

(11) EP 3 845 477 A1

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 153(4) EPC

(43) Date of publication: 07.07.2021 Bulletin 2021/27

(21) Application number: 19855987.4

(22) Date of filing: 20.08.2019

(51) Int Cl.: **B65H 55/04** (2006.01)

(86) International application number: **PCT/JP2019/032407**

(87) International publication number: WO 2020/045161 (05.03.2020 Gazette 2020/10)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME KH MA MD TN

(30) Priority: 29.08.2018 JP 2018160115

(71) Applicant: Toray Industries, Inc. Tokyo, 103-8666 (JP) (72) Inventors:

 OSHIMA, Fumito lyo-gun, Ehime 791-3193 (JP)

• KAWAMOTO, Takashi Iyo-gun, Ehime 791-3193 (JP)

 MURAKAMI, Tetsuya lyo-gun, Ehime 791-3193 (JP)

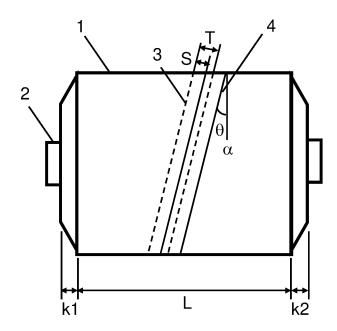
(74) Representative: Mewburn Ellis LLP
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) ACRYLIC YARN PACKAGE

(57) Provided is an acrylic yarn package which prevents winding yarn collapse during transportation when an acrylic yarn having a high total fineness is wound around a core bobbin. The acrylic yarn package includes

an acrylic yarn wound around a bobbin and having a total fineness of 8000 dtex or more. The acrylic yarn on the package has a yarn width of 0.22 mm/1000 dtex or more and hardness of 60 or more.

Fig. 1



EP 3 845 477 A1

Description

5

10

15

20

30

35

40

50

55

TECHNICAL FIELD

[0001] The present invention relates to an acrylic yarn package, and relates to an acrylic yarn package having a good package shape and less troubles during transportation and unwinding. In particular, the present invention is suitable as an acrylic precursor yarn package used for production of carbon fibers.

BACKGROUND ART

[0002] Polyacrylonitrile long fibers have been used as not only clothing but also precursors of carbon fibers in recent years, and many improvement techniques have been disclosed to obtain carbon fibers having excellent performance and to increase their productivity.

[0003] The carbon fibers are obtained by winding an acrylonitrile fiber varn as a precursor once in a yarn-making process of spinning the acrylonitrile fiber yarn, and then sending the acrylonitrile fiber yarn to a carbonization process, in which the fiber is heated in an air atmosphere at 200 to 300°C to convert the fiber into an oxidized fiber (oxidation process), and the oxidized fiber is further heated to 300 to 3000°C in an inert atmosphere such as nitrogen, argon, or helium to convert the oxidized fiber into a carbon fiber (carbonizing process). The carbon fibers are widely utilized as reinforcing fibers for composite materials in aerospace applications, sports applications, and general industrial applications and the like.

[0004] The carbon fiber generally includes a multifilament composed of filaments having 1000 or more monofilaments as one yarn unit, but because of a difference in production yarn speed between a yarn-making process and a carbonization process as a subsequent process, an acrylic yarn as a raw material is generally wound once in the yarn-making process, and then sent to the carbonization process. In order to increase the productivity in the carbonization process, it is effective to increase the amount of an acrylic yarn which can be processed per one time. However, the acrylic yarn is usually wound around a core bobbin, so that, if a large amount of yarn is wound around one bobbin, the bobbin may sag in a vertical direction during the transportation of the bobbin to the carbonization process, or bulge in side surfaces may increase, to result in winding yarn collapse causing unwinding failure in the carbonization process.

