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(54) **HYGROSCOPIC CORE-SHEATH CONJUGATE YARN AND PRODUCTION METHOD THEREFOR**

(57) A hygroscopic core-sheath composite fiber which includes: a polyetheresteramide copolymer as a core polymer; and a polyamide as a sheath polymer, and which has a degree of shrinkage with boiling water of

6-11%. Provided is a core-sheath composite fiber which has high hygroscopicity and laundering durability of the hygroscopicity which makes the fiber withstand practical use, and which is capable of attaining a soft feeling.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a hygroscopic core-sheath composite fiber which is excellent in terms of feeling.

BACKGROUND ART

[0002] Synthetic fibers including thermoplastic resins such as polyamides and polyesters are excellent in terms of strength, chemical resistance, heat resistance, etc., and are hence used extensively in clothing applications, industrial applications, etc.

[0003] In particular, polyamide fibers not only have properties such as the peculiar softness, high tensile strength, colorability by dyeing, and high heat resistance but also have excellent hygroscopicity, and are hence in extensive use in applications such as inner wear and sportswear. However, polyamide fibers are insufficient in hygroscopicity as compared with natural fibers such as cotton, and have problems such as stuffiness and stickiness. There is hence a problem in that the polyamide fibers are inferior in comfortableness to natural fibers.

[0004] Under such circumstances, a synthetic fiber which shows excellent moisture absorbing/releasing properties for eliminating stuffiness and stickiness and has comfortableness substantially comparable to that of natural fibers is desired mainly in inner wear applications and sportswear applications.

[0005] Methods in which a hydrophilic compound is added to polyamide fibers have been most commonly investigated for that purpose. For example, Patent Document 1 proposes a method in which polyvinylpyrrolidone is blended as a hydrophilic polymer with a polyamide and the blend is spun to thereby improve the hygroscopicity.

[0006] Meanwhile, investigations are being made enthusiastically in which a fiber is made to have a core-sheath structure in which a highly hygroscopic thermoplastic resin is used as the core and a thermoplastic resin having excellent mechanical properties is used as the sheath, thereby attaining both hygroscopicity and mechanical properties.

[0007] For example, Patent Document 2 describes a core-sheath composite fiber which has a shape including a core and a sheath, the core being unexposed on the fiber surface, in which the core is a polyether-block-amide copolymer including nylon-6 as a hard segment, the sheath is a nylon-6 resin, and the areal proportion between the core and the sheath in a fiber cross-section is 3/1 to 1/5.

[0008] Patent Document 3 describes a core-sheath composite fiber including a polyetheresteramide as the core and a polyamide as the sheath and having high hygroscopicity, as a core-sheath type composite fiber having excellent hygroscopicity. This composite fiber is a core-sheath type composite fiber including a thermoplastic resin as the core and a fiber-forming polyamide resin as the sheath, in which the main component of the thermoplastic resin constituting the core is a polyetheresteramide and the proportion of the core is 5-50% by weight of the overall weight of the composite fiber.

[0009] Furthermore, Patent Document 4 describes a composite fiber having moisture absorbing/releasing properties, which includes a polyamide or a polyester as a sheath component and a water-absorbing thermoplastic resin including crosslinked poly(ethylene oxide) as a core component. Described therein is a highly hygroscopic core-sheath composite fiber including a highly hygroscopic water-insoluble modified poly(ethylene oxide) disposed as the core and a polyamide disposed as the sheath.

BACKGROUND ART DOCUMENT

PATENT DOCUMENT

[0010]

Patent Document 1: JP-A-9-188917

Patent Document 2: WO 2014/10709

Patent Document 3: JP-A-6-136618

Patent Document 4: JP-A-8-209450

SUMMARY OF THE INVENTION

PROBLEMS THAT THE INVENTION IS TO SOLVE

[0011] However, the fiber described in Patent Document 1 has a problem in that although this fiber has moisture absorbing/releasing properties substantially comparable to those of natural fibers, the performance is not fully satisfactory,

and even higher moisture absorbing/releasing properties are required to be attained.

[0012] Meanwhile, the core-sheath composite fibers of Patent Documents 2 to 4 have moisture absorbing/releasing properties equal to or higher than those of natural fibers. However, the core deteriorates due to repetitions of practical use, and there has been a problem in that the hygroscopicity decreases with repetitions of use. In addition, fabrics formed therefrom have softness equal to that of nylons and are hence insufficient in feeling. A soft feeling superior to that of any existing article has been strongly desired.

MEANS FOR SOLVING THE PROBLEMS

[0013] An object of the present invention is to provide a core-sheath composite fiber which overcomes the problems of the background-art techniques, and which is capable of attaining: comfortableness superior to that of natural fibers with high hygroscopicity; laundering durability of the hygroscopicity, which makes the fiber withstand practical use; and a soft feeling that has been impossible so far.

[0014] In order to solve the above-described problem, the present invention includes the following configurations.

(1) A hygroscopic core-sheath composite fiber which includes: a polyetheresteramide copolymer as a core polymer; and a polyamide as a sheath polymer, and which has a degree of shrinkage with boiling water of 6-11%.

