Nov. 9, 1971 I. M. JONKOFF 3,618,307

ACRYLIC FIBERS AND PROCESS FOR PREPARING THE FIBERS

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FIG. 1

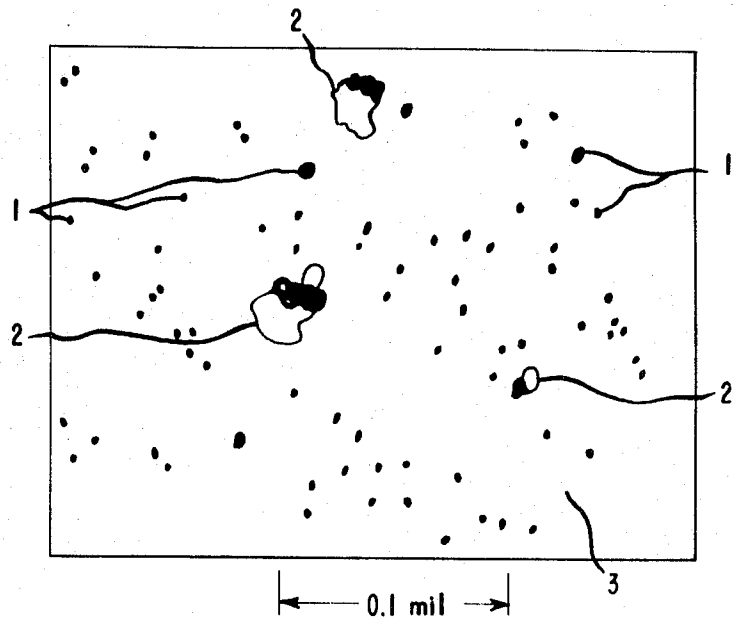
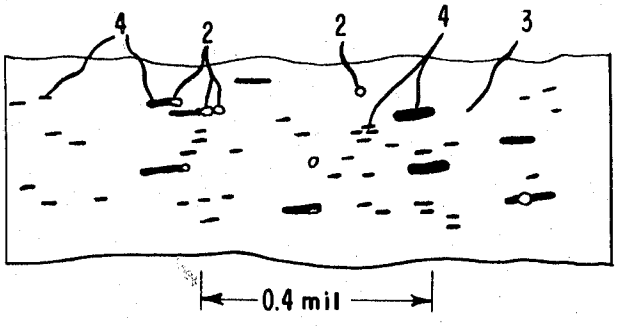


FIG. 2



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ACRYLIC FIBERS AND PROCESS FOR PREPARING THE FIBERS

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U.S. Cl. 57—140 R 14 Claims

ABSTRACT OF THE DISCLOSURE

Textile fibers of synthetic acrylonitrile polymer having dispersed throughout the cross section of the fiber a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol; said salt being present in the amount of about 0.05% to about 3% by weight of the polymer to reduce waste in fiber processing operations and to provide a yarn of the fibers having improved quality. Also, the process for preparing the above fibers.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to an improved acrylic fiber that resists mechanical degradation and forms very little waste when stretch-broken as a multifilamentary tow to form staple sliver and subsequently processed to staple yarn. The invention relates also to a novel process for preparing the improved fibers.

(2) Description of the prior art

In the production of acrylic staple yarns, one widely used commercial method involves conversion of a multifilamentary tow to a staple sliver by a stretch-breaking process on apparatus such as that described by Wyatt in U.S. Pat. 2,748,426. In this process, the acrylic filaments are stretched between feed nip rolls and delivery nip rolls while being struck by breaker bars positioned between the pairs of rolls. The breaker bars increase the tension upon the filaments in the tow sheet, inflicting stress concentration points upon the filaments to break them progressively to staple fiber length without destroying the continuity of the resulting sliver. The sliver so produced is then processed to conventional staple yarns by known methods, such as by spinning on the worsted system.

