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(54) **GLOSSY PILLING-RESISTANT ACRYLIC FIBER, METHOD FOR PRODUCING SAME, AND SPUN YARN AND KNITTED FABRIC INCLUDING SAID ACRYLIC FIBER**

(57) The present invention provides: an acrylic fiber having a fineness of 0.5 to 3.5 dtex and having excellent gloss, pilling resistance, and texture; a method for producing said acrylic fiber; and a spun yarn and a knitted fabric containing said acrylic fiber. Provided is an acrylic fiber having a filament fineness of 0.5 to 3.5 dtex, wherein the product K of the value of knot strength (cN/dtex) and the value of knot elongation (%) is from 8 to 30 inclusive, and the number of recesses having a depth of 0.1 μ m or greater is 10 or fewer. In this method for producing said acrylic fiber, an acrylonitrile-based copolymer containing 92 to 96.8 mass% of an acrylonitrile unit, 2 to 6 mass% of a vinyl-based monomer unit, and 0.2 to 2.0 mass% of a sulfonic acid group-containing vinyl monomer unit is

dissolved in an organic solvent, to prepare a spinning dope. A coagulated fiber bundle is formed by discharging the spinning dope from discharge holes into a coagulation bath having a solvent concentration of 40 to 60 mass% and a temperature of 35 to 50 °C. The coagulated fiber bundle is drawn in hot water at a draw ratio of 2 to 3.8 times, an oil agent is applied, the fiber bundle is dried, and then the fiber bundle is drawn under dry heat at a draw ratio of 1.2 to 3 times.

The product S of said draw ratio in hot water and said draw ratio under dry heat is from 4 to 6 times. Further, the fiber bundle is subjected to a thermal relaxation treatment.

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Description

Technical Field

5 **[0001]** The present invention relates to a pilling-resistant acrylic fiber that exhibits excellent gloss and soft texture, to a method for producing the acrylic fiber, and to a spun yarn and a knitted fabric that contain the acrylic fiber.

Background Art

10 **[0002]** Acrylic fibers have excellent characteristics such as soft texture, heat retention capability, shape stability, weather resistance and dyeability, and are widely used in apparel and interior applications the same as other synthetic fibers such as nylon and polyester fibers. However, when fiber products made of acrylic fibers are in use, pilling tends to occur. Accordingly, the appearance and texture of knitted fabrics are significantly lowered and their commercial value is reduced. Therefore, technological development has been sought for a so-called pilling-resistant acrylic fiber in which pilling rarely occurs.

15 **[0003]** Meanwhile, to achieve softer texture in apparel products, degrees of fiber fineness have become even smaller recently, and development of products using fibers with a smaller fiber fineness is in progress. Since pilling is more likely to occur when the degree of fiber fineness is smaller, demand for improved pilling-resistance properties is on the rise.

20 **[0004]** In addition to improving the texture of apparel products, it has been proposed to enhance gloss to express high quality similar to that of silk. For example, Patent Literature 1 (JP H11-222716A) proposes an acrylic fiber having a large single fiber fineness of 6~34 dtex with a flat cross section, which is set to have enhanced gloss by forming smooth portions of at least a certain size on the fiber surface. Patent Literature 2 (JP2012-36512A) proposes a glossy acrylic fiber which is set to have a circular, or an elliptical but almost circular, fiber cross section and to have a recessed curvature on the edge of the cross section. Those fibers are each set to have a large single fiber fineness of 6 dtex or greater, while having a flat or broad-bean shaped cross-section.

25 **[0005]** Moreover, Patent Literature 3 (JP2006-176937A) and Patent Literature 4 (JP2008-38309A) each propose a yarn containing a pilling-resistant acrylic fiber with a smaller fiber fineness along with its manufacturing method. However, none of such smaller-fineness acrylic fibers has achieved both pilling-resistance and glossy properties.

30 **[0006]** Patent Literature 5 (JP2011-12363A) proposes a carbon-fiber-precursor acrylic fiber which is structured to have fewer irregularities on fiber surfaces and to have a single fiber fineness of 1.1 dtex. However, since the strength of the carbon-fiber-precursor acrylic fiber is enhanced, the knot strength and knot elongation are smaller. Accordingly, the carbon-fiber-precursor acrylic fiber tends to break during the spinning process and thus is not suitable for forming yarn.

CITATION LIST

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PATENT LITERATURE

[0007]

40 Patent Literature 1: JP H11-222716A

Patent Literature 2: JP2012-36512A

Patent Literature 3: JP2006-176937A

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Patent Literature 4: JP2008-38309A

Patent Literature 5: JP2011-12363A

50 SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

55 **[0008]** Considering the above, the objective of the present invention is to provide an acrylic fiber with a fiber fineness of 0.5~3.5 dtex, which is set to exhibit excellent gloss and pilling resistance while having soft texture, and to provide its manufacturing method. The present invention also provides a spun yarn and knitted product containing such an acrylic fiber.

SOLUTIONS TO THE PROBLEMS

[0009] An acrylic fiber related to the present invention is set to have a center-line mean roughness (Ra) of 3 nm to 12 nm on a single fiber surface, and a single fiber fineness of 0.5 dtex to 3.5 dtex.

[0010] The acrylic fiber related to the present invention is preferred to have a product (K) of 10 to 30 obtained by multiplying the value of knot strength (cN/dtex) and the value of knot elongation (%).

[0011] The acrylic fiber related to the present invention is structured to have a center-line mean roughness (Ra) of 3 nm to 12 nm on a single fiber surface, and to have a product (K) of 10 to 30 obtained by multiplying the value of knot strength (cN/dtex) and the value of knot elongation (%).

[0012] The acrylic fiber related to the present invention is preferred to have a single fiber fineness of 0.5 dtex to 3.5 dtex.

[0013] On the surface of an acrylic fiber related to the present invention, it is preferred that a maximum height (Ry) of the profile be set at 40 nm to 150 nm, a 30-point mean roughness (Rz) at 20 nm to 80 nm, and a distance (S) at 800 nm to 1100 nm between peaks of convex portions.

[0014] Regarding the acrylic fiber related to the present invention, the number of recesses of 0.1 μm or deeper that are present on the surface of a single fiber is preferred to be no greater than 10 when counted in the cross section perpendicular to the fiber axis.

[0015] The acrylic fiber related to the present invention is preferred to contain 92 mass% to 96.8 mass% of an acrylonitrile unit, 2 mass% to 6 mass% of a vinyl monomer unit, and 0.2 mass% to 2.0 mass% of a sulfonic acid group-containing vinyl monomer unit, and to have a single fiber tensile strength of 1.8 cN/dtex to 3.0 cN/dtex, a single fiber knot strength of 1.0 cN/dtex to 1.8 cN/dtex, and a single fiber knot elongation of 8% to 12%.