[0005] Patent Document 1 describes a technique for defining winding conditions such as a taper angle and winding tension in an acrylic yarn package for precursors of carbon fibers in order to obtain a good package shape during winding. However, Patent Document 1 describes no winding yarn collapse during transportation. Patent Document 2 describes a technique for obtaining a good package shape by taking a specific yarn width and yarn shift ratio for a thick acrylic yarn of 33000 dtex or more. However, unless moisture is applied to the yarn before winding to improve the bundling property, deterioration in the package shape and troubles during unwinding cannot be completely prevented, which causes a problem that winding yarn collapse occurs even during transportation. Because of the application of the moisture, the technique has the problem that the running cost increases and it is not suitable for long-distance movement due to a mass increase.

[0006] Furthermore, Patent Documents 3 and 4 describe techniques for defining the hardness of a package for fibers having a total fineness of several tens to several hundreds dtex in order to prevent winding yarn collapse during transportation. However, the technique cannot be directly applied to an acrylic yarn package for precursors of carbon fibers having a high total fineness exceeding 1000 dtex.

PRIOR ART DOCUMENTS

45 PATENT DOCUMENTS

[0007]

Patent Document 1: Japanese Patent Laid-open Publication No. 11-263534 Patent Document 2: Japanese Patent Laid-open Publication No. 2002-3081 Patent Document 3: Japanese Patent Laid-open Publication No. Sho51-23322

Patent Document 4: Japanese Patent Laid-open Publication No. 2005-273106

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] The present invention solves such problems of the conventional techniques, and an object of the present

invention is to provide an acrylic yarn package which prevents winding yarn collapse during transportation when an acrylic yarn having a high total fineness is wound around a core bobbin.

SOLUTIONS TO THE PROBLEMS

[0009] In order to solve the above-described problems, the present invention includes the following means. That is, an acrylic yarn package of the present invention is an acrylic yarn package including an acrylic yarn wound around a bobbin and having a total fineness of 8000 dtex or more, wherein the acrylic yarn on the package has a yarn width of 0.22 mm/1000 dtex or more and hardness of 60 or more.

EFFECTS OF THE INVENTION

[0010] The present invention can provide an acrylic yarn package which has a good package shape and prevents collapse during transportation of an acrylic yarn package having a high total fineness to a next process when the acrylic yarn is wound around a core bobbin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

20

5

10

15

Fig. 1 is a schematic view showing an acrylic yarn package.

Fig. 2 is a schematic view showing an acrylic yarn package having warpage occurring in its center.

EMBODIMENTS OF THE INVENTION

25

30

35

50

[0012] The present invention has made a diligent study on a carbon fiber precursor acrylic thick yarn package having a good package shape without collapsing even during transportation when an acrylic yarn having a high total fineness is wound around a core bobbin as the above problems, and has clarified that the problems are solved by setting the yarn width and hardness of the package to a certain level or higher.

[0013] A carbon fiber precursor acrylic yarn used in the present invention is composed of a so-called acrylic polymer, for example, preferably a polymer obtained by polymerizing 90% by mass or more of acrylicnitrile and less than 10% by mass of a comonomer. Examples of the comonomer which can be used include at least one selected from acrylic acid, methacrylic acid, itaconic acid, and methyl ester, ethyl ester, propyl ester, and butyl ester of these acids; alkali metal salt, ammonium salt, or allyl sulfonic acid, methallyl sulfonic acid, and alkali metal salts thereof, and the like.

[0014] Such an acrylic polymer can be obtained by using a known polymerization method, for example, a polymerization method such as emulsion polymerization, suspension polymerization, or solution polymerization. When an acrylic fiber is produced from these polymers, a polymer solution containing a solvent selected from, for example, dimethyl acetamide, dimethyl sulfoxide (hereinafter referred to as DMSO), dimethylformamide, aqueous solutions of nitric acid, zinc chloride, and sodium rhodanide is used as a spinning raw yarn, and spinning is performed by a wet spinning method or a dry spinning method.

[0015] The spun yarn is then subjected to bath draw, but the spun-out yarn may be directly subjected to the bath draw, or the spun-out yarn may be washed with water once to remove the solvent, followed by subjecting the spun yarn to the bath draw. In such bath draw, the spun yarn is preferably drawn about 2 to 6 times in a drawing bath at 50 to 98°C. After drawing, an oil agent is preferably applied to the spun yarn, and the spun yarn is subjected to drying and densification with a hot roller or the like. Then, the spun yarn is subjected to steam drawing, and then wound around a core bobbin to form a package.

[0016] When such a package is formed, a plurality of yarns may be combined, and then wound. It is effective to carbonize multifilament yarns at one time in order to improve the productivity of carbon fibers. Therefore, the total fineness of the yarn wound in the present invention is 8000 dtex or more. The moisture percentage of the yarn is preferably 3% or less in order to avoid an increase in mass during transportation. The total amount of the acrylic yarn obtained by subtracting a bobbin mass and an amount of moisture from the mass of the entire package is preferably large, preferably 120 kg or more, and more preferably 200 kg or more in order to reduce the set number of the acrylic yarn in a carbonization process to improve the work efficiency.

[0017] It is important that the hardness of a bobbin end measured by a durometer is set to 60 or more in order to eliminate winding yarn collapse during transportation. If the hardness is less than 60, the package is apt to loosen, which is apt to cause winding yarn collapse during transportation and yarn drop during unwinding to occur. The hardness of 60 or more can be achieved by setting the tension of the yarn during winding to an appropriate value. A large amount of yarn is commonly wound while a large tension is gradually attenuated, but the value may be an appropriate value

depending on the fineness of the yarn and the number of filaments.

[0018] In the acrylic yarn package of the present invention, it is necessary to wind the acrylic yarn on the package with the yarn width of the acrylic yarn set to 0.22 mm/1000 dtex or more. If the yarn width is smaller than 0.22 mm/1000 dtex, the thickness of the yarn becomes large, so that a gap causing yarn slip occurs between a yarn and another yarn adjacent to the yarn, which is apt to cause winding yarn collapse during transportation. If the yarn width is more than 0.54 mm/1000 dtex, the yarn convergency is deteriorated, which may cause troubles such as yarn drop and monofilament wrapping to occur during unwinding in the carbonization process, whereby the yarn width of the acrylic yarn on the package is preferably within a range of 0.22 mm to 0.54 mm/1000 dtex. The method for setting the yarn width on the package within the above range is not particularly limited, but when the yarn is wound with a winder, a method for winding the yarn after causing a group of free rollers for bundling to pass at a certain level or more is suitably used.

[0019] In the acrylic yarn package of the present invention, when the coefficient of static friction between the acrylic yarns is less than 0.13, bulge in side surfaces may occur during winding even if the yarn width and the hardness are controlled to specific conditions to prevent the winding yarn collapse. Therefore, the coefficient of static friction is preferably set to 0.13 or more by applying an appropriate type and amount of an oil agent.

[0020] In the acrylic yarn package of the present invention, it is preferable to set a yarn shift ratio to 15 to 59% and a taper angle on the package to 6 to 14°. The yarn shift ratio is a ratio of a yarn shift length S to a yarn width T in two yarns passing through the closest points on the package in parallel. That is, this yarn shift ratio is obtained by $(S/T) \times 100$ shown in Fig. 1. This will be conceptually described using Fig. 1. An acrylic yarn 4 is a yarn passing through the closest point on an acrylic yarn package 1 in parallel to an acrylic yarn 3. The yarn shift ratio is a ratio of the yarn shift length S between the acrylic yarn 3 and the acrylic yarn 4 to the yarn width T. The yarn width T and the yarn shift length S are values measured by methods to be described later.

[0021] As shown in Fig. 1, the taper angle is an angle (θ) between a straight line perpendicular to the axis of a core bobbin 2 (line α perpendicular to the axis direction of the core bobbin) and the direction of the acrylic yarn 4 to be wound. [0022] The yarn shift ratio and the taper angle can be usually controlled by setting the number of revolutions of a winder spindle per thread traverse, i.e., a so-called winding ratio to appropriate values. If the winding ratio is an integer, the yarn passes through the exactly same yarn passage before and after one traverse, whereby the yarn passage before and after one traverse can be shifted by setting the fractional portion of the winding ratio to an appropriate value, to control the yarn shift ratio. The taper angle can be controlled by setting the size of the entire winding ratio including an integer portion to an appropriate value. If the yarn shift ratio is less than 15%, the package has large undulations. Even if a winding tension is increased, the hardness may be decreased, which is apt to cause the winding yarn collapse to occur during transportation. When the yarn shift ratio is more than 59%, a contact surface between an inner layer yarn and an outer layer yarn is small, so that the pressing of the outer layer yarn during winding causes the inner layer yarn to slip, to push out the inner layer yarn, which causes bulge in side surfaces. Therefore, the yarn shift ratio is set within a range of 15% to 59%, whereby both the hardness and the end face shape can have good values.

[0023] If the taper angle is less than 6°, the yarn drop during unwinding is likely to occur. If the taper angle is more than 14°, the bulge in side surfaces is large, so that the taper angle is preferably within a range of 6 to 14°. When the yarn is wound with a constant winding ratio, the taper angle linearly decreases as the diameter of the package wound around the core bobbin increases, whereby the yarn can be wound while the taper angle is kept within a certain range by changing the winding ratio during winding depending on the winding amount of the yarn. For example, by providing a mechanism such that spindle drive and traverse drive are made to be independent from each other, the number of revolutions of the spindle is detected, calculation is performed so as to provide the set winding ratio, and then the number of revolutions of the traverse drive is controlled, the winding ratio can be freely set depending on the wilding amount in the winding process. Examples

[0024] Hereinafter, the present invention will be described in detail with reference to Examples and Comparative Examples. Measurement methods used in Examples and Comparative Examples will be described below.

<Total Fineness>

10

20

30

35

40

45

50

55

[0025] A sample yarn of 20 m was collected from a package to be measured, and a total fineness was determined by a method according to JIS L1013: 2010.

<Coefficient of Static Friction>

[0026] A sample yarn of 1.5 m was collected from a package to be measured, and wrapped around the collected package. At this time, the sample yarn was wound around the center of the package along the circumferential surface of the package. After the sample yarn was wound so that a contact angle with the package was set to 540°, a weight of 150 g was attached to each of both ends of the sample yarn. Then, the mass of the weight on one end side of the yarn was increased, and a mass of the weight when the yarn started to slip on a separate roll was measured. A coefficient

of static friction was calculated from the following formula.

Coefficient of static friction (μs) = $3/\pi \times Ln$ (T1/150)

 π : Circumference ratio

T1: Mass of weight (g) when yarn starts to slip.

<Yarn Width>

5

10

15

30

35

45

50

55

[0027] Using a caliper, the yarn width of the acrylic yarn on the package was measured at a total of five points of places within 2 cm from both ends of the package (hereinafter referred to as both ends), a center of the package, a place between one of both the ends and the center, and a place between the other end and the center, and a value obtained by dividing the measured value with the total fineness was taken as the yarn width.

<Yarn Shift Ratio>

[0028] For two yarns passing through the closest points on the package in parallel, a yarn shift length (S) shown in Fig. 1 was measured at a total of five points of both ends of the package, a center of the package, a place between one of both the ends and the center, and a place between the other end and the center using a caliper, and a value obtained by dividing the average value with the yarn width was taken as the yarn shift ratio.

25 < Taper Angle Range>

[0029] While the wound package was subjected to unwinding, an angle (θ) between a straight line (α) perpendicular to the axial direction of a core bobbin 2 shown in Fig. 1 and the direction of a yarn 4 to be wound was measured at the center of the package every 10 kg until all the yarns were discharged, and the range of the measured value was taken as a taper angle range.

<Hardness>

[0030] Using HARDNESS TESTER "Type C" (for Cellular Rubber & Yarn Package) manufactured by KOBUNSHI KEIKI CO.,LTD., values were measured at two places within 2 cm from both ends of the package, and the average value thereof was taken as the hardness of the yarn package.

