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ANTISTATIC POLYAMIDE FIBER CONTAINING SULFONIC ACID POLYETHER REACTION PRODUCT

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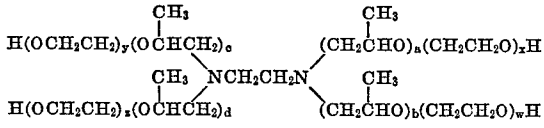
U.S. Cl. 260—857 PG 10 Claims

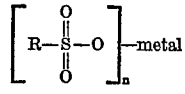
ABSTRACT OF THE DISCLOSURE

It has been suggested that the utility of synthetic fibers of polyamide could be increased by dispersing in the polyamide a minor proportion of an antistatic polyether compound derived from the reaction of an amine having at least one primary group with at least one alkylene oxide having 2 to 4 carbon atoms, e.g., a compound represented by the formula :

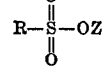


where *a*, *b*, *c*, *d* *w*, *x*, *y* and *z* are each a whole number and the total of *a*, *b*, *c*, and *d* is between 8 and 850 and the total of *w*, *x*, *y*, and *z* is between 8 and 1,000.

However, with incorporation of this antistatic additive in the polyamide, serious problems have been encountered in melt-spinning due to the frequent occurrence of "drips" of the molten polymer as it emerges from the spinneret. It has now been found that the occurrence of said drips can be eliminated or greatly reduced by reacting the antistatic polyether additive with a compound of the formula:



or a compound of the formula:



wherein R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl, *n* is a whole number corresponding to the valence of the metal, and Z is selected from the group consisting of hydrogen, ammonium cation and substituted ammonium cation.

Moreover, it has been found that the antistatic properties and dyeability of the resulting polyamide fiber are improved.

BACKGROUND OF THE INVENTION

This invention relates to a process for the melt-spinning of a filamentary structure from a synthetic polyamide polymer. More particularly, it is concerned with an improved process for the formation of an improved antistatic filament, yarn or the like by melt-spinning a synthetic linear fiber-forming polyamide.

It has been suggested that the utility of synthetic fibers could be increased and their properties, in particular their antistatic properties, could be improved if a polyalkylene ether of high molecular weight is included in the polymer. More specifically, it is disclosed in U.S. Pat. 3,475,898 to Magat and Sharkey to use poly(ethylene-propylene)ether glycols for this purpose. More recently, U.S. Pat. 3,657,386 discloses that certain propylene oxide-ethylene oxide copolymers based on ethylene diamine are especially useful in preparation of an antistatic fiber of polyamide.

Polyamide fibers containing antistatic polyalkylene ethers of high molecular weight have been prepared but serious problems were encountered in melt-spinning due to the frequent occurrence of "drips" of the molten polymer as it emerges from the spinneret. The term "drips" is conventionally applied and is used herein to mean drops of molten polymer which obviate the normal jetting action of the polymer and the production of any filaments whatsoever. It is then necessary to wipe the extrusion face of the spinneret at frequent intervals during spinning in order that the normal spinning action may be resumed. Often, the denier of the filaments being prepared will vary as the drips form. The frequent interruptions are inhibitive to commercial operations.

SUMMARY OF THE INVENTION

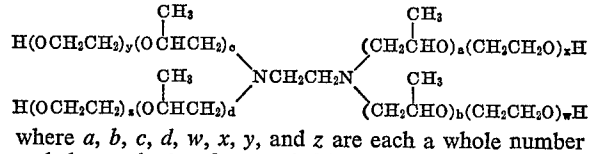
It is an object of the present invention, therefore, to provide a synthetic polyamide fiber with improved dyeability and antistatic properties and an improved melt-spinning process for its preparation.

Another object is to provide an improved melt-spinning process for preparing an antistatic polyamide fiber whereby drips are eliminated or substantially reduced.

Yet another object is to provide an improved antistatic additive for use in a melt-spinning process for preparing a synthetic polyamide fiber.

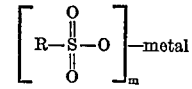
Other objects will become aparent from the disclosure and the appended claims.