[0016] A method for producing acrylic fiber related to the present invention includes the following steps: forming a spinning dope by dissolving in an organic solvent an acrylonitrile-based copolymer that contains 92 mass% to 96.8 mass% of an acrylonitrile unit and 0.2 mass% to 2.0 mass% of a sulfonic acid group-containing vinyl monomer unit; forming a coagulated fiber bundle by discharging the spinning dope in a 35°C to 50°C coagulation bath through multiple discharge ports of a spinning nozzle at a jet-stretch ratio of 0.4 to 2.2 times; stretching the coagulated fiber bundle in 80°C to 98°C hot water at a stretch ratio of 2 to 3.8 times; applying oil to the fiber bundle and drying thereafter; stretching the fiber bundle by applying dry heat to have a fiber temperature of 150°C to 170°C at a stretch ratio of 1.2 to 3 times; and setting the value of a product (S) to be 4 to 6 when obtained by multiplying the hot-water stretch ratio and the dry-heat stretch ratio.

[0017] In the method for producing the acrylic fiber related to the present invention, it is preferred that the acrylonitrile-based copolymer further contain 2 mass% to 6 mass% of a vinyl monomer unit, the solvent concentration of the coagulation bath be 40 mass% to 60 mass%, and a thermal relaxation process be conducted after hot-dry stretching.

[0018] In the method for producing an acrylic fiber related to the present invention, the thermal relaxation process is preferred to have an annealing temperature of 120°C to 135°C and a fiber relaxation ratio of 5% to 20%.

[0019] A spun yarn related to the present invention contains the acrylic fiber at 40 mass% or greater, and has a cotton count of 40 to 70.

[0020] The spun yarn is preferred to contain a cellulose-based fiber at 10 mass% to 40 mass%.

[0021] A knitted fabric related to the present invention contains the spun yarn at 40 mass% or greater, has a basis weight of 150 g/m² to 230 g/m², and the pilling resistant property is rated at 4 or higher.

[0022] The knitted fabric related to the present invention is preferred to exhibit a heat-retention rate of 15% to 50%.

EFFECTS OF THE INVENTION

[0023] According to the present invention, an acrylic fiber is provided to be used in inner apparel applications, especially in applications for undergarments. Using the acrylic fiber, such fiber products exhibit a soft texture while showing high-grade gloss and excellent pilling resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024]

FIG. 1 is a cross-sectional view of a single fiber surface, showing a center-line mean roughness (Ra);
 FIG. 2 is a cross-sectional view of a single fiber surface, showing a maximum height (Ry) of the profile;
 FIG. 3 is a cross-sectional view of a single fiber surface, showing a 30-point mean roughness (Rz); and
 FIG. 4 is a cross-sectional view of a single fiber surface, showing a distance (S) between peaks of convex portions.

DETAILED DESCRIPTION OF THE EMBODIMENTS

<Polymer Composition of Acrylic Fiber>

[0025] In the acrylic fiber related to the present invention, the copolymer is preferred to be formed by copolymerizing 92 mass% to 96.8 mass% of an acrylonitrile unit. When the copolymerization ratio of an acrylonitrile unit is 92 mass% or greater, it is easier to obtain the fiber strength required for forming apparel fibers.

[0026] From the above viewpoint, the ratio of an acrylonitrile unit in a copolymer is more preferred to be 95 mass% or greater.

[0027] In addition, when the copolymerization ratio of an acrylonitrile unit is 96.8 mass% or lower, excellent dyeability, fiber strength and elongation are expected to be achieved.

[0028] In the copolymer, the ratio of a vinyl monomer unit copolymerizable with acrylonitrile is preferred to be set at 3.0 mass% to 6.0 mass%. When the polymerization ratio of a vinyl monomer unit is set in such a range, sufficient physical characteristics and dyeability necessary for knitted products are achieved.

[0029] Moreover, the copolymerization ratio of a sulfonic acid group-containing vinyl monomer unit in the copolymer is preferred to be set at 0.2 mass% to 2.0 mass%. When the copolymerization ratio of the sulfonic acid group containing-vinyl monomer is 0.2 mass% or greater, excellent dyeability is expected to be achieved, and when the ratio is 2.0 mass% or lower, an increase in cost is suppressed.

[0030] Examples of vinyl monomers copolymerizable with acrylonitrile are methyl acrylate, methyl methacrylate, esters of (meth)acrylic acids, vinyl acetate, styrene, acrylamide, 2-hydroxyethyl methacrylate, glycidyl methacrylate and the like. Preferred examples of sulfonic acid group-containing vinyl monomers are allyl sulfonic acid, methallylsulfonic acid, styrene sulfonic acid, vinylsulfonic acid, isoprene sulfonic acid, 2-acrylamide-2-methylpropanesulfonic acid, their metal salts and amine salts, and so on. However, those listed above are not the only option to be used in the embodiments of the present invention. To prepare acrylonitrile-based copolymers, suspension polymerization carried out in an aqueous medium is preferred.

<Single Fiber Fineness of Acrylic Fiber>

[0031] The single fiber fineness of acrylic fiber related to the present invention is preferred to be set at 0.5 dtex to 3.5 dtex. Generally, the finer the fiber is, the lower the color sharpness is when dyed. However, the acrylic fiber related to the present invention exhibits color sharpness even though its fineness is 1.2 dtex or lower. A single fiber fineness of 0.5 dtex or higher contributes to achieving the effects of color sharpness, while a single fiber fineness of 3.5 dtex or lower makes it easier to obtain a soft texture when the fiber is formed into a knitted fabric. Considering those viewpoints, the single fiber fineness is more preferred to be 0.7 dtex to 2.0 dtex, even more preferably 0.8 dtex to 1.2 dtex.

<Product (K)>

[0032] The acrylic fiber related to the present invention is preferred to have a product (K) of 10 to 30 obtained by multiplying the value of knot strength (cN/dtex) and the value of knot elongation (%). The value of product (K) is used as an index of pilling resistance by people skilled in the art.

[0033] When the product (K) is 10 or greater, fly waste caused by finely broken single fibers is less likely to occur during a spinning process. When the product (K) is 30 or lower, excellent pilling resistance is achieved.

[0034] From the above viewpoints, the product (K) is more preferred to be 12 to 25, even more preferably 14 to 20.

<Center-line Mean Roughness (Ra) on Single Fiber Surface>

[0035] The acrylic fiber related to the present invention has fewer recesses on the surface, resulting in excellent gloss. The center-line mean roughness (Ra) on a single fiber surface is 3 nm to 12 nm. An (Ra) of 3 nm or greater is preferred since the fiber is unlikely to slip because of the friction generated between the roll and the fiber during spinning. An (Ra) of 12 nm or less is preferred since it is easier to express gloss. From such viewpoints, the (Ra) is more preferred to be 4 nm to 10 nm, even more preferably 5 nm to 9 nm.

