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3,698,994

ACRYLIC SYNTHETIC FIBERS HAVING IMPROVED PROPERTIES AND PROCESS FOR PRODUCING THE SAME

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ABSTRACT OF THE DISCLOSURE

Acrylic fibers containing streaky inclusions of 2-25% polyvinyl cyanoethyl ether of DS value between 55% and 75% having improved luster, softness, hygroscopic, and antistatic properties. Such fibers are made by wet-spinning a solution of the polyvinyl cyanoethyl ether and the acrylonitrile polymer in a common solvent, water-washing, stretching, and dry-heat drying the fibers so spun.

This invention relates to acrylic fibers containing distributed therein a poly(vinyl cyanoethyl ether) as a separate phase continuous throughout the fiber length, said polyether phase being detached from said polyacrylonitrile phase and separated therefrom by void space. The invention also relates to a process by which the desired fibres are obtained.

In particular, this invention relates to acrylic fibers in which improvements in hydroscopic, antistatic, lustrous and softness properties are obtained. The process involves wet-spinning a polymer solution comprising a blend of an acrylonitrile polymer and a poly(vinyl cyanoethyl ether) wherein during the spinning procedure a phase separation of polymers occurs with the result that the poly(vinyl cyanoethyl ether) is distributed within said fiber as a separate phase continuous throughout the fiber length detached from the acrylonitrile polymer and separated therefrom by void space. The resulting fiber presents an appearance in which the poly-(vinyl cyanoethyl ether) tends to be seen as a streak-like dispersion within the fiber.

It is known in the prior art that improvements in acrylic fiber properties can be achieved by blending a poly(vinyl cyanoethyl ether) with an acrylonitrile polymer. For example, in U.S. Pat. 2,938,008, May 24, 1960, Hare, there is disclosed a fiber of improved properties, which fiber is based on a homogenous blend of an acrylonitrile polymer and a poly(vinyl cyanoethyl ether). The property improvements resulting are in abrasion resistance, anti-fibrillation, and dyeability. In this reference, the polymers are not only mutually soluble in the polymer solvent but are compatible with one another in fiber form. The property improvements resulting are those associated with a homogeneous distribution of polymers throughout the fiber structure and there is no phase separation of the compatible polymers.

In accordance with the product aspect of the present invention there is provided an acrylic fiber comprising an acrylonitrile polymer and a poly(vinyl cyanoethyl ether), said ether being present in an amount ranging from about 2% to 25%, by weight, based on the total weight of the fiber and being distributed as a separate phase within said fiber, said ether phase extending continuously throughout the fiber length and being detached from said acrylonitrile polymer and separated therefrom by void space, the poly(vinyl cyanoethyl ether) being etherified with cyanoethyl groups to an extent which is between about 55% and 75% of full theoretical etherification with acrylonitrile.

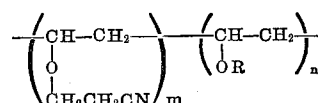
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In accordance with the process aspect of the present invention there is provided a procedure for preparing the above-described fibers which comprises preparing a homogeneous spinning solution in a suitable polymer solvent of an acrylonitrile polymer and from about 2% to 25%, by weight, based on the total weight of polymer in said solution of a poly(vinyl cyanoethyl ether) which is etherified to an extent which is from about 55% to 75% of full theoretical etherification with acrylonitrile, wet-spinning said polymer solution into a coagulant for said polymers, washing the coagulated wet-gel filament thus formed, stretching the wet-gel filament, and drying the stretched filament.

The fibers of the present invention are improved over conventional acrylic fibers in such properties as luster, hydroscopicity, and softness and have a reduced tendency to accumulate static electrical charges. The fibers exhibit the appearance of having a streaky dispersion of the poly(vinyl cyanoethyl ether) therein although said polyether is dispersed as a separate phase within the fiber extending continuously throughout the fiber length as a separate phase detached from the acrylonitrile polymer phase and separated therefrom by void space.

As the acrylonitrile polymer that may be employed in the present invention are included those conventional fiber-forming acrylonitrile polymers and copolymers which contain at least 70% by weight of acrylonitrile. A mixture of two or more such polymers may also be employed. Numerous vinyl type monomers are known which are copolymerizable with acrylonitrile and provide desirable fiber-forming copolymers. Such vinyl type monomers may be employed singly or in mixture with acrylonitrile so long as their total concentration in the copolymer does not exceed about 30% by weight.

As the poly(vinyl cyanoethyl ethers) useful in the present invention are those having the formula



wherein $m+n$ represents the total content of the polymer and m represents from about 55 to about 75% of the total content and R represents hydrogen or an acetyl group. The molecular weight of the polymer may vary widely and is not critical. Typically, polymers corresponding to those wherein the unsubstituted polyvinyl alcohol has a molecular weight in the range of about 10,000 to about 100,000 are employed.

A customary procedure for obtaining a poly(vinyl alcohol) is by polymerizing vinyl acetate and subsequently saponifying the resulting polymer. The percentage of hydroxyl groups produced will depend upon the degree to which saponification is effected. To obtain the cyanoethyl ether, the saponified poly(vinyl acetate) is reacted with acrylonitrile under alkaline conditions and, since such conditions also effect saponification, it is possible to effect saponification and etherification concurrently. Thus, the useful poly(vinyl cyanoethyl ethers) are readily obtained by controlled saponification and etherification of poly(vinyl acetate). As stated above, the usage of poly(vinyl cyanoethyl ether) must be between about 2% to 25%, by weight, based on the total polymer weight.

If the value of m in the formula given above is less than about 55%, the poly(vinyl cyanoethyl ether) is dissolved out of the extruded filament in the coagulating bath, in the washing step immediately following, or both and will not be present in the final fiber. On the other hand, if the value of m is greater than about 75%, the poly(vinyl cyanoethyl ether) will become compatible with

the acrylonitrile polymer and the desired separate and detached phase will not be obtained. If the content of poly(vinyl cyanoethyl ether) is less than about 2%, by weight, based on the total polymer weight, such content does not effect any significant improvements in the resulting fiber properties. On the other hand, if the content of poly(vinyl cyanoethyl ether) is above about 25%, by weight, based on the total polymer weight, the swollen gel fibers upon drying, regardless of drying temperature, tend to stick together, apparently due to inability to confine the poly(vinyl cyanoethyl ether) as a separate phase within the fiber.

As the solvent for preparing the spinning solution of the polymers, one may use organic solvents or inorganic salt and inorganic acid solvents. As organic solvents, for example, one may use dimethyl formamide, dimethyl acetamide, and dimethyl sulfoxide. As inorganic salt solvents for example, one may use concentrated aqueous solutions of thiocyanates, such as sodium, potassium, ammonium, and calcium thiocyanates and mixtures thereof, concentrated aqueous solutions of zinc chloride, and concentrated aqueous solutions of lithium chloride. As inorganic acid solutions, for example, one may use concentrated aqueous nitric and sulfuric acids.

As the coagulant for the spun polymer solution, typically one uses those liquid coagulants normally employed in wet-spinning, taking into account those subtle relationships between polymer solvent and coagulant as are well known in the art. Among the suitable coagulants, for example, are water, aqueous solutions of the above-mentioned inorganic salts or acids in which the concentration of salt or acid does not exceed 20% by weight thereof, aqueous solutions of the above-mentioned organic solvents in which the concentration of organic solvent is in the range of 20% to 70% by weight thereof, or polyethylene glycol.

In carrying out the process of the present invention, a spinning solution is prepared by dissolving the acrylonitrile polymer and poly(vinyl cyanoethyl ether) in the selected solvent. Preferably, this solution is prepared by first dissolving the poly(vinyl cyanoethyl ether) in at least a portion of the selected solvent and then adding the acrylonitrile, while making any necessary adjustment as to solvent content. It is generally preferable to adjust the polymer content of the spinning solution to between about 10% and 30%, by weight, based on the total weight of the spinning solution. However, it is not necessary to restrict the polymer content of the spinning bath to this specific range since such factors as solution viscosity, temperature of the spinning solution, and solvent nature influence the useful polymer concentrations in specific instances.

The polymer solution is wet-spun into an appropriate coagulant according to conventional procedures. Following coagulation, the filaments are washed, stretched and dried in accordance with conventional procedures, except that the drying temperature should not exceed about 115° C., since drying of the wet-gel filaments at higher temperatures tends to cause the fibers to stick together. Subsequent to drying other conventional steps normally employed may be carried out as desired.

Although it is not known for certain what mechanism is responsible for the fibers of the present invention and the inventors do not wish to be bound by any particular theory, the following theory is suggested. Both polymers are coagulated by the coagulating bath as it penetrates into the extruded polymer solution but the rate of coagulation differs among the two polymers. The acrylonitrile polymer coagulates first upon contact with the coagulant and forms the outer periphery of the wet gel filament. Since the poly(vinyl cyanoethyl ether) is incompatible with the coagulated acrylonitrile polymer and is not immediately precipitated by the coagulant, the poly(vinyl cyanoethyl ether) in solution form is displaced toward the center of the filament by the penetrating coagulant

and the increasing content of coagulated polyacrylonitrile building up within the peripheral wall of the gel filament. Although the coagulant can penetrate the porous nature of the gel filament, the poly(vinyl cyanoethyl ether) is incapable of such penetration and remains within the gel structure. Eventually, as coagulation continues the poly(vinyl cyanoethyl ether) is coagulated within the fiber as a separate phase from the acrylonitrile polymer but, because the poly(vinyl cyanoethyl ether) remained as an interconnected solution within the gel filament, the poly(vinyl cyanoethyl ether) phase remains connected along the length of the formed filament. As first formed, the separate poly(vinyl cyanoethyl ether) phase is joined to the inner portion of the acrylonitrile phase. Subsequently, after washing, stretching, and drying, due to differences in the swollen states of the polymers and differential shrinkages thereof, the poly(vinyl cyanoethyl ether) becomes detached from the acrylonitrile polymer and void space forms between the polymer structures. This ultimate structure is felt to give rise to the streaky dispersion effect noted. It is also felt that the unique structure of the fiber gives rise to the improved properties noted.

The invention is further illustrated by the examples which follow, in which all parts and percentages are by weight unless otherwise specifically noted.

The various tests by which the data recorded in the following examples are obtained are conducted as follows.

(1) K/S value

1.5 grams of the fiber to be measured are immersed in a solution at 70° C. of the following:

	Percent
C.I. Basic Blue 22	0.5
Acetic acid	1.0
Sodium sulfate	10.0

wherein the percentages are based on the weight of fibers. The volume of solution is 50 times the weight of fibers. Upon immersion of the fibers, the bath is heated to 100° C. at the rate of 1° C. per minute and the bath is then maintained at 100° C. for 30 minutes. The fibers are then gradually cooled in the bath, removed, and dried. One gram of the dyed fibers are then taken and the reflectance determined using a source of monochromatic light. The K/S value is determined from the Kubelka-Munk equation:

$$K/S = (1 - R)^2 / 2R$$

wherein R is the reflectance measured, K is the absorption coefficient of the fibers, and S is the scattering coefficient of the fibers.

The K/S value quantitatively represents the magnitude of the internal reflecting surface area and smaller K/S values indicate larger internal reflecting surface areas. Thus, the K/S value indicates the degree of streaky dispersion formed within the fibers by the poly(vinyl cyanoethyl ether).

(2) 60-degree mirror surface luster (G_s^{60})

Samples of fiber from any crimp has been removed are arranged in parallel and laid flat on a cardboard to present a rectangular fiber surface of size 6 centimeters by 4.5 centimeters. The G_s^{60} value is then determined according to the method described in JIS 2-8741 using a GM-5 luster meter (manufactured by Murakami Color Technical Laboratory). Measurements of luster were obtained with the angle of incidence parallel to the axial direction of the fiber.

