore, substantially wholly a carbon chain. Among suitable monomers for such polymerization may be mentioned vinyl fluoride, vinyl chloride, vinylidene chloride, ethylene, propylene and the like and fiber-forming copolymers thereof. In general, such polymers, whether of the condensation or addition variety are substantially free from aliphatic unsaturation, since they must be non-reactive in their wide fields of utility.

By "high energy particle radiation" is meant an emission of highly accelerated electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, beta particles, or the like, directed so that the said particle impinges upon the polymer containing the polyether. The charged particles may be accelerated to high speeds by means of a suitable voltage gradient, using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron, cyclotron, or the like, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g., beryllium) targets with high energy positive particles. In addition, particle radiation suitable for carrying out the process of the invention may be obtained from an atomic pile, or from radioactive isotopes or from other natural or artificial radioactive materials.

The "66 nylon yarn" employed in many of the examples is a 70 denier hexamethylene adipamide continuous filament, having a denier per filament of 2.0. The polyamide is produced from hexamethylene diamine and adipic acid (ergo, "66"). The "standard washing" to which samples are subjected consists of a 30 minute immersion in 70° C. water containing 0.5% of detergent (sold under the trademark "Tide" by Procter and Gamble Co. of Cincinnati, Ohio) in an agitation washer. Radiation dosages are given in units of "mrep." (millions of roentgen equivalents physical), a "rep." being the amount of high energy particle radiation which results in an energy absorption of 83.8 ergs per gram of water or equivalent absorbing material.

The static propensity of the fabrics reported herein is given in terms of the direct current resistance in ohms per square (the units of area being immaterial), measured parallel to the fabric surface at the given temperature and humidity according to the A/A.T.C.C. method, C–76–59. Numerical values are reported as "log R," which is the logarithm (to the base 10) of the resistance in ohms. High values indicate a tendency to acquire and retain a static charge. Adequate static protection is attained when performance equivalent to cotton is attained; cotton has a log R of 13.1, a 30% RH.

The "D wash" used to simulate home laundering is carried out as follows. The fabrics are washed in a tumble-type washing machine with a water temperature of 38° C.; the washed fabrics are given a final spin to extract excess water, followed by tumble drying at 77° C.

Throughout the specification and claims, by "average molecular weight" it is meant the number average molecular weight.

By the term "stable" under melt spinning conditions, it is meant that the poly(alkylene ether) is not decomposed or volatilized during the spinning step.

By the term "microscopic" it is meant having a particle size about 0.05 to 2 mircons or more in diameter. The length of the polyether particles or "fibrils" is estimated to be from ½ to 50 times the fiber diameter. These particles are almost always visible in a light microscope.

The following examples, in which parts and percentages are by weight unless otherwise specified, further illustrate the present invention.

Example I

Polyhexamethylene adipamide flake is coated with polyethylene glycol of 20,000 average molecular weight (sold under the name of "Carbowax" 20,000 by the Carbide & Carbon Chemicals Company of New York), the weight of glycol used being 2% of the weight of the flake. The coated flake is then melted and thereafter spun into yarn, substantially as described in U.S. Patent 2,217,743. After drawing, a skein of the yarn is wrapped in polyethylene film and irradiated by an electron beam from a Van de Graaff electron accelerator, which is operated at an accelerating voltage of 2 mev. (million electron volts) with a tube current of 290 microamperes. The yarn sample is traversed back and forth under the electron beam on a conveyor at a speed of 40 inches per minute. The radiation dose per pass is 2 mrep. and a total of 20 passes is used, giving a total dosage of 40 mrep. The yarn is then knitted into fabric. The test fabric has improved antistatic properties over a non-irradiated control, after repeated standard washings. The test yarn also shows a smaller weight loss than the control after the washings.

Example II

Polyhexamethylene adipamide flake is coated with polyethylene glycol 20,000, as in Example I, the weight of the glycol used being 5% of the weight of flake. The coated flake is spun into 40 denier 13 filament yarn. Skeins of this yarn are prepared, wet with water, wrapped in polyethylene film and irradiated as shown in Table 1, using the equipment of Example I. In this case, the dose per pass is 1 mrep., or 12.5 watt sec./cm.^{2} of sample. After the irradiation exposure, a skein of the yarn is extracted with water in a Soxhlet extractor for 24 hours, and wickability is then tested by immersing the end of a piece of yarn in ink. The wickability (the rate at which moisture is absorbed) is measured by the height to which the ink is wicked up into a length of yarn which has been suspended with one immersed in writing ink for one minute. A wickability rating of 7.5 is observed as reported for sample F in Table 1 below. This value is compared with wickability ratings of similar skeins of non-irradiated polyhexamethylene adipamide (C), irradiated polyhexamethylene adipamide (D), non-irradiated polyhexamethylene adipamide containing 5% polyethylene glycol 20,000 (E) and mercerized cotton (G).

TABLE 1

Skein No.	Yarn (40-13)	Irradiation Dose (passes)	Height of Ink Wicked in 1 Min., cm.
C	66 Nylon	0	2.6
D	66 Nylon	40	2.4
E	66 Nylon [1] (5% P.G.)	0	4.5
F	66 Nylon [1] (5% P.G.)	40	7.5
G	Mercerized Cotton	0	7.5

[1] Polyhexamethylene adipamide containing 5% (based on flake weight) of polyethylene glycol 20,000.

The extracted non-irradiated sample E is more opaque than irradiated extracted sample F. Both are more opaque than either control sample C or D, which appear unchanged after the extraction treatment.

These results show that the wickability of the polyether glycol modified nylon is approximately twice that of unmodified nylon, while the modified, irradiated nylon is three times control, and, surprisingly, equivalent to mercerized cotton.

Example III

This example illustrates the effect of increased irradiation exposure in decreasing the amount of modifier which can be extracted from the condensation polymer matrix. Polyhexamethylene adipamide flake is coated with polyethylene glycols of two different molecular weight ranges, the weight of the glycol used being 5% of the weight of the flake. The coated flake samples are then melted, extruded as filaments and drawn as in Example I. The yarn samples are given irradiation exposures as shown in Table 2. After the irradiation exposure, skeins of the yarn are heated in water for 2 hours at 60°, the skeins are then dried and the weight loss after the extraction treatment is determined. The results are shown in the table.

TABLE 2

Irradiation Exposure		Weight Loss, Percent		
No. of Passes	Watt Sec./cm.^{2}	66 Nylon Control	66 Nylon [1] (5% P.G. 6,000)	66 Nylon [1] (5% P.G. 20,000)
0	0	0.6	2.2	2.1
10	125	0.4	2.1	1.9
20	250	0.7	1.6	1.4

[1] Polyethylene glycol, the numeral indicating average molecular weight.

Example IV

A 48% aqueous solution of hexamethylene diammonium adipate (66 nylon salt) and 0.3 mol percent (based on salt) of a 25% aqueous acetic acid solution (viscosity stabilizer) are charged to an evaporator and concentrated to 60% at atmospheric pressure. The 60% salt solution is transferred to an autoclave equipped with stirrer, and is heated in the closed vessel, until the steam pressure reaches 250 lbs./in.^{2} (temperature, 210° C.) over a period of about twenty minutes. The autoclave stirrer is then started. Heating is continued until the temperature attains 235° C. at which time a 25% aqueous solution of a polyethylene ether glycol of 20,000 molecular weight is pumped in. Sufficient of the polyether is added to correspond to 15%, of the weight of unmodified polyhexamethylene adipamide. Heating is continued, the temperature increasing, while maintaining a pressure of 250 pounds by bleeding off steam. When the temperature reaches 240° C. steam is bled off more rapidly, reducing the pressure continuously over about 90 minutes to atmospheric pressure.

Heating at atmospheric pressure is continued at about 275° C. to complete the polymerization. The autoclave is discharged by extruding the polymer as a ribbon at 100 pounds pressure of inert gas, discharging the molten polymer as a ribbon by extrusion through a narrow slit. The ribbon is quenched on a water cooled casting wheel and cut to flake. The polymer flake has a relative viscosity of 34.4 (relative viscosity defined in U.S. Patent 2,385,890). This batch of modified polymer is coded sample A. An analysis for adipic acid content indicates (by difference) a polyether content of 15.6%.

The polymer flake thus prepared is melted on a grid blanketed with steam, extruded through a filter pack and a thirteen hole spinneret, in conventional manner. The filaments are quenched, wound up and subsequently drawn to produce an approximately 40 denier yarn. Processing conditions used for unmodified polyhexamethylene adipamide (66 nylon) are employed.

The thus-produced yarn is twisted, sized and woven to a taffeta fabric. Portions of the fabric sample are finished in conventional manner using a jig scour under minimum tension at the boil for thirty minutes. The fabric is then dried at 120° C. on a pin tenter, followed by heat setting at 205° C. for twenty seconds using 5% overfeed and 5% underwidth.

In like manner, fabrics (sample B) containing 10% of the 20,000 molecular weight polyether compound are prepared and finished. A third fabric (C) is similarly prepared from polymer containing 10% polyethylene ether glycol of 200,000 molecular weight.