<Maximum Height (Ry) of the Profile, 30-point Mean Roughness (Rz), Distance (S) between Peaks of Convex Portions>

[0036] Regarding the surface of a single acrylic fiber related to the present invention, it is preferred that a maximum height (Ry) of the profile be set at 40 nm to 150 nm, a 30-point mean roughness (Rz) at 20 nm to 80 nm, and a distance (S) between peaks of convex portions at 800 nm to 1100 nm.

[0037] An (Ry) of 40 nm or greater is preferred since friction is generated between fibers to improve processability in

a spinning process, while an (Ry) of 150 nm or less is preferred since regular reflection is expected to occur. From such viewpoints, the (Ry) is more preferred to be 50 nm to 100 nm, even more preferably 55 nm to 90 nm.

[0038] An (Rz) of 20 nm or greater is preferred since processability during spinning is better, and an (Rz) of 80 nm is preferable since the gloss is enhanced. From such viewpoints, the (Rz) is more preferred to be 30 nm to 65 nm, even more preferably 35 nm to 50 nm.

[0039] An (S) of 800 nm or greater is preferred in view of fiber spinnability, while an (S) of 1100 nm or less is preferred since irregularities are fewer on a fiber surface and random reflection is less likely to occur. From such viewpoints, the (S) is more preferred to be 900 nm to 1000 nm.

<Number of Recesses on Fiber Surface>

[0040] Furthermore, regarding the acrylic fiber related to the present invention, the number of recesses of 0.1 μm or deeper is preferred to be 10 or fewer when counted on the cross section of a single fiber cut in a direction perpendicular to the fiber axis. When observed in a cross section perpendicular to the fiber axis using a later-described method, the number of recesses of 0.1 μm or deeper is preferred to be no greater than 10 on a fiber surface, since gloss is enhanced. When recesses of 0.1 μm or deeper are present on a fiber surface, light reflects randomly. Thus, when the number of recesses of 0.1 μm or deeper is 10 or fewer on the acrylic fiber surface related to the present invention, gloss is enhanced since random reflections are less likely to occur, and a decrease in gloss is suppressed. From such viewpoints, the number of recesses of 0.1 μm or deeper is more preferred to be 5 or fewer. To reduce irregularities on a fiber surface, it is effective to lower the stretch ratio when the coagulated fiber is stretched by wet heat.

[0041] The tensile strength of a single acrylic fiber related to the present invention is preferred to be 1.8 cN/dtex or greater, more preferably 2.0 cN/dtex or greater, considering processability during a spinning process or the like. The upper limit of the tensile strength is not particularly specified, and 3.0 cN/dtex is sufficient.

[0042] The knot strength of a single acrylic fiber related to the present invention is preferred to be 1.0 cN/dtex to 1.8 cN/dtex.

[0043] When the knot strength is 1.0 cN/dtex or greater, fly waste is less likely to occur during a spinning process and processability is excellent. When the knot strength is 1.8 cN/dtex or less, pilling resistance is improved. From such viewpoints, the knot strength is more preferred to be 1.2 cN/dtex to 1.6 cN/dtex, even more preferably 1.4 cN/dtex to 1.5 cN/dtex.

[0044] To enhance pilling resistance, the knot elongation of a single acrylic fiber related to the present invention is preferred to be at least 8% but no greater than 20%, more preferably no greater than 15%.

<Method for Producing Acrylic Fiber>

[0045] The acrylic fiber related to the present invention is produced by wet spinning or dry wet spinning. Wet spinning is preferred in terms of productivity and cost performance.

<Composition of Copolymer>

[0046] In the method for producing acrylic fiber related to the present invention, it is preferred to use an acrylonitrile-based copolymer that contains 92 mass% to 96.8 mass% of an acrylonitrile unit, 2 mass% to 6 mass% of a vinyl monomer unit and 0.2 mass% to 2.0 mass% of a sulfonic acid group containing-vinyl monomer unit.

[0047] A spinning dope is formed by dissolving the acrylonitrile-based copolymer in an organic solvent.

[0048] The spinning dope is preferred to contain 15 mass% to 30 mass% of the acrylonitrile-based copolymer and 70 mass% to 85 mass% of an organic solvent. The acrylonitrile-based copolymer is preferred to have a concentration of 15 mass% to 30 mass% in the spinning dope. Such a concentration is preferred to achieve excellent spinnability, since yarn breakage is less likely to occur and productivity is high. The copolymer concentration is more preferred to be 18% to 25% in view of spinnability.

[0049] The solvent is required to be an organic solvent, for example, dimethylacetamide, dimethylformamide, dimethyl sulfoxide and the like. Among them, dimethylacetamide is preferred from the viewpoint of productivity in fiber manufacturing and balancing the color sharpness and anti-pilling properties of the obtained pilling-resistant acrylic fiber.

[0050] A temperature of 40°C or higher is preferred for dissolving the acrylonitrile-based copolymer in an organic solvent, since fewer undissolved components will remain, thus prolonging the life span of a filter medium in a filtration system such as a filter press while preventing a decrease in thread-forming properties. On the other hand, a dissolving temperature of 95°C or lower is preferred since the copolymer is less likely to undergo color change.

[0051] The temperature of the spinning dope after the acrylonitrile-based copolymer is dissolved in an organic solvent is preferred to be 40°C to 95°C. If the temperature is set at 40°C to 95°C, an increase in nozzle pressure due to low viscosity, gelation of the spinning dope or the like is prevented, thus optimizing thread-forming properties and spinnability.

<Temperature of Coagulation Bath>

[0052] Next, a coagulated fiber bundle is formed by discharging the spinning dope through multiple discharge ports of a spinning nozzle into a coagulation bath set to have a solvent concentration of 40 mass% to 60 mass% and a temperature of 35°C to 50°C.

[0053] When the solvent concentration and temperature are set in the above ranges, coagulation at an undesired faster speed is prevented and recessed wrinkles are less likely to be formed on a fiber surface.

<Jet-Stretch Ratio, Hot-water Stretch Ratio, Dry-heat Stretch Ratio, Multiplication Product of Stretch Ratios>

[0054] The jet-stretch ratio is preferred to be 0.4 to 2.2 when the spinning dope is discharged through spinning nozzle ports. The jet-stretch ratio is obtained when the draw velocity of coagulated fiber is divided by the extrusion velocity.

[0055] A jet-stretch ratio of 0.4 to 2.2 is preferred since fiber breakage is less likely to occur in the spinning bath and spinnability is thereby excellent. From such viewpoints, the jet-stretch ratio is more preferred to be 0.6 to 2.0.

