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# (11) EP 4 560 060 A1

(12)

## **EUROPEAN PATENT APPLICATION**

published in accordance with Art. 153(4) EPC

(43) Date of publication: **28.05.2025 Bulletin 2025/22** 

(21) Application number: 23842749.6

(22) Date of filing: 22.06.2023

(51) International Patent Classification (IPC): **D01F 8/14** (2006.01)

(52) Cooperative Patent Classification (CPC): **D01F 8/14** 

(86) International application number: **PCT/JP2023/023193** 

(87) International publication number: WO 2024/018818 (25.01.2024 Gazette 2024/04)

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR

**Designated Extension States:** 

BA

**Designated Validation States:** 

KH MA MD TN

(30) Priority: 22.07.2022 JP 2022116919

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

 NAKAMICHI, Shinya Otsu-shi, Shiga 520-2141 (JP)

YOSHIGAI, Taichi
 Otsu-shi, Shiga 520-2141 (JP)

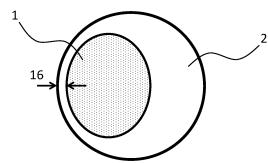
 INADA, Kojiro Otsu-shi, Shiga 520-2141 (JP)

(74) Representative: Kador & Partner Part mbB Corneliusstraße 15 80469 München (DE)

## (54) COMPOSITE FIBER, STRUCTURAL YARN, WOVEN AND KNITTED FABRIC, AND CLOTHING

In order to provide a composite fiber that satisfies both properties of stretchability and wear resistance, and exhibits high sensitiveness of a carded wool material, among wool materials, characterized by softness, deep color development, and bulkiness, and combined filament composite fiber, woven or knitted fabric, and clothing including the composite fiber, the composite fiber of the present invention includes a polyester-based thermoplastic resin A and a polyester-based thermoplastic resin B, and satisfies following requirements: (1) a difference (MA - MB) between a weight-average molecular weight  $\mathbf{M}_{\mathbf{A}}$  of the polyester-based thermoplastic resin  $\mathbf{A}$ and a weight-average molecular weight M<sub>R</sub> of the polyester-based thermoplastic resin B is 2000 to 15000; (2) an apparent thick-to-thin ratio ( $D_{thick}/D_{thin}$ ) of the composite fiber is 1.00 to 1.04; (3) a crimp elongation rate of the composite fiber is 3.0 to 25.0%; (4) in a cross-section of the composite fiber, the polyester-based thermoplastic resin B covers the polyester-based thermoplastic resin A, and a ratio  $(t_{min}/D)$  of a minimum value  $t_{min}$  of a thickness t of the polyester-based thermoplastic resin B to a fiber diameter D of the composite fiber is 0.01 to 0.10; and (5) In the cross-section of the composite fiber, a length Ct of a portion in which a region having the thickness t satisfying  $1.00t_{min} \leq t \leq 1.05t_{min}$  and a circumferential line of the composite fiber are overlapped satisfies  $Ct \ge 0.33C$  with respect to a circumferential length C of the entire composite fiber.

[Fig. 1]



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#### Description

#### **TECHNICAL FIELD**

5 [0001] The present invention relates to a composite fiber, a structural yarn, a woven or knitted fabric, and a clothing.

#### **BACKGROUND ART**

[0002] Conventionally, among wool materials, a carded-wool touch fabric is required having softness, deep color development, feelings of a carded wool material characterized by bulkiness, and both functions such as stretchability and wear resistance and durability.

**[0003]** Until now, as a wool touch fabric, for example, as disclosed in Patent Document 1, a fabric made by mixing and entangling two types of latent crimping fibers having different thermal shrinkage rates has been proposed. Citation List

15 PRIOR ART DOCUMENT

PATENT DOCUMENT

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[0004] Patent document 1: Japanese Patent Laid-open Publication No. 2004-197231

SUMMARY OF THE INVENTION

#### PROBLEMS TO BE SOLVED BY THE INVENTION

- [0005] As a method for obtaining a grain appearance of wool touch, a method of imparting thickness and thinness in a fiber longitudinal direction at a draw ratio of a natural draw ratio or less is known, and in this method, a grain appearance, which is one feature of various wool materials, can be obtained. On the other hand, the characteristics of wool such as uniform deep color development, bulkiness, and softness are insufficient, and wear resistance is also difficult to obtain because a fiber structure of a thick portion in the thickness and thinness is undeveloped.
- [0006] In addition, as one of means for obtaining soft and bulky feelings of carded-wool touch, means for obtaining a fabric with entangled mixed yarn of long fibers having a crimp (crimpiness) structure found in wool is considered. However, in a technique as disclosed in Patent Document 1, when the boiling water shrinkage rate of the high-shrinkable fiber is 10% or more, the fiber is constrained in the fabric, and sufficient softness cannot be obtained. Furthermore, the low-shrinkage fiber disclosed in Patent Document 1 has a problem that durability and feelings cannot be achieved simultaneously because physical properties are significantly deteriorated by alkali treatment. That is, the carded-wool touch feelings such as softness, deep color development, and bulkiness, stretchability, and wear resistance could not be satisfied simultaneously.
  - **[0007]** The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a composite fiber, a structural yarn, a woven or knitted fabric, and clothing that satisfy both properties of stretchability and wear resistance, and exhibit high sensitiveness of a carded wool material, among wool materials, characterized by softness, deep color development, and bulkiness, particularly, soft carded-wool touch.

#### SOLUTIONS TO THE PROBLEMS

- <sup>45</sup> **[0008]** The present invention has the following structures.
  - [1] A composite fiber including a polyester-based thermoplastic resin A and a polyester-based thermoplastic resin B, and satisfying the following requirements.
    - (1) A difference ( $M_A$   $M_B$ ) between a weight-average molecular weight  $M_A$  of the polyester-based thermoplastic resin A and a weight-average molecular weight  $M_B$  of the polyester-based thermoplastic resin B is 2000 to 15000.
    - (2) An apparent thick-to-thin ratio ( $D_{thick}/D_{thin}$ ) of the composite fiber is 1.00 to 1.04.
    - (3) The crimp elongation rate of the composite fiber is 3.0 to 25.0%.
    - (4) In a cross-section of the composite fiber, the polyester-based thermoplastic resin B covers the polyester-based thermoplastic resin A, and a ratio  $(t_{min}/D)$  of a minimum value  $t_{min}$  of a thickness t of the polyester-based thermoplastic resin B to a fiber diameter D of the composite fiber is 0.01 to 0.10.
    - (5) In the cross-section of the composite fiber, a length  $C_t$  of a portion in which a region having the thickness t satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and the circumferential line of the composite fiber are overlapped satisfies  $Ct \ge 1.05t_{min}$

0.33C with respect to a circumferential length C of the entire composite fiber.

- [2] The composite fiber according to the above [1], in which at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing.
- [3] The composite fiber according to the above [2], in which the other thread is a latent crimping yarn.
  - [4] A structural yarn in which cracks are made on an entire circumference of the surface of the composite fiber according to the above [1].
  - [5] The structural yarn according to the above [4], in which at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing.
- [6] The structural yarn according to the above [5], in which the other thread is an explicit crimping yarn.
  - [7] A woven or knitted fabric obtained by weaving or knitting, using the composite fiber according to any one of the above [1] to [3] in at least a portion of the woven or knitted fabric.
  - [8] A woven or knitted fabric including the structural yarn according to any one of the above [4] to [6] in at least a portion of the woven or knitted fabric.
  - [9] Clothing including the woven or knitted fabric according to the above [7] or [8] in at least a portion of the woven or knitted fabric.

#### **EFFECTS OF THE INVENTION**

20 [0009] According to the present invention, it is possible to obtain a composite fiber that satisfies both properties of stretchability and wear resistance, and exhibits high sensitiveness of carded wool material, among wool materials, characterized by softness, deep color development, and bulkiness, particularly, soft carded-wool touch. In particular, the structural yarn, the woven or knitted fabric, and the clothing using the composite fiber of the present invention can be an item in the field of outerwear worn as a women's or men's wear, for example, clothing such as a jacket, a suit, or a lower garment.

#### BRIEF DESCRIPTION OF THE DRAWINGS

#### [0010]

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- Fig. 1 is a cross-sectional view illustrating an existence form of a polyester-based thermoplastic resin A and a polyester-based thermoplastic resin B of a composite fiber of the present invention.
- Fig. 2 is a perspective view illustrating one embodiment of a surface of the composite fiber of the present invention. Fig. 3 is a schematic view of a draw and relaxation heat treatment device used in production of the composite fiber of the present invention.
- Fig. 4 is a schematic view of a final distribution plate according to Example 1 of the composite fiber of the present invention.
- Fig. 5 is a schematic view of a final distribution plate according to Comparative Example 5 of the composite fiber of the present invention.

#### **EMBODIMENTS OF THE INVENTION**

[0011] A composite fiber of the present invention includes a polyester