A significant problem in the commercial preparation of sliver from multifilamentary tows employing stretch-breaking apparatus incorporating breaker bars is that mechanical degradation of the fibers occurs during the process, with formation of airborne waste, known as "fly," which consists mainly of short fibers. Approximately 80% of the fly consists of fibers less than two inches in length. This waste material becomes detached from the sliver during its preparation on the stretch-breaking apparatus, resulting in reduced yield of the product. Not only does this result in economic loss in proportion to the amount of fly which is formed, but also the accumulation of the fly on the equipment and in adjacent areas creates a cleaning and equipment maintenance problem. Also, it is found that only a part of the short fiber waste material drops out during the manufacture of the staple sliver on the stretch-breaking apparatus. Additional quantities of the waste material become detached at each stage of the conversion of the staple sliver to the staple yarn, resulting in additional cleaning and maintenance problems and reduced yield at each stage. In roving and spinning, fly waste picked up by the thread-line causes breaks, resulting in loss of spindle operation time, and quality defects in the yarn. Slubs of wound-in waste in the yarn frequently cause needle breaks, resulting in fabric defects.

SUMMARY OF THE INVENTION

The present invention provides an improved acrylic fiber which, in the form of a multifilamentary tow, undergoes relatively little mechanical degradation to waste in the form of short fibers when stretch-broken to staple fiber and processed to staple yarn. Another advantage is to provide a novel process for preparing the improved acrylic fiber.

In accordance with the invention, a fiber is provided comprised of an acrylonitrile polymer and containing throughout the cross section of the fiber, a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol; said salt being present in the amount of 0.05 to 3.0%, based on the weight of the polymer.

Surprisingly, up to 70% lower waste is encountered in the stretch-breaking of multifilamentary tows of the acrylic fiber of the invention, as contrasted with conventional acrylic fibers which do not contain the salt of a partial ester of phosphoric acid. Greatly reduced waste in subsequent processing steps is similarly observed. Yarns made from the fiber of the invention also exhibit improved uniformity, with respect to yarns made from conventional acrylic fibers.

The invention also provides a novel process for preparing the improved fibers, in which a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol is dispersed in a solution of an acrylonitrile polymer to form a homogeneous spinning solution, and the spinning solution is then extruded through orifices of a spinneret to form fibers.

The product of this invention in its narrower scope is defined as textile fibers of synthetic acrylonitrile polymer having dispersed throughout the cross section of the fiber a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol; said salt being present in the amount of about 0.05% to about 3% by weight of the polymer to reduce waste in fiber processing operations and to provide a yarn of the fibers having improved quality. Included within the scope are the embodiments wherein: a paraffin wax is dispersed as an extender throughout the cross section of the fiber along with the salt; the salt is a sodium salt of a lauryloxypoly(ethyleneoxy) acid phosphate of the formula

$$[C_{12}H_{25}O(CH_2CH_2O)_x]_n\text{—}\overset{\overset{O}{\|}}{P}\text{—}(ONa)_{3-n}$$

wherein n is 1 or 2 and x is about 4; the salt is in the form of rod-like globules with the longitudinal axes of the globules extending in the direction of the fiber length; and staple yarns of said fibers.

The process of the present invention is more specifically described as being in the production of synthetic fibers of acrylic polymer in which the polymer is dissolved in a solvent to provide a spinning solution and the resulting solution is extruded in a spinning zone to form filaments which are subsequently processed to produce acrylic fibers; the improvement which comprises including in said spinning solution a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol, said salt being present in said solution in the amount of about 0.05% to about 3% by weight of the polymer to provide a dispersion of the salt throughout the cross section of the filaments.

BRIEF DESCRIPTION OF THE DRAWING

The invention will be better undestood by reference to the attached figures, which illustrate sections of the fiber of the present invention.

FIG. 1 is an interior portion of a greatly magnified cross section of the fiber of the present invention contain-

ing a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol; and

FIG. 2 is a greatly magnified longitudinal section of the fiber of the present invention, along its axis.

In FIG. 1, a portion of the interior of a cross section of the fiber of the invention, perpendicular to its axis, is seen. In this cross section, globules **1** of substantially round cross section of the salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol are seen together with particles **2** of TiO_2 delusterant of irregular cross section embedded within the matrix of acrylonitrile polymer **3**.