[0056] Moreover, the coagulated fiber bundle is stretched in hot water to have a stretch ratio of 2 to 4 times, and an oil agent is applied and dried on the fiber bundle. Then, the fiber bundle is stretched by applying dry heat to have a stretch ratio of 1.2 to 3 times. During those procedures, the value of a product (S), obtained by multiplying the hot-water stretch ratio and the dry-heat stretch ratio, is set to be 4 to 6.

[0057] A dry-heat stretch ratio of at least 1.2 times is preferred, since recesses on a fiber surface are elongated to increase the area of smooth surface, thus enhancing the gloss of the fiber. A dry-heat stretch ratio of no greater than 3 times is preferred, since pilling resistance is improved and fiber breakage is reduced during a spinning process.

[0058] To reduce recesses on a fiber surface and to enhance gloss, the dry-heat stretch ratio is more preferred to be at least 1.5 times, even more preferably at least 1.7 times. To improve processability, the stretch ratio is preferred to be no greater than 2 times.

[0059] In addition, the product (S) is preferred to be 4 to 6, since processability during spinning is excellent, and appropriate fiber strength is achieved. Also, pilling resistance is expected to be excellent. The product (S) is more preferred to be 4.5 to 5.5.

<Temperature of Hot Water, Fiber Temperature for Dry-heat Stretching>

[0060] When the fiber is stretched in hot water, the water temperature is preferred to be 80°C to 98°C. In such a temperature range, fiber breakage is less likely to occur during hot-water stretching.

[0061] In addition, the fiber temperature at the time for stretching by dry heat is preferred to be 150°C to 170°C. A temperature of at least 150°C makes it easier to stretch wrinkles on the fiber surface, and a temperature of no higher than 170°C reduces color change caused by heat while decreasing fiber breakage during dry-heat stretching.

[0062] Applying heat on a fiber bundle for dry-heat stretching may be conducted by using a hot roll, contact heating on a hot plate, or non-contact heating by hot air. Among them, hot roll heating is preferred because heat is efficiently applied on a fiber bundle.

[0063] By using a hot roll to apply heat on a fiber bundle, the fiber temperature is appropriately increased by adjusting the temperature of the hot roll and the time for the fiber bundle to be in contact with the hot roll. It is preferred to use multiple hot rolls so that both surfaces of the fiber bundle are heated.

[0064] The temperature of a hot roll is preferred to be 150°C to 190°C. A temperature of 190°C or lower suppresses the color change of the fiber caused by heat.

[0065] Then, the dry-heat stretched fiber bundle is crimped and stored in a container.

[0066] The swelling degree of fiber that is stretched in hot water is preferred to be set at 80% to 130%. A swelling degree of 80% to 130% is preferred since dryness and productivity of the fiber are excellent. In addition, fewer wrinkles are expected to appear on the fiber surface.

<Thermal Relaxation>

[0067] Lastly, thermal relaxation is conducted on the fiber to have a thermal shrinkage rate of 5% to 20% to obtain the final product of acrylic fiber. Conditions for thermal relaxation are determined based on the thermal shrinkage rate of fiber. A fiber thermal shrinkage rate of 5% to 20% is preferred since knot strength and knot elongation are set to have a value that is sufficient for exhibiting pilling resistance.

[0068] The thermal shrinkage rate means the rate of fiber shrinkage determined when the fiber is compared before and after thermal relaxation treatment.

[0069] The temperature for thermal relaxation is set at 120°C to 135°C. A temperature of 120°C or higher is preferred since the strength and elongation of a single fiber are set to achieve excellent carding processability during spinning,

and a temperature of 135°C or lower makes it easier to obtain excellent pilling-resistant single fibers.

[0070] An acrylic fiber bundle produced by the above-described method is cut into short fibers. The acrylic fiber was cut by a cutter to form short fibers and then spun. Spun yarn may be formed with 100% of acrylic fiber related to the present invention, or may be formed by blending other fibers, for example, synthetic or chemical fibers such as generic acrylic fibers, polyester fibers, nylon fibers and rayon fibers and/or natural fibers such as cotton, wool and silk.

<Fiber Content of Spun Yarn>

[0071] The spun yarn related to the present invention is preferred to contain the aforementioned acrylic fiber at 40 mass% or greater. A content of 40 mass% or greater contributes to expressing gloss and pilling resistance characterized in the acrylic fiber related to the present invention. From such viewpoints, the content is more preferred to be 60 mass% or greater, even more preferably 80 mass% or greater.

<Yarn Count of Spun Yarn>

[0072] The yarn count of the spun yarn related to the present invention is preferred to be a cotton count of 40 to 70. A cotton count of 40 or higher makes it easier to form soft fabrics based on the effects derived from a smaller fiber fineness of the acrylic fiber related to the present invention. In addition, a cotton count of 70 or lower makes it easier to provide the strength required for the spun yarn during its use.

[0073] The coefficient of variation (CV) of yarn unevenness in the spun yarn is preferred to be 11.5% or lower. When a CV is 11.5% or lower, a knitted fabric has good appearance with enhanced gloss. The CV is more preferred to be 11% or lower, even more preferably 10% or lower.

<Blending Ratio of Cellulose Fiber>

[0074] The spun yarn related to the present invention is preferred to contain a cellulose fiber at 10 mass% to 40 mass%. A content of cellulose fiber at 10 mass% or greater enhances moisture-absorption and heat-generation properties of the spun yarn. A content of 40 mass% or lower improves the pilling resistance and heat retention rate.

<Yarn Content of Knitted Fabric>

[0075] The knitted fabric related to the present invention is preferred to contain the spun yarn at 40 mass% or greater. A content of 40 mass% or greater contributes to achieving the effects of enhancing the gloss and pilling resistance of the knitted fabric. From such viewpoints, the content is more preferred to be 50 mass% or greater, even more preferably 60 mass% or greater.

<Basis Weight of Knitted Fabric>

[0076] The knitted fabric related to the present invention is preferred to have a basis weight of 150 g/m² to 230 g/m². A basis weight of 150 g/m² or greater increases the strength, and the knitted fabric is less likely to be torn. A basis weight of 230 g/m² or less contributes to obtaining a lightweight, soft, knitted fabric suitable for undergarments.

<Pilling Resistance>

[0077] The knitted fabric related to the present invention is preferred to exhibit a pilling resistance rated at 4 or higher. A pilling resistance rated at 4 or higher reduces the amount of pilling so as to give the fabric a clean appearance. The pilling resistance rating is more preferred to be 4.5 or higher.

<Heat Retention>

[0078] The knitted fabric related to the present invention is preferred to have a heat retention rate of 15% to 50%. When the knitted fabric is made into undergarments, a heat retention rate of 15% or higher provides warmth, and a heat retention rate of 50% or lower prevents excessive warmth.