Portions of the original fabrics are tested for log R with the results shown in Table 3. The fabrics are then scoured at the boil for one hour and dried; log R is again determined. The polyether content of the scoured fabrics is estimated by determining the weight loss on scouring, making allowance for the normal amount of finish and size that is also removed by this step. The estimated amounts are shown in Table 3, and indicate that approximately 2–4% polyether compound remains in the fabric, depending in part on the initial concentration. When the high molecular weight polyether compound is employed (sample C), approximately 8% polyether remains in the fabric. It is noted that the fabrics in unscoured and scoured state have attained a satisfactory degree of static protection, since cotton, a satisfactory fabric in this respect, has a log R of 13. In comparison, unmodified 66 nylon has a log R of over 15. A drop of oil placed on scoured fabric sample A spreads to a lesser extent, and is more completely removed by blotting, than is a drop of oil placed on an unmodified nylon fabric.

TABLE 3

Sample	A	B	C
Polyether, mol. wt	20,000	20,000	200,000
Amt. added, Percent	15	10	10
Log R,[1] initial	12.1	12.5	11.2
Percent remaining after scour [2]	3–4	2 3	8
Log R after scour, 40 wash	12.8	13.3	--------
Log R after mild scour and heat set	11.4	11.9	11.6
Log R after heat set and one hour severe scour	13.0	13.1	12.7
Log R after heat set and 40 wash	12.2	12.5	--------
Log R after heat set and 10 dry clean [3]	11.4	12.0	--------

[1] At 25° C., 30% RH.

[2] Severe scour, one hour at the boil, in aqueous 0.125% sodium lauryl sulfate, 0.1% trisodium phosphate.

[3] Dry cleaned in perchloroethylene, using 4% of a sodium mahogany oil sulfonate dry cleaning soap.

Other swatches of the original fabrics are given a conventional size-removing scour, heat-set, and tested for log R. Other treatments include severe scour following the heat setting, forty home laundry washings, and ten standard dry cleaning cycles using a conventional dry cleaning soap. The log R of these samples is shown in Table 3.

It is apparent that permanent antistatic protection, substantially equivalent to cotton, is obtained with both the 10 and 15% modification using a polyether of 20,000 molecular weight. Improved retention of the polyether compound is observed when a higher molecular weight polyether is used. These advantages are retained through conventional home laundering, as well as during dry cleaning.

Swatches of sample A, prior to scour, are irradiated with 2 mev. electrons to various doses, as shown in the following table. The swatches are wetted with water, and wrapped in aluminum foil prior to exposure to the electron beam. After irradiation, the samples are scoured for one hour at the boil. They are then dried, and the weight loss and log R are determined. The results are listed in Table 4.

TABLE 4

Sample	Dose, Mrep.	Weight Loss on Extraction, Percent	Log R
A	0	12.8	[1] 12.1
AB	10	11.5	11.3
AC	15	8.4	11.4
AD	20	8.4	11.4

[1] From Table 3.

The results show that the irradiation bonds about half the polyether to the nylon, so that it is not extractable. There is a corresponding improvement in log R. Doses above 15 Mrep. apparently provide little improvement in bonding.

There is no significant advantage in irradiating the scoured samples since the polyether is already sufficiently resistant to extraction.

When the fabric samples are irradiated dry, there is a much smaller improvement in bonding between polyether and polyamide.

Fabric samples A, B, and C contain no delusterant, and retain the surface luster typical of bright polyamide yarns. Prior to boil-off (scour) they have the relatively low covering power typical of bright (non-delustered) yarn. However, after scour, the fabrics have covering power which exceeds that of fabrics of similar construction containing from 0.3% to 2.0% TiO_2. In addition, the fabrics have a dry hand.

Fabric sample A, after scouring, has better covering power than irradiated, scoured samples AC and AD, since a smaller amount of the polyether is extracted from AC and AD.

When longitudinal sections of the scoured fibers of fabric sample A are examined under the microscope, it is observed that the yarn is full of narrow channels which appear as circular voids in the cross-section. The voids, of course, represent volume elements from which the polyether phase has been extracted. The channels are of the order of one micron in diameter. These narrow channels vary in length; many are at least several fiber diameters long. These voids scatter incident light, producing a fabric of high covering power. Examination of the surface of these fibers shows that a few of the channels extend to the fiber surface.

Scoured sample B has somewhat greater covering power than scoured sample C, since a greater proportion of the polyether is removed in scouring.

It is observed that the dimensions of a dry fiber removed from fabric A are substantially the same prior to and after scour. Since the scoured fiber contains voids, it is necessarily less dense. Density determination for fabric A shows a density of 1.04 after scour, as compared to 1.14 before scouring; the latter figure corresponds to that of unmodified 66 nylon. Thus, a lighter weight fabric is produced.

During the step in which the polyether is extracted from the polyamide filaments, a highly unusual swelling phenomenon is observed. The diameter of a filament of sample A (prior to scour), immersed in water, is measured at gradually increasing temperatures, with the results shown in Table 5, reported as percent swelling, based on the initial fiber diameter, dry, at room temperature (about 25° C.).

TABLE 5

Temperature, ° C.:	Percent swelling
25, dry	0
25, wet	5
50, wet	5
75, wet	5
100, wet	65

In comparison, unmodified 66 nylon swells no more than about 5–6% at the boil.

When the test is repeated on a scoured fiber, the fiber swells only about 5–6%, showing that the high swellability occurs once only, when the polyether is extracted from the filament. The high swellability produces changes in fabric geometry whereby fabrics of higher bulk and silklike hand are produced, as shown in Example VII which follows later herein.

Example V

When very high molecular weight polyethylene ether glycols are used, it is generally desirable to melt-blend the additive with the polymer substrate, since even dilute solutions of the polyether have a very high viscosity. Such high viscosity dilute solutions are not only hard to transfer, but also require elimination of objectionably large quantities of water, during polyamidation. Polyhexamethylene adipamide of 60 relative viscosity is melted in a screw extruder and fed to a polymer blender. Simultaneously, polyethylene ether glycol of 200,000, 500,000, and 3,000,000 molecular weight is melted, in separate runs (A, B, and C, respectively), in a second screw melter which also feeds the polymer blender where the polymers are mechanically mixed. Feed rates are adjusted to make a product containing 7.5% of the polyether compound. The molten polymer blend is fed to a meter pump, then to a filter pack and spinneret in conventional manner. The yarn is spun and drawn, and woven to a taffeta fabric. Each of the greige fabrics has a log R of 11.6, which increases to 13.1 after a one hour scour. The opacity of the samples after scour is in inverse order of the molecular weights of the polyethylene oxide additives as indicated in Table 6.

Irradiating wetted samples A, B, C to a dose of 20 mrep., as previously described, decreases the covering power of the extracted fiber, but increases its wickability.

TABLE 6

	Sample		
	A	B	C
Molecular weight of Polyether	200,000	500,000	3,000,000
Opacity after scour	Most	Intermediate	Least

Example VI

Polymer flake of polyethylene terephthalate, free from delusterant, and having an intrinsic viscosity of 0.76 is mixed by tumbling with 15% by weight (based on polyethylene terephthalate) of polyethylene ether glycol having a molecular weight of 20,000. The mixture is melted in a screw extruder and spun into yarn at a temperature of about 290° C. The yarn is drawn at a draw ratio of 3.55, to produce a yarn having a break elongation of about 25%. The yarn is then twisted seven turns per inch, twist set, and is woven into a plain weave taffeta of 104 x 72 construction.

The test fabric is divided into a number of swatches for subsequent tests.

A swatch of the test fabric is scoured for one hour at the boil in 0.5% aqueous solution of sodium salt of unsaturated long-chain alcohol sulfate. The surface luster of the original fabric is retained but its covering power (opacity) is increased so that it is equivalent to that of a similarly constructed fabric from unmodified polymer containing 0.3% TiO_2 delusterant. A wetted sample irradiated to a dose of 20 mrep. shows an increase in wickability, but a lower covering power.

The density of the unextracted yarn is 1.350; the scoured yarn has a density of 1.317. This compares with a value, for unmodified control, of 1.373. Based on the observed density change, it is estimated that from 10–20% of the polyether glycol initially present has been extracted. After 25 successive scourings in aqueous synthetic detergent, the scoured fabric has a log R value of 13.1. Another swatch is bleached in peroxide, followed by ten scourings; the log R is 12.8. A swatch of the extracted fabric is exposed to five dry cleaning cycles; the log R is 12.6. Another swatch of the scoured fabric is Soxhlett extracted in methylene chloride for 15 hours; the log R is 13.2. A comparably treated control (without polyether modifier) has a log R of 14.8, which is typical of unmodified polyethylene terephthalate.

The polyether glycol is present in the polyester fiber as a second phase, which may be seen by photo (FIG. V) of the fiber at about 700× magnification. Faint striations appearing parallel to the fiber length are due to the high molecular weight polyether glycol phase. After scouring, the yarn has even more pronounced striations (FIG. VI) and these appear to be voids within the fiber. A second sample, differing only in that 5% of the polyether glycol (20,000 molecular weight) is employed, shows fewer striations than are seen in the first sample.

When yet another sample is prepared following the above procedures, using, however, 10% of polyether glycol of 9,000 molecular weight, the fiber does not show striations (FIG. VII). There is some indication of a two-phase system, since there appear to be globules of the polyether compound in the fiber. However, this product does not retain its antistatic properties after scouring; a log R of 13.8 is obtained (after scour).