(3) Hygroscopicity

About two grams of fibers to be measured are predried for one hour at 80° C. and then conditioned at 20° C. and 65% relative humidity for 24 hours. The conditioned fibers are weighed and the weight designated A. The fibers are then dried for 20 hours at 60° C. at a pressure equivalent to 50 millimeters of mercury em-

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ploying a vacuum dryer containing phosphorus pentoxide. The fibers thus dried are weighed and the weight designated B. The hygroscopicity is calculated from the following formula employing the weights designated above:

$$\text{Hygroscopicity (percent)} = \frac{A-B}{B} \times 100$$

(4) Antistatic activity

The fibers are conditioned for 16 hours at 20° C. and 65% relative humidity. The electrical resistivity of the fiber surface is then measured using an appropriate meter (Textrome® Model GR-54, manufactured by Chuo Electronic Industrial Company, Ltd.).

(5) Water-absorption length

Fibers to be measured are spun into a 36 cotton count single yarn having 325 twists per meter. Two such single yarns are plied employing 540 twists per meter in plying. The yarn thus obtained is knitted into a plain weave fabric having a weight of 200 milligrams per square centimeter. A test specimen 3 centimeters wide and 12 centimeters long is cut from the fabric. The test specimen is hung vertically at a fixed height with its lower end held submerged in a water tank by tension. The test is conducted in a conditioned room at 20° C. and 65% relative humidity employing water at 20° C. After the specimen has been maintained in the position stated for 10 minutes, the height to which water has risen in the fabric is measured and reported. In the event the height exceeds 95 millimeters within the ten minute time limit, the testing is modified so that the time required to reach the 95 millimeter height is reported.

EXAMPLE 1

A ploy(vinyl acetate) which has been saponified to an extent which exceeds 95% is employed in preparing a poly(vinyl cyanoethyl ether). One part of the resulting poly(vinyl alcohol), which has a degree of polymerization of 1700, i.e. a molecular weight of about 75,000, is dissolved in 10 parts of 1% aqueous sodium hydroxide solution. To this solution are added 3 parts of acrylonitrile and the mixture is stirred and reacted at 50° C. for 150 minutes. The reaction mixture was then filtered, the filter cake washed with water and recovered. There was obtained a poly(vinyl cyanoethyl ether) which contained 60.2% of the full theoretical content of cyanoethyl groups. The resulting polymer contained water in the amount of 45%.

In 7.2 parts of 60% aqueous sodium thiocyanate solution was dissolved 1 part of the poly(vinyl cyanoethyl ether) obtained above. As the acrylonitrile polymer there was employed a copolymer of the following monomer composition:

	Percent
Acrylonitrile	91
Methyl acrylate	8.73
Sodium methallylsulfonate	0.27

9 parts of this polymer and 6.9 parts of water were added to the solution of poly(vinyl cyanoethyl ether) and stirred to obtain a uniform slurry. To the slurry was then added 24.1 parts of 60% aqueous sodium thiocyanate solution and the mixture was stirred at 60° C. for 75 minutes to obtain a clear solution. The solution obtained, which had a ratio of acrylonitrile polymer to poly(vinyl cyanoethyl ether) of 90:10, was then heated to 70° C., spun through a spinnerette into an aqueous coagulation bath which consisted of a 12% aqueous solution of sodium thiocyanate maintained at a temperature of -3° C. The filaments thus formed were water-washed while being stretched at a stretch ratio of 2:1, further stretched at a stretch ratio of 5:1 in boiling water and then dried at 90° C. The dried fibers were then relaxed of an atmosphere of steam at 115° C. to produce acrylic fibers in the present invention.