EXAMPLES

[0079] The acrylic fiber related to the present invention is described by referring to the examples below.

(Method for Measuring Irregularities on Fiber Surface)

[0080] The depths of irregularities on the surface of an acrylic fiber related to the present invention are determined by the center-line mean roughness (Ra), maximum height (Ry) of the profile, 30-point mean roughness (Rz), and distance (S) between peaks, which are described below. They are measured by using a laser microscope.

[0081] FIGs. 1~4 are schematic views, each showing the surface of a single acrylic fiber related to the present invention observed in a cross section perpendicular to a fiber longitudinal direction.

(Center-line Mean Roughness <Ra> on Single Fiber Surface)

[0082] As shown in FIG. 1, the center-line mean roughness (Ra) on the surface of a single fiber is the value expressed in nanometers (nm), which is determined in base length (L) taken out of the roughness curve to be parallel to the center line (m) when the distances from the center line (m) to the roughness-curve line are measured and the absolute deviation values are totaled to obtain the mean absolute deviation.

(Maximum Height <Ry> of the Profile of Single Fiber Surface)

[0083] As shown in FIG. 2, the maximum height (Ry) of the profile of a single fiber surface is the value expressed in nanometers (nm), which is determined in base length (L) taken out of the roughness curve to be parallel to the center line (m) when the distance (Rp) from the highest peak line to the center line (m) and the distance (Rv) from the lowest valley line to the center line (m) are measured and the sum (Rp+Rv) is obtained.

(30-point Mean Roughness <Rz> on Single Fiber Surface)

[0084] As shown in FIG. 3, the 30-point mean roughness (Rz) on the surface of a single fiber is the value expressed in nanometers (nm), which is determined in the base length taken out of the roughness curve to be parallel to the center line when the mean absolute value of elevations (Yp) from the highest peak to the 15th highest peak and the mean absolute value of elevations (Yv) from the lowest valley to the 15th lowest valley, both measured in a vertical direction of the profile, and the sum (Yp+Yv) is obtained.

(Distance <S> between Peaks on Single Fiber Surface)

[0085] As shown in FIG. 4, the distance (S) between peaks on the surface of a single fiber is the value expressed in nanometers (nm), which is determined in base length (L) taken out of the roughness curve to be parallel to the center line when the lengths corresponding to the distances between adjacent peaks are measured and the mean distance value of multiple lengths between peaks of the convex portions is obtained.

(Tensile Strength and Elongation, Knot Strength and Knot Elongation)

[0086] Measurement was conducted in accordance with JIS L1015.

(Number of Recesses of 0.1 μm or Deeper on Single Fiber Surface)

[0087] After hot air was applied from a dryer on 200 to 300 acrylic fibers related to the present invention to stretch the shrunk fibers, the fibers were put into a tube. The tube was made of polyethylene that shrinks only in a circumferential direction.

[0088] Next, the polyethylene tube filled with the acrylic fibers related to the present invention was cut into approximately 2 mm lengths using a new razor blade in an approximate perpendicular direction to the axis.

[0089] One of the cut surfaces was fixed on a stage using a double-sided tape, and gold was deposited on the other cut surface set for observation using a low-temperature ion sputtering apparatus (JFC1100, made by JEOL Ltd.) under conditions of 1200 V and 5 mA for 8 minutes. Accordingly, an observation sample of acrylic fibers related to the present invention was prepared.

[0090] Using a scanning electron microscope (model number XL-20, made by Philips Electronics Company), a fiber cross section of the sample was captured at a magnification of 5000 times. The depth of a recess was determined as the length of a line, which starts at the tangent line connecting convex portions on both sides of the recess and is drawn vertically down to the deepest spot of the recess. Then, the number of recesses of 0.1 μm or deeper was counted on the fiber surface. The same procedure was conducted on three samples, and the average value was set as the number of recesses of 0.1 μm or deeper present on a fiber cross section.

(Evaluation of Gloss)

[0091] The gloss was evaluated as follows.

[0092] Acrylic fibers of Examples 1 and 2 and Comparative Example 1 were used 100% to form spun yarns respectively under the same conditions, which were then formed into fabrics under the same conditions. The gloss of each fabric was visually evaluated.

○ : excellent gloss

× : poor gloss

(Example 1)

[0093] An acrylonitrile-based copolymer with a reduced viscosity of 1.8 containing 95% of acrylonitrile, 4.4% of vinyl acetate and 0.6% of sodium methallylsulfonate was dissolved in dimethylacetamide. Accordingly, a spinning dope was obtained, having a copolymer concentration of 24% and a viscosity at 50°C of 200 poise.

[0094] The spinning dope was discharged in a 41 °C coagulation bath with a dimethylacetamide concentration of 56% through multiple discharge ports with a port diameter of 0.045 mm. Then, the obtained fiber was stretched to be 2.5 times in 98°C hot water while the solvent was washed out. An oil agent was applied on the fibers and dried using multiple hot rollers set to have a surface temperature of 150°C. The fibers were further heated to 160°C by applying heat using a 180°C hot roller. The fibers were stretched in air to be twice as long, crimped and put into a container.

[0095] Furthermore, thermal relaxation treatment was conducted on the fiber bundle to have a thermal shrinkage rate of 7% to 9%. Accordingly, acrylic fiber with a single fiber fineness of 1.0 dtex was prepared. Conditions are specified in Table 1 and results are shown in Table 2.

[0096] The product (K), obtained by multiplying knot strength (cN/dtex) and knot elongation (%) was 15.9, sufficient for exhibiting excellent pilling resistance. The number of recesses of 0.1 μm or deeper was two, and excellent gloss was obtained relative to comparative examples.

(Example 2)

[0097] The same spinning process as in Example 1 was conducted except that the wet-heat stretch ratio and the dry-heat stretch ratio were changed. The conditions are specified in Table 1 and results are shown in Table 2.

[0098] Accordingly, the product (K) obtained by multiplying knot strength (cN/dtex) and knot elongation (%) was 16.6, sufficient for exhibiting excellent pilling resistance. The number of recesses of 0.1 μm or deeper was four, and excellent gloss was obtained relative to comparative examples.

(Examples 3~11)

[0099] Acrylic fibers were prepared by conducting the same process as in Example 1 except that conditions for forming acrylic fibers were changed as respectively specified in Table 1. Physical properties of each acrylic fiber are shown in Table 1.

(Comparative Example 1)

[0100] Acrylic fiber was prepared the same as in Example 1 except that no dry-heat stretching was conducted but the hot-water stretch ratio was increased to set the overall stretch ratio to be the same. The conditions are specified in Table 1 and results are shown in Table 2.

[0101] Accordingly, the product (K) obtained by multiplying knot strength (cN/dtex) and knot elongation (%) was 25.7, at which pilling resistance was exhibited, but the rating was not so high as that in the acrylic fiber related to the present invention. In addition, the number recesses of 0.1 μm or deeper was 15, and gloss was poor.

(Comparative Example 2)

[0102] Acrylic fiber was prepared the same as in Example 3 except that no dry-heat stretching was conducted but the hot-water stretch ratio was increased to set the overall stretch ratio to be the same. The conditions are specified in Table 1 and results are shown in Table 2.

[0103] Accordingly, the product (K) obtained by multiplying knot strength (cN/dtex) and knot elongation (%) was 20, at which pilling resistance was exhibited, but the rating was not so high as that in the acrylic fiber related to the present invention. In addition, gloss was poor.

(Comparative Example 3)

[0104] Acrylic fiber was prepared by the conditions described in JP2013-209771A for producing a carbon-fiber-precursor acrylic fiber. The conditions are specified in Table 1 and results are shown in Table 2.

[0105] The carbon-fiber-precursor acrylic fiber had a low value of product (K) obtained by multiplying knot strength and knot elongation. During the spinning process the fiber broke, indicating that the physical properties of the acrylic fiber were so low that the fiber could not be spun.

(Comparative Example 4)

[0106] According to the conditions described in JP H11-222716A for producing glossy fibers, acrylic fiber was prepared to have a single fiber fineness of 22 dtex and a flatness rate of 22. The conditions are specified in Table 1 and results are shown in Table 2.

[0107] Accordingly, the product (K) was at a value sufficient for exhibiting pilling resistance, but the fiber fineness level was too high for achieving soft texture. Thus, the fiber is not suitable for apparel products.

Table 1

	AN/AV/MS (mass%)	Spin- ning dope temp. (°C)	Coagula- tion bath temp. (°C)	Coagula- tion bath concentra- tion (mass%)	Hot- water stretch ratio (times)	Dry- heat stretch ratio (times)	Ther- mals re- laxation temp. (°C)	Single fiber fine- ness (dtex)	Tensile strength (cN/dte x)	Knot strength (cN/dte x)	Knot elonga- tion (%)	Product (K) (knot strength × knot elonga- tion)	Center- line mean rough- ness (Ra) (nm)	30-point mean rough- ness (Rz) (nm)	Maxi- mum height of pro- file (Ry) (nm)	Dis- tance (S) be- tw. peaks (nm)	Num- ber of recess- es of 0.1 μm or deeper	Glos s
Exam- ple 1	95/4.4/0.6	75	41	56	2.5	2	128	1.0	2.6	1.42	11.2	15.9					2	○
Exam- ple 2	95/4.4/0.6	75	41	56	3.3	1.5	128	1.0	3	1.44	11.5	16.6	5.7	38	64	940	4	○
Exam- ple 3	95/4.4/0.6	80	45	56	2.25	2	123	0.8	2.69	1.69	11.5	19.4	8.4	46	80	988		○
Exam- ple 4	95/4.4/0.6	80	45	56	2.25	2	128	0.8	2.55	1.42	12.1	17.2						○
Exam- ple 5	95/4.4/0.6	80	45	56	2.25	2	132	0.8	2.7	1.48	13.9	20.6						○
Exam- ple 6	95/4.4/0.6	80	45	56	2.65	1.7	123	0.8	2.78	1.4	13.4	18.8	8.7	57	99	988		○
Exam- ple 7	95/4.4/0.6	80	45	56	2.65	1.7	128	0.8	2.55	1.25	10.6	13.3						○
Exam- ple 8	95/4.4/0.6	80	45	56	2.65	1.7	132	0.8	2.48	1.28	13.7	17.5						○
Exam- ple 9	95/4.4/0.6	80	35	56	2.25	2	123	0.8	2.42	1.59	17.3	27.5	9.5	56	98	988		○
Exam- ple 10	95/4.4/0.6	75	45	56	2.25	2	123	0.8	2.46	1.51	15.4	23.3	10	63	103			○
Exam- ple 11	95/4.4/0.6	80	41	56	3	1.5	132	0.8	3.17	1.62	9.5	15.9	9	50	92			○
Comp. Exam- ple 1	95/4.4/0.6	75	41	56	5	-	128	1.0	2.8	1.76	16.7	29.4	14.6	105	194	984	15	×

(continued)

	AN/AV/MS (mass%)	Spin- ning dope temp. (°C)	Coagula- tion bath temp. (°C)	Coagula- tion bath concen- tration (mass%)	Hot- water stretc h ratio (times)	Dry- heat stretc h ratio (times)	Ther- mals re- laxation temp. (°C)	Single fiber fine- ness (dtex)	Tensile strengt h (cN/dte x)	Knot strengt h (cN/dte x)	Knot elonga- tion (%)	Product (K) (knot strength × knot elonga- tion)	Center- line mean rough- ness (Ra) (nm)	30-point mean rough- ness (Rz) (nm)	Maxi- mum height of pro- file (Ry) (nm)	Dis- tance (S) be- tw. peaks (nm)	Num- ber of recess- es of 0.1 μm or deeper	Glos s
Comp. Exam- ple 2	95/4.4/0.6	80	45	56	4.5	-	123	0.8	2.77	1.35	14.8	20	15.6	93	185		15	×
Comp. Exam- ple 3	AN/AAm/MA=96.5 /5.7/0.8	70	38	65	5.4	1.4	-	1.2	8.00	1.19	1.4	1.7	80		460	720	13	×
Comp. Exam- ple 4	AN/AV=93/7	85	30	30	2	2	140	22.0	1.63	1.31	14.1	18.5	6.3	40	70		4	○

(Example 12)

[0108] By blending 70 mass% of the acrylic fiber prepared in Example 1 and 30 mass% of MicroModal (1.0 dtex, made by Lenzing Corporation), a spun yarn was formed to have a cotton count of 50 and a twist count of 873 t/m. Its physical properties are shown in Table 2.

(Example 13)

[0109] Using 100% of the acrylic fiber prepared in Example 1, a spun yarn was formed to have a cotton count of 60 and a twist count of 1139 t/m. Its physical properties are shown in Table 2.

(Examples 14, 15)

[0110] Spun yarns were obtained the same as in Example 13 except that their cotton counts were changed respectively as specified in Table 2. Their physical properties are shown in Table 2.

(Example 16)

[0111] A spun yarn was formed by using 100 mass% of the acrylic fiber prepared in Example 11. The cotton count was 40 and the twist count 820 t/m. Their physical properties are shown in Table 2.

(Comparative Example 5)

[0112] By blending 70 mass% of the acrylic fiber prepared in Comparative Example 1 and 30 mass% of MicroModal (1.0 dtex, made by Lenzing Corporation), a spun yarn was formed to have a cotton count of 50 and a twist count of 900 t/m. Its physical properties are shown in Table 2.