In FIG. 2, a segment of a longitudinal section of the fiber, substantially along its axis, is shown. In this longitudinal section, rod-like streaks **4** of the salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol are seen together with particles **2** of TiO_2 of irregular cross section embedded within the matrix of acrylonitrile polymer **3**. The fact that the phosphate ester salt is seen as round globules in the fiber cross section and in rod-like streaks in the fiber longitudinal section results from the drawing of the fiber after it has been spun.

DESCRIPTION OF PREFERRED EMBODIMENTS

In a preferred embodiment of the present invention, the salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol is the sodium salt and the said monoalkyl group contains at least about 10 carbon atoms. In a highly preferred embodiment of the invention, the salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol is a sodium salt of a lauryloxypoly(ethyleneoxy) acid phosphate of the formula

$$[C_{12}H_{25}O(CH_2CH_2O)_x]_n-\overset{\overset{O}{\|}}{P}-(ONa)_{3-n}$$

wherein n is 1 or 2 and x is about 4.

Other additives may also be present in the improved acrylic fiber of the invention. In a highly preferred embodiment of the invention, the acrylic fiber contains paraffin wax together with the salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol throughout the cross section of the fiber. Titanium dioxide may also be present as a delusterant. Additional additives, such as an optical brightener, may be present.

In a preferred process embodiment of the invention, paraffin wax and a sodium salt of a lauryloxypoly(ethyleneoxy) acid phosphate are dispersed in a solution of the acrylonitrile polymer in dimethyl formamide to form a homogeneous spinning solution, and the spinning solution is then extruded through orifices of a spinneret to form fibers. In a highly preferred embodiment, an aqueous emulsion of the paraffin wax and sodium salt of the lauryloxypoly(ethyleneoxy) acid phosphate are dispersed in the polymer solution.

The term "acrylonitrile polymer," as used herein, refers to any long chain synthetic polymer composed of at least 85% by weight of acrylonitrile units of the formula,

$$(-CH_2-\underset{\underset{CN}{|}}{CH}-)$$

in the polymer chain. As is well understood, the term includes both the homopolymer of acrylonitrile and copolymers of acrylonitrile and monoethylenically unsaturated monomers polymerizable with acrylonitrile. Nonlimitative examples of preferred comonomers include methyl acrylate, methyl methacrylate, vinyl acetate, styrene, methacrylamide, methacrylonitrile, vinyl chloride, vinylidene chloride, methyl vinyl ketone, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, and sodium styrene sulfonate.

The term "acrylic fiber," as used herein, refers to a fiber of acrylonitrile polymer, as defined above, which may contain additives such as the phosphate ester salt or other additives.

EXAMPLES

Preferred embodiments of the invention will be illustrated by the examples that follow. Parts and percentages are by weight unless otherwise indicated.

Example I

An N,N-dimethylformamide (DMF) solution containing 31% by weight total solids of the following materials is prepared:

(A) a terpolymer consisting essentially of 93.6% acrylonitrile, 6% methyl acrylate, and 0.4% sodium styrenesulfonate

(B) 0.4% TiO_2, based on polymer weight, as a delusterant

(C) 0.25%, based on polymer weight, of a mixture of 40% paraffin wax and 60% of the sodium salt of a mixture of mono- and di-esters of phosphoric acid and an alcohol prepared by condensing lauryl alcohol with 4 mols of ethylene oxide. To facilitate addition of this mixture, 10% by weight of water is added to it to prepare an emulsion.

The solution is continuously dry-spun to a multifilamentary tow which, after simultaneous drawing 4.5× and extracting in a water bath maintained near its boiling point, has a denier per filament of about 3. The tow is designated as "Tow I." Examination of surface replicas of fiber cross sections and fiber longitudinal sections, using an electron microscope (Stereoscan electron microscope manufactured by the Cambridge Instrument Company), reveals the presence of the TiO_2 and the phosphate ester salt in dispersed form.

As a control, a multifilamentary tow is prepared following the identical procedure, except that the paraffin wax/phosphate ester sodium salt of item (C) is omitted from the spinning solution. This tow is designated as "Tow C–I."