These objects are accomplished by the present invention which provides an improvement in the process for the formation of an antistatic polyamide fiber from a synthetic linear fiber-forming polyamide polymer containing a minor proportion of an antistatic polyether compound derived from the reaction of an amine having at least one primary group with at least one alkylene oxide having 2 to 4 carbon atoms, preferably a polyether compound represented by the formula:

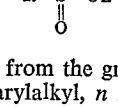


where *a*, *b*, *c*, *d*, *w*, *x*, *y*, and *z* are each a whole number and the total of *a*, *b*, *c*, and *d* is between 8 and 850 and the total of *w*, *x*, *y*, and *z* is between 8 and 1,000; by extruding the molten polymer through an orifice into a quenching medium, the improvement comprising:

(a) Reacting said polyether compound with at least 0.01 mol, preferably 0.1 to 3 mols, per mol of polyether compound of a sulfur compound soluble in the polyether compound and selected from the group consisting of a compound of the formula:



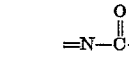
and a compound of the formula:



wherein R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl, *n* is a whole number corresponding to the valence of the metal, and Z is selected from the group consisting of hydrogen, ammonium cation and substituted ammonium cation; and

(b) Dispersing in the polyamide polymer prior to extrusion about 1 percent to 12 percent, based on the weight of the polyamide polymer, of the reaction product of said polyether compound and said sulfur compound.

By "a synthetic linear fiber-forming polyamide polymer" is meant a wholly synthetic polymer which contains a preponderance of recurring units containing a hydrogen atom on the carbon alpha to the nitrogen atom of the amide unit of the chain. Such polymers may be broadly defined as polyamides since they contain the carbonamide unit



as the linking units in the polymer chain.

The expression "by extruding the molten polymer through an orifice into a quenching medium" is employed to mean the conventional melt-spinning process whereby the melted polymer is forced through a hole into a medium such as a liquid or gas, generally an inert gas, to cool and solidify the polymer into a long substantially continuous structure.

The reaction of the polyether compound with the sulfur compound may be carried out by simply mixing the reactants at a temperature of about 25° C. or higher, preferably at a temperature of about 75° to 110° C.

As indicated hereinabove, the present invention is an improvement over the disclosure of U.S. Pat. 3,657,386 and other prior art patents that are directed to antistatic polyamide fibers containing polyether compounds such as propylene oxide-ethylene oxide copolymers based on ethylene diamine. The sulfur compounds useful in the present invention are known compounds and some are commercially available at low cost. For example, p-toluenesulfonic acid, p-toluenesulfonic acid sodium salt and methane sulfonic acid are readily available and give excellent results as shown in the specific examples hereinafter.

It has been discovered that the viscosity of the polyether compounds of the invention are substantially increased by the instant reaction with the sulfur compounds. Moreover, this high viscosity is a primary requirement for improved dispersion of the polyethers into molten polyamide for antistatic fibers. Therefore, it is postulated that the increased viscosity of the antistatic additive of the present invention is a major factor in the improvement in melt-spinning of the polyamide polymer, i.e., the substantial elimination of "drips" of the molten polymer as it emerges from the spinneret. Accordingly, we prefer that the improved antistatic additive of the invention have a melt viscosity of at least 3000 cps. at 100° C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will now be further described in the following specific examples which are to be regarded solely as illustrative and not as restricting the scope of the invention.

The propylene oxide-ethylene oxide copolymers based on ethylene diamine used in the preferred process of the present invention are described in U.S. Pats. 2,979,528 and 3,657,380. These compounds are commercially available as "Tetronic" series block copolymers having molecular weights between 1,650 and over 26,000. This series varies in length of poly(oxyethylene) chain and poly(oxypropylene) chain. A 3 and 4 digit code number indicates the molecular composition. When four digits are employed, the first two explain the average molecular weight of the hydrophobe (poly(oxypropylene) branches on the alkylene-diamine). When three digits are used only the first number serves this purpose. The last digit of each code number represents the weight percentage of hydrophilic (poly(oxethylene)) units to the nearest 10%. The "Tetronic" compounds in the examples are described this way.

EXAMPLE 1

About 200 grams of "Tetronic 1504" was placed in a 500 milliliter glass beaker and heated to 80° C. "Tetronic 1504" is a propylene oxide-ethylene oxide block copolymer based on ethylene diamine, having a molecular weight

of about 12,500 and containing 40% ethylene oxide moiety. About 6.08 grams of p-toluene-sulfonic acid monohydrate was added to the "Tetronic 1504" with agitation over a period of 15 minutes. The reaction mixture was maintained at about 80° C. and stirred for an additional 30 minutes. The melt viscosity of the resulting reaction product was 9,600 centipoises measured at 100° C. with a Brookfield viscometer. The original "Tetronic 1504" had a viscosity of only 200 centipoises at 100° C.