X-ray diagrams of polyethylene terephthalate fibers modified with high molecular weight polyether show features characteristic of an oriented crystalline polyether glycol phase, and also features characteristic of an oriented crystalline polyethylene terephthalate phase. In contrast, a terephthalate polyester containing polyethylene ether units as an integral part of the polymer chain, described by D. Coleman in J. Polymer Sci., 14, 15 (1954) shows no difference between X-ray photographs of the modified polymer containing both polyethylene terephthalate and polyether terephthalate blocks and the unmodified polyethylene terephthalate. Moreover, fibers are not antistatic.

Example VII

Seventy denier, thirty-four filament polyhexamethylene adipamide yarn of Y-shaped cross-section is prepared according to the procedure for sample A of Example IV; the polymer blend contains 15% polyether glycol of 20,000 molecular weight. A similar 70 denier, 34 filament yarn of unmodified polyhexamethylene adipamide (of the same cross-section) is also prepared as a control. Fabrics of similar construction are woven from these yarns, both in a plain weave and a twill construction. The fabrics are scoured at the boil for one hour in 0.5% synthetic detergent, and then heat set, in relaxed condition, for three minutes at 180° C. followed by dyeing. The bulk of these fabrics is measured with the results shown in Table 7.

TABLE 7

	Loom Construction	Finish Construction	Finished Fabric Weight, oz./yd.^{2}	Finished Fabric Bulk, cc./gm.
Plain Weave:				
Polyether Blend	100 x 68	120 x 80	1.82	2.8
Unmodified Control	100 x 80	112 x 94	2.16	1.77
Twill:				
Polyether Blend	100 x 86	120 x 100	1.92	2.58
Unmodified Control	100 x 90	114 x 108	2.27	1.75

A cross-section (perpendicular to the warp yarn) of the plain weave test fabric containing polyether glycol (prior to scour) is photographed at a magnification of 700×, FIG. VIII; the yarn consists of fairly loose fiber bundles. The fabric is then scoured at the boil for one hour, dried, and again photographed, FIG. IX. A comparison shows that the fiber bundles have become more compact and the filling yarn has acquired a more pronounced weave crimp, increasing the fabric bulk. In contrast, a photograph of the unmodified control, FIG. X (after boil-off) shows the yarn bundle to be flattened, and the weave crimp is not better than the test fabric before boil-off.

Example VIII

A solution of 3860 gm. caprolactam, 681 gm. polyethylene oxide glycol of 20,000 MW and 454 gm. H_2O is charged to an autoclave and heated according to the schedule used in Example I, except that the mixture is held for thirty minutes at 250 p.s.i.g. and 270° C. before pressure reduction is begun. The 6 nylon polymer contains 15% of the polyether compound. Yarn is spun from the polymer blend, as in Example V.

The yarn has a log R of 12.8, which increases only to 13.1 after boil-off. The log R of unmodified 6 nylon is 15.0. When the wetted yarn is irradiated prior to boil-off, to a dose of 15 mrep., the log R is 10.0 after boil-off.

Example IX

A melt blend is prepared by stirring 95 parts of polyhexamethylene adipamide flake with 5 parts of polyethylene ether glycol of 20,000 molecular weight for one-half hour under nitrogen at 285° C. The polymer blend thus prepared is melted in a screw melter and extruded from a spinneret to form filaments which are drawn and then scoured at the boil for one hour. The fiber has a log R of 12.2. A photomicrograph of the fiber A shows a striated appearance characteristic of properly distributed polyether glycol.

The experiment is repeated except that 95 parts of polyhexamethylene adipamide flake is heated to 100° C., and is tumbled with 5 parts of polyethylene ether glycol of 20,000 molecular weight. The polyether is a liquid at 100° C., so that it becomes relatively evenly distributed over the surface of the nylon flakes. The polymer mixture (coded batch B) is placed in a N_2 blanketed, heated cylinder, one end of which is closed with a sand filter and a spinneret. After heating until the polymer is completely melted, a piston forces the molten mixture through the orifices to form filaments, which are quenched and drawn as before. The log R of this yarn, after drawing and scouring, is 13.9. Although the filament shows a striated appearance, the polyether phase in B is less uniformly distributed than in A.

The NMR peak ratio of A is 5.5, compared to 2.5 for B, as determined at 50% R.H., by nuclear magnetic resonance. The comparable value for unmodified 66 nylon is 2.8. When the samples are dried by blowing dry N_2 over them for 15 min., the difference in the peak ratio is even more outstanding. Yarn A shows a value of 4.1 as compared to 1.4 for B. Unmodified 66 is 0.3.

A portion of the polymer of sample A in Example IV is dissolved in 98% formic acid, and fibers are formed by dry spinning. After drawing and scouring, the log R of the dry-spun fiber is 14.0.

Example X

Eighty-five parts of polyhexamethylene adipamide and fifteen parts of polypropylene ether glycol having a molecular weight of 2,000 are melt blended by stirring for one-half hour under nitrogen at 285° C. The melt is extruded through a spinneret and the yarn is drawn and scoured for one hour at the boil. The log R after scouring is 12.2. A photomicrograph of the fiber shows the presence of highly striated inclusions of the polypropylene ether glycol.

When the test is repeated, using instead of the polypropylene ether glycol a polytetramethylene ether glycol of 2,000 molecular weight, the log R of the scoured fiber is 14.6, substantially equivalent to unmodified nylon control. The static protection is unsatisfactory.

Example XI

Polymer is prepared in an autoclave, from 55% aqueous solution of the salt of bis(para-aminocyclohexyl) methane and azelaic acid. 7.9 millimols of acetic acid are added for every mol of the polyamide salt. One-half percent (base on weight of final polymer) of sodium phenyl phosphinate antioxidant is added. The salt solution is heated under 280 lbs./in.^{2} pressure for two hours while the temperature is raised to 206° C. During the heating period, when the temperature reaches 220° C., a 25% aqueous solution of a polyethylene ether glycol of 20,000 molecular weight is added in sufficient amount to make concentrations indicated in Table 8. The pressure is then reduced to atmospheric and the temperature raised to 300° C. and the polymer held under these conditions for one hour. It is then extruded and cut to flake. The polymer is melted and filaments are extruded at a temperature of 280° C. through a five-hole spinneret, and the yarn is wound up at 200 yds./min. The yarn is then drawn three times its extruded length over a three inch diameter pin at a temperature of 150° C., at a speed of 50 yd./min. After a scour of one hour, the log R values indicated in Table 8 are observed. In a second test on unscoured filaments, the percent volume increase at various water temperatures is indicated. An exceptional degree of swelling is observed, especially in the sample B containing the larger amount of additive. The scoured yarns have an opaque appearance.

TABLE 8

	Run	
	A	B
Molecular Weight of Polyether Glycol	20,000	20,000
Amount, Polyether Glycol, Percent	15	30
Log R after Aqueous Scour	12.6	12.1
	Percent Volume Swelling	
Percent Swelling in Water—Water Temperature, ° C.:		
25	0	−13
40	0	+123
60	0	+143
75	0	+334
90	−19	+60
100	+40	+40
110	+25	+40

It is important to note that this polyamide appears to be especially compatible with the polyether. A 4% mixture shows no evidence of a separate polyether phase, and is not antistatic. A 5% mixture does show a separate polyether phase, as well as antistatic properties, as shown in Example XX.

Example XII

Polyhexamethylene adipamide polymer flake containing 10% polyethylene ether glycol of 20,000 molecular weight is prepared following the procedure for sample B of Example IV. The flake is melted, extruded through a spinneret and drawn to form a bristle of 14 mil diameter. The bristle is evaluated as an antistatic broom for use in explosive areas. Its antistatic properties are equivalent to those of one of the natural cellulosic fibers, Tampico, and are at least ten times better than horsehair which is acceptable for use in such areas. The bristle retains over 75% of its antistatic properties after boiling in water for four hours followed by reconditioning at 50% R.H. for four days.

When the above test is repeated, using polyhexamethylene sebacamide, similar results are obtained.

Example XIII

This example illustrates the use in nylon of a polyethylene ether compound which is capped on one end with a nonyl phenyl group. The average molecular weight of this compound is about 590. The procedure of Example IV is repeated, with suitable amounts (Table 9) of this polyethylene ether being added as a 50% solution during polyamidation. Polymerization, casting, spinning, and drawing are carried out as in Example IV. The log R of the drawn yarn is determined after a two hour scour, with the results indicated in the table. The fiber appearance under the microscope is also tabulated.

TABLE 9

Run	Amount Added, Percent	Log R (After 2 hr. Scour)	Fiber Appearance Under Microscope
A	2.5	14.5	No visible second phase (no striations).
B	5	13.2	Striations appear.
C	7.5	12.3	Striations more prominent.
D	10	12.0	Do.

When run B is repeated, using a polyethylene ether compound with hydroxyl ends (i.e., a glycol) and an average molecular weight of 600, the additive is soluble in the fiber (sample E). No striated polyether phase is produced. Log R of the scoured sample E is 14.0. Due to reaction between adipic acid and the low molecular weight glycol during polyamidation, the polymer has a low molecular weight.

This confirms the observation that antistatic properties require the presence of a second phase, which must be present as striations within the fiber.

It is also noted that the nonyl phenyl capped polyether is more highly dispersed than when the polyether is a glycol. At 10% concentration, voids corresponding to the polyethylene ether glycol particles of run B, Example IV range in size from one-quarter to three-quarters micron while the polyethylene ether compound voids of run D of this example are about half this size.