<Winding Yarn Collapse during Transportation>

[0031] An acrylic yarn package was set at a trolley with a spindle, and one acrylic yarn package was subjected to a transportation vibration test according to JIS Z 0232: 2004 once to determine the presence or absence of winding yarn collapse according to the following two levels.

Good: No increase of 5.0 mm or more of bulge in side surfaces and no increase of 10 mm or more of warpage. Poor: Increase of 5.0 mm or more of bulge in side surfaces and increase of 10 mm or more of warpage.

[0032] A distance (U) between a straight line 5 connecting both ends of an upper part of the package shown in Fig. 2 and the farthest point on a curve 6 following the upper part of the package was measured, and taken as warpage U.

<Bulge in Side Surfaces>

[0033] Bulge length in side surfaces (k1, k2), which was a height of a point where a side surface of the package bulges on the outermost side, with respect to a yarn traverse width (L) on the outermost surface of the package, as shown in Fig. 1 was measured on each of both the side surfaces of the package, and the average value thereof was taken as bulge in side surfaces.

<Troubles during Unwinding>

[0034] When the package was set on a creel, and the entire amount was subjected to unwinding, those which did not cause yarn drop or monofilament wrapping were taken as good, and those which caused yarn drop or monofilament wrapping were taken as poor.

(Example 1)

5

10

30

35

40

50

55

[0035] Using a 19% DMSO solution of an acrylic polymer having an intrinsic viscosity [n] of 1.80 and containing 99.6% by mass of acrylonitrile and 0.4% by mass of itaconic acid as a raw spinning solution, and a spinneret having 6000 pores, semi-wet spinning was performed in a coagulation bath containing 30% of DMSO and 70% of water at 8°C to obtain a coagulated yarn. The coagulated yarn was drawn 2.8 times in hot water while being washed with water. Furthermore, the remaining DMSO was washed with water until the DMSO amount became 0.01% or less in the yarn, and a silicone-based oil agent was then applied, followed by drying and densification at 150 to 160°C. Subsequently, the yarn was drawn 4.3 times in pressurized steam, and then dried again. Two 6000-filament yarns were combined, and a 12000-filament yarn having a total fineness of 13300 dtex was wound around an FRP core bobbin having an outer diameter of 145 mm with a winder so that the total amount of the acrylic yarn obtained by subtracting the bobbin mass and the amount of moisture from the mass of the entire package was set to 120 kg in a yarn width, a yarn shift ratio, and a taper angle range shown in Table 1. The amount of moisture was determined by collecting a yarn of about 12 m to be wound in advance, measuring a moisture percentage by a method according to JIS L1013: 2010, and multiplying the moisture percentage by the amount of the wound yarn.

[0036] As a result, as shown in Table 1, a good package which did not cause winding yarn collapse during transportation was provided.

(Examples 2 to 5 and Comparative Examples 1 to 4)

[0037] An acrylic yarn was wound in a yarn width, a yarn shift ratio, and a taper angle range shown in Table 1 in the same manner as in Example 1 except that the total weight of the acrylic yarn obtained by subtracting a bobbin mass and an amount of moisture from the mass of an entire package was set to 240 kg, and a yarn width during winding, and a winding ratio and tension of a winder were changed.

[0038] As a result, as shown in Table 1, Examples 2 to 5 provided a good package which did not cause winding yarn collapse during transportation, but Example 4 caused a high yarn shift ratio of 60% or more during winding, to result in a small contact surface between an inner layer yarn and an outer layer yarn, so that the outer layer yarn pressed the inner layer yarn during winding, and the inner layer yarn slid and was pushed out, to result in a package having large bulge in side surfaces. Example 5 caused a large yarn width of 0.55 mm/1000 dtex or more to result in poor yarn convergency, so that yarn drop and monofilament wrapping occurred during unwinding in a carbonization process. Comparative Examples 1 to 3 had hardness of less than 60 as compared with Example 2, and caused winding yarn collapse during transportation. Comparative Example 4 had a yarn width of less than 0.22 mm/1000 dtex as compared with Example 2, and caused winding yarn collapse during transportation.

(Examples 6 and 7)

[0039] A yarn was wound in a yarn width and a yarn shift ratio shown in Table 1 in the same manner as in Example 2 except that the amount of an oil agent deposited was adjusted to change the coefficient of static friction of the yarn. As a result, as shown in Table 1, a good package which did not cause winding yarn collapse during transportation was provided. Example 6 had a low coefficient of static friction of less than 0.13 and caused yarn lateral sliding during winding, to result in a package having large bulge in side surfaces.

(Example 8)

[0040] A 24000-filament yarn having a total fineness of 26600 dtex was wound in a yarn width and a yarn shift ratio shown in Table 1 in the same manner as in Example 2 except that four 6000-filament yarns were combined.

[0041] As a result, as shown in Table 1, a good package which did not cause winding yarn collapse during transportation was provided.

(Example 9)

[0042] A 24000-filament yarn having a total fineness of 29100 dtex was wound in a yarn width and a yarn shift ratio

shown in Table 1 in the same manner as in Example 8 except that a drawing ratio in pressurized steam was set to 3.9. **[0043]** As a result, as shown in Table 1, a good package which did not cause winding yarn collapse during transportation was provided.

5 (Example 10)

[0044] A 36000-filament yarn having a total fineness of 26600 dtex was wound in a yarn width and a yarn shift ratio shown in Table 1 in the same manner as in Example 2 except that six 6000-filament yarns having a monofilament fineness of 0.74 dtex were combined.

[0045] As a result, as shown in Table 1, a good package which did not cause winding yarn collapse during transportation was provided.

[Table 1-1]

during unwinding No winding yarn collapse: good Less than 15mm: very good No troubles: good Winding yarn collapse: poor Less than 25 mm: good Troubles: poor 25 mm or more: poor Troubles Good Good Good Good Good Good Good Good Poor Good Good Good Good Poor 5 Determination Very good Bulge in side surfaces Good Poor Poor Poor 10 value [mm] Numerical 4 26 23 20 24 28 7 24 22 22 22 29 22 15 collapse during Winding yarn transportation Good Poor Poor Poor Poor 20 25 Hardness \equiv 75 75 2 62 22 8 74 7 28 29 22 65 17 8 [Table 1] angle 7 to 13 range 16 30 \Box 7 to , 10 1 7 to 3 to, ratio [%] Yarn shift 54 54 19 9 20 20 54 57 4 28 10 54 54 50 35 Yarn width 1000dtex] [mm/ 0.40 0.40 0.40 0.38 0.40 0.26 0.30 0.29 0.40 0.40 0.37 0.67 0.37 0.21 40 of static friction [-] Coefficient 0.15 0.15 0.15 0.15 0.14 0.16 0.16 0.16 0.22 45 Winding amount 240 240 240 240 240 240 240 240 [kg] 120 240 240 240 240 240 fineness 50 13300 13300 13300 13300 13300 13300 13300 26600 29100 26600 13300 13300 13300 13300 Total [dtex] Comparative Comparative Comparative Comparative Example 10 Example 5 Example 8 Example 3 Example 4 Example 2 Example 3 Example 6 Example 9 Example 1 Example 2 Example 4 Example 7 Example 1 55 [0046]

DESCRIPTION OF REFERENCE SIGNS

[0047]

- 5 1: Acrylic yarn package
 - 2: Core bobbin
 - 3: Acrylic yarn
 - 4: Acrylic yarn
 - 5: Straight line connecting both ends of upper part of package
- 6: Curve following upper part of package
 - L: Yarn traverse width
 - k1, k2: Bulge length in side surfaces
 - S: Yarn shift length
 - T: Yarn width
- 15 U: Warpage
 - θ: Taper angle
 - $\alpha \mbox{:}\ \mbox{Line}$ perpendicular to core bobbin axis direction

20 Claims

25

30

35

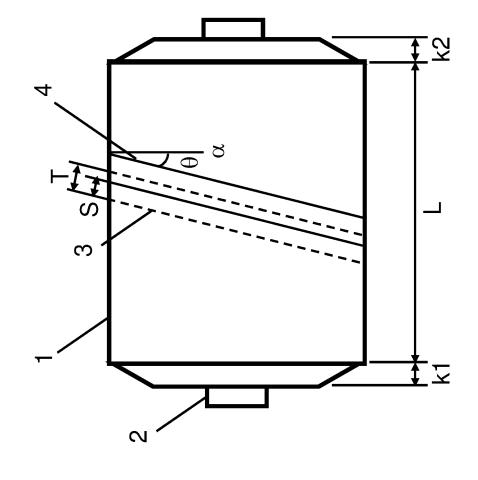
- 1. An acrylic yarn package comprising an acrylic yarn wound around a bobbin and having a total fineness of 8000 dtex or more, wherein
 - the acrylic yarn on the package has a yarn width of 0.22 mm/1000 dtex or more and hardness of 60 or more.
- 2. The acrylic yarn package according to claim 1, wherein a total amount of the acrylic yarn is 120 kg or more.
- 3. The acrylic yarn package according to claim 1 or 2, wherein the acrylic yarn has a coefficient of static friction of 0.13 or more.
- **4.** The acrylic yarn package according to any one of claims 1 to 3, wherein the acrylic yarn on the package has a yarn width of 0.22 to 0.54 mm/1000 dtex, a yarn shift ratio of 15 to 59%, and a taper angle of 6 to 14°.

40

45

50

55



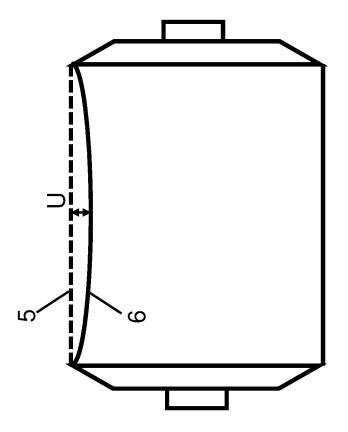


Fig. 2

INTERNATIONAL SEARCH REPORT International application No. PCT/JP2019/032407 A. CLASSIFICATION OF SUBJECT MATTER 5 Int.Cl. B65H55/04(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) 10 Int.Cl. B65H55/04 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2019 Registered utility model specifications of Japan 1996-2019 15 Published registered utility model applications of Japan 1994-2019 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages JP 2002-3081 A (TORAY INDUSTRIES, INC.) 09 January Υ 1 - 42002, paragraphs [0014]-[0022], fig. 1-2 (Family: 25 Υ JP 2016-69160 A (TORAY INDUSTRIES, INC.) 09 May 1 - 42016, paragraphs [0006], [0011], [0015] (Family: none) Υ JP 3827672 B2 (ASAHI KASEI FIBERS CORP.) 27 1 - 430 September 2006, paragraph [0021] (Family: none) 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 45 document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 07 October 2019 (07.10.2019) 21 October 2019 (21.10.2019) Name and mailing address of the ISA/ Authorized officer Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan Telephone No. 55 Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/032407

5	C (Continuation)	C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
10	Y	JP 2003-335457 A (TOYOBO BOSEKI KABUSHIKI KAISHA) 25 November 2003, paragraphs [0010], [0025] (Family: none)	3-4	
	Α	JP 10-120302 A (TORAY INDUSTRIES, INC.) 12 May 1998 (Family: none)	1-4	
15	A	JP 2003-34466 A (TORAY INDUSTRIES, INC.) 07 February 2003 (Family: none)	1-4	
	A	JP 58-212563 A (TORAY INDUSTRIES, INC.) 10 December 1983 (Family: none)	1-4	
20	Α	JP 2004-123296 A (TORAY INDUSTRIES, INC.) 22 April 2004 (Family: none)	1-4	
25				
30				
35				
40				
45				
50				
55	E DOTTIGA (0.1	10 (continuation of second sheet) (January 2015)		

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 11263534 A [0007]
- JP 2002003081 A **[0007]**

- JP 51023322 A **[0007]**
- JP 2005273106 A **[0007]**