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Comparative Example A

In this example, the acrylonitrile polymer of Example 1 was the sole polymer in spinning fibers. 10 parts of the acrylonitrile polymer of Example 1 were dissolved in 90 parts of a 48% aqueous sodium thiocyanate solution. The spinning solution thus obtained was spun into filaments following the procedure of Example 1. The coagulated filaments were water-washed and stretched as in Example 1. The stretched fibers were dried at a dry bulb temperature of 120° C. at 20% relative humidity and then relaxed in an atmosphere of steam at 120° C. for 10 minutes.

Properties of the fibers obtained in Example 1 and Comparative Example A are given in Table I which follows.

TABLE I

Property	Fibers Example 1	From Comp. Example A
20 K/S value	0.997	1.600
Hygroscopicity, percent	3.0	1.8
60-degree mirror surface luster (G_s^{60})	48	33
Surface resistivity, ohms	10 ⁹	10 ¹²

It can readily be seen from the data in Table I, that the fibers of the present invention are improved in the streaky dispersion effect (as indicated by K/S values) over conventional fibers and also have improved hygroscopicity, luster, and antistatic properties thereover.

In addition, evaluation of the fibers by touch reveals an improved softness of the fibers of the present invention relative to conventional fibers.

EXAMPLE 2

One part of the poly(vinyl cyanoethyl ether) prepared in Example 1 was dissolved in 4.8 parts of 60% aqueous sodium thiocyanate solution. To this solution were added 4.6 parts water and 5.7 parts of a copolymer containing 45% water and having the following monomer composition:

	Percent
Acrylonitrile	91
Methyl acrylate	8.73
Sodium methallylsulfonate	0.27

The mixture was stirred to form a slurry and then 16.1 parts of 60% aqueous sodium thiocyanate solution were added and the mixture stirred for 75 minutes while maintaining the temperature of 60° C. so that a homogeneous solution was obtained. The ratio of acrylonitrile polymer to poly(vinyl cyanoethyl ether) was 85:15. The solution was then heated to 70° C. and spun through a spinnerette into a coagulating bath of 12% aqueous sodium thiocyanate maintained at -3° C. The filaments thus obtained were water-washed and concurrently stretched at a stretch ratio of 2X. The filaments were then further stretched in boiling water at a stretch ratio of 5X. After stretching, the fiber was dried at 115° C. and then relaxed in an atmosphere of steam at 115° C. Properties of the fibers obtained are given in Table II.

TABLE II

Property:	
K/S value	0.701.
Hygroscopicity	5.5%.
G_s^{60}	41.
65 Surface resistivity	10 ⁹ ohms.
Water absorption	3 min. 50 seconds for 95 millimeter height.

When the fibers of Comparative Example A were tested for water absorption, it was found that the length was only 76 millimeters after 10 minutes.

EXAMPLE 3

Following the procedure of Example 1 a poly(vinyl cyanoethyl ether) was prepared. In this example, the

amount of acrylonitrile employed in forming the ether was 2.4 parts per part of poly(vinyl alcohol). There was obtained a poly(vinyl cyanoethyl ether) which contained 55.2% of the full theoretical content of cyanoethyl groups.

Employing this poly(vinyl cyanoethyl ether), fibers were prepared following the procedure of Example 2. Fiber properties are given in Table III.

Comparative Example B

The procedure of Example 3 was followed except that the amount of acrylonitrile employed was 1.8 parts per part of poly(vinyl cyanoethyl ether) which contained 49.7% of the full theoretical content of cyanoethyl groups.

Employing this poly(vinyl cyanoethyl ether), fibers were prepared following the procedure of Example 2. Fiber properties are also given in Table III.

TABLE III

Property	Exam- ple 3	Comp. Exam- ple B
K/S value.....	1.0	1.5
G _s ⁶⁰	40	27

The data indicate that when the poly(vinyl cyanoethyl ether) has 49.7% of the full theoretical content of cyanoethyl groups, the fibers obtained do not possess the desired streaky dispersion effect or luster. The data also indicate that a poly(vinyl cyanoethyl ether) having 55.2% of the full theoretical content of cyanoethyl groups produces the desired properties.

EXAMPLE 4

1.8 parts of the poly(vinyl cyanoethyl ether) obtained in Example 1 were dissolved in 40 parts of dimethyl formamide. To this solution were added 9 parts of a dried powdered copolymer obtained from a monomer content of:

	Parts
Acrylonitrile	91
Methyl acrylate	8.73
Sodium methallylsulfonate	0.27

The mixture was stirred for 120 minutes at 50° C. to prepare a homogeneous spinning solution. The spinning solution at 50° C. spun into a coagulation bath maintained at 70° C. and consisting of polyethylene glycol of molecular weight 400. The filaments thus obtained were stretched at a stretch ratio of 5× in a bath of polyethylene glycol of molecular weight 600 and maintained at 120° C. The filaments were then water-washed at room temperature and dried at 115° C. The fibers were then relaxed in an atmosphere of steam at 120° C. Properties of the fibers obtained are given in Table IV.

TABLE IV

Property:	
K/S value	0.701
Hygroscopicity, percent	6.2
G _s ⁶⁰	38
Surface resistivity, ohms	10 ⁷

This example shows the usefulness of an organic polymer solvent in the present invention.

EXAMPLE 5

One part of the poly(vinyl cyanoethyl ether) prepared in Example 1 was dissolved in 36.1 parts of an aqueous 60% solution of sodium thiocyanate. To this solution were then added 49 parts of a copolymer containing 45% water and based on a monomer composition of:

Percent

Acrylonitrile	91
Methyl acrylate	8.73
Sodium methallylsulfonate	0.27

34.4 parts of water were also added and the mixture stirred to form a uniform slurry. There were then added 120.5 parts of an aqueous 60% sodium thiocyanate solution and stirring was effected for 75 minutes while maintaining the composition at 60° C. so as to produce a homogeneous solution. The solution contained the acrylonitrile polymer and poly(vinyl cyanoethyl ether) at a ratio of 98:2, respectively.

The solution was then spun into fibers following the procedure of Example 2. The fibers obtained exhibited a K/S value of 0.759.

We claim:

1. An acrylic fiber comprising an acrylonitrile polymer of at least 70% acrylonitrile and a poly(vinyl cyanoethyl ether), said ether being present in an amount ranging from about 2% to about 25%, by weight, based on the total weight of the fiber, and being distributed as a separate phase within said fiber, said ether phase extending continuously throughout the fiber length and being detached from said acrylonitrile polymer and separated therefrom by void space, the poly(vinyl cyanoethyl ether) being etherified with cyanoethyl groups to an extent which is between about 55% and 75% of full theoretical etherification with acrylonitrile.

2. The fiber of claim 1 wherein the amount of poly(vinyl cyanoethyl ether) in said fiber is about 10% to 15%, by weight, based on the total weight of said fiber.

3. The fiber of claim 1 wherein the extent of etherification of said poly(vinyl cyanoethyl ether) is about 60% of the full theoretical etherification with acrylonitrile.

4. A process for preparing an acrylic fiber comprising preparing a homogeneous spinning solution in a suitable polymer solvent of an acrylonitrile polymer of at least 70% acrylonitrile and from about 2% to about 25%, by weight, based on the total weight of polymer, of a poly(vinyl cyanoethyl ether) which is etherified to an extent which is from about 55% to about 75% of full theoretical etherification with acrylonitrile, wet-spinning said polymer solution into a coagulant for said polymers, washing the coagulated wet-gel filaments, stretching the washed filaments and drying the stretched filaments.

5. The process of claim 4 wherein an aqueous inorganic salt solution is employed as the polymer solvent.

6. The process of claim 4 wherein an organic solvent is employed as the polymer solvent.

7. The process of claim 4 wherein drying of the stretched fibers is at a temperature of up to 115° C.

8. The process of claim 4 wherein partial stretching is accomplished in the washing step.

9. The process of claim 5 wherein said aqueous inorganic salt is a thiocyanate salt.

10. The process of claim 6 wherein said organic solvent is dimethyl formamide.

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