Example XIV

This example illustrates the use in nylon of varying molecular weight, singly capped polyethylene ether compounds. The polyethylene ether compounds are capped on one end with a nonyl phenyl group. Ten percent (10%) of the compound is employed. The procedure for run D of Example XIII is followed. The results are indicated in Table 10, showing log R after a one-hour scour.

TABLE 10

Run	Average Mol. Wt.	Log R, after one-hour scour
A	385	14.2
B	640	12.3
C	1,600	12.0
D	4,600	12.0

It is noted that the low molecular weight compound of run A provides insufficient static protection. Good static protection is obtained using the other additives.

When samples B, C and D are given continual extraction in boiling distilled water, changing the water every hour up to four hours, it is shown that all but about 2% of the antistatic additive is removed. This is sufficient to give satisfactory permanent static protection. However, when samples C and D are irradiated wet to a dose of 20 mrep. prior to the extraction, a greater amount of the polyether is retained after scour, and the samples have improved wickability.

Example XV

This example illustrates the relationship between the concentration of the poly(alkylene ether) and the antistatic effect provided.

66 nylon polymer is melt blended with polyethylene ether glycol of 20,000 molecular weight. The fibers are melt extruded, drawn 4 times their extruded length and boiled off (in skeins) for one hour in aqueous 0.1% trisodium phosphate, 0.125% sodium lauryl sulfate. The yarn is wound on polytetrafluoroethylene cards; log R is determined in a direction parallel to the filaments. Values obtained are indicated in Table 11.

TABLE 11

Run	Concentration of Polyether, Percent	Log R (after one-hour boil-off)
A	0 (control)	15.3+
B	1	13.4
C	2	13.3
D	3	12.9
E	4	12.4
F	5	12.2
G	8	11.8

It is apparent from the table that at least 3% of this polyethylene ether glycol must be added to the nylon in order to obtain an antistatic effect equivalent to cotton, which has a log R of about 13.1.

When the test is repeated using nonyl phenoxy capped polyethylene ether alcohol of 1600 mol. wt., the addition of only 2% will give an acceptably antistatic fiber.

Example XVI

Polyethylene terephthalate is polymerized conventionally by reacting dimethyl terephthalate with ethylene glycol, with evolution of methanol. When the evolution of methanol is complete, the reaction product is transferred to an autoclave and the vacuum cycle is begun. Glycol is evolved as high molecular weight polymer is formed. Midway in the polymerization cycle, a polyether glycol is added in a glycol slurry. Polymerization is continued until polymer of spinnable molecular weight is produced. Following the polymerization, the polymer is extruded as ribbon, cut to flake and then spun to yarn using a screw melter.

The polyethylene ether compounds added during the various runs are inticated in Table 12, along with the concentrations employed. The compound used in run B is the nonyl phenyl capped polyether used in run D of Example XIV. In C, D, and E, polyether glycols are added. The spun yarn is drawn and woven into a filling face satin. A sample representative of each run (including an unmodified control A) is given five washing cycles, each of which is followed by hand ironing at the temperature setting customary for synthetic fabrics. Following the five wash-press cycles, each sample is subjectively rated for static against the control A at 25% relative humidity. The rating scale goes from 1, severe static, up to 5, no static. Cotton, which is acceptable, has a rating of 3 to 4.

TABLE 12

Run	Average Mol. Wt.	Concen., Percent	Static Rating after 5 Wash/Press Cycles
A	None	----------	1.0
B	4,600	6	4.6
C	500,000	8	4.2
D	200,000	3	3.0
E	200,000	5	4.2

It is observed that increasing the amount of polyether glycol in E (vs. D) gives improved antistatic effect, as expected. Examination of the filaments of sample E with a light microscope shows no visible striations, but when examined at high magnification in an electron microscope, minute striations are evident.

Example XVII

The procedure of Example VI is repeated; however, for this test 2 mol percent of the terephthalate component is replaced by an equivalent amount of sulfonated isophthalate. The polyethylene ether glycol added, 8% by weight, to the flake, and screw melter spun, has a molecular weight of 20,000. After five wash-press cycles, fabric from this polymer has a subjective static rating of 4.5.

The test is again repeated, using a terephthalate copolymer in which 10 mol percent of the terephthalate component is replaced by an equivalent amount of hexahydroterephthalate. 5% of the 20,000 molecular weight polyethylene ether glycol is added to the flake before screw melting. Fabric produced from filaments of this composition have satisfactory static properties.

The process of this example is again repeated, preparing a polymer of para-hexahydroxylylene terephthalate (65% trans, 35% cis isomer) to which is added 8% of the same polyethylene ether glycol. When tested according to the procedures described above, it is found to have an antistatic rating equivalent to cotton.

Example XVIII

A study of the effect of reacting a polyether glycol and a polyester, so that the antistatic becomes part of the polymer chain, has shown that such reaction should be minimized. The harmful effects become evident in a number of ways. A very sensitive criterion is the effect on lightfastness of the dyed fiber.

It has been discovered that substantially all of the unreacted polyether glycol can be extracted from polyethylene terephthalate filaments which have not been irradiated using a solvent which has a swelling effect upon the substrate polymer, e.g., methylene chloride. In this way, the extent of reaction can be evaluated; harmful results become serious when more than 10% of the added polyether glycol reacts with the polyester.

Polyethylene terephthalate filaments are prepared in accordance with the procedure of Example VI to contain 15% of polyethylene ether glycol of 20,000 molecular weight. The filaments are spun, drawn and woven into a filling face satin. A swatch A is extracted with methylene chloride for one-half hour, removing about 65% of the added polyether glycol. Swatch A, an untreated swatch B, and a control swatch C containing no polyether glycol are dyed by the same procedure, and are exposed to the ultraviolet light of a xenon arc. Examination after 40 hours shows equivalent fading of samples A and B, whereas very little fading is noted on control sample C. This indicates that it is not the total amount of polyether glycol which causes the fading, but rather the amount which has become a part of the polymer molecule.

Example XIX

Following the procedure of Example XVIII 6% of (a) polyether compound of 20,000 molecular weight having hydroxyl ends and 6% of (b) polyether compound of 20,000 molecular weight having methoxy ends is incorporated in polyethylene terephthalate polymer which is spun to yarn and woven to filling face satin as before. Representative samples are coded A and B, respectively. The static rating after five wash-press cycles is listed in Table 13 along with a similar result for an unmodified control C. Swatches of the fabric are dyed with a dispersed dye and exposed for 40 hours in a Xenotester to determine dye lightfastness. It is noted that there is no fading for the control C, very slight change in shade for the methyl capped polyether product B, and a severe change in shade for the sample of run A. Skeins of these yarns are boiled in dilute sodium hydroxide solution and the rate at which they lose weight is compared to that of control C.

TABLE 13

	Run		
	A	B	C (Control)
Polyether Compound, Mol Wt	20,000	20,000	----------
Amount added, percent	6	6	None
Static rating, 5 Wash/Press Cycles	4.2	4.3	1.0
Disperse Dye Lightfastness	(1)	(2)	(3)
Caustic Sensitivity, percent of control	880	200	100

[1] Severe change.
[2] Slight change.
[3] No change.

It is noted that sample B shows a caustic sensitivity (rate of weight loss) close to that of control, whereas the rate of weight loss for sample A is over four times as fast. It is believed that the rapid rate of caustic attack is because the polyether glycol has, in part, become a component of the polyethylene terephthalate chain. The polyether compound capped with methyl groups would not be expected to react during polymerization, and, hence, would be present as a polymer blend component only.

Example XX

Nylon polymer is prepared from the salt of bis-(para-aminocyclohexyl)methane and azelaic acid, following the procedure of Example XI. No antioxidant is added. At 220°, sufficient TiO_2 slurry is added to give 0.3% TiO_2 in the final polymer. At 245° C., sufficient 40% aqueous solution of the polyether of run C of Example XIV is added to make a final concentration of 5.0%. The polymer is extruded and cut to flake, which is subsequently steam-spun from a heated grid melting unit. The yarn is drawn 3.2× over a 110° C. hot pin.

A filling face satin woven from the test yarn gave a log R of 11.3 after boiling in water for one hour. A corresponding control without antistat has a log R of over 14.5.

Only 1.7% (on weight of fabric) of the antistat is removed after 8 hours extraction in boiling water. However, the extracted test fabric is noticeably more opaque than the similarly treated control. Examination of the filaments show a striated structure.

Example XXI

Forty denier, 13 filament nylon yarn containing 15% polyethylene ether glycol of 20,000 molecular weight, prepared like run A of Example IV is tricot knitted into test slips (A) and compared to conventional dull (2% TiO_2) nylon tricot (B) and cotton batiste (C) control garments in subjective slip comfort static tests. Each of the items is worn and evaluated by two female subjects for the discomforting effects attendant with static build-up under controlled humidity and temperature conditions (20% R.H. and 78° F.). Prior to testing each slip was given 10 standard washes.

No perceptible evidence of static or of its effects is encountered with either the test A or the cotton control C; both are rated static-free. The nylon control (B), however, develops a considerable degree of static, causing it to cling to the wearer and to produce an audible static discharge (crackle) upon removal.

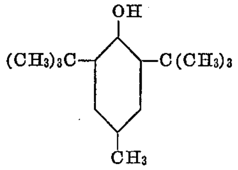
The covering power of the test fabric A and dull nylon control fabric B are compared by measuring light transmittance and light reflectance. The results adjusted to a fabric weight of 2.5 oz./yd. in each case, are shown in Table 14.

