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METHOD OF INCORPORATING A PHOSPHINATE AND PARTICULATE MATERIAL IN A POLYAMIDE TO MAKE LOW FRICTION FILAMENT

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This invention relates to improved synthetic linear polyamide filaments. More particularly, it relates to filaments having improved surface characteristics and to a process for the preparation of such filaments.

Synthetic linear polyamide textile fibers are well known in the art and because of their outstanding properties have found application in many end uses. These fibers are produced by melt-spinning the polymer into filaments and orienting the filaments by drawing to several times the original length. Filaments of this type have a relatively smooth surface as compared to natural fibers which have rough surfaces. This smooth surface has made processing of these filaments into fabric more difficult because of the higher dynamic friction resulting when the filaments are passed over guide surfaces at high speeds.

The relatively high dynamic friction exhibited by synthetic polyamide filaments has proved to be troublesome, particularly in the knitting of hosiery. This difficulty arises from the fact that in knitting hosiery from a given package of yarn the tension varies appreciably due to the fact that the yarn in the middle of the package has a microcrimp as a result of having been compressed by the overlying filaments; such microcrimp reduces the area of contact with guide surfaces and therefore reduces the effective yarn coefficient of friction relative to that in the inner and outer layers of the package. The end result is a variation in length of successive hose knitted from the same yarn package. The higher the coefficient of friction in non-microcrimped lengths, the greater the variation in hose length. Both the variation in tension between different lengths of a monofil and the consequent variation in hose length can be minimized if the filaments exhibit a substantially reduced coefficient of friction in the non-microcrimped lengths.

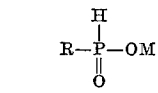
Prior processes for roughening filament surfaces have usually involved physical damage to the surface with the resultant loss in tensile and other desirable properties or have required the use of relatively large quantities of particulate materials. The latter alternative also leads to undesirably high losses in tensile properties and in some cases produces undesirable luster effects.

It is the most important object of the present invention to provide a synthetic linear polyamide filament which develops less tension when passed over guiding surfaces. A further important object is to provide polyamide filaments which exhibit less variation in tension between microcrimped and non-microcrimped lengths. Another object is to provide an improved process for the production of such filaments.

These and other objects are accomplished in a filament which contains dispersed throughout its structure from 0.003–0.045% by weight of a phospinate compound and from 0.025–0.65% by weight of a finely divided inert particulate material having an average particle size of 0.3–3.0 microns, the filament having a rough surface which is characterized by a coefficient of dynamic friction below 0.70 in non-microcrimped lengths. Such filaments are produced by adding a phosphinate to polyamide-forming reactants, heating the reactants under condensation temperature-pressure conditions, extruding, cutting and the extrusion to flake, coating the flake with a sufficient amount of finely divided particulate material

to provide 0.025–0.65% by weight, melting the coated flake, extruding the molten polymer to form filaments, and quenching and drawing the filaments.

The phosphinate compound employed has the formula



wherein R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl radicals and M is selected from the group consisting of sodium, potassium and lithium ions.

The finely divided inert material is preferably titanium dioxide (Example I) but other materials such as calcium terephthalate (Example II) or diatomaceous earth may be employed.

Where referred to herein, the coefficient of dynamic friction is measured by draping a single filament over a cylindrical polished mandrel (180° contact), with one end of the filament attached to a strain guage and the other end attached to a free-hanging weight of 0.3 gram. The mandrel surface is flooded with No. 50 mineral oil and the mandrel rotated at a surface speed of 120 centimeters/second, in a direction which exerts tension on the strain gauge. The coefficient of friction f is calculated from the equation $T_2/T_1=e^{fa}$, where T_2 is the gauge reading when the mandrel is rotating, T_1 is the gravitational effect of the 0.3 gram weight and a is the angle of wrap in radians.