[0113] When compared with the fiber in Example 12, the variations in yarn unevenness were greater.

[0114] When spun yarns prepared in Example 12 and Comparative Example 5, each wound on a cone, were visually compared, it was verified that the spun yarn of Example 12 had better gloss.

[0115] Using 100 mass% of the acrylic fiber prepared in Comparative Example 1, a spun yarn was formed to have a cotton count of 60 and a twist count of 1139 t/m. Its physical properties are shown in Table 2.

[0116] Variations in yarn unevenness were greater than those in the spun yarn of Example 13.

(Comparative Examples 7, 8)

[0117] A spun yarn was formed the same as in Comparative Example 6 except that the cotton count was changed as specified in Table 2. Its physical properties are shown in Table 2.

(Comparative Example 9)

[0118] Using 100 mass% of the acrylic fiber of Comparative Example 2, a spun yarn was formed to have a cotton count of 40 and a twist count of 820 t/m. Its physical properties are shown in Table 2.

[0119] When spun yarns prepared in Examples 13~16 and Comparative Examples 6~9, each wound on a cone, were visually compared, it was verified that spun yarns of the examples had better gloss than those of the comparative examples.

(Example 17)

[0120] Using the spun yarn of Example 15, a jersey weft-knit fabric was prepared by setting the gauge at 14G. The basis weight was 210 g/m², the anti-pilling rating was 4.5, and the heat retention rate was 45.1 %.

(Comparative Example 10)

[0121] Using the spun yarn of Comparative Example 8, a jersey weft-knit fabric was prepared by setting the gauge at 14G. The basis weight was 210 g/m², the anti-pilling rating was 4.5, and the heat retention rate was 44.9%.

[0122] However, the gloss was not as good as that of Example 17.

Table 2

	Yarn structure	Blend ratio (mass%)	Cotton count	Twist count (t/m)	Strength of single yarn (g)	CV of strength (%)	Elongation (%)	CV of yarn unevenness (%)
Example 12	acrylic fiber of Examp. 1 MicroModal	70 30	50	873		7.01	12.98	9.56
Example 13	acrylic fiber of Examp. 1	100	60	1139		9.49	14.37	12.22
Example 14	acrylic fiber of Examp. 1	100	50	1038		8.73	15.4	11.16
Example 15	acrylic fiber of Examp. 1	100	40	921		9.72	16.76	9.82
Example 16	acrylic fiber of Examp. 11	100	40	820	210.6	11.1	16.8	11.7
Comp. Example 5	acrylic fiber of Comp. Examp. 1 MicroModal	70 30	40	921			14.6	14.3
Comp. Example 6	acrylic fiber of Comp. Examp. 1	100	60	1100	118	9	13	14.3
Comp. Example 7	acrylic fiber of Comp. Examp. 1	100	50	1000	178	11.3	14	14
Comp. Example 8	acrylic fiber of Comp. Examp. 1	100	40	890	229	10.1	16	13.8
Comp. Example 9	acrylic fiber of Comp. Examp. 2	100	40	820	227.2	10.1	16.9	11.9

Table 3

	Spun yarn	Basis weight (g/m ²)	Pilling resistance (rating)	Heat retention rate (%)
Example 17	Example 15	210	4.5	45.1
Comp. Example 10	Comp. Example 8	210	4.5	44.9

Claims

1. An acrylic fiber, configured to have a center-line mean roughness (Ra) of 3 nm to 12 nm on the surface of a single fiber, and a single fiber fineness of 0.5 dtex to 3.5 dtex.
2. An acrylic fiber, configured to have a center-line mean roughness (Ra) of 3 nm to 12 nm on the surface of a single fiber, and a product (K) of 10 to 30 obtained by multiplying the value of knot strength (cN/dtex) and the value of knot elongation (%).
3. The acrylic fiber according to Claim 1, wherein the value of a product (K), obtained by multiplying the value of knot strength (cN/dtex) and the value of knot elongation (%), is set to be 10 to 30.

4. The acrylic fiber according to Claim 2, wherein a single fiber fineness is set at 0.5 dtex to 3.5 dtex.
5. The acrylic fiber according to any of Claims 1~4, wherein the surface of a single fiber is configured to have a maximum height (R_y) of the profile set at 40 nm to 150 nm, the 30-point mean roughness (R_z) at 20 nm to 80 nm and the distance (S) between peaks of convex portions at 800 nm to 1100 nm.
6. The acrylic fiber according to any of Claims 1~5, wherein the number of recesses of 0.1 μm or deeper that are present on the surface of a single fiber is no greater than 10 when observed in a cross section perpendicular to the fiber axis.
7. The acrylic fiber according to any of Claims 1~6, comprising 92 mass% to 96.8 mass% of an acrylonitrile unit, 2 mass% to 6 mass% of a vinyl monomer unit, and 0.2 mass% to 2.0 mass% of a sulfonic acid group-containing vinyl monomer unit, wherein a single fiber tensile strength is set at 1.8 cN/dtex to 3.0 cN/dtex, a single fiber knot strength is set at 1.0 cN/dtex to 1.8 cN/dtex, and a single fiber knot elongation is set at 8% to 20%.
8. A method for producing an acrylic fiber, comprising:
 - forming a spinning dope by dissolving in an organic solvent an acrylonitrile-based copolymer that contains 92 mass% to 96.8 mass% of an acrylonitrile unit and 0.2 mass% to 2.0 mass% of a sulfonic acid group containing-vinyl monomer unit;
 - forming a coagulated fiber bundle by discharging the spinning dope in a 35°C to 50°C coagulation bath through the discharge ports of a spinning nozzle at a jet-stretch ratio of 0.4 to 2.2;
 - stretching the coagulated fiber bundle in 80°C to 98°C hot water at a stretch ratio of 2 to 3.8 times;
 - applying oil to the fiber bundle and drying the fiber bundle; and
 - stretching the fiber bundle by applying dry heat to have a fiber temperature of 150°C to 170°C at a stretch ratio of 1.2 to 3 times,
 - wherein the value of a product (S), obtained by multiplying the hot-water stretch ratio and the dry-heat stretch ratio, is set to be 4 to 6.
9. The method for producing an acrylic fiber according to Claim 8, wherein the acrylonitrile-based copolymer is configured to further comprise 2 mass% to 6 mass% of a vinyl monomer unit, the solvent concentration of the coagulation bath is set to be 40 mass% to 60 mass%, and a thermal relaxation process is conducted after hot-dry stretching.
10. The method for producing an acrylic fiber according to Claim 8 or 9, wherein the temperature for the thermal relaxation process is set at 120°C to 135°C, and a fiber relaxation ratio is set at 5% to 20%.
11. A spun yarn, comprising:
 - an acrylic fiber according to any of Claims 1~7 at 40 mass% or greater,
 - wherein the cotton count is set at 40 to 70.
12. The spun yarn according to Claim 11, further comprising a cellulose-based fiber at 10 mass% to 40 mass%.
13. A knitted fabric, comprising:
 - a spun yarn according to Claim 11 or 12 at 40 mass% or greater,
 - wherein the basis weight is set at 150 g/m² to 230 g/m², and
 - the pilling-resistant property is rated at 4 or higher.
14. The knitted fabric according to Claim 13, wherein a heat-retention rate is set to be 15% to 50%.