Tow I is converted to a sliver of staple fibers on a commercially available stretch-breaking machine of the type shown in U.S. Pat. 2,748,426 to W. K. Wyatt (manufactured by the Turbo Machine Company and designated as the "Turbo Stapler") and processed to 1/30 worsted count staple yarn in conventional manner on the worsted spinning system. As a control, Tow C–I is stretch-broken to staple sliver and processed to staple yarn under identical conditions. The amount of waste collected at various stages of processing the tow and staple sliver to yarn is listed in Table I, together with the quality of the resulting yarns as measured by the yarn unevenness. The yarn unevenness as measured by the coefficient of variation is defined as the square root of the average of the squares of the deviation of linear density from the average linear density, expressed as a percentage of the average linear density within the tested length of strand. A higher number corresponds to a more uneven yarn.

TABLE I

	Tow C–I	Tow I
Turbo waste (grains/100 lbs.)	185	56
Roving waste (grains/100 lbs.)	101	69
Spinning waste (grains/100 lbs.)	208	88
Yarn fly waste (percent)	0.095	0.052
Yarn unevenness, percent coefficient of variance (CV)	14.1	12.3

Example II

A series of multifilamentary tows is prepared, converted to sliver, and processed to staple yarns in general accordance with the procedure of Example I, except that the drawn fibers have a denier per filament of 6 and the staple yarn produced is a 1/20 worsted count staple yarn. Item (C) of the spinning solution of Example I is omitted in each instance and replaced by the following:

(1) No additive is incorporated in a control identified as "Tow C–II."

(2) 0.15%, based on polymer weight, of paraffin wax is incorporated as the sole additive in a second control identified as "Tow C–P."

(3) 0.15%, based on polymer weight, of the sodium salt of a mixture of mono- and di-esters of phosphoric acid and an alcohol prepared by condensing lauryl alcohol with 4 mols of ethylene oxide is incorporated as the additive in a tow designated as "Tow II."

(4) 0.15%, based on polymer weight, of a mixture of 40% paraffin wax and 60% of the sodium salt of a mixture of mono- and di-esters of phosphoric acid and an alcohol prepared by condensing lauryl alcohol with 4 mols of ethylene oxide is incorporated as the additive in a tow designated as "Tow II–P."

The results are listed in Table II.

As a further comparison 6 denier per filament tow in which no additive is incorporated is prepared and a finish comprising a mixture of 40% paraffin wax and 60% of the sodium salt of a mixture of mono- and di-esters of phosphoric acid and an alcohol prepared by condensing lauryl alcohol with 4 mols of ethylene oxide is applied to the tow in 20% aqueous emulsion in the amount of 0.42%, based on the dry weight of the tow, after the tow has been crimped. When this tow is stretch-broken to staple sliver and processed to staple yarn under the same conditions employed with the tows of Table II, the total waste collected is 917 grains/100 lbs. and the yarn fly waste (percent) is 0.1005.

TABLE II

	Control results		Results from fibers of the invention	
	Tow C–II	Tow C–P	Tow II	Tow II–P
Turbo and rebreaker waste (grains/100 lbs.)	370	354	302	196
Pindrafer waste (3 drafts) (grains/100 lbs.)	252	216	183	153
Roving waste (grains/100 lbs.)	87	94	40	50
Spinning waste (grains/100 lbs.)	134	180	96	112
Total waste (grains/100 lbs.)	843	844	621	511
Yarn fly waste (percent)	0.1367	0.1165	0.0649	0.0604

Example III

To illustrate the feasibility of spinning filaments readily at high levels of the phosphate ester salt additive, a spinning solution is prepared containing the following materials:

(A) 5,000 g. of N,N-dimethylformamide,

(B) 2,300 g. of a terpolymer consisting essentially of 93.6% acrylonitrile, 6% methyl acrylate, and 0.4% sodium styrenesulfonate,

(C) 9.7 g. TiO_2 as a delusterant,

(D) 1.62 g. of citric acid as a color inhibitor,

(E) 35 g. of a pure, saturated, hydrocarbon mineral oil, and

(F) 35 g. of the sodium salt of a mixture of mono- and di-esters of phosphoric acid and an alcohol prepared by condensing lauryl alcohol with 4 mols of ethylene oxide.