EXAMPLE 2

The procedure of Example 1 was followed except that 6.21 grams of p-toluenesulfonic acid sodium salt was substituted for the p-toluene sulfonic acid. The molar ratio of said sodium salt to the polyether was about 2. The melt viscosity of the resulting reaction product was 30,000 centipoises measured at 100° C. with a Brookfield viscometer. Thermogravimetric analysis of this product showed only 6 percent loss of weight in 30 minutes at 285° C.

EXAMPLE 3

The product of Example 2 was used to prepare an antistatic polyamide fiber containing polyether compound in accordance with the following procedure:

A glass reactor equipped with a heater and stirrer was charged with a mixture of 1,520 grams of ε-caprolactam and 80 grams of aminocaproic acid. The mixture was then flushed with nitrogen and was stirred and heated to 255° C. over a one hour period at atmospheric pressure to produce a polymerization reaction. The heating and stirring was continued at atmospheric pressure under a nitrogen sweep for an additional four hours in order to complete the polymerization. During the last thirty minutes of the polymerization, 60 grams of the antistatic agent prepared in accordance with the procedure of Example 2 was added to the polycaproamide and stirring was continued to thoroughly mix the antistatic agent throughout the polymer. Nitrogen was then admitted to the glass reactor and a small pressure was maintained while the polymer was extruded from the glass reactor in the form of a polymer ribbon. The polymer ribbon was subsequently cooled, pelletized using a Wiley mill, washed and then dried. The polymer was a white solid having a relative viscosity of about 55 to 60, as determined at a concentration of 11 grams of polymer in 100 ml. of 90 percent formic acid at 25° C. (ASTM D-789-62T). Particles of antistatic additive were dispersed throughout the polymer chips with a particle diameter of about 3–5 microns.

The polycaproamide pellets containing the antistatic agent were melted at about 285° C. and then melt extruded under a pressure of 1,500 p.s.i.g. through a 16-orifice spinneret, each of the orifices having a diameter of 0.014 inch, to produce a 250 denier fiber. No problems were encountered in melt-spinning the antistatic polyamide fiber and there was no evidence of the formation of "drips" of the molten fiber as it emerged from the spinneret. The fiber was collected at about 1,000 feet per minute and was drawn about 3.5 times its extruded length to produce a 70 denier yarn, hereinafter designated yarn A. A control yarn containing no antistatic agent was produced in the same manner as described above and designated yarn B.

EXAMPLE 4

The 70 denier polycaproamide yarn containing an antistatic agent and the control yarn which was produced in Example 3 were woven into conventional plain weave fabrics. The yarns contained ½ Z twist.

The fabrics were cut into fabric test samples having a width of 3 inches and a length of 9 inches. The fabric samples were tested for their antistatic property in accordance with the general procedure described in the Technical Manual of the American Association of Textile Chemists and Colorists, 1969 ed., vol. 45 at pp. 206

and 207. This test procedure is entitled "Electrostatic Clinging of Fabrics: Fabric-to-Metal Test" and is numbered A.A.T.C.C. 115–1969.

The time for each fabric sample to decling completely of its own accord was recorded. Fresh test and rubbing fabrics were used for each determination and the fabric samples were tested in triplicate in both warp and filling directions with nylon and polyester rubbing fabrics.

The fabric samples were subjected to repeated washings to evaluate the permanency of the antistatic property imparted by the antistatic agent. The fabrics were washed in a commercial washing machine having conventional washing and rinsing cycles at a temperature of about 70° C. using a conventional laundry detergent. The fabrics were then dried in a commercial dryer at a temperature of about 80° C. for a period of time of about 30 minutes. Prior to testing, the fabric samples were pressed free of creases with a clean, dry iron at the appropriate settings and were then conditioned from the dry side at 20 percent relative humidity and a temperature of 24° C. for at least 24 hours (Technical Manual of the A.A.T.C.C., p. 206, paragraph 4.3, note 9.5).

The average times for each respective set of fabric samples to decling completely of their own accord after 0 and 25 wash cycles are contained in Table I below. The antistatic measurements were made at 20 percent relative humidity and a temperature of 24° C. as in the A.A.T.C.C. procedure.

TABLE I

[Electrostatic clinging of fabrics; fabric-to-metal test results]

Antistatic agent in fabric	Average times for fabric samples to decling from metal completely on their own accord, seconds	
	Unwashed	25 wash cycles
Yarn A	0	60
Yarn B	0	>300

The textile industry at present accepts a cling time of 300 seconds or less as passing, indicating significant antistatic properties, thus the control was not acceptable while the additive of this example was effective in rendering the yarn antistatic.

EXAMPLE 5

The procedure of Example 2 was used except that only 3.1 grams of p-toluenesulfonic acid sodium salt was reacted with the 200 grams of "Tetronic 1504." The resulting antistatic agent had a melt viscosity of 16,000 centipoises at 100° C.

EXAMPLE 6

The procedure of Example 3 (yarn A) was followed except that 90 grams of the antistatic additive of Example 5 was used. The average particle size of the antistatic additive in the polyamide was about 4 to 6 microns. The polyamide fiber produced was evaluated as described in Example 4, and the cling test on fabric showed an average cling time after 25 washes of 78 seconds.

EXAMPLE 7

The procedure of Example 3 (yarn A) was followed except that 90 grams of the antistatic additive of Example 2 was used. The polymer was spun and drawn without any occurrence of "drips" of the molten polymer as it emerged from the spinneret. Fabric was woven and tested as in Example 4, and the cling test showed an average cling time after 25 washes of 47 seconds.

EXAMPLE 8

The procedure of Example 3 (yarn A) was followed except that 90 grams of the antistatic additive of Example 1 was used. The polymer was spun and drawn without any occurrence of "drips" of the molten polymer as it emerged from the spinneret. Fabric was woven and tested as in Example 4. The cling test showed an average cling time of 43 seconds after 25 washes.

EXAMPLE 9

The procedure of Example 3 was followed except that the following changes were made: The polycaproamide pellets containing the antistatic agent were melted at about 285° C. and then melt extruded under pressure of 15 p.s.i.g. to a 70-orifice spinneret, each of the orifices having a diameter of 0.018 inch to produce a 4,500 denier fiber. The fiber was collected at 1,000 feet per minute and was drawn about 4 times the extruded length to produce 1,125 denier yarn. A control yarn containing no antistatic agent was prepared in the same manner as described above.

The yarns were textured using a steam jet and then two-plied. The yarns were tufted into a level loop carpet at 6.5 stitch rate, $^{9-10}/_{32}$ inch pile height, mock dyed and latexed. Static buildup of the carpet was tested by measuring the electrostatic voltage build-up on a person walking with a series of short shuffling steps on a piece of carpet. This test is an adaptation of the C.R.I. Stroll Test, for use as a screening method for smaller carpet samples. The carpet was conditioned at 70° F. at 20% relative humidity. The voltage generated was 2.9 kv. while a control carpet generated 10 kv.

EXAMPLE 10

The procedure of Example 1 was followed except that 3.08 grams of methanesulfonic acid was reacted with the "Tetronic 1504." The resulting antistatic agent had a melt viscosity of 6,400 centipoises at 100° C.

EXAMPLE 11

The procedure of Example 3 (yarn A) was followed except that 90 grams of the antistatic additive of Example 10 was used. The polymer was spun and drawn without any occurrence of "drips" of the molten polymer as it emerged from the spinneret. Fabric was woven and tested as in Example 4, the cling test showed an average cling time after 25 washes of 63 seconds.

EXAMPLE 12

The procedure of Example 1 was followed except that the 200 grams of "Tetronic 1504" was replaced with 200 grams of ethylene oxide-propylene oxide block copolymer of triethylene tetramine having a molecular weight of 34,500 and containing 70% ethylene oxide moiety. Also, only 4.37 grams of p-toluenesulfonic acid was used. The melt viscosity of the resutling reaction product was 2,800 centipoises measured at 100° C. The melt viscosity of the original copolymer was 1,720 centipoises at 100° C.

EXAMPLE 13

The procedure of Example 3 (yarn A) was followed except that 90 grams of the antistatic additive of Example 12 was used. The polymer was spun and drawn without any occurrence of "drips" of the molten polymer as it emerged from the spinneret. Fabric was woven and tested as in Example 4, and the cling test showed an average cling time after 25 washes of 79 seconds.

EXAMPLE 14

The procedure of Example 3 (yarn A) was followed except that the polyamide was polymerized from poly (hexamethylene) adipamide salt. A fiber was produced and a fabric knit and tested as in Example 4. The average cling time after 25 washes was 60 seconds.

DISCUSSION

In additional tests it was determined that the molecular weight of the propylene oxide-ethylene oxide copolymers based on ethylene diamine used to form the antistatic additive of this invention is preferably in excess of 1,500, more preferably, between about 4,000 and about 50,000, the ethylene oxide moieties making up about 20% to

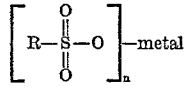
about 80% of the molecular weight of said compound. Preferably, the antistatic fiber contains from about 2% to about 8% of the novel antistatic additive.

By "antistatic" fiber is meant fibers that will pass the cling test and the shuffle test as described in U.S. Pat. 3,657,386. By "fiber" is meant multifilament yarn, monofilament, and all the known physical forms of synthetic fibers. By "ethylene oxide moiety" is meant the portion of the chemical molecule —(CH_2CH_2O)—.

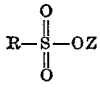
Desirably, the antistatic polyether additive is substantially uniformly dispersed in the polyamide.

We claim:

1. In a process for the formation of an antistatic polyamide fiber from a synthetic linear fiber-forming polyamide polymer containing a minor proportion of an antistatic polyether compound derived from reaction of an amine having at least one primary group with a least one alkylene oxide having 2 to 4 carbon atoms, by extruding the molten polymer through an orifice into a quenching medium, the improvement comprising reducing the occurrence of drips during extrusion by (a) reacting said polyether compound with at least 0.01 mol per mol of polyether compound, of a sulfur compound soluble in the polyether compound and selected from the group consisting of a compound of the formula:

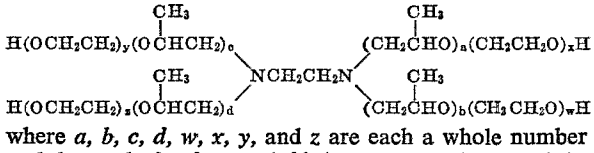


and a compound of the formula:



wherein R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl, *n* is a whole number corresponding to the valence of the metal, and Z is selected from the group consisting of hydrogen, ammonium cation and substituted ammonium cation; and (b) dispersing in the polyamide polymer prior to extrusion about 1 percent to 12 percent, based on the weight of the polyamide polymer, of the reaction product of said polyether compound and said sulfur compound.

2. The process of claim **1** wherein the polyether compound is represented by the formula:



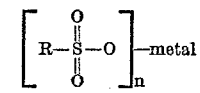
where *a, b, c, d, w, x, y,* and *z* are each a whole number and the total of *a, b, c,* and *d* is between 8 and 850 and the total of *w, x, y,* and *z* is between 8 and 1,000, the molecular weight of said polyether compound being in excess of 1,500 prior to reaction with the sulfur compound.

3. The process of claim **1** wherein the sulfur compound is selected from the group consisting of p-toluenesulfonic acid, p-toluenesulfonic acid sodium salt, and methane sulfonic acid.

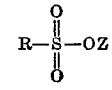
4. The process of claim **1** wherein 1 mol of the polyether compound is reacted with about 0.1 to 3 mols of the sulfur compound.

5. The process of claim **1** wherein the polyether compound is reacted with the sulfur compound at a temperature of about 75° to 110° C.

6. An antistatic polyamide fiber containing between about 1% and about 12% by weight based on the weight of the polyamide, of the reaction product of (a) a polyether compound having a molecular weight in excess of 1,500, derived from reaction of an amine having at least one primary group with at least one alkylene oxide having 2 to 4 carbon atoms, with (b) a sulfur compound selected from the group consisting of a compound of the formula:

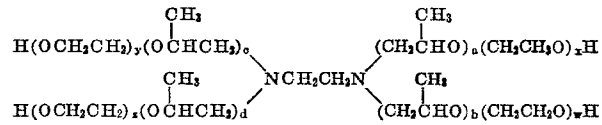


and a compound of the formula:



wherein R is selected from the group consisting of alkyl, cycloalkyl, aryl and arylalkyl, *n* is a whole number corresponding to the valence of the metal, and Z is selected from the group consisting of hydrogen ammonium cation and substituted ammonium cation, the mol ratio of the sulfur compound to the polyether compound being at least 0.01.

7. The fiber of claim **6** wherein the polyether compound is represented by the formula:



where *a, b, c, d, w, x, y,* and *z* are each a whole number and the total of *a, b, c,* and *d* is between 8 and 850 and the total of *w, x, y,* and *z* is between 8 and 1,000, the molecular weight of said polyether compound being in excess of 1,500 prior to reaction with the sulfur compound.

8. The fiber of claim **7** wherein the sulfur compound is selected from the group consisting of p-toluenesulfonic acid, p-toluenesulfonic acid sodium salt, and methane sulfonic acid.

9. The fiber of claim **6** wherein 1 mol of the polyether compound is reacted with about 0.1 to 3 mols of the sulfur compound.

10. The fiber of claim **6** wherein the polyether compound is reacted with the sulfur compound at a temperature of about 75° to 110° C.

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PAUL LIEBERMAN, Primary Examiner

U.S. Cl. X.R.

260—78 SC