EXAMPLE I

An aqueous solution of hexamethylenediammonium adipate (66 salt solution) is polymerized to form polyhexamethylene adipamide in a conventional melt-polymerization, following the general procedure of U.S. Patent No. 2,163,636. The polymer is extruded from the autoclave in the form of a ribbon onto a water-cooled casting wheel and cut into flake, following the procedure of U.S. Patent No. 2,289,860. Polymer batches A–N are prepared in this manner to yield flake having a relative viscosity of 36.5. Titanium dioxide having an average particle size of 0.5 micron and/or sodium phenylphosphinate are added to the different batches in the concentrations given in Table 1 below. The sodium phenylphosphinate is added, as a 25% aqueous solution, to the salt solution prior to polymerization. Addition of titanium dioxide to batches B–D and K–N is accomplished by injection of a 20% aqueous slurry into the autoclave when the temperature reaches 180–200° C. and the pressure about 250 p.s.i. Titanium dioxide is added to batches E–N by tumbling the flake with a dry powder until it has been coated with the tabulated amounts.

The various batches of flake are melted on a grid and extruded in the conventional manner to form monofils, which are quenched by passing air transversely across the filaments in the conventional manner and wound up at a speed of 461 y.p.m. The filaments are subsequently drawn on a drawtwister at a ratio of 4.4 to give 15-denier monofils.

Measurements are made, as previously described, to determine the coefficients of dynamic friction of the different filaments. The results are shown in Table 1 below. Also shown, for some of the filaments, are the tensions developed when a filament is run through a tension device and then over a glazed porcelain guiding surface. In the case of filament H, the tension was adjusted to 1.5 grams. Others were tested under the same conditions and thus show the relative difference in tension with the various additives.

Filaments A–E show that the addition of a small amount of TiO_2 to the autoclave reduces the coefficient of dynamic friction slightly. A comparison of filaments

B and D shows, however, that there is no additive effect as a consequence of the phosphinate addition. A comparison of filaments B and E shows that the addition of TiO_2 by flake-coating without the addition of the phosphinate compound gives no improvement over addition to the autoclave. Filaments F–J, prepared in accordance with the present invention, illustrate the synergistic effect obtained when the titanium dioxide is added by coating flake which contains the phosphinate compound. Filaments K–N show the results of using various concentrations of titanium dioxide in both the autoclave and by flake-coating in combination with various concentrations of the phosphinate compound.

TABLE 1

Filament	TiO_2 Added, Percent		Sodium Phenyl-phos-phinate, Percent	Coefficient of Friction	Tension, grams
	Autoclave	Flake			
A	None	None	0.012	0.89	
B	0.3	None	None	0.79	8.1
C	0.2	None	0.012	0.81	8.1
D	0.3	None	0.012	0.79	8.1
E	None	0.3	None	0.79	8.1
F	None	0.05	0.006	0.74	
G	None	0.05	0.024	0.65	
H	None	0.25	0.012	0.59	1.5
I	None	0.45	0.006	0.65	
J	None	0.45	0.024	0.54	
K	0.3	0.1	0.012	0.57	
L	0.2	0.05	0.012	0.69	
M	0.2	0.25	0.012	0.59	1.5
N	0.4	0.45	0.024	0.56	

Filaments B and H are knitted into ladies' hosiery in the conventional manner. When the hose are inspected, it is found that filament H performs much better than filament B with respect to length variations and tension rings (a few rows of short stitches which occur as the result of variations in the knitting tension). The results are recorded in Table 2.

TABLE 2

	H	B
Number of hose inspected, dozen pairs	99	82
First grade hose outside ±0.5 in. length variation limits, percent	2.2	11.4
Hose with tension rings, percent	0.09	6.2

EXAMPLE II

Calcium terephthalate is prepared by heating a quantity of dimethylterephthalate overnight on a steam bath with 10% excess sodium hydroxide added as a 10% solution in methyl alcohol. The excess alkali is neutralized to phenolphthalein with hydrochloric acid and the calcium terephthalate precipitated in a finely divided condition by addition of a concentrated aqueous solution of calcium chloride.

Polyamide flake containing 0.012% of sodium phenylphosphinate but no titanium dioxide is prepared as described in Example I. The flake is coated by tumbling with the finely divided calcium terephthalate to provide a concentration of 0.1% calcium terephthalate based on the weight of the polymer. It is then melted, extruded and processed into drawn filaments as described in Example I. A monofil is run over a porcelain guide under a tension of 1.5 grams. With the same settings, a control filament gives a tension of 4.5 grams.

The foregoing examples illustrate the advantages of the claimed improvements in reducing filament-to-guide friction with a consequent improvement in processing as evidenced by a substantial reduction in the percent of second-grade hose.

The roughening effect obtained in the present invention is not due in any appreciable degree to finely divided particles of TiO_2 or other particulate material having been embedded in the surface of the filament, but appears to be related in some manner to the formation of crystalline polymer particles at the fiber surface. This effect is not obtained if the particulate material is added to the polymer during the polymerization cycle but only when the material is added to or coated on the flake prior to melt-extrusion. Likewise, the effect is not obtained in the absence of the phosphinate compound.

The term "flake" as used herein refers to relatively small bits of polymer which are commonly called flakes, pellets, chips, etc., and which result from cutting, breaking, or otherwise subdividing extruded polymer.

If desired, a suitable material may be added in the coating step to hold the finely divided particulate material on the surface of the flake and prevent its dusting off. A suitable procedure is to add a sufficient amount of a material such as Santicizer 8 (a mixture of ortho- and para-N-ethyltoluene sulfonamides) to provide about 0.1% concentration based on the weight of the polymer. As exemplified, the particulate material may be coated on the flake in the form of a dry powder or, with TiO_2, a slurry containing about 5 to 20% by weight of the TiO_2 may be prepared and used for coating the flake.

The amount of finely divided particulate material should be in the range of about 0.025 to 0.65% and is preferably in the range of from 0.05 to 0.3% by weight of the polyamide. Lower concentrations do not give effective results, while higher concentrations detract from the properties of the filament. Higher concentrations of titanium dioxide, for instance, produce a chalky effect in hose knitted from the fiber.

The preferred inert particulate material is titanium dioxide because of the ready availability of suitable pigments of this material and because it imparts to the filament a desirable delustering effect. Other inert materials such as insoluble metal salts of terephthalic acid, aluminum oxide, aluminum silicate and diatomaceous earth may be employed, however.

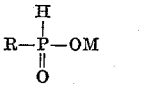
Suitable phosphinate compounds are those conforming to the formula given above. Specific compounds in addition to sodium phenylphosphinate are the sodium or potassium salts of iso-octyl-, iso-butyl-, n-pentyl-, cyclohexyl-, p-tolyl-, p-ethylphenyl-, 2,5-dimethylphenyl-, p-isopropylphenyl- and ethyl-phosphinic acids. The concentration of the phosphinate compound, based on the weight of the polymer, should fall in the range 0.003 to 0.045%. Lower concentrations do not give effective results, while higher concentrations not only do not contribute to increased roughening but also contribute to poor spinnability of the polymer and are therefore undesirable. The preferred range is 0.006 to 0.03% by weight of the polyamide from which filaments are spun.

Preferably, the filament denier should be relatively high, i.e., at least about 5 and preferably 10–30. Lower deniers tend to reduce the surface roughening effect and are less desirable.

In addition to polyhexamethylene adipamide, other polyamides such as polycaproamide or polyhexamethylene sebacamide may be employed. Other suitable polyamides are those disclosed in U.S. Patents Nos. 2,071,250 and 2,071,253. The preparation and spinning of such polyamides is disclosed in U.S. Patents Nos. 2,130,948, 2,163,-636 and 2,477,156.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. In the production of a low friction yarn from a polyamide, the steps of: adding from 0.003–0.045% by weight, based on the weight of said polyamide, of a phosphinate having the formula



wherein R is selected from the group consisting of phenyl, iso-octyl, iso-butyl, n-pentyl, cyclohexyl, p-tolyl, p-ethylphenyl, 2,5-dimethylphenyl, p-isopropylphenyl, and ethyl

radicals, and M is selected from the group consisting of sodium, potassium, and lithium ions, to polyamide-forming reactants; heating said reactants under condensation temperature-pressure conditions to produce said polyamide; extruding said polyamide; dividing the extrusion into flake; coating said flake with from 0.025–0.65% by weight of an inert, particulate material selected from the group consisting of titanium dioxide and calcium terephthalate; and melt-spinning filaments from said coated flake.

2. In the process of claim 1, the steps of: coating flake comprised of polyhexamethylene adipamide and containing about 0.012% by weight of sodium phenylphosphinate with about 0.25% by weight of titanium dioxide; and melt-spinning filaments from said coated flake.

3. In the process of claim 1, the steps of: coating flake comprised of polyhexamethylene adipamide and containing about 0.012% by weight of sodium phenylphosphinate with about 0.1% by weight of calcium terephthalate; and melt-spinning filaments from said coated flake.

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