In the above mixture the additive incorporated in accordance with the process of the present invention therefore comprises 3.0%, based on polymer weight, of a mixture of 50% mineral oil and 50% of the phosphate ester salt. The solution is continuously dry-spun to form filaments and then simultaneously drawn 4.5× and extracted in a water bath maintained near its boiling point. The resulting filaments are readily processed to staple fibers and converted to staple yarn. The fibers have a denier per filament of 5.2, a tenacity of 2.31 g.p.d., an elongation of 26.9%, a modulus of 50.4 g.p.d., and a work-to-break of 0.41 g.p.d. Control filaments spun from the same ingredients listed above, excepting that no mineral oil and no phosphate ester salt is added, have a denier per filament of 5.0, a tenacity of 2.36 g.p.d., an elongation of 27.3%, a modulus of 50.4 g.p.d., and a work-to-break of 0.43 g.p.d. This experiment illustrates that good fiber physical properties are retained even when high levels of the additive are employed.

What is claimed is:

1. Multifilament tow of textile fibers of acrylonitrile polymer having dispersed throughout the cross section of the fibers a salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol; said salt being present in the amount of about 0.05% to about 3% by weight of the ploymer.

2. The fibers as in claim **1** wherein said salt is a sodium salt of a lauryloxypoly(ethyleneoxy) acid phosphate of the formula

$$[C_{12}H_{25}O(CH_2CH_2O)_x]_n-\overset{\overset{O}{\|}}{P}-(ONa)_{3-n}$$

wherein n is 1 or 2 and x is about 4.

3. The fiber as in claim **1** wherein said salt is in the form of rod-like globules with the longitudinal axes of the globules extending in the direction of the fiber length.

4. The fibers as in claim **1** having a denier within the range of about 1 to about 20.

5. Fibers prepared from the tow of claim **1** in the form of a staple yarn having a worsted count within the range of 1/10 to about 1/40.

6. The fibers as in claim **1** in which the polymer comprises at least 85% acrylonitrile and up to 15% of a monoethylenically unsaturated monomer copolymerizable with acrylonitrile.

7. The fibers as in claim **1** wherein a paraffin hydrocarbon having a chain length of at least a length corresponding to an oil is dispersed as an exterior through out the cross section of the fiber along with said salt.

8. The fibers as in claim **7** wherein said hydrocarbon is mineral oil.

9. The fibers as in claim **7** wherein said hydrocarbon is paraffin wax.

10. In the production of synthetic fibers of acrylic polymer in which the polymer is dissolved in a solvent to provide a spinning soluiton and the resulting solution is extruded in a spinning zone to form filaments which are subsequently processed to produce acrylic fibers; the improvement which comprises including in said spinning solution of salt of a partial ester of phosphoric acid with a monoalkyl ether of a polyoxyalkylene glycol, said salt being present in said solution in the amount of about 0.05% to about 3% by weight of the polymer to provide a dispersion of the salt throughout the cross section of the filaments.

11. The process as in claim **10** wherein said salt is a sodium salt of a lauryloxypoly(ethyleneoxy) acid phosphate of the formula

$$[C_{12}H_{25}O(CH_2CH_2O)_x]_n-\overset{\overset{O}{\|}}{P}-(ONa)_{3-n}$$

wherein n is 1 or 2 and x is about 4.

12. The process as in claim **10** wherein the polymer comprises at least 85% acrylonitrile and up to 15% of a monoethylenically unsaturated monomer copolymerizable with acrylonitrile, and the solvent is N,N-dimethylformamide.

13. The process as in claim **10** wherein a paraffin hydrocarbon is included in said spinning solution as an extender along with said salt.

14. The process as in claim 11 wherein said salt and said paraffin hydrocarbon are added to the spinning solution as an aqueous emulsion.

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117—139.5 CQ; 161—174; 260—28.5 R, 30.6R, 33.6 UA, DIG. 23; 264—176 F

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,618,307 Dated November 9, 1971

Inventor(s) Imre M. Jonkoff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, Claim 1, line 6: "ploymer" should read --polymer--.

Column 6, Claim 7, line 3: "exterior" should read --extender--.

Column 6, Claim 10, line 3: "soluiton" should read --solution--.

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents