(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 138 940 A1**

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
08.03.2017 Bulletin 2017/10

(21) Application number: **15786320.0**

(22) Date of filing: **28.04.2015**

(51) Int Cl.:
D01F 8/08 $^{(2006.01)}$ ***D02J 1/22*** $^{(2006.01)}$

(86) International application number:
PCT/JP2015/062863

(87) International publication number:
WO 2015/166956 (05.11.2015 Gazette 2015/44)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **30.04.2014 JP 2014093278**

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(54) ACRYLIC FIBERS, METHOD FOR MANUFACTURING SAME, AND SPUN YARN AND KNITTED FABRIC USING SAID FIBERS

(57) Provided are: acrylic fibers having 2-7% boiling water shrinkage and formed by the side-by-side conjugation of a copolymer A, which contains 5-10 mass% of an unsaturated monomer that can form a copolymer with acrylonitrile units, and a copolymer B, which contains 2-5 mass% of unsaturated monomer units that can form a copolymer with acrylonitrile units and 0.2-1.5 mass% of sulfonic acid group-containing monomer units; a method for manufacturing said fibers; a spun yarn containing said fibers; and a knitted fabric obtained from said spun yarn. The single fiber fineness of the heat-treated acrylic fibers is 1.7-6.6 dtex, the bulkiness is at least 380 cm3/g, the percentage of crimp is at least 15%, and the product (DKSDKE) of the knot strength (cN/dtex) and the knot elongation (%) is 10-25. The acrylic fibers have excellent crimp characteristics and anti-pilling properties.

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention relates to acrylic fibers with excellent crimp and anti-pill properties, and a method for manufacturing such acrylic fibers. The present invention also relates to spun yarns and knitted fabrics formed using such acrylic fibers.

Background Art

[0002] Acrylic fibers have bulkiness and heat-retention properties similar to those of wool, and are dyeable to distinct colors with excellent fastness, while having excellent properties such as lightfastness and anti-corrosion. Acrylic fibers are used in a wide range of apparel, interior and materials applications.

[0003] Wool exhibits excellent bulkiness, compression resistance and elasticity, and acrylic fibers are said to have similar properties to those of wool. However, the compression resistance and elasticity of acrylic fibers have not reached the level of wool. Studies have been conducted accordingly to make acrylic fibers more similar to wool.

[0004] For example, JP S63-190019A (Patent Literature 1) and JP H01-104825A (Patent Literature 2) disclose technologies for forming a double- or multi-layer fiber structure through composite spinning of two or more copolymers having different copolymerization compositions. These bicomponent fibers are manufactured by layering spinning dopes using a multi-layer system, but it is difficult to achieve a stable side-by-side formation and sufficient bulkiness.

[0005] Also, JP H07-197323A (Patent Literature 3), for example, discloses technology for forming an eccentric-radiated or parallel fiber structure through bicomponent spinning of two types of acrylonitrile polymers with different hydrophilic properties. Such bicomponent fibers are self-crimping fibers with crimps that are reversible depending on wet or dry conditions. However, the target texture has not been achieved as they do not exhibit bulkiness and resilience similar to those of wool.

[0006] Moreover, JP S59-192717A (Patent Literature 4), for example, discloses technology to conduct side-by-side bicomponent spinning using two types of polymers with different shrinkage rates. Bicomponent fibers formed by such a method have bulkiness and are capable of producing bulky fabrics. However, when the fibers undergo hot water treatment during a dyeing process, shrinkage along the fiber axis direction tends to occur, causing the texture to harden after shrinkage.

[0007] Since bicomponent fibers produced by conventional technology have a higher shrinkage rate in the fiber axis direction, it is necessary to use a skein when the yarn is dyed (hank dyeing). , In the case of fabric dyeing, it is necessary to make a loosely-knitted fabric based on the calculated size of the shrunk fabric. The shrinkage rate is controlled during the dyeing process. Advanced processing technology is required.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Literature 1: JP S63-190019A

Patent Literature 2: JP H01-104825A

Patent Literature 3: JP H07-197323A

Patent Literature 4: JP S59-192717A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009] The objective of the present invention is to solve the aforementioned problems in conventional technology by providing acrylic fibers with excellent crimp and anti-pill properties.

SOLUTIONS TO THE PROBLEMS

[0010] An acrylic fiber related to the present invention has a crimp rate of 15% or higher measured in accordance with JIS L1015 (2010), and bulkiness measured by the method below is 380 cm^3/g or greater.

(Method for Measuring Bulkiness)

[0011]

(1) collect approximately 10 grams of an acrylic fiber cut into 51 mm-long pieces, and open the fiber until almost no adhesion is observed;
(2) take 1.5 grams of the opened acrylic fiber;
(3) divide the fiber into batches of approximately 0.15 grams each, and softly drop each batch into a 1000 mL graduated cylinder with a bottom area of 33.17 cm^2 to fill the cylinder homogenously without creating any gap;
(4) lower a 6-gram load disc into the cylinder and measure the volume, "v" cm^3, occupied by the acrylic fiber two minutes later; and
(5) calculate the degree of bulkiness by the following formula:

$$\text{degree of bulkiness } (cm^3/g) = v \div 1.5$$

The above procedure is conducted on three samples, and their average value is entered as the result.

[0012] Acrylic fibers related to the present invention are preferred to have a single fiber fineness of 1.7 dtex~6.6 dtex, and the value obtained by multiplying knot strength (cN/dtex) and knot elongation (%) is preferred to be 10~25.

[0013] The number of crimps in the acrylic fibers related to the present invention is preferred to be 20 per 2.54 cm~50 per 2.54 cm.

[0014] Acrylic fibers related to the present invention are preferred to have a side-by-side bicomponent structure of an acrylonitrile copolymer (A) with an acrylonitrile unit content of 90 mass%~95 mass% and an acrylonitrile copolymer (B) with an acrylonitrile unit content of 93.5 mass%~97.8 mass%, which are arranged in an area ratio of 1:3~3:1 at a fiber cross-section perpendicular to the fiber axis.

[0015] Acrylic fibers related to the present invention are preferred to have a difference of 2 or greater between the value of acrylonitrile unit content (mass%) in the copolymer (A) and the value of acrylonitrile unit content (mass%) in the copolymer (B).

[0016] In the acrylic fibers related to the present invention, the copolymer (A) is preferred to be formed by copolymerizing 90 mass%~95 mass% of an acrylonitrile unit and 5 mass%~10 mass% of an unsaturated monomer copolymerizable with the acrylonitrile unit, and the copolymer (B) is preferred to be formed by copolymerizing 93.5 mass%~97.8 mass% of an acrylonitrile unit, 2 mass%~5 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit, and 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit.

[0017] In the acrylic fibers related to the present invention, the monomer unit contained as an unsaturated monomer unit copolymerizable with the acrylonitrile unit in the copolymers (A) and (B) is preferred to be a vinyl acetate unit, and the sulfonic acid group-containing monomer unit is preferred to be a sodium methallyl sulfonate unit.

[0018] The shrinkage rate of the acrylic fibers related to the present invention is preferred to be 2%~7%.

[0019] A method for manufacturing an acrylic fiber according to the present invention is to form a side-by-side bicomponent fiber by discharging the following dopes from a nozzle into a coagulation bath with a solvent concentration of 35%~60%: a spinning dope (A') prepared by dissolving a copolymer (A) with an acrylonitrile unit content of 90 mass%~95 mass% in a solvent, and a spinning dope (B') prepared by dissolving a copolymer (B) with an acrylonitrile unit content of 93.5 mass%~97.8 mass% in a solvent. In such a fiber, the difference between the value of acrylonitrile unit content (mass%) in the copolymer (A) and the value of acrylonitrile unit content (mass%) in the copolymer (B) is 2 or greater.

[0020] In the method for manufacturing an acrylic fiber according to the present invention, the copolymer (A) is preferred to be formed by copolymerizing 90 mass%~95 mass% of an acrylonitrile unit and 5 mass%~10 mass% of an unsaturated monomer copolymerizable with the acrylonitrile unit, and the copolymer (B) is preferred to be formed by copolymerizing 93.5 mass%~97.8 mass% of an acrylonitrile unit, 2 mass%~5 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit, and 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit.

[0021] In the method for manufacturing an acrylic fiber related to the present invention, the unsaturated monomer unit copolymerizable with the acrylonitrile unit in the copolymers (A) and (B) is preferred to be a vinyl acetate unit, and the sulfonic acid group-containing monomer unit is preferred to be a sodium methallyl sulfonate unit.

[0022] The method for manufacturing an acrylic fiber related to the present invention is preferred to have a step for forming a side-by-side bicomponent fiber by discharging the spinning dope (A') and spinning dope (B') from a nozzle into a spinning bath; a step for conducting primary drawing at a draw ratio of 3.0~5.0 times; a step for conducting relaxation heat treatment under saturated steam pressure of 90 kPa~230 kPa; and a step for conducting secondary drawing at a draw ratio of 1.05~1.20 times.

[0023] The spun yarn related to the present invention contains the above acrylic fiber at 30 mass% or greater. The spun yarn related to the present invention is preferred to contain a conductive acrylic fiber in a range of 3 mass%~15 mass%.

[0024] The knitted fabric related to the present invention contains the spun yarn at 50 mass% or greater and has an anti-pill grade of 4 or higher.

[0025] After washing 10 times, the dimensional change in the knitted fabrics related to the present invention is preferred to be ±3% or lower in both vertical and horizontal directions.

EFFECTS OF THE INVENTION

[0026] The acrylic fibers related to the present invention have excellent anti-pill, bulkiness, compression resistance and elasticity properties, while showcasing a texture similar to that of wool. Apparel products manufactured by using the acrylic fibers have a bulkiness and texture similar to those in wool products, while exhibiting easy-care characteristics with an anti-pill property to compensate for drawbacks inherent in wool.

[0027] In the following, the present invention is described in detail.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0028] Acrylic fibers of the present invention have a crimp rate of 15% or higher and bulkiness of 380 cm^3/g or greater.

[0029] A crimp rate of 15% or higher provides fiber products with excellent bulkiness and resilience. From such viewpoints, a crimp rate is preferred to be at least 17%, more preferably at least 20%, and its upper limit is preferred to be no greater than 30% because such a rate can prevent the texture of the fiber products from hardening.

[0030] A degree of bulkiness of 380 cm^3/g or greater provides fiber products with excellent bulkiness and resilience. From such viewpoints, the degree of bulkiness is more preferred to be at least 440 cm^3/g, and its upper limit is preferred to be no greater than 600 cm^3/g, because such a degree of bulkiness prevents the texture of the fiber products from hardening.

[0031] Acrylic fibers related to the present invention are preferred to have a single fiber fineness of 1.7 dtex~6.6 dtex, and the value obtained by multiplying knot strength (cN/dtex) and knot elongation (%) is preferred to be 10~25.

[0032] A single fiber fineness of at least 1.7 dtex provides fiber products with excellent bulkiness and resilience similar to those of wool. A single fiber fineness of no greater than 6.6 dtex prevents fiber products from developing a hardened rough texture. From such viewpoints, the single fiber fineness is more preferred to be 2.2 dtex~5.6 dtex.

[0033] The value obtained by multiplying knot strength (cN/dtex) and knot elongation (%) is preferred to be 10~25, more preferably 15~25 in the acrylic fibers related to the present invention. In the present application, knot strength (cN/dtex) may be referred to as "DKS," and knot elongation (%) as "DKE."

[0034] If the value of DKS×DKE is 10 or greater, problems such as formation of fly waste in post-processing steps (for example spinning), and decrease in yarn strength are unlikely to happen. Moreover, if the value of DKS×DKE is no greater than 25, an excellent anti-pill property is maintained.

[0035] The value of DKS×DKE is used as an index of anti-pill property by those skilled in the art.

[0036] In the acrylic fibers related to the present invention, the number of crimps is preferred to be 20-50 per 2.54 cm, more preferably 25~45 per 2.54 cm.

[0037] It is preferred for acrylic fibers to have at least 20 crimps per 2.54 cm so that fiber products can achieve a texture of elasticity, compression resistance and bulkiness, whereas a number of crimps no greater than 50 per 2.54 cm can prevent the fiber products from hardening.

[0038] Acrylic fibers related to the present invention are preferred to have a side-by-side bicomponent structure of acrylonitrile copolymer (A) with an acrylonitrile unit content of 90 mass%~95 mass% and acrylonitrile copolymer (B) with an acrylonitrile unit content of 93.5 mass%~97.8 mass%, which are laid in an area ratio of 1:3~3:1 at a fiber cross-section perpendicular to the fiber axis.

[0039] When the copolymers (A) and (B) are arranged to have a side-by-side bicomponent structure, fine crimps are formed. Elasticity, rate of crimps and degree of bulkiness tend to be higher.

[0040] If the area ratio is in a range of 1:3~3:1, fiber products exhibit excellent bulkiness and resilience without decreasing spinning stability. From these viewpoints, the area ratio is more preferred to be 2:3~3:2.

[0041] When an acrylic fiber related to the present invention is spun, the side-by-side bicomponent fiber formed with copolymers (A) and (B), which are arranged in an area ratio of 1:3~3:1 at a fiber cross-section perpendicular to the fiber axis direction, is preferred to be contained at 80 mass% or greater in a fiber bundle discharged from one nozzle.

[0042] When a side-by-side bicomponent fiber is contained at 80 mass% or greater, fiber products have excellent bulkiness and resilience. From such viewpoints, the content of a side-by-side bicomponent fiber is more preferred to be 90 mass% or greater.

[0043] The copolymer (A) is preferred to have an acrylonitrile unit content of 90 mass%~95 mass% to maintain physical properties, especially dimensional stability necessary for apparel fibers ,and sufficient shrinkage.

[0044] The copolymer (B) is preferred to have an acrylonitrile unit content of 93.5 mass%~97.8 mass% so that the shrinkage difference with copolymer (A) is easier to be present to provide bulkiness and resilience.

[0045] Acrylic fibers related to the present invention are preferred to have a difference of 2 or greater between the value of acrylonitrile unit content (mass%) in the copolymer (A) and the value of acrylonitrile unit content (mass%) in the copolymer (B).

[0046] If the content difference is 2 or greater, fine crimp is likely to be formed , resulting in a higher crimp rate and improved bulkiness.

[0047] Considering the above, the content difference is more preferred to be 3 or greater.

[0048] In the acrylic fibers related to the present invention, the copolymer (A) is preferred to be formed by copolymerizing 90 mass%~95 mass% of an acrylonitrile unit and 5 mass%~10 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit. The copolymer (B) is preferred to be formed by copolymerizing 93.5 mass%~97.8 mass% of an acrylonitrile unit, 2 mass%~5 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit, and 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit.

[0049] It is preferred to copolymerize 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit in copolymer (B). Dyeability differences between copolymers (A) and (B) will not be too great, and color shades variations are prevented.

[0050] Examples of an unsaturated monomer unit copolymerizable with the acrylonitrile unit are acrylic acid, methacrylic acid and their derivatives, vinyl acetate, acrylamide, methacrylamide, vinyl chloride, vinylidene chloride and the like. Among them, vinyl acetate is preferred due to its availability and cost.

[0051] Examples of a sulfonic acid group-containing monomer unit are sodium vinylbenzenesulfonate, sodium methallylsulfonate, sodium acrylamide methyl sulfonate, sodium p-sulfophenyl methallyl ether and the like. Among them, sodium methallylsulfonate is preferred due to its availability and cost.

[0052] The content of an unsaturated monomer copolymerizable with the acrylonitrile unit in the copolymer (A) is sufficient if it is 5 mass%~10 mass%. When the content is 5 mass% or greater, sufficient shrinkage is maintained, and when the content is 10 mass% or less, physical properties, especially dimensional stability necessary for apparel fibers, are maintained.

[0053] Regarding an unsaturated monomer copolymerizable with the acrylonitrile unit in the copolymer (B), a content of 2 mass%~5 mass% is sufficient. Such a range of content causes a difference in shrinkage between copolymers (A) and (B), and thus provides fibers with excellent bulkiness and resilience. Also, as for a sulfonic acid group-containing monomer unit, a content of 0.2 mass%~1.5 mass% is sufficient. Such a range of content prevents an overly large difference in dyeability between copolymers (A) and (B), and color shades variations are prevented.

[0054] The shrinkage rate of acrylic fibers related to the present invention is preferred to be 2%~7%. A shrinkage rate of 2% or higher makes latent fine crimps to provide bulky texture, whereas a shrinkage rate of 8% or less prevents hardened texture after shrinkage. Considering these features, a shrinkage rate of 4%~7% is more preferred.

[0055] Also, due to a relatively low shrinkage rate, it is easier to dye the fiber without experiencing much trouble. It is also easier to conduct piece fabric dyeing in addition to commonly used yarn dyeing processes such as cheese dyeing and hank dyeing.

[0056] To determine polymerization degrees of copolymers (A) and (B), each of their specific viscosities is preferred to be 0.12~0.21 (when measured at 30°C by dissolving 0.5 grams of a polymer in 100 mL of dimethylformamide). In addition, each of their molecular weights is not limited specifically as long as the value is within a normal range for manufacturing acrylic fibers. It is usually preferred to be 10,000~1,000,000.

[0057] Acrylic fibers related to the present invention are manufactured by the following method, for example.

[0058] Copolymers (A) and (B) are each dissolved in a solvent normally used for spinning acrylic fibers, for example, dimethylacetamide, dimethylformamide, dimethyl sulfoxide, and the like, and are each made into a spinning dope with a solid content of 20 mass%~28 mass%. The viscosity of the spinning dope is preferred to be 50-500 poise (measured at 50°C in accordance with JIS Z8803, using a falling ball viscometer.) A solid content of 20 mass% or greater prevents a decrease in quality of the spinning dope when it is spun out, and a solid content of 28 mass% or less prevents lowered spinnability, caused by insufficient chronological stability.

[0059] Bicomponent fibers related to the present invention are manufactured when two types of spinning dope prepared as above are discharged simultaneously from a spinning nozzle. The spinning method may be selected appropriately from among known methods, but it is preferred to select a method for forming side-by-side bicomponent fibers.

[0060] Acrylic fibers related to the present invention are formed by discharging two types of spinning dope from a side-by-side bicomponent spinning nozzle into a wet-spinning coagulation bath containing a solvent. The solvent concentration

in the spinning bath is preferred to be 35 mass%~60 mass%, more preferably 40 mass%~55 mass%.
When the solvent concentration of the spinning bath is 35 mass%~60 mass%, the value of DKS×DKE will be in a desired range, and an excellent anti-pill property is achieved. In addition, the temperature of the spinning bath is preferred to be 20°C~45°C. If the temperature of the spinning bath is 20°C or higher, it is relatively easy to control the temperature, and if the temperature is 50°C or lower, an efficient spinning process is maintained. Also, when the temperature of the spinning bath is in such a range, the value of DKS×DKE will be within a desired range, and an excellent anti-pill property is thereby achieved.

[0061] Next, primary drawing is conducted in hot water to have a draw ratio of 3~5 times. When the ratio of primary drawing is 3 times or higher, strength and elongation necessary for apparel fibers are maintained. When the draw ratio is 5 times or lower, the value of DKS×DKE will be within a desired range, and an excellent anti-pill property is thereby achieved.

[0062] The draw ratio is more preferred to be 4~5 times.

[0063] To obtain acrylic fibers with excellent crimp and anti-pill properties as targeted in the present invention, it is necessary to conduct relaxation heat treatment in saturated steam pressure at 90 kPa~230 kPa, preferably 95 kPa~170 kPa. By setting the steam pressure at 95 kPa or higher, excellent crimps are obtained, and dyeability is stabilized. By setting the steam pressure at 230 kPa or lower, the value of DKS×DKE will be within a desired range, and an excellent anti-pill property is thereby achieved.

[0064] When fine crimps are apparent in fibers, such fibers are difficult to open due to intense crimps, likely causing trouble during the spinning process. Therefore, it is necessary to conduct secondary drawing so as to set the fine crimps to be temporarily latent. In the present invention, it is sufficient if the draw ratio of secondary drawing is 1.05~1.20 times, preferably 1.05~1.10 times. When a draw ratio of secondary drawing is 1.05 times or higher, the fine crimps are set to be latent. A draw ratio of 1.20 times or lower does not cause excessive shrinkage, and a decrease in dimensional stability and hardened texture after shrinkage are prevented.

<Spun Yarn>

[0065] When a spun yarn is formed to contain the acrylic fiber manufactured as above at 30 mass% or greater, the latent crimps are made apparent by the heat treatment during the dyeing process or the like, and the texture tends to be similar to that of wool. By containing 30 mass% or greater of an acrylic fiber related to the present invention, an excellent anti-pill property is achieved.

[0066] When the spun yarn contains the acrylic fiber at 100 mass%, the obtained knitted fabric exhibits excellent bulkiness and resilience along with excellent anti-pill property.

[0067] Fibers to be blended with the acrylic fiber in spun yarn are not limited specifically. Both synthetic fibers and natural fibers may be used. To enhance the anti-pill property, it is preferred to blend with anti-pill synthetic fibers.

[0068] When natural fibers are blended in spun yarn, the rate of blending natural fibers is preferred to be 70 mass% or less, more preferably 30 mass% or less to prevent a decrease in the anti-pill property.

[0069] The yarn count of the spun yarn related to the present invention is preferred to be 60 or lower in metric count because bulkiness is easier to obtain if the yarn is not too thin.

[0070] The twist coefficient is preferred to be 70~120. A twist coefficient of 70 or higher makes it strong enough to not cause trouble during spinning. A twist coefficient of 120 or lower makes it easier to obtain bulkiness and prevents hardened texture in knitted fabrics.

[0071] A twist coefficient satisfies the relationship in the formula below to determine the number of twists from the yarn count.

$$\text{number of twists (times/meter)} = \text{twist coefficient} \times \sqrt{\text{(yarn count)}}$$

[0072] The spun yarn related to the present invention is preferred to contain a conductive acrylic fiber at 3 mass%~15 mass%. Including a conductive acrylic fiber in such a range suppresses unpleasant sensations caused by static electricity when the fiber product is put on or taken off. The content of conductive acrylic fiber is more preferred to be 5 mass%~12 mass% from the viewpoints of antistatic performance and cost effectiveness.

<Knitted Fabric>

[0073] Knitted fabrics related to the present invention contain the above spun yarn at 50 mass% or greater. To maintain an excellent anti-pill property and easy-care features, using the spun yarn of the present invention at 100% is preferable. However, it is also an option to interknit other spun yarn within a range that does not spoil the knitted texture, anti-pill property and easy-care features. A spun yarn that may be interknitted with the spun yarn of the present invention is not limited specifically; for example, it may be made of 100% natural fiber, 100% synthetic fiber, blended yarn of natural and synthetic fibers or the like. To obtain wool-like texture having an excellent anti-pill property of grade 4 or higher and easy-care features, it is preferred to contain an acrylic fiber related to the present invention at 30 mass% or greater of the entire knitted fabric.

[0074] Furthermore, after being washed 10 times, the dimensional change of the knitted fabric related to the present invention is preferred to be ±3% or lower in both vertical and horizontal directions.

[0075] The present invention is described in details in the following examples.

EXAMPLES

[0076] Physical properties of acrylic fibers are measured by the following methods.

[0077] When fine crimps are still in a latent state, they are made apparent by conducting heat relaxation as a pretreatment for 20 minutes in boiling water. Then, acrylic fibers are dried by blowing air until the moisture content is 3 mass% or less, and opened until almost no fiber adhesion is observed.

(Single Fiber Fineness)

[0078] The fineness was determined in accordance with JIS L 1015 (vibration testing method). Testing was conducted on 50 fiber strands and the average value was used.

(Boiling Water Shrinkage Rate)

[0079] The hot water shrinkage rate was determined in accordance with JIS L 1015. Shrinking treatment was conducted in boiling water.

(Bulkiness)

[0080] An acrylic fiber of 1.5 grams, opened until almost no fiber adhesion is observed and divided into batches of approximately 0.15 grams each, is softly dropped batch by batch into a 1000 mL graduated cylinder with a bottom area of 33.17 cm^2 to fill the cylinder homogenously without creating any gap. Then, a 6-gram load disc is lowered into the cylinder to determine the volume, "v" (cm^3), occupied by the acrylic fiber two minutes later. The degree of bulkiness is calculated by the following formula:

$$\text{degree of bulkiness (cm}^3\text{/g)} = v \div 1.5$$

[0081] The above procedure is conducted on 3 samples and the average value was entered as the result.

(Crimp Rate)

[0082] The crimp rate was determined in accordance with JIS L 1015 (2010).

(Number of Crimps)

[0083] The number of crimps was determined in accordance with JIS L 1015 (2010).

(Value Obtained by Multiplying Knot Strength and Knot Elongation (DKS×DKE))

[0084] The knot strength was determined in accordance with JIS L 1015 (2010) (testing under normal conditions). The elongation rate at that time was determined as knot elongation, and the multiplication product was calculated.

(Anti-pill Property)

[0085] The anti-pill property was tested in accordance with pilling test method "A" specified in JIS L 1076 (2012) (ICI-type tester, running time: five hours), and classified as grades 1~5 based on the appearance of the fabric after testing.

(Dimensional Change Rate in Knitted Fabric)

[0086] In the center of 30 cm×30 cm fabric test piece with a 20 cm square marking was washed 10 times according to the method 103 (hanging method) specified in JIS L 0217. The length of each side was measured after washing, and the dimensional change rate was calculated by the following formulas.

$$\text{vertical dimensional change rate} = (20 - (\text{lengths of two vertical sides after washing} / 2)) / 20 \times 100 \quad (\%)$$

$$\text{horizontal dimensional change rate} = (20 - (\text{lengths of two horizontal sides after washing} / 2)) / 20 \times 100 \quad (\%)$$

(Texture)

[0087] Ten people were assigned to check the texture of a knitted fabric by touch, and evaluated it based on the following criteria:

[+ +]: all 10 people evaluated the texture to be excellent, having the same level of bulkiness and resilience as that of wool;
[+]: 5~9 people evaluated the texture to be excellent; and
[-]: 4 or fewer people evaluated the texture to be excellent.

[Example 1]

[0088] Spinning dopes were prepared by respectively dissolving copolymers (A) and (B) specified in Table 1 in a dimethylacetamide (DMAc) solvent to have a solid content of 24 mass%. In a 40°C wet-spinning bath consisting of dimethylacetamide (DMAc) and water with a solvent concentration of 55%, the spinning dopes were discharged at a ratio of 50 mass% of copolymer (A) and 50 mass% of copolymer (B) from a bicomponent spinning nozzle and coagulated to be side-by-side. Next, after primary drawing was conducted in hot water at a draw ratio of 4.5 times, an oil agent was applied, dried by using a 150°C hot roller, and then the fiber was crimped. Then, relaxation heat treatment was conducted on the fiber bundle under saturated steam pressure of 160 kPa to make fine crimps apparent. The fine crimps were set to be temporarily latent by conducting secondary drawing at a draw ratio of 1.1 times, and crimped again for spinning. The fiber was then cut into 51 mm-long pieces. A fiber with a single fiber fineness of 2.2 dtex was obtained. The fiber was spun to have a metric count of 1/30, and the spun yarn was formed into a tubular knitted fabric using an 18G knitting machine. The knitted fabric was dyed with a cationic dye (Cathilon Blue CD-RLH, made by Hodogaya Chemical Co., Ltd.). The results are show in Table 1.

[Example 2]

[0089] A fiber was obtained through the same process as that employed in Example 1 except that the solvent concentration, the spinning bath temperature and the single fiber fineness were changed to those specified in Table 1. The fiber was spun, knitted and dyed in the same way as in Example 1.The results are shown in Table 1.

[Example 3]

[0090] A fiber was obtained through the same process as that employed in Example 1 except that the composition of copolymer (A) and single fiber fineness were changed to those specified in Table 1. The fiber was spun, knitted and dyed in the same way as in Example 1.The results are shown in Table 1.

[Comparative Example 1]

[0091] A fiber was obtained through the same process as that employed in Example 3 except that only the copolymer (A) of Example 3 was used. The fiber was spun, knitted and dyed in the same way as in Example 1. The results are shown in Table 1.

[Comparative Example 2]

[0092] A fiber was obtained through the same process as that employed in Example 1 except that only the copolymer (B) of Example 1 was used and the solvent concentration was set at 30 mass%. The fiber was spun, knitted and dyed in the same way as in Example 1. The results are shown in Table 1.

[Comparative Example 3]

[0093] The copolymers (A) and (B) of Example 1 were made into spinning dopes respectively and homogenously mixed. The mixture was then discharged from a spinning nozzle and coagulated so as to obtain a heterogeneous polymer composite acrylic fiber. The fiber was spun, knitted and dyed in the same way as in Example 1. The results are shown in Table 1.

[Comparative Example 4]

[0094] A fiber was obtained through the same process as that employed in Example 1 except that the solvent concentration was changed as specified in Table 1. The fiber was spun, knitted and dyed in the same way as in Example 1. The results are shown in Table 1.

[0095] Note that conditions set in Comparative Example 4 correspond to those described in Prior Art Literature 4 (JP S59-192717A).

Table 1

	Copolymer (A)	Copolymer (B)	Spinning bath conditions (solvent concentration / temp)	Shrinkage rate in boiling water (%)	Single fiber fineness (dtex)	Side-by-side ratio (%)	Bulkiness (cm^3/g)	Number of crimps (per 2.54cm)	Crimp elongation rate (%)	DKS×DKE	Anti-pill grade	Texture
Example 1	AN: 91% AV: 9%	AN: 95% AV: 4.5% MS: 0.5%	55% / 40°C	6.5	2.2	93.5	400	37.2	20.7	13.9	4.5	++
Example 2	AN: 91% AV: 9%	AN: 95% AV: 4.5% MS: 0.5%	40% / 30°C	5.8	5.6	92.3	485	32.5	17.5	22.5	4	++
Example 3	AN: 93% AV: 7%	AN: 95% AV: 4.5% MS: 0.5%	55% / 40°C	4.5	5.6	89.6	440	25.8	17.1	14.1	4.5	++
Comp. Example 1	AN: 93% AV: 7%	-	55% / 40°C	1.2	5.6	0	265	8.7	10.6	35.9	3	-
Comp. Example 2	-	AN: 95% AV: 4.5% MS: 0.5%	30% / 40°C	0.8	2.2	0	220	10.1	11.5	18.5	4	-
Comp. Example 3	AN: 91% AV: 9%	AN: 95% AV: 4.5% MS: 0.5%	55% / 40°C	3.8	5.6	65.5	350	16.5	13.9	28.8	3.5	+
Comp. Example 4	AN: 91% AV: 9%	AN: 95% AV: 4.5% MS: 0.5%	30% / 40°C	12.6	2.2	90.5	305	20.4	14.8	18.7	3.5	-

AN: acrylonitrile, AV: vinyl acetate, MS: sodium methallyl sulfonate

[Example 4]

[0096] A spun yarn with a metric count of 1/30 was prepared by blending 70 mass% of the acrylic fiber obtained in Example 1 and 30 mass% of wool (66's). The spun yarn underwent a boiling water treatment at 100°C×30 minutes by using a cheese dyeing machine. Then, two strands of the spun yarn were aligned and put onto a 12G flat knitting machine to form a knitted fabric.

[0097] The knitted fabric exhibited wool-like texture, showed hardly any dimensional change after washing, and had an excellent anti-pill grade of 4.0. The results are shown in Table 2.

[Example 5]

[0098] A spun yarn with a metric count of 1/30 was prepared by blending 40 mass% of the acrylic fiber obtained in Example 1, 30 mass% of an anti-pill acrylic fiber with a single fiber fineness of 2.2 dtex (item type: H616, made by Mitsubishi Rayon), and 30 mass% of wool (66's). After the spun yarn underwent a boiling water treatment by using a cheese dyeing machine the same as in Example 4, the spun yarn was put onto a 12G flat knitting machine to form a knitted fabric.

[0099] As shown in Table 2, the knitted fabric exhibited a wool-like texture, showed hardly any dimensional change after washing, and had an excellent anti-pill grade of 4.5. The results are shown in Table 2.

[Example 6]

[0100] A spun yarn with a metric count of 1/30 was prepared by blending 90 mass% of the acrylic fiber obtained in Example 1, and 10 mass% of a conductive acrylic fiber with a single fiber fineness of 3.3 dtex (item type: TB10, made by Mitsubishi Rayon). After the spun yarn underwent a boiling water treatment by using a cheese dyeing machine the same as in Example 4, the spun yarn was put onto a 12G flat knitting machine to form a knitted fabric.

[0101] As shown in Table 2, the knitted fabric exhibited wool-like texture, showed hardly any dimensional change after washing, and had an excellent anti-pill grade of 4.5. The results are shown in Table 2.

[Comparative Example 5]

[0102] A spun yarn with a metric count of 1/30 was prepared to have a 100% wool (66's) content. After the spun yarn underwent a boiling water treatment by using a cheese dyeing machine the same as in Example 4. Then, two strands of the spun yarn were aligned and put onto a 12G flat knitting machine to form a knitted fabric.

[0103] The knitted fabric exhibited excellent bulkiness and resilience. However, as shown in Table 2, a significant dimensional change was observed after washing, and it had low anti-pill grade of 2. The results are shown in Table 2.

Table 2

	Composition of spun yarn	Blending ratio	Anti-pill grade	Dimensional change rate (vertical / horizontal)	Texture
Example 4	acrylic fiber of Example 1 wool	70% 30%	4	-1.9% /-1.2%	++
Example 5	acrylic fiber of Example 1 anti-pilling acrylic fiber wool	40% 30% 30%	4.5	-1.2% /-0.9%	++
Example 6	acrylic fiber of Example 1 conductive acrylic fiber	90% 10%	4.5	-0.9% /0.5%	++
Comp. Example 5	wool	100%	2	-5.2% /-5.8%	++
		30 or higher	4 or higher	±3 or lower	
* "_" in dimensional change rate column indicates shrinkage					

INDUSTRIAL APPLICABILITY

[0104] The acrylic fibers related to the present invention have excellent crimp and anti-pill properties, and are preferable for apparel such as sweaters and jackets along with handcraft yarn.

Claims

1. An acrylic fiber, wherein
a crimp rate is 15% or higher measured in accordance with JIS L1015 (2010); and
bulkiness measured by the method below is 380 cm^3/g or greater.
(Method for Measuring Bulkiness)

    (1) collect approximately 10 grams of the acrylic fiber cut into 51 mm-long pieces, and open the fiber until almost no fiber adhesion is observed;
    (2) collect 1.5 grams of the opened acrylic fiber;
    (3) divide the collected fiber into batches of approximately 0.15 grams each, and softly drop each batch into a 1000 mL graduated cylinder with a bottom area of 33.17 cm^2 to fill the cylinder homogenously without creating any gap;
    (4) lower a 6-gram load disc into the cylinder, and measure the volume, "v" cm^3, occupied by the acrylic fiber two minutes later; and
    (5) calculate the degree of bulkiness by the following formula:

$$\text{degree of bulkiness } (cm^3/g) = v \div 1.5$$

    The above procedure is conducted on three samples and their average value is entered as the result.

2. The acrylic fiber according to Claim 1, wherein the single fiber fineness is set at 1.7 dtex~6.6 dtex, and the value obtained by multiplying knot strength (cN/dtex) and knot elongation (%) is set to be 10~25.

3. The acrylic fiber according to Claim 1 or 2, wherein the number of crimps is set at 20 per 2.54 cm~50 per 2.54 cm.

4. The acrylic fiber according to any of Claims 1~3, wherein an acrylonitrile copolymer (A) with an acrylonitrile unit content of 90 mass%~95 mass% and an acrylonitrile copolymer (B) with an acrylonitrile unit content of 93.5 mass%~97.8 mass% are arranged to form a side-by-side bicomponent structure with an area ratio of 1:3~3:1 at a fiber cross-section perpendicular to the fiber axis direction.

5. The acrylic fiber according to Claim 4, wherein the difference between the value of acrylonitrile unit content (mass%) in the copolymer (A) and the value of acrylonitrile unit content (mass%) in the copolymer (B) is set to be 2 or greater.

6. The acrylic fiber according to Claim 4 or 5, wherein the copolymer (A) is formed by copolymerizing 90 mass%~95 mass% of an acrylonitrile unit and 5 mass%~10 mass% of an unsaturated monomer copolymerizable with the acrylonitrile unit, and the copolymer (B) is formed by copolymerizing 93.5 mass%~97.8 mass% of an acrylonitrile unit, 2 mass%~5 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit, and 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit.

7. The acrylic fiber according to Claim 6, wherein the monomer unit contained as an unsaturated monomer unit copolymerizable with the acrylonitrile in the copolymers (A) and (B) is a vinyl acetate unit, and the sulfonic acid group-containing monomer unit is a sodium methallyl sulfonate unit.

8. The acrylic fiber according to any of Claims 1~7, wherein the shrinkage rate is set at 2%~7%.

9. A method for manufacturing an acrylic fiber, comprising:

    preparing a spinning dope (A') by dissolving a copolymer (A) with an acrylonitrile unit content of 90 mass%~95 mass% in a solvent;

preparing a spinning dope (B') by dissolving a copolymer (B) with an acrylonitrile unit content of 93.5 mass%~97.8 mass% in a solvent; and
forming a side-by-side bicomponent fiber by discharging spinning dopes (A') and (B') from a nozzle into a coagulation bath with a solvent concentration of 35%~60%,
wherein the difference between the value of acrylonitrile unit content (mass%) in the copolymer (A) and the value of acrylonitrile unit content (mass%) in the copolymer (B) is set to be 2 or greater.

10. The method for manufacturing an acrylic fiber according to Claim 9, wherein the copolymer (A) comprises 90 mass%~95 mass% of an acrylonitrile unit and 5 mass%~10 mass% of an unsaturated monomer copolymerizable with the acrylonitrile unit, and the copolymer (B) comprises 93.5 mass%~97.8 mass% of an acrylonitrile unit, 2 mass%~5 mass% of an unsaturated monomer unit copolymerizable with the acrylonitrile unit, and 0.2 mass%~1.5 mass% of a sulfonic acid group-containing monomer unit.

11. The method for manufacturing an acrylic fiber according to Claim 9 or 10, wherein the unsaturated monomer copolymerizable with the acrylonitrile unit in the copolymers is a vinyl acetate, and the sulfonic acid group-containing monomer is a sodium methallyl sulfonate.

12. The method for manufacturing an acrylic fiber according to any of Claims 9~11, further comprising a step for forming a side-by-side bicomponent fiber by discharging spinning dope (A') and spinning dope (B') from a nozzle into a spinning bath;
a step for conducting primary drawing at a draw ratio of 3.0~5.0 times;
a step for conducting relaxation heat treatment under saturated steam of 90 kPa~230 kPa; and
a step for conducting secondary drawing at a draw ratio of 1.05~1.20 times.

13. A spun yarn, comprising:
the acrylic fiber according to any of Claims 1-8 at 30 mass% or greater.

14. The spun yarn according to Claim 13, further comprising a conductive acrylic fiber in a range of 3 mass%~15 mass%.

15. A knitted fabric, comprising:

the spun yarn according to Claim 13 or 14 at 50 mass% or greater,
wherein the anti-pill grade is set at four or higher.

16. The knitted fabric according to Claim 15, wherein the dimensional change after washing 10 times is set to be ±3% or lower in both vertical and horizontal directions.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/062863

A. CLASSIFICATION OF SUBJECT MATTER
D01F8/08(2006.01)i, *D02J1/22*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01F6/00-9/04, D02G1/00-3/48, D02J1/00-13/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 54-68417 A (Mitsubishi Rayon Co., Ltd.), 01 June 1979 (01.06.1979), claims; page 4, lower left column, line 18 to lower right column, line 2; examples 1, 3 & GB 2007587 A	1,3-7,9-11, 13-16 2,8,12
Y A	JP 10-266019 A (Mitsubishi Rayon Co., Ltd.), 06 October 1998 (06.10.1998), claims; paragraphs [0026] to [0034]; tables 1 to 3 (Family: none)	1-15 16
Y A	JP 2004-44026 A (Mitsubishi Rayon Co., Ltd.), 12 February 2004 (12.02.2004), claims; paragraphs [0015], [0031] (Family: none)	1-15 16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 30 July 2015 (30.07.15)	Date of mailing of the international search report 11 August 2015 (11.08.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/062863

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55-112316 A (Rhone Poulenc Textile), 29 August 1980 (29.08.1980), claims; page 4, lower right column, lines 2 to 8; page 4, lower right column, line 16 to page 5, upper left column, line 9 & US 4297412 A & GB 2036121 A & DE 2948298 A & FR 2442901 A & BE 880336 A & MX 159140 A & NL 7908290 A & ES 486362 A & BR 7907792 A & DD 147556 C & IT 1126462 A & LU 81941 A & DD 147556 A & IT 1126462 B & IT 7927769 A0	1-16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/062863

The invention in claim 1 includes a specified feature wherein the acrylic fibers have a percentage crimp of 15% or greater and a bulkiness, as measured by a given method, of 380 cm^3/g or greater, but the makeup and structure thereof are unspecified. The invention hence involves acrylic fibers having any structure.

The description indicates that the present invention can address the problem of providing acrylic fibers that have excellent crimping properties and have crimps excellent in terms of antipilling property.

However, the description presents examples in which acrylic fibers formed only from a composition composed of AN and AV and acrylic fibers formed only from AN, AV, and MS are inferior in crimping property and antipilling property.

Generally, it is common technical knowledge that the crimping properties of composite fibers composed of two components result from a difference in makeup in the fibers.

As such, the modes disclosed in the meaning of PCT Article 5 are limited to acrylic fibers of a side-by-side type obtained by compositing acrylic compositions that differ in makeup. The invention in claim 1, which involves acrylic fibers having any structure, and in claims 2-4, which depend on claim 1, lacks a support in the meaning of PCT Article 6.

This international search was made only for the acrylic fibers of a side-by-side type obtained by compositing acrylic compositions that differ in makeup.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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- JP H07197323 A **[0005] [0008]**
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- JP 63190019 A **[0008]**
- JP 59192717 A **[0008]**