(2) The hygroscopic core-sheath composite fiber according to (1), which has an elongation of 60-90%.

(3) A false-twist textured yarn including the hygroscopic core-sheath composite fiber according to (1) or (2).

(4) A fabric at least a part of which includes the hygroscopic core-sheath composite fiber according to any one of (1) to (3).

(5) A process for producing the hygroscopic core-sheath composite fiber according to (1) or (2), the process including: ejecting a filament from a spinneret; cooling and solidifying the ejected filament with a cooling wind; thereafter applying an aqueous solution (oil emulsion) twice to the filament; and then winding up the filament,

in which a time gap between the first-stage application and the second-stage application is 20 msec or longer.

ADVANTAGE OF THE INVENTION

[0015] According to the present invention, it is possible to provide a core-sheath composite fiber which is capable of attaining: comfortableness superior to that of natural fibers with high hygroscopicity; laundering durability of the hygroscopicity, which makes the fiber withstand practical use; and a soft feeling that has been impossible so far.

MODE FOR CARRYING OUT THE INVENTION

[0016] The core-sheath composite fiber of the present invention employs a polyamide as the sheath and a thermoplastic polymer having high hygroscopicity as the core. The term "thermoplastic polymer having high hygroscopicity as the core" means a polymer which, when examined in a pellet form, has a ΔMR of 10% or higher, and examples thereof include polyetheresteramide copolymers, poly(vinyl alcohol), and cellulosic thermoplastic resins. Of these, a polyetheresteramide copolymer is used from the standpoint that this polymer has satisfactory thermal stability and satisfactory compatibility with the polyamide as the sheath and has excellent separation resistance. By thus-configuring a core-sheath composite fiber, the fiber can be made to have a high ΔMR , and a textile which has excellent hygroscopicity and is comfortable can be achieved. ΔMR is an index to humidity regulation, and is expressed by the difference in the coefficient of moisture absorption between an in-garment temperature and humidity condition during light to medium works or light to medium exercises which is represented by 30°C×90% RH and an outside-air temperature and humidity condition represented by 20°C×65% RH. The larger the ΔMR , the higher the hygroscopicity and the better the comfortableness during wear.

[0017] The polyetheresteramide copolymer is a block copolymer which has an ether linkage, an ester linkage, and an amide linkage in the same molecular chain. More specifically, the copolymer is a block copolymer obtained by subjecting a polyamide ingredient (A) including one or more members selected from among lactams, aminocarboxylic acids, and salts of diamines with dicarboxylic acids and a polyetherester ingredient (B) including a dicarboxylic acid and a poly(alkylene oxide) glycol to polycondensation reaction.

[0018] Examples of the polyamide ingredient (A) include lactams such as ϵ -caprolactam, dodecanolactam, and undecanolactam, ω -aminocarboxylic acids such as aminocaproic acid, 11-aminoundecanoic acid and 12-aminododecanoic acid, and diamine-dicarboxylic acid nylon salts which are precursors for nylon-66, nylon-610, nylon-612, etc. A preferred polyamide-forming ingredient is ϵ -caprolactam.

[0019] The polyetherester ingredient (B) is an ingredient including a dicarboxylic acid having 4-20 carbon atoms and a poly(alkylene oxide) glycol. Examples of the dicarboxylic acid having 4-20 carbon atoms include aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid and dodecanedioic acid,

aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid, and alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid; one of these or a mixture of two or more thereof can be used. Preferred dicarboxylic acids are adipic acid, sebacic acid, dodecanedioic acid, terephthalic acid, and isophthalic acid. Examples of the poly(alkylene oxide) glycol include polyethylene glycol, poly(1,2- and 1,3-propylene oxide) glycol, poly(tetramethylene oxide) glycol, and poly(hexamethylene oxide) glycol. Preferred is polyethylene glycol, which has especially satisfactory hygroscopicity.

[0020] The number-average molecular weight of the poly(alkylene oxide) glycol is preferably 300-10,000, more preferably 500-5,000. In cases when the molecular weight of the poly(alkylene oxide) glycol is 300 or higher, this glycol is less apt to fly off from the system during the polycondensation reaction and a fiber having stable hygroscopicity is obtained. Such molecular weights are hence preferred. In cases when the molecular weight thereof is 10,000 or less, an even block copolymer is obtained to attain stable spinning. Such molecular weights are hence preferred.

[0021] It is preferable that the proportion of the polyetherester ingredient (B) is 20-80% by mole. Proportions thereof not less than 20% are preferred because satisfactory hygroscopicity is obtained. Meanwhile, proportions thereof not higher than 80% are preferred because satisfactory color fastness and laundering durability are obtained.

[0022] Commercial examples of such polyetheresteramide copolymer are "MH 1657" and "MV 1074", both manufactured by Arkema Inc.

[0023] Examples of the polyamide as the sheath include nylon-6, nylon-66, nylon-46, nylon-9, nylon-610, nylon-11, nylon-12, nylon-612, and the like and copolyamides including these nylons and comonomer components such as compounds having an amide-forming functional group, e.g., laurilactam, sebacic acid, terephthalic acid, isophthalic acid, and 5-sodiumsulfoisophthalic acid. Preferred of these are nylon-6, nylon-11, nylon-12, nylon-610, and nylon-612, from the standpoint of spinning because the difference in melting point between such nylons and the polyetheresteramide copolymer is so small that the polyetheresteramide copolymer can be inhibited from thermally deteriorating during melt spinning. Preferred of these is nylon-6, which has excellent dyeability.

[0024] Various additives may have been copolymerized with or incorporated into the sheath polyamide in the present invention according to need in a total additive content in the range of 0.001-10% by weight. Examples of the additives include a delustering agent, flame retardant, antioxidant, ultraviolet absorber, infrared absorber, nucleator, fluorescent brightener, antistatic agent, hygroscopic polymer, and carbon.

[0025] The core-sheath composite fiber of the present invention must have a degree of shrinkage with boiling water of 6-11%. By regulating the degree of shrinkage with boiling water thereof so as to be within the specified range, a soft feeling which has not been attained with any conventional nylon is rendered possible in cases when a false-twist textured yarn is obtained from the core-sheath composite fiber and a textile is then obtained from the yarn. In case where the degree of shrinkage with boiling water thereof is less than 6%, this core-sheath composite fiber has undergone crystallization before false twisting and, hence, cannot be crimped in false twisting, making it impossible to attain fluffiness and a soft feeling. Meanwhile, in case where the degree of shrinkage with boiling water thereof is higher than 11%, the shrinkage is so large that the textile may give a hard feeling. A more preferred range of the degree of shrinkage with boiling water is 6-10%, and an even more preferred range thereof is 7-9.5%.

[0026] From the standpoint of attaining a degree of shrinkage in boiling water of 6-11%, it is preferable that when producing the core-sheath composite fiber described above, an oil is applied in two stages. Although an oil is essential for improving the smoothness and collectibility of fibers, the degree of shrinkage with boiling water can be easily reduced by applying an aqueous solution (emulsion) to a filament which has been cooled and solidified and, after the lapse of a certain time period, applying an emulsion again. This is thought to be because the first-stage application simultaneously supplies water to the fiber and crystallization proceeds thereupon, and the second-stage oil supply ensures smoothness and collectibility. It is preferable that the time gap between the first-stage application and the second-stage application is 20 msec or longer, because this time gap makes it easy to regulate the degree of shrinkage with boiling water so as to be within the specified range according to the present invention. Although longer application time gaps are preferred, the longer gaps necessitate a prolongation of the step. It is therefore preferred to set a time gap while taking account of efficient production. Incidentally, in cases when the spinning speed is 3,000 m/min and the distance between the first-stage and second-stage oil application positions is 1.5 m, then the application time gap is 30 msec. Furthermore, from the standpoint of regulating the degree of shrinkage with boiling water so as to be within the specified range, it is preferable that the tension of the fiber during the oil application is in the range of 0.15-0.40 cN/dtex, because the orientation of the fiber is accelerated thereby. The fiber tension is measured at a position between the first-stage and second-stage oil application positions. It is also preferable that the core-sheath composite fiber of the present invention has an elongation of 60-90%. It is desirable to false-twist the core-sheath composite fiber from the standpoint of improving the softness, and an elongation of 60-90% is preferred for the false twisting because the crimp is less apt to change with the lapse of time or less apt to be weakened by repeated stretching and because the softness of the fiber can be further improved.

[0027] The core-sheath composite fiber of the present invention is not particularly limited in total fineness and the number of filaments (in the case of long fibers) and in length and the number of crimp waves (in the case of short fibers), and can be made to have any desired cross-sectional shape in accordance with the intended use of the fabric to be

obtained, etc. In view of use as a long-fiber material for clothing, it is preferable that the core-sheath composite fiber of the present invention has, as a multifilament, a total fineness of 5-235 dtex and the number of filaments of 1-144. The cross-sectional shape preferably is circular, triangular, flat, Y-shaped, star-shaped, eccentric, or laminate-type.

[0028] The proportion of the core in the core-sheath composite fiber of the present invention is preferably 20-80 parts by weight, more preferably 30-70 parts by weight, per 100 parts by weight of the composite fiber. By regulating the proportion thereof so as to be within that range, not only a satisfactory ΔMR is obtained but also the processability during false twisting is rendered satisfactory.

[0029] Chips of the polyamide to be used as the sheath in the present invention have a sulfuric-acid relative viscosity of preferably 2.3-3.3, more preferably 2.6-3.3. By regulating the sulfuric-acid relative viscosity so as to be within that range, not only the degree of shrinkage with boiling water can be easily regulated but also the laundering durability of ΔMR is improved, easily rendering comfortable textiles possible.

[0030] It is preferable that chips of the polyetheresteramide copolymer to be used as the core in the present invention have an o-chlorophenol relative viscosity (OCP relative viscosity) of 1.2-2.0. In cases when the o-chlorophenol relative viscosity thereof is 1.2 or higher, not only optimal stress is imposed on the sheath in spinning to cause the crystallization of the sheath polyamide to proceed, thereby facilitating control of the degree of shrinkage with boiling water, but also the laundering durability of ΔMR improves. Such o-chlorophenol relative viscosities are hence preferred.

[0031] Besides being produced by the preferred production process described above, the core-sheath composite fiber of the present invention can be obtained by known techniques of melt spinning or composite spinning. Examples thereof are as follows.

[0032] For example, a polyamide (sheath) and a polyetheresteramide copolymer (core) are separately melted, and the melts are metered and transported with gear pumps, then put together to form a composite flow by an ordinary method so as to result in a core-sheath structure, and ejected from a spinneret. A cooling wind is blown against the resultant filament with a filament cooler, such as a chimney, thereby cooling the filament to room temperature. In this method, an oil is supplied in two stages, and the oiled filament is passed through take-up rollers. The peripheral speed of the take-up rollers is preferably 3,000-3,900 m/min. The filament which has passed through the take-up rollers is stretched preferably in a stretch ratio of 1.0-1.1 and is passed through the stretching rollers. Thereafter, the winder (winding device) is regulated so as to impose a winding tension which results in a preferred package form, and the filament is then wound up therewith.

[0033] By false-twisting the core-sheath composite fiber obtained by the present invention, the softness thereof is improved and a feeling which has not been attained so far is obtained. The false twisting can be conducted using a known technique such as friction processing, pin processing, or belt nip processing. When cost, etc. are taken into account, friction processing is preferred. When crimping performance is taken into account, pin processing is preferred. In any processing, it is preferred to set the elongation of the false-twisted textured yarn at 25-40%, when the change of the crimp with the lapse of time, processability in the false twisting, and the subsequent weaving or knitting are taken into account. It is preferred to perform heat setting at 140-170°C in order to obtain satisfactory crimp and to inhibit the crimp from changing with the lapse of time.

[0034] The core-sheath composite fiber of the present invention is advantageously used in fabric and garments. With respect to the type of fabric, it is possible to select woven fabric, knitted fabric, nonwoven fabric, etc. according to purposes, and clothing is also included. The garments can be various clothing products including inner wear and sports-wear.

EXAMPLES

[0035] The present invention will be explained below in more detail by reference to Examples. In the Examples, property values were determined by the following methods.

(1) Sulfuric-acid Relative Viscosity

[0036] A 0.25-g portion of a sample was dissolved in sulfuric acid having a concentration of 98% by weight, so that the sample amount was 1 g per 100 mL of the sulfuric acid. Using an Ostwald viscometer, the solution was examined for flow time (T1) at 25°C. Subsequently, the sulfuric acid having a concentration of 98% by weight was examined alone for flow time (T2). The ratio of T1 to T2, i.e., $T1/T2$, was taken as the sulfuric-acid relative viscosity.

(2) o-Chlorophenol Relative Viscosity (OCP relative viscosity)

[0037] A 0.5-g portion of a sample was dissolved in o-chlorophenol so that the sample amount was 1 g per 100 mL of the o-chlorophenol. Using an Ostwald viscometer, the solution was examined for flow time (T1) at 25°C. Subsequently, the o-chlorophenol was examined alone for flow time (T2). The ratio of T1 to T2, i.e., $T1/T2$, was taken as the OCP

relative viscosity.

(3) Fineness

[0038] A fiber sample was set on a counter reel having a peripheral length of 1.125 m, and the counter reel was caused to make 200 revolutions to form a hank in a loop form. The hank was dried in a hot-air drying oven ($105 \pm 2^\circ\text{C} \times 60 \text{ min}$) and then weighed with a balance. The measured mass was multiplied by an official moisture regain, and the fineness was calculated from the resultant product. The official moisture regain of the core-sheath composite fiber was taken as 4.5% by weight.

(4) Strength and Elongation

[0039] A fiber sample was examined with "TENSILON" (registered trademark) UCT-100, manufactured by Orientec Co., Ltd., under the constant-speed stretching conditions shown in JIS L1013 (Test Methods for Chemical-Fiber Filament Yarns, 2010). The elongation was determined from the tensile strength/elongation curve by obtaining the elongation at the point on the curve where a maximum strength was observed. Meanwhile, a value obtained by dividing the maximum strength by the fineness was taken as the strength. The measurement was made ten times, and average values were taken as the strength and the elongation.

(5) Degree of Shrinkage with Boiling Water

[0040] A hank of a fiber was taken, and the sample length S_0 was measured under a load of 0.09 cN/dtex. Thereafter, the hank under no load was treated by immersion in boiling water for 15 minutes. After the treatment, the hank was air-dried and the sample length S_1 was measured under a load of 0.09 cN/dtex. The degree of shrinkage with boiling water was calculated using the following equation.

$$\text{Degree of shrinkage with boiling water} = (S_0 - S_1) / S_0 \times 100\% \quad (1)$$

(6) Recovery of Stretchability (CR)

[0041] The recovery of stretchability is an index to the crimp properties of false-twisted textured yarns.

[0042] A hank of a false-twisted texture yarn was taken, and was subjected, in a free state, to a 20-minute treatment with 90°C water and then air-dried. Subsequently, in 25°C water, a load of 0.0018 cN/dtex was imposed on the hank, and the hank length L_1 was measured at 2 minutes thereafter. Next, in the same water, the load of 0.0018 cN/dtex was removed and a load of 0.09 cN/dtex was imposed on the hank, and the hank length L_0 was measured at 2 minutes thereafter. The recovery of stretchability was calculated using the following equation.

$$\text{CR} = (L_0 - L_1) / L_0 \times 100\% \quad (2)$$

(7) ΔMR

[0043] Using a circular knitting machine, a cylindrical knitted fabric was produced so as to result in a stitch density of 50. In the case of fibers having a low fineness based on corrected weight, the fibers were suitably put together so that the fibers being supplied to the circular knitting machine had a total fineness of 50-100 dtex. In the case of a yarn having a total fineness exceeding 100 dtex, a single yarn was supplied to the circular knitting machine and knitted so as to result in a stitch density of 50 as in the case shown above. An about 1-2 g portion of the cylindrical knitted fabric is weighed out and introduced into a weighing bottle, dried by holding it at 110°C for 2 hours, and then weighed (W_0). Next, the specimen being examined is held at 20°C and a relative humidity of 65% for 24 hours and then weighed (W_{65}). Furthermore, this specimen is held at 30°C and a relative humidity of 90% for 24 hours and then weighed (W_{90}). ΔMR was calculated using the following equations.

$$\text{MR1} = [(W_{65} - W_0) / W_0] \times 100\% \quad (3)$$

$$MR2 = [(W90-W0)/W0] \times 100\% \quad (4)$$

$$\Delta MR = MR2 - MR1 \quad (5)$$

(8) Δ MR after Laundering

[0044] The cylindrical knitted fabric was repeatedly laundered 20 times by the method No. 103 described in JIS L0217 (1995), appended table 1. Thereafter, this fabric was examined to calculate the Δ MR (moisture absorbing/releasing properties) in the manner described above.

[0045] Fabrics having a Δ MR of 7.0% or larger were rated as S, and fabrics having a Δ MR of 5.0% or larger were rated as A.

(9) Retention of Δ MR after Laundering

[0046] The retention of Δ MR after laundering was calculated as an index to a change in Δ MR through laundering, using the following equation.

$$[(\Delta \text{MR after laundering}) / (\Delta \text{MR before laundering})] \times 100 \quad (6)$$

[0047] Fabrics having a retention of Δ MR of 95% or higher were rated as S, and fabrics which had a retention of Δ MR of 90% or higher and had laundering durability and which were regarded as giving satisfactory comfortableness during wear were rated as A. The others were rated as C.

(10) Feeling of Fabric

[0048] A core-sheath composite fiber of the present invention and a 22-dtex elastic polyurethane fiber were used to produce a bare plain knitted fabric using a 28G single circular knitting machine, and the knitted fabric was subjected to scouring, heat setting, dyeing, and finish setting to obtain a fabric. Meanwhile, an ordinary, nylon-6, 44-dtex, 26-filament, false-twist textured yarn (CR, 26%) was prepared, and a bare plain knitted fabric was produced therefrom in the same manner as described above. The fabrics obtained were evaluated for feeling and compared. S and A were acceptable.

S ... Far softer than the ordinary fabric formed using nylon-6.

A ... Superior in softness to the ordinary fabric formed using nylon-6.

C ... Equal to the ordinary fabric formed using nylon-6.

(11) Overall Evaluation

[0049] In the case where all of the Δ MR after laundering, retention of Δ MR after laundering, and feeling of fabric were rated as S, the fabric not only had comfortableness with satisfactory moisture absorbing properties but also had excellent softness; the overall evaluation in this case was S. In the case where all these properties were rated as A or higher, the overall evaluation was A. In the case where any of those properties was rated as C, the overall evaluation was C.

(12) Tension Measurement

[0050] Tension values were measured using TENSION METER and FT-R pickup sensor, both manufactured by Toray Engineering Co., Ltd.

[0051] With respect to fiber tension at the time of first-stage oil application, the value of tension was measured between the first-stage and second-stage oil application devices, and the tension value was divided by the fineness. The resultant quotient (cN/dtex) was taken as the fiber tension.

[0052] Winding tension was determined by measuring the tension value (cN) between the second roller and the winder.

[Example 1]

[0053] A polyetheresteramide copolymer (MH 1657, manufactured by Arkema Inc.; o-chlorophenol relative viscosity,

1.69) including nylon-6 as a polyamide component and polyethylene glycol having a molecular weight of 1,500 as a polyether component (poly(alkylene oxide)glycol) in which the proportion of the polyether component was about 76% by mole was used for the core, and nylon-6 having a sulfuric-acid relative viscosity of 2.71 and a terminal amino group content of 5.95×10^{-5} mol/g was used for the sheath. The polyetheresteramide copolymer and the nylon-6 were melted at 270°C and spun with a spinneret for concentric core-sheath formation so as to result in a core-sheath ratio (parts by weight) of 50/50. The terminal amino group content had been regulated with hexamethylenediamine and acetic acid during the polymerization.

[0054] During the spinning, the rotational speeds of the gear pumps were set so as to give core-sheath composite fibers having a total fineness of 57 dtex, and the core ingredient and the sheath ingredient were each ejected at a rate of 19.6 g/min. The filaments ejected from the spinneret nozzle were cooled and solidified with a filament cooler, and were then subjected to first-stage oil application in which an oil emulsion having a concentration of 1% was applied thereto with an oiling device. The tension of the fibers at this moment was 0.30 cN/dtex. A second-stage oiling device was disposed at a position 2.0 m downstream from the first-stage oiling, and an oil emulsion having a concentration of 15% was used to conduct oil application. Thereafter, the fibers were temporarily taken up by a first roller which was rotating at a speed of 3,500 m/min, and were subsequently wound up, via a second roller which was rotating at the same speed, by a winder having a peripheral speed regulated to 3,430 m/min so as to result in a winding tension of 5 cN. In this case, the time gap between the first-stage oil application and the second-stage oil application was 34 msec. The core-sheath composite fibers obtained had the properties shown in Table 1. Thus, core-sheath composite fibers having a degree of shrinkage with boiling water of 8.5% and an elongation of 75% were obtained.

[0055] Using a friction type false-twist texturing machine, the core-sheath composite fibers were processed under the conditions of a processing ratio of 1.3, processing speed of 400 m/min, and heater temperature 150°C, thereby obtaining a 44-dtex, 26-filament, false-twist textured yarn having an elongation of 34%. These false twisting conditions were common among the Examples and the Comparative Examples.

[0056] The false-twist textured yarn obtained was evaluated and, as a result, was found to have a Δ MR of 12.1% and a Δ MR after laundering of 11.8%, that is, the retention of Δ MR was 98%. The yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. The fabric showed an excellent feeling and was superior in softness to the ordinary nylon. Consequently, the overall evaluation was S.

[Example 2]

[0057] The speeds of the first roller and second roller were regulated to 3,200 m/min, and spinning was conducted using the same positional relationship between the first stage and the second stage as in Example 1, i.e., 2.0 m. Namely, spinning was conducted in which the oil application time gap was 38 msec. Incidentally, the speed of the winder was regulated so as to result in a winding tension of 5 cN, as in Example 1. The polymer ejection rates were regulated so as to give a false-twist textured yarn having a fineness of 44 dtex. The core-sheath composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 7.2%, and the elongation was 81%.

[0058] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated to 1.35 so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0059] The false-twist textured yarn obtained had a Δ MR after laundering of 11.2% and a retention of Δ MR of 97%. The yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. The fabric showed an excellent feeling and was superior in softness to the ordinary nylon. Consequently, the overall evaluation was S.

[Example 3]

[0060] The stretch ratio was regulated to 1.05. Namely, the speeds of the first roller and the second roller were regulated to 3,500 m/min and 3,675 m/min, respectively, to conduct spinning. The oil application time gap was the same as in Example 1, and the other conditions were set from the same standpoint as in Example 1. The core-sheath composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 9.5%, and the elongation was 66.

[0061] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0062] The false-twist textured yarn obtained had a Δ MR after laundering of 12.8% and a retention of Δ MR of 98%. The yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. Meanwhile, the feeling of the fabric was slightly rough and hard

because the degree of shrinkage with boiling water of the core-sheath composite fibers was higher than that in Example 1. However, the fabric showed better softness than the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was A.

[Example 4]

[0063] Spinning was conducted in which the core-sheath ratio (parts by weight) was 30/70, the speeds of the first roller and the second roller was 3,000 m/min each, and the oil application time gap was 40 msec. The core-sheath composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 6.1%, and the elongation was 69%.

[0064] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0065] The false-twist textured yarn obtained had a Δ MR after laundering of 7.2% and a retention of Δ MR of 91%. The yarn showed highly satisfactory moisture absorbing/releasing properties. Meanwhile, it is thought that since the roller speed had been lower than that in Example 1, the orientation of the core-sheath composite fibers had been affected thereby and the composite fibers had a slightly poor retention of Δ MR. However, the moisture absorbing/releasing properties had satisfactory laundering durability. With respect to the feeling of the fabric, the crimp was slightly weak and the fabric was slightly poor in fluffiness, because the degree of shrinkage with boiling water was lower than that in Example 1. However, the fabric showed better softness than the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was A.

[Example 5]

[0066] The procedure was changed so that the core-sheath ratio (parts by weight) was 20/80, the speeds of the first roller and the second roller were 3,800 m/min each, and the second-stage oil application was conducted at a position 1.25 m downstream from the first-stage oil application. Namely, spinning was conducted in which the oil application time gap was 20 msec. The core-sheath composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 10.8%, which was slightly high because the time gap had been set at a shorter period. The elongation was 58%.

[0067] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0068] The false-twist textured yarn obtained had a Δ MR after laundering of 5.9% and a retention of Δ MR of 98%. The yarn showed satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. Meanwhile, the feeling of the fabric was slightly rough and hard because the degree of shrinkage with boiling water of the core-sheath composite fibers was higher than that in Example 1. However, the fabric showed better softness than the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was A.

[Example 6]

[0069] Spinning was conducted in the same manner as in Example 1, except that nylon-6 having a sulfuric-acid relative viscosity of 3.30 and a terminal amino group content of 4.78×10^{-5} mol/g was used for the sheath. The core-sheath composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 9.3%, and the elongation was 70%.

[0070] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0071] The false-twist textured yarn obtained had a Δ MR after laundering of 12.2% and a retention of Δ MR of 99%. The yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. The fabric showed an excellent feeling and was superior in softness to the ordinary nylon. Consequently, the overall evaluation was S.

[Example 7]

[0072] Spinning was conducted in the same manner as in Example 1, except that nylon-6 having a sulfuric-acid relative viscosity of 2.40 and a terminal amino group content of 3.95×10^{-5} mol/g was used for the sheath. The core-sheath

composite fibers obtained had the properties shown in Table 1. The degree of shrinkage with boiling water was 6.7%, and the elongation was 84%.

[0073] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was regulated so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0074] The false-twist textured yarn obtained had a Δ MR after laundering of 9.2% and a retention of Δ MR of 93%. The yarn showed highly satisfactory moisture absorbing/releasing properties. Meanwhile, it is thought that since the sulfuric-acid relative viscosity had been lower than that in Example 1, the orientation of the core-sheath composite fibers had been affected thereby and the composite fibers had a slightly poor retention of Δ MR. However, the moisture absorbing/releasing properties had satisfactory laundering durability. With respect to the feeling of the fabric, the crimp was slightly weak and the fabric was slightly poor in fluffiness, because the degree of shrinkage with boiling water was lower than that in Example 1. However, the fabric showed better softness than the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was A.

[Comparative Example 1]

[0075] Spinning was conducted in which nylon-6 having a sulfuric-acid relative viscosity of 2.15 and a terminal amino group content of 4.70×10^{-5} mol/g was used for the sheath, the speeds of the first roller and second roller were regulated to 4,000 m/min, and the positional relationship between the first stage and the second stage was the same as in Example 1, i.e., 2.0 m. Namely, spinning was conducted in which the oil application time gap was 30 msec. The core-sheath composite fibers obtained had the properties shown in Table 2. The degree of shrinkage with boiling water was 11.5%, and the elongation was 68%.

[0076] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was set so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0077] The false-twist textured yarn obtained had a Δ MR after laundering of 7.5% and a retention of Δ MR of 70%. This yarn was poor in the laundering durability of moisture absorbing/releasing properties. The feeling of the fabric was considerably rough and hard because the degree of shrinkage with boiling water was higher than those in the Examples. The fabric obtained was nothing but one which was equal in feeling to the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was C.

[Comparative Example 2]

[0078] Spinning was conducted in which the speeds of the first roller and second roller were regulated to 4,200 m/min, and the positional relationship between the first stage and the second stage was the same as in Example 1, i.e., 2.0 m. Namely, spinning was conducted in which the oil application time gap was 7 msec. The core-sheath composite fibers obtained had the properties shown in Table 2. The degree of shrinkage with boiling water was 14.5%, and the elongation was 70%.

[0079] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was set so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0080] The false-twist textured yarn obtained had a Δ MR after laundering of 10.6% and a retention of Δ MR of 96%. This yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. Meanwhile, the feeling of the fabric was considerably rough and hard because the degree of shrinkage with boiling water was higher than those in the Examples. The fabric obtained was nothing but one which was equal in feeling to the fabric obtained using ordinary nylon-6. The feeling was rated as C. Consequently, the overall evaluation was C.

[Comparative Example 3]

[0081] Spinning was conducted in the same manner as in Example 1, except that the speed of the second roller was changed to 3,465 m/min and the surface temperature of the second roller was changed to 130°C. The core-sheath composite fibers obtained had the properties shown in Table 2. The degree of shrinkage with boiling water was 5.2%, and the elongation was 70%.

[0082] False twisting was conducted in the same manner as in Example 1, except that the processing ratio was set so as to give a false-twist textured yarn having an elongation of 35%. Thus, a 44-dtex, 26-filament, false-twist textured yarn was obtained.

[0083] The false-twist textured yarn obtained had a Δ MR after laundering of 11.5% and a retention of Δ MR of 96%.

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This yarn showed highly satisfactory moisture absorbing/releasing properties, and the moisture absorbing/releasing properties had highly satisfactory laundering durability. Meanwhile, with respect to the feeling of the fabric, the false-twist textured yarn had not been crimped because the degree of shrinkage with boiling water had been higher than those in the Examples and because the crystallization of the core-sheath composite fibers had proceeded. The fabric obtained was poor in fluffiness and was nothing but one which was equal in feeling to the fabric obtained using ordinary nylon-6. Consequently, the overall evaluation was C.

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Table 1

Core component	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6		Example 7	
	Polymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer
Sheath component	OCP relative viscosity	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69
	Polymer	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6	nylon-6
Core-sheath ratio	Sulfuric-acid relative viscosity	2.71	2.71	2.71	2.71	2.71	2.71	2.71	2.71	2.71	3.30	2.40	2.40	2.40
	Core/sheath	50/50	50/50	50/50	50/50	50/50	30/70	20/80	50/50	50/50	50/50	50/50	50/50	50/50
Spinning conditions	Oil application time gap between first stage and second stage (msec)	34	38	34	34	40	20	34	34	34	34	34	34	34
	Fibertension at first-stage oil application (cN/dtex)	0.30	0.25	0.29	0.35	0.30	0.22	0.37	0.30	0.37	0.22	0.37	0.22	0.22
	Speed of first roller (m/min)	3500	3200	3500	3500	3800	3500	3500	3800	3500	3500	3500	3500	3500
	Stretch ratio	1.0	1.0	1.05	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Speed of second roller (m/min)	3500	3200	3675	3500	3800	3500	3500	3800	3500	3500	3500	3500	3500

(continued)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Properties of unprocessed fibers	2.6	2.5	2.7	2.5	2.7	3.0	2.2
Strength (cN/dtex)							
Elongation (%)	75	81	66	69	58	70	84
Degree of shrinkage with boiling water (%)	8.5	7.2	9.5	6.1	10.8	9.3	6.7
Recovery of stretchability false-twist yarn	30	31	27	25	21	31	25
CR (%)							
ΔMR (%)	12.1	11.6	13.0	7.9	6.0	12.3	9.9
ΔMR after laundering (%)	S 11.8	S 11.2	S 12.8	S 7.2	A 5.9	S 12.2	S 9.2
Retention of ΔMR after laundering (%)	S 98	S 97	S 98	A 91	S 98	S 99	A 93
Sensory test	S	S	A	S	A	S	A
Overall evaluation	S	S	A	A	A	S	A

Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3
5	Core component	polyetheresteramide copolymer	polyetheresteramide copolymer	polyetheresteramide copolymer
		OCP relative viscosity	1.69	1.69
10	Sheath component	nylon-6	nylon-6	nylon-6
		Sulfuric-acid relative viscosity	2.15	2.71
15	Core-sheath ratio	Core/sheath	50/50	50/50
20	Spinning conditions	Oil application time gap between first stage and second stage (msec)	30	7
		Fiber tension at first- stage oil application (cN/dtex)	0.14	0.52
		Speed of first roller (m/min)	4000	4200
		Stretch ratio	1.0	1.0
		Speed of second roller (m/min)	4000	4200
30	Properties of Unprocessed fibers	Strength (cN/dtex)	2.2	2.4
		Elongation (%)	68	70
		Degree of shrinkage with boiling water (%)	11.5	14.5
35	Property of false- twist yarn	Recovery of stretchability CR (%)	23	29
40	Hygroscopicity	Δ MR (%)	10.7	11.0
		Δ MR after laundering (%)	S 7.5	S 10.6
		Retention of Δ MR after laundering (%)	C 70	S 96
45	Feeling of fabric	Sensory test	C	C
	Overall evaluation		C	C

INDUSTRIAL APPLICABILITY

[0084] According to the core-sheath composite fiber of the present invention, high hygroscopicity, laundering durability of the hygroscopicity, which makes the fiber withstand practical use, and a soft feeling can be attained.

Claims

1. A hygroscopic core-sheath composite fiber which comprises: a polyetheresteramide copolymer as a core polymer; and a polyamide as a sheath polymer, and which has a degree of shrinkage with boiling water of 6-11%.

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2. The hygroscopic core-sheath composite fiber according to claim 1, which has an elongation of 60-90%.

3. A false-twist textured yarn comprising the hygroscopic core-sheath composite fiber according to claim 1 or 2.

5 4. A fabric at least a part of which comprises the hygroscopic core-sheath composite fiber according to any one of claims 1 to 3.

10 5. A process for producing the hygroscopic core-sheath composite fiber according to claim 1 or 2, the process comprising: ejecting a filament from a spinneret; cooling and solidifying the ejected filament with a cooling wind; thereafter applying an aqueous solution (oil emulsion) twice to the filament; and then winding up the filament, wherein a time gap between the first-stage application and the second-stage application is 20 msec or longer.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/063971

A. CLASSIFICATION OF SUBJECT MATTER

D01F8/12(2006.01)i, D02G1/02(2006.01)i, D03D15/00(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)

D01F8/00-8/18, D02G1/00-3/48, D02J1/00-13/00, D01D1/00-13/02, D03D1/00-27/18

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	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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.
A	JP 6-136618 A (Toray Industries, Inc.), 17 May 1994 (17.05.1994), claims; examples (Family: none)	1-5
A	JP 58-104220 A (Teijin Ltd.), 21 June 1983 (21.06.1983), claims; page 3, upper right column, line 19 to lower left column, line 10; examples (Family: none)	1-5
A	JP 9-41204 A (Toray Industries, Inc.), 10 February 1997 (10.02.1997), claims; examples (Family: none)	1-5

☒ 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
04 August 2016 (04.08.16)Date of mailing of the international search report
16 August 2016 (16.08.16)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/JP2016/063971

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 51-84921 A (Toray Industries, Inc.), 24 July 1976 (24.07.1976), claims; examples (Family: none)	1-5
A	JP 9-256224 A (Teijin Ltd.), 30 September 1997 (30.09.1997), claims; examples (Family: none)	1-5

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 9188917 A [0010]
- WO 201410709 A [0010]
- JP 6136618 A [0010]
- JP 8209450 A [0010]