TABLE 14

	Test A	Control B
Percent Light Transmitted	10.0	14.0
Percent Light Reflected	75.0	67.0

The test fabric A containing no TiO_2 has better covering power than control B which contains 2.0% of the delusterant.

The test is repeated, using melt blending techniques to prepare an antistatic yarn (D). One component of the blend is 66 nylon polymer containing about 0.3% sodium phenyl phosphinate; the other is polyethylene ether glycol of 20,000 mol. wt., containing about 6.2% (based on weight of glycol) of a phenolic antioxidant of the formula:



The two components are melted in individual screw melters, and are fed to a power driven homogenizer. The feed ratio is such that the final composition contains 7.5% of the glycol, 0.3% of the phosphinate, and 0.5% of the antioxidant. The blended melt is immediately pumped to a sand pack and spinneret, and spun to yarn as before. The yarn is drawn, knitted and made into slips, as before. Slips from D, like A, are free from static, and are superior in whiteness, being equivalent to B in this respect.

Example XXII

Polymer is prepared by carrying out the polymerization cycle as described in Example IV except that a 25% aqueous solution of poly-N-vinyl pyrrolidone (PVP) of molecular weight 150,000 is pumped into the autoclave before the polyethylene ether glycol solution is added. The final polymer has a composition of 10% polyethylene ether glycol, of 20,000 molecular weight, 10% PVP, 80% 66 nylon. The polymer is melt spun under a steam atmosphere, and drawn to 40 denier 13 filament yarn (sample A). Yarn A is compared to sample B of Example IV which cotnains 10% of the polyethylene ether glycol and 90% 66 nylon. Under the electron microscope, the striations of the polyethylene ether glycol are found to be much smaller in diameter and more numerous when PVP is present (sample A) than in sample B. The filaments A are less opaque than the B yarn after scouring. The resulting fabrics A have reduced covering power, lower luster and much higher dye yield than sample B without PVP. Both A and B are antistatic.

Example XXIII

Two batches, A and B, of 1040 denier, 68 filament, round cross section nylon yarn containing 3% and 15% 20,000 molecular weight linear polyethylene ether glycol (PEG) respectively, are steam bulked substantially as described in Belgian Patent 573,230 and tufted into continuous filament carpets. The carpets are mock dyed (dye bath at the boil, without dye) during which the antistat concentration is reduced (by extraction) to about 2.5% and 4% for carpets A and B, respectively. The mock dyed carpets are coded AA and BB respectively. The carpets are tested for static propensity by measuring the electrostatic voltage built up on an individual while walking on the carpets at 70° F., 20% R.H. Results are listed below (further controls are given in Example XV).

TABLE 15

Carpet	PEG, Percent	Voltage (kilovolts)
AA	3	8.5
BB	15	4.5
Soiled wool	None	5

These results illustrate the permanent antistatic protection obtained with the test carpets, especially B, which is equivalent to soiled wool.

The above carpets are also tested in a hallway for soiling resistance with results as follows:

TABLE 16.—SUBJECTIVE SOIL RATING [1]

Carpet	Traffic Cycles		
	4,000	8,000	12,000
A—3% PEG, as-tufted [2]	2.1	1.9	1.4
B—15% PEG, as-tufted [2]	2.3	2.2	1.5
AA—3% PEG, mock dyed	3.9	3.2	2.4
BB—15% PEG, mock dyed	4.1	3.3	2.5
Type 501 nylon (trilobal cross section, 0.15% TiO_2)	3.0	2.5	2.1
Type 101 nylon (round cross section, 0.02% TiO_2)	2.1	2.0	1.5

[1] 5=no change from original; 1=severe change.

[2] Finish removed by extraction with perchloroethylene, which does not extract PEG.

These results show that carpets A and B, prior to mock dyeing, show no soiling improvement over control type 101 having the same (round) cross-section. Soiling properties are inferior to type 501 trilobal control. After mock dyeing (scour), however, carpets AA and BB show significantly improved soil repellence vs. both unmodified controls.

When the test is repeated, after irradiating yarns A and B to a dose of 20 mrep., the mock dyed samples show a better resistance to static but greater soilability than corresponding samples AA and BB. It is thus seen that improved antisoiling is obtained when more of the PEG is extractable, at some sacrifice in static protection.

By means of extended tests of this type, it is discovered that at least about 0.5% PEG (based on weight of fiber) must be extracted to obtain an improvement in soiling protection.

Example XXIV

The polymer blend of this invention is well suited for spinning fibers of two polymer components, in side by side or sheath-core arrangement, as disclosed in U.S. Patents 2,389,173 and 2,931,091.

Polymer batch A is prepared as in Example IV (sample A) to contain 7.5% polyethylene ether glycol of 20,000 molecular weight. Polymer B is unmodified polyhexamethylene adipamide (41 relative viscosity). In successive runs, 1020 denier 68 filament yarns are prepared in which (1) the entire filament consists of B; (2) A is in the sheath, B in the core; (3) B is in the sheath, A in the core; and (4) A and B are spun side by side. About equal amounts of A and B appear in each filament. The yarns (1020 denier, 68 filament) are spun, drawn and steam-bulked. They are then made into tufted carpets and tested for static propensity by electric charge accumulation when a person walks across the carpet. The data are shown in the following table.

TABLE 17

Run	Sample	Static Voltage Kilovolts	
		Before Scour	After Scour and Mock Dye
1	B 66 nylon control	12.5	12.5
2	A in sheath of filaments, B in core	0.5	8.8
3	A in core of filaments, B in sheath	4.3	6.0
4	Side-by-Side filaments, A and B	3.1	7.6
	Soiled wool control	6.0	----------

When the polyether is in the sheath of the filaments (Run 2), a major portion (80%) of the amount added is extracted during scouring and mock dyeing, resulting in an unacceptable decrease in static protection. However, when the polyether is in the core of the filaments, loss due to extraction is largely prevented, thus retaining a higher level of static protection. A similar result is obtained by irradiating any of such combinations with high energy radiation.

Example XXV

Following the procedure of Run 4 of Example XXIV a two component fiber is spun, in which one component is polyethylene terephthalate and the other is 66 nylon containing 15% of linear polyethylene ether glycol of 20,000 molecular weight.

The yarn is spun with a trilobal cross-section using two screw melters. The yarn is conventionally draw-twisted over a 90° C. hot pin. Fabric is woven and finished using conventional techniques.

The test fabric has cotton-like static properties even though the antistatic nylon component accounts for only 37% (by weight) of the fabric. Before scouring, the fabric contained an average 5.5% of the polyether, overall. After scouring, the residual polyether is only about 1%, based on weight of fabric. Even this low level of antistatic agent is sufficient to produce cotton-like static properties. The unusual efficiency of the very small amount of antistatic agent is believed to be due to the fact that it is concentrated in some of the filaments in sufficient quantity to make these filaments conductive. The log R (30% R.H.) after conventional finishing is 12.8–13.0 (vs. 13.1 for cotton); the charge decay is 10 sec. vs. 13 sec. for cotton.

The test is repeated, using 2.5% of the nonyl phenyl capped polyethylene ether alcohol of run C, Example XIV, instead of the polyether glycol. The scoured fabric shows antistatic behavior superior to cotton. This is achieved because at least 2% of the PEO modifier was mixed with the nylon component, which thus serves to conduct away static charges developed on the unmodified polyethylene terephthalate component.

Example XXVI

Modified nylon carpet staple (A) is prepared from a melt blend of polyhexamethylene adipamide containing 10% of polyethylene ether glycol of 20,000 molecular weight. This staple is scoured and mock dyed, as in Example XXIII, and is then blended with an equal weight of unmodified hexamethylene adipamide staple (B) which had been scoured in perchloroethylene for ½ hour to remove any spin finish. The blend of A and B is carded on the woolen system, spun and woven into a 27-inch wide loop pile carpet. No finish is added to the staple blend during processing. A 4-foot length of this carpet is tested for static propensity by the electrostatic voltage build-up test of Example XXIII. The voltage build-up observed is 6.6 kv. This is much better than 10 to 12 kv. for an unmodified nylon carpet of fiber B, and is close to the value of 5 kv. for a soiled wool carpet. Analysis of the modified nylon B indicates that the scoured staple contains 4.1% of the polyethylene ether glycol.

A third lot C of carpet staple is prepared, containing 15% polyethylene ether glycol of 20,000 molecular weight. When as little as 10% of staple C is blended with 90% of unmodified 66 nylon, staple yarn spun from the staple blend has a log R of 13.2. This compares favorably with a log R of 14.8 for yarn from unmodified nylon B. When wet staple fiber C is irradiated prior to blending to a dose of 15 mrep., the log R of the blend containing 10% C. is 12.0.

It is thus apparent that as little as 10% by weight of the modified antistatic nylon staple of this invention produces significant antistatic effect when blended with as much as 90% of conventional 66 nylon fiber.

Example XXVII

Two batches of polymer, A and B, are prepared according to the procedure of Example IV. Batch A is polyhexamethylene adipamide, and Batch B is a copolymer of 92 parts hexamethylene adipamide and 8 parts of hexamethylene isophthalamide. Each batch contains 3% of nonyl phenoxy capped polyethylene ether alcohol of about 1600 mol. wt. These polymers are co-spun from a divided spinneret, drawn as a combined bundle then woven to fabric. After scouring, the fabric develops a silk-like bulk and hand, due to the differential shrinkage of the cospun yarn. The scoured fabric has a log R of 12.5, vs. over 15 for control yarn containing no polyether.

The test is repeated, using 2.5% of the polyether compound in the 66 nylon yarn, cospun with unmodified copolymer B. The fiber shows more satisfactory spinning and drawing behavior than in the previous test. The fabric bulks on boil-off, and is antistatic. When dyed, it shows a pleasing heather effect, due to the differing dye rates of the two components.

When the test is again repeated, except that 2.5% of the same polyether compound is added to the copolymer component B (but not to A), improved processability is observed, and an antistatic, bulked fabric is obtained, after boil-off. When dyed, a uniform color is obtained, since the decrease in dye rate produced by the polyether additive compensates for the higher dye rate of the copolymer B.

Example XXVIII

Polyether blends are prepared from the sulfonated isophthalate-terephthalate copolymer of Example XVII, and various amounts of a polyether glycol (PEG) of 20,000 mol. wt., using the melt blending-spinning technique described for sample D of Examples XXI. Yarns are spun, drawn and scoured, then are tested for log R, and NMR peak ratio, with the results given in Table 18. The amount of PEG is determined by analysis.

TABLE 18

Sample	Percent PEG	Log R	NMR Peak Ratio at 26° C.	
			50% RH	Dry N_2 [1]
A	0	>15	3.0	1.6
B	~1.0	>15	2.7	1.4
C	5.2	13.3	6.8	5.0
D	6.4	13.0	7.5	4.9
E	7.0	12.2	8.8	7.0

[1] Peak ratio determined after exposing sample to a stream of dry N_2 for 15 minutes.

It is noted that there is a good correlation between amount of PEG, log R and the NMR peak ratio.

Example XXIX

Following the melt blending-spinning procedure of the previous example, taffeta fabrics are prepared from melt blends of 100 parts polyethylene terephthalate and 6 parts of various polyether compounds. Using this technique, less than 10% of the polyether glycol reacts with the polyethylene terephthalate.

The fabrics are evaluated for static rating after 15 "C" wash cycles, using the scale given in Example XVI. The polyethers used have the formula:

$$R—O(CH_2CH_2O)_x—R'$$

R and R′ are as shown in Table 19.

TABLE 19

Polyether			Static Rating After 15 "C" Wash Cycles
R	R′	Molecular Weight	
Nonyl phenyl	H	20,000	4.5
Nonyl phenyl	H	13,500	3.8
Phenyl	H	16,000	4.4
Nonyl phenyl	CH_3	11,000	3.1
Phenyl	CH_3	16,000	3.3
CH_3	H	15,000	4.1
CH_3	CH_3	15,000	4.1
H	H	21,000	3.8

Example XXX

A melt blend is prepared by mixing 85 parts of linear polypropylene and 15 parts of a polyethylene ether glycol of 20,000 molecular weight. The melt is extruded through a spinneret, and the thus-produced fiber is drawn and scoured for one hour at the boil. After scouring, the fiber shows a log R of 12.1. A photomicrograph of the fiber shows the characteristic striated structure. Unmodified polypropylene has a log R greater than 15.

When the test is repeated, using linear polyethylene as the hydrophobic polymer, similar results are obtained.

The one-time swelling of polyether-modified polyamide fiber may be exploited to produce changes in fabric geometry, as explained previously, to produce a synthetic fabric having a silk-like hand. It is believed that the fiber is swollen due to absorption of water by hydration of the polyether; at elevated temperatures, sufficient force is developed to distend the fiber. In the distended condition, part of the polyether glycol is extracted leaving voids which produce opacity. On cooling, the swollen fiber is dehydrated and returns to its former size. Since a large part of the polyether glycol has been removed, the swelling does not occur on a second boil-off. However, the once-only swelling (superior even to silk which swells approximately 45% in water at 100° C.) is believed to be responsible for the silk-like properties observed in fabrics from polyamides which have been modified by polyether glycol and then extracted.

It has long been the goal to produce a fabric that approaches more closely the aesthetic characteristics of silk. Two characteristics in which nylon and silk fabrics differ are that the silk has a high flexural rigidity, as measured for example by the hanging heart test, combined with a liveliness which may be measured by the rate at which induced vibrations are damped out of the fabric. In comparable construction, and at substantially constant flexural rigidity, the scoured, polyether glycol modified, nylon fabric has a damping factor which is reduced more than 20% below that of the unmodified 66 nylon control thus approaching silk fabric aesthetics more closely than any wholly synthetic fabric known heretofore.

An additional surprising property of fabric prepared from the filaments of this invention is the resistance to soiling. Resistance to oil spotting has already been mentioned. In addition, the fabric shows less effect from oily and dry soil. This effect is enhanced by high extractability of the polyether. For antisoil effect, at least 1% of the polyether (based on fiber weight) and preferably 4% should be extractable. This property is especially desirable in carpets.

The hydrophobic synthetic fiber-forming polymer to be modified by the process of the instant invention is characterized by a low moisture regain, e.g., the moisture regain will normally be 5% or less at a relative humidity of 78% at 25° C. Filaments of such polymers have a high static propensity, and typically have a log R.H. of 14.5 and above at 25° C. and 30% R.H. The filaments may be used or produced in any state of aggregation, e.g., plexifilament, fiber, staple, floc, yarn, tow, cord, fabric or the like.

The modified polymer of this invention may be used as a component of a cospun yarn in which filaments of two or more different compositions are spun simultaneously to make a mixed filament yarn, as a component of a side-by-side or a sheath core yarn. The yarn bundle may also be separated and given different treatments wherein a differential shrinkage, bulkable yarn is produced, as disclosed, for example, in British Patent 787,157. The polymer is also suitable for the process of British Patent 839,418.

The polymers suitable for the process of this invention must be shaped by melt spinning processes. It has been shown (Example IX) that dry spun fibers are not adequately antistatic.

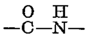
As illustrated in many of the examples, the filament produced from the synthetic polymer acts as a matrix in which the polyalkylene ether is dispersed and to which it becomes bonded by means of the high energy irradiation bombardment. As previously mentioned, these compounds includes the polyamides, the polyureas, the polyurethanes, the polyesters, the polysulfonamides and the like. Typical processes for producing suitable condensation polymers are disclosed in United States Patent Nos. 2,071,250, 2,071,253, 2,130,523, 2,130,948, 2,190,770, 2,321,890, 2,321,891, 2,465,319, 2,604,689, 2,647,104, 2,752,328.

By the term "synthetic condensation polymer" is meant a polymer which can be formed by polymerization with elimination of small molecules such as HCl, H_2O, NaCl, NH_3 and the like as well as those polymers which on chemical degradation (e.g. by hydrolysis) yield monomeric end products differing compositon from the structural units. Among such polymers may be mentioned polyamides, polyoxymethylenes, polyureas, polyurethanes, polyesters, polysulfonamides, and the like and copolymers of such materials.

Suitable polyamides are those melt-spinnable synthetic linear polyamides which are prepared from polymerizable monoamino monocarboxylic acids or their amide-forming derivatives, or from suitable diamines and suitable dicarboxylic acids or from amide-forming derivatives of these compounds. Typical of such polyamides are those formed from an aliphatic diamine and an aliphatic acid containing the repeating unit

$$-X-Z-Y-Z-$$

wherein —X— and —Y— represent divalent aliphatic, cycloaliphatic or mixed aliphatic-cycloaliphatic groups and —Z— represents the



$$-\overset{O}{C}-\overset{H}{N}-$$

linkage. Especially useful polyamides are those in which —X— and —Y— are $(CH_2)_{n-1}$, where n is a positive integer of from 1 to 12 inclusive, except that n may not be 1 for both —X— and —Y— simultaneously. —X— and —Y— may be the same or different. Polyhexamethylene adipamide, polycaproamide (i.e., "66" and "6" nylons) and polyundecanoamide are typical. Other suitable polyamides are those having the repeating structure

$$-A-Z-X-Z-$$

wherein —A— is a divalent aromatic radical and —X— and —Z— are as previously defined. Polyhexamethylene isophthalamide is illustrative of such polymer. Additionally polyamides having repeating units such as

$$-A-Z-B-Z-$$

and

$$-X-Z-B-Z-$$

wherein —B— is divalent alkaryl (such as xylylene) may be used; only those polymers and copolymers which are melt spinnable are intended. Another class of suitable polyamides containing other than aromatic intracarbonamide repeating units are those prepared from piperazine, such as those from piperazine and adipic acid, and the like.

Melt spinnable copolyamides and polyamide mixtures may also be used in accord with this invention.

Another preferred group of polymers for the practice of this invention are the melt spinnable fiber-forming synthetic linear condensation polyesters of bifunctional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain includes at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain (para-relationship in the case of a single six-membered ring). The polyesters may be derived from any suitable combination of bifunctional ester-forming compounds. Such compounds include hydroxy acids such as 4-(2-hydroxyethyl)benzoic acid, hydroxypivalic acid and 4-(2-hydroxyethoxy)benzoic acid, or mixtures of the various suitable bifunctional acids or derivatives thereof and the various suitable dihydroxy compounds and derivatives thereof. The repeating structural units of the polymer chain comprise recurring divalent ester radicals separated by predominantly carbon atom chains comprising hydrocarbon radicals, halogen-substituted hydrocarbon radicals, and chalcogen-containing hydrocarbon radicals wherein each chalcogen atom is bonded to carbon or a different chalcogen atom, and no carbon is bonded to more than one chalcogen atom. Thus, the repeating units may contain ether, sulfonyl, sulfide, or carbonyl radicals. Sulfonate salt substituents may also be present in minor amount, up to about 5 mol percent total sulfonate salt substituents in the polyester based on the number of ester linkages present in the polyester. Other suitable substituents may also be present.

Among the various suitable dicarboxylic acids are terephthalic acid, bromoterephthalic acid, 4,4′-sulfonyldibenzoic acid, 4,4′-diphenic acid, 4,4′-benzophenone-dicarboxylic acid, 1,2-bis(4-carboxylphenyl)ethane, 1,2-bis(p-carboxyphenoxy)ethane, bis-4-carboxyphenyl ether and various of the naphthalenedicarboxylic acids, especially the 1,4-, 1,5-, 2,6-, and 2,7-isomers. Isophthalic acid is also suitable, especially when used in combination with a 1,4-dihydroxyaromatic compound. Carbonic acid is similarly suitable.

Among the various suitable dihydroxy compounds are the glycols, such as ethylene glycol and other glycols taken from the series $HO(CH_2)_nOH$, where *n* is 2 to 10; cis- or trans-p-hexahydroxylylene glycol; diethylene glycol; quinitol; neopentylene glycol; 1,4-bis(hydroxyethyl)benzene; and 1,4-bis-(hydroxyethoxy) benzene. Other suitable compounds include dihydroxyaromatic compounds such as 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, hydroquinone, and 2,5- or 2,6-dihydroxynaphthalene.

The mixing step is essential in order to distribute the polyether compound sufficiently uniformly throughout the hydrophobic polymer. Melting the components in a screw extruder is usually satisfactory, although mechanical mixers are more effective, due to the high melt viscosity of the polymer and normally very different viscosity of the poly(alkylene ether). Excessive mixing must be avoided, since this has been found to disperse the poly(alkylene ether) into such small particles that they do not form microscopic elongated particles oriented parallel to the fiber axis; instead, the polyether appears as minute globules, and the fiber has inferior antistatic properties.

It has been pointed out previously that it is advantageous to choose a polyether free from groups which may react during the process of blending the polyether with the fiber-forming polymer. For example, where the polyether compound is to be mixed with a polyamide during polyamidation, amine and carboxyl end groups on the polyether should be especially avoided. This can be done by using a polyether glycol, or alternatively using a polyether compound which is capped with monofunctional ether ends, e.g., methyl, ethyl, phenyl, alkylphenyl, or the like. Analogous precautions must be observed when it is desired to add the polyether compound during polyesterification, where carboxyl, hydroxyl or ester ends may be reactive. Alternatively, it will often be possible to employ a polyether compound having reactive ends if the polymers are blended so late in the process (e.g. after the polymerization is completed or preferably during melting prior to spinning) that there are few reactive ends remaining and the chances of reaction between the polyether compound and the substrate polymer are remote; and the chance for reaction is decreased by reducing contact time during the melting stage. As a guide, reaction with the fiber-forming polymer should be kept to less than 10% of the polyether added.

The poly(alkylene ethers) which may be incorporated in the hydrophobic polymers are either ethylene oxide, propylene oxide or ethylene oxide-propylene oxide condensation products, i.e., the products contain from two to three carbon atoms in the alkylene group with two of the carbon atoms being intralinear carbon atoms connecting intralinear ether-oxygen atoms. Preferably, the poly(alkylene ether) is an ethylene oxide polymer. The poly(alkylene ether) may be a glycol ether, and thus terminated or "capped" by hydroxyl groups, or it may be an oxyalkylated ether of a monohydric or polyhydric alcohol. Suitable alcohols are methanol, ethanol, i-octanol, decanol, laurol, tridecanol, glycerol, pentaerythritol, sorbitol, mannitol, their partial esters and the like. Alternatively, the poly(alkylene ether) may be an oxyalkylated condensation product of a phenol. The preferred poly(alkylene ethers) are those which are substantially linear, and are terminated by hydroxyl groups, or by one or two ether end groups of the formula —OR, where R is an alkyl, aryl, or aralkyl, such as methyl, ethyl, i-octyl, decyl, lauryl, tridecyl, nonylphenyl, dodecylphenyl, phenyl, naphthyl and the like. They are preferably water soluble or readily water dispersible. Residues of coupling compounds or chain-initiating agents, such as bis-phenol, may be present. The poly(alkylene ether) may, as just mentioned, be a propylene oxide polymer or an ethylene oxide-propylene oxide copolymer. Indeed, when the specified number of ethylene oxide units are present, copolymer constituents in addition to those mentioned may be included in the polymer chain. Other elements or radicals may be introduced into the R groups provided they are not reactive with the hydrophobic polymer. The necessity for the absence of groups which are reactive with the hydrophobic polymer will be readily apparent since durability, molecular weight and other physical properties of the hydrophobic polymer are adversely affected by copolymerization with poly(alkylene ether).

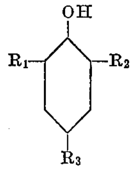
It should be noted that the poly(alkylene ether) compounds are preferably free from aliphatic unsaturation. Such unsaturation is not necessary for chemical bonding when using ionizing particle irradiation, and will usually have an adverse effect on the color and heat stability of the additive.

In order to provide the particulate striated form in the hydrophobic polymer, the poly(alkylene ether) must be substantially insoluble in the hydrophobic polymer. In addition, it must be stable under melt spinning conditions for the hydrophobic polymer.

For products which need not develop opacity, for which maximum wickability and static protection are required, polyethers are selected which are not easily extracted, such as the intermediate molecular weight polyethers capped with at least one nonyl phenyl end, or high molecular weight polyethylene ether glycols or the polypropylene ether glycols. These may be added at a minimum concentration of about 2% to provide permanent antistatic effect with a minimum loss of additive on scouring. It will usually be desirable to irradiate those compositions to enhance retention of the polyether.

The polyether compound employed should preferably be of very high purity. In addition, it should be free from color forming compounds, particularly those of an aldehyde nature. This is especially important where the polyether compound is to be subjected to the high temperatures involved in melt spinning.

It is often advantageous to add an antioxidant to the melt blended composition, thereby giving whiter filaments. Preferably the antioxidant is dissolved in the polyalkylene ether before mixing with the hydrophobic condensation polymer. Suitable antioxidants are high boiling substituted phenols, for example, those of the formula:



where R_1, R_2, R_3 may be lower alkyl or aryl. The R's may be the same or different. Suitable examples are R_1 and R_2=methyl, ethyl, isopropyl or t-butyl; R_3 may be methyl, ethyl or phenyl. Polyols such as sorbitol may also be employed. Such antioxidants are added in amounts up to 1.0% of the fiber composition; from 0.2 to 0.5% is preferred.

The preferred molecular weight of the polyether compound, and its concentration, will depend in part on the polymer to which it is to be added and in part on the relative balance between delustering and antistatic properties desired. In any event, polyether compound of sufficiently high molecular weight and in sufficient amount is required so that a two-phase system exists in the fiber.

The polyether-modified filaments of this invention may also contain suitable light stabilizers, ultraviolet absorbers, delusterants, pigments, dyes, and the like. Delusterants and pigments may be added before, along with, or after the polyether. It is often desirable to added polyamide antioxidant, such as, for example, those disclosed in U.S. Patents 2,510,777 and 2,981,715. Of these, sodium phenyl phosphinate is a preferred species.

Other polymer additives (e.g., polyvinyl pyrrolidone) may be present in the fibers of this invention, for example to enhance solubility of the polyether, to improve or to decrease ease of extraction, or to affect dyeability, soiling, crease resistance, hand, water repellance, wickability, strength, elongation, modulus, or melting point of the fiber.

The removal of a portion of the polyether compound from the synthetic fiber is achieved by a simple aqueous extraction. The product then becomes more opaque and still retains its original surface luster. The opacity results from the creation of a multiplicity of elongated microscopic voids due to the extraction of a portion of the poly(ethylene ether). It will usually be unnecessary, and may even be undesirable, to irradiate such products prior to scouring. Since the product must contain about 1% of the poly(alkylene ether) after extraction to provide permanent antistatic protection a minimum of about 2% of the polyether should be present before scouring. The balance between the level of wickability and antistatic properties and the opacity after scouring can be varied by adjusting either the concentration of the polyether, the molecular weight of the polyether, or by varying the radiation dose. To obtain a noticeable improvement in covering power, at least 3% of the poly(alkylene ether) should be added. This step may be carried out upon the fiber at any stage of processing, i.e., on spun yarn, after drawing, prior to twisting, setting or crimping, in a skein, as a cake, on a dye package or the like. Staple, tow, floc, or spun yarn may be scoured. However, it is preferred that the fiber be extracted when in fabric form, due to the beneficial effect on fabric properties.

A simple boil-off treatment is usually satisfactory to remove the desired amount of the polyether compound, but the process may be suitably combined with dirt removal by use of an alkaline scouring agent and/or a detergent, which may be natural or synthetic. Highly alkaline solutions must be avoided when treating alkali-sensitive fibers. It may sometimes be desirable to include a swelling agent, for maximum extraction of the polyether with maximum opacification of fiber, especially if antistatic properties are unimportant. Conventional scouring procedures are very satisfactory. Alternatively, polyether may be removed during dyeing or other hot, aqueous step.