FIG.1

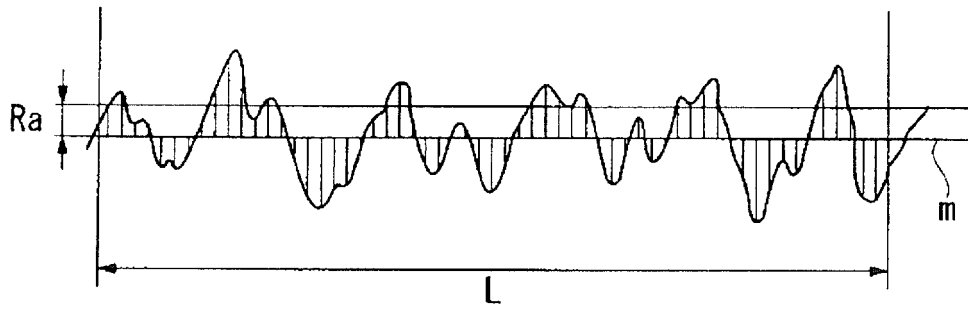


FIG.2

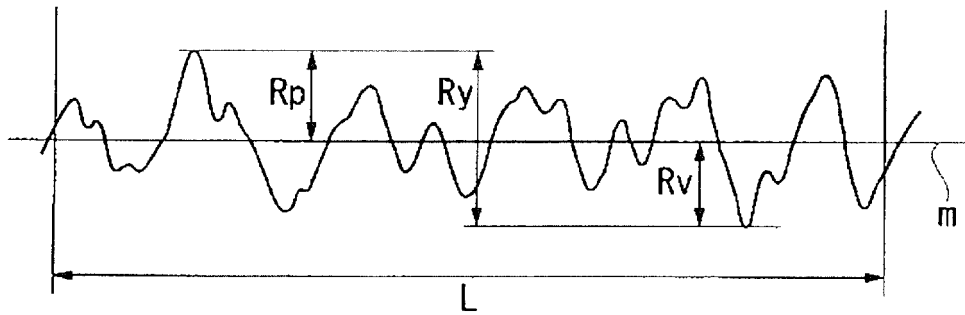


FIG.3

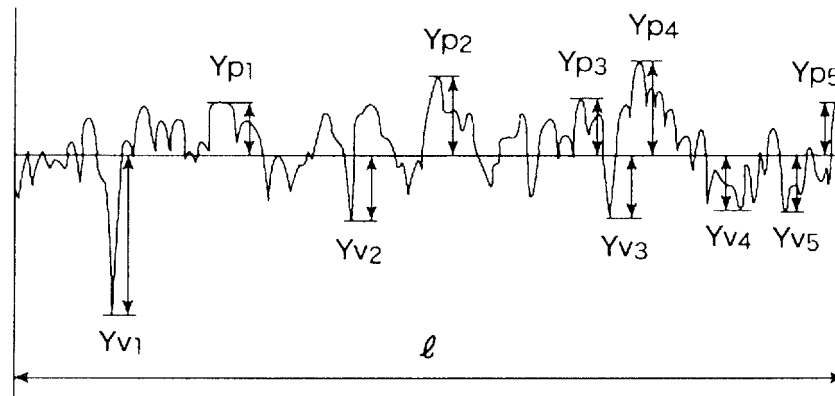
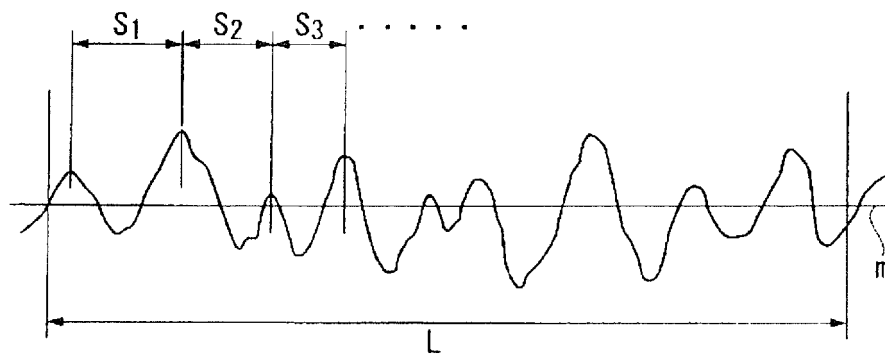


FIG.4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/073883

A. CLASSIFICATION OF SUBJECT MATTER

D01F6/18(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)

D01F1/00-6/96, D01F9/00-9/04, D04B1/00-1/28, D04B21/00-21/20

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015

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	WO 2010/143680 A1 (Mitsubishi Rayon Co., Ltd.), 16 December 2010 (16.12.2010), claims; paragraph [0044] & JP 4945684 B & US 2012/0088104 A1 claims; paragraph [0060] & EP 2441865 A1 & CA 2764661 A & CN 102459722 A & KR 10-2012-0023181 A & TW 201114960 A & CA 2820810 A & CA 2820976 A & ES 2534649 T	1, 5, 6 2-4, 7-14
X A	JP 2009-46770 A (Mitsubishi Rayon Co., Ltd.), 05 March 2009 (05.03.2009), claims; paragraph [0021] (Family: none)	1 2-14

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

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Date of the actual completion of the international search
05 November 2015 (05.11.15)Date of mailing of the international search report
24 November 2015 (24.11.15)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/073883

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 5-295615 A (Mitsubishi Rayon Co., Ltd.), 09 November 1993 (09.11.1993), claims; paragraphs [0006], [0029] (Family: none)	1-14
A	JP 5-279912 A (Mitsubishi Rayon Co., Ltd.), 26 October 1993 (26.10.1993), claims; paragraph [0008] (Family: none)	1-14
A	JP 7-216637 A (Mitsubishi Rayon Co., Ltd.), 15 August 1995 (15.08.1995), claims; paragraphs [0006], [0018], [0023] (Family: none)	1-14

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2012036512 A [0004] [0007]
- JP 2006176937 A [0005] [0007]
- JP 2008038309 A [0005] [0007]
- JP 2011012363 A [0006] [0007]
- JP 2013209771 A [0104]