Large concentrations of the polyether compound are usually more easily extracted to low levels than small ones. For those products in which maximum covering power and surface luster are required, high concentrations (i.e., 7–15%) of linear polyethylene ether glycol are used. After scour, the residual polyether content in polyamide fiber is about 2–3%, providing satisfactory static protection.

In general, more than 30% of the poly(alkylene ether) in filaments offers no advantage, and often is undesirable, making spinning difficult or impossible. However, larger concentrations may be mixed with the base polymer for subsequent mixing with the spinning composition.

By combining suitable proportions of the more easily extractable polyether glycol, the less easily extractable nonyl phenoxy capped polyethylene ether, TiO_2 delusterant, and radiation dose, fibers can be prepared having almost any desired degree of wickability, antistatic property, covering power and surface luster.

The extraction step may be carried out while the filaments (in any form) are restrained from shrinking; alternatively, shrinkage of any desired extent may be permitted. Maximum increase in fabric bulk and liveliness will be attained by extracting the fabric while free to retract.

For washfast static protection of polyesters, polyethylene ether glycol molecular weight should exceed 9,000. Compatible groups on the terminal ether oxygen will usually permit use of lower molecular weight compounds.

As previously indicated, the particular poly(alkylene ether) utilized will depend on the properties of the hydrophobic polymer as well as the properties desired in the final product. As a general rule for most hydrophobic polymers, the higher molecular weight poly(alkylene ethers), e.g., those having molecular weights from about 20,000 to about 200,000 are preferred.

For use with polyamides, polyethylene ethers having —OH ends (i.e., glycols) are preferably of 12,000 to 50,000 molecular weight, and are added in concentrations of from about 3 to about 30%. For polyester filaments, polyethylene ether glycols should have a molecular weight of from about 10,000 to about 500,000. From 3 to about 15% is satisfactory.

When these poly(ethylene oxides) are capped on one or more ends with ether radicals which are compatible with the polymer, lower molecular weight polyethers may be used. For polyamides, the polyether part of the chain should constitute at least 50% by weight of the capped poly(ethylene oxide). A very suitable end group is nonyl phenoxy. From 2 to about 30% should be added.

For polyesters, singly, and especially doubly capped polyethylene oxides are preferred; these should have at least about 30 ethylene oxide units in the chains, corresponding to a molecular weight (for the polyether portion) of at least about 1300. Higher molecular weight compounds are even more effective, in the molecular weight range of about 19,000 to 20,000. Especially suitable ends for these polyethers are nonyl phenoxy or methoxy radicals.

When irradiation is employed, it may be accomplished over a wide range of temperatures. However, a low temperature decreases the tendency towards oxidation. Since the absorption of the radiation frequently causes a temperature increase in the range of about 2° C. for each mrep. absorbed, if high tube current is employed so that absorption is complete within a short time interval, it is usually advisable to provide means to remove the heat generated to avoid injury to the sample. The use of Dry Ice to maintain a low temperature is very satisfactory for this purpose. In general, irradiation at a higher temperature promotes the speed with which bonding occurs, thus promoting a higher throughput of a given piece of equipment at a constant radiation dosage. Temperatures as low as −80° C. and as high as 150° C. may be employed. Maintenance of the temperature of the sample within the range from about 0 to about 75° C. is preferred.

Although charged particle radiation having energy equivalent to about 50 electron volts (ev.) can break the bonds required for chemical attachment, penetration is too low for more than surface modification, even when operating in a vacuum. It is therefore preferred to use ionizing particle radiation having an energy of at least about 100,000 ev. A suitable dose for such radiation is from 1 to 80 mrep; it is preferable to use a dose of from about 1 to about 20 mrep. When shaping (after irradiation) is required, the maximum dose should be not over about 40 mrep.

The filaments produced in accord with this invention may be used, prior to or after the extraction step, to produce any type of fabric, whether knitted, felted or woven. They are suitable as bristles up to 125 mils in diameter for brushes, brooms and the like. The filaments may be used alone, or may be plied or blended with other natural, synthetic or man-made fiber. The filaments of the invention are readily dyed, bleached, pigmented, printed or the like. They may be textured, bulked, heat-set, twisted, crimped, or any combination of these processes. Due to decreased dye sensitivity to steam bulking conditions, they are especially suitable for this use. In addition to steam bulking, hot air bulking as described in Belgian Patent 573,230 may be used. They may be knitted to tricot, jersey, tissue, satinette or circular knit or full-fashioned hose. They may be woven, alone or in combination with other fiber, to taffeta, twill, satin, sand crepe and the like. The fibers are especially useful in the pipe of pile fabrics, such as velvet, plush, rugs, carpets and artificial fur. Rugs and carpets of these fibers are especially useful due to their antistatic properties, attractive luster, fiber opacity combined with an unexpected degree of soil repellance. Their antistatic behavior is often so effective that a minor proportion serves to reduce to an acceptable level, the static propensity of a fabric in which they are combined with unmodified hydrophobic filaments.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. A filament of melt-spun fiber-forming synthetic linear polymer from the class consisting of (1) a condensation polyester of bifunctional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain include at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain, (2) a condensation polymer wherein recurring amide linkages form an integral part of the main polymer chain from the class consisting of (a) a polyamide, (b) a polyurea, (c) a polyurethane, (d) a polysulfonamide, (3) polypropylene and (4) polyethylene having dispersed therethrough, in the form of elongated shapes giving the appearance of multiple striations parallel to the longitudinal axis of the said filament at least about 2% by weight based on the final filament of a poly(alkylene ether) containing only the elements carbon, hydrogen and oxygen, the said poly(alkylene ether) having a molecular weight between about 600 and 3,000,000 and being substantially inert to the said synthetic polymer during the melt-spinning of the said filament.

2. The filament of claim 1 wherein said poly(alkylene ether) is a polyethylene ether glycol.

3. The filament of claim 2, wherein said fiber-forming polymer is polyhexamethylene adipamide.

4. The filament of claim 3 wherein said poly(alkylene ether) has a molecular weight from about 1,000 to about 500,000 and is present in said polymer in an amount from about 3% to about 30% by weight.

5. The filament of claim 2 wherein said fiber-forming polymer is polyethylene terephthalate.

6. The filament of claim 5 wherein said poly(alkylene ether) has a molecular weight from 10,000 to about 500,000 and is present in said fiber-forming polymer in an amount from about 3% to about 15%.

7. The filament of claim 1 wherein said fiber-forming polymer is polypropylene.

8. A low-density static-resistant melt-spun textile filament prepared from a synthetic fiber-forming linear polymer from the class consisting of (1) a condensation polyester of bifunctional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain include at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain, (2) a condensation polymer wherein recurring amide linkages form an integral part of the main polymer chain from the class consisting of (a) a polyamide, (b) a polyurea, (c) a polyurethane, (d) a polysulfonamide, (3) polypropylene and (4) polyethylene having dispersed therein at least about 1% by weight of a poly(alkylene ether) containing only the elements carbon, hydrogen and oxygen, the said poly(alkylene ether) having a molecular weight of at least about 600 and having from two to three carbon atoms in the alkyl chain, with two of said carbon atoms being intralinear carbon atoms connecting intralinear ether-oxygen atoms, said filament having a multiplicity of elongated microscopic voids distributed throughout its length.

9. The filament of claim 8 wherein said poly(alkylene ether) is a polyethylene ether glycol.

10. The filament of claim 9 wherein said polyethylene ether glycol has a molecular weight in the range from about 1,000 to about 3,000,000.

11. The filament of claim 10 wherein said polyethylene ether glycol is present in an amount from about 1% to about 10% by weight of said fiber-forming polymer.

12. The filament of claim 8 wherein said polymer is polyhexamethylene adipamide.

13. The filament of claim 8 wherein said fiber-forming polymer is polyethylene terephthalate and said polyethylene ether glycol has a molecular weight in the range from about 9,000 to about 500,000.

14. The filament of claim 8 wherein the said fiber-forming polymer is polypropylene.

15. The structure of claim 1 wherein the said poly(alkylene ether) is chemically bonded as a graft copolymeric component of the said melt-spun polymer.

16. A process for preparing a filament of melt-spun fiber-forming synthetic linear polymer from the class consisting of (1) a condensation polyester of bifunctional ester-forming compounds wherein at least about 75% of the repeating structural units of the polymer chain include at least one divalent carbocyclic ring containing at least six carbon atoms present as an integral part of the polymer chain and having a minimum of four carbon atoms between the points of attachment of the ring in the polymer chain, (2) a condensation polymer wherein recurring amide linkages form an integral part of the main polymer chain from the class consisting of (a) a polyamide, (b) a polyurea, (c) a polyurethane, (d) a polysulfonamide, (3) polypropylene and (4) polyethylene having dispersed therethrough in the form of elongated shapes giving the appearance of multiple striations parallel to the longitudinal axis of the said filament at least about 2% by weight based on the final filament of a poly(alkylene ether) containing only the elements carbon, hydrogen and oxygen, the said poly(alkylene ether) having a molecular weight between about 600 and 3,000,000 and being substantially inert to the said synthetic polymer during the melt-spinning of the said filament which comprises mixing the melt of the said synthetic fiber-forming linear polymer and the said poly(alkylene ether), thereafter melt-spinning the resulting composition into a filament and drawing the said filament.

17. The process of claim **16** wherein the drawn filament is subjected to aqueous scour to partially remove the said poly(alkylene ether).

18. The process of claim **17** wherein the scour is applied to a fabric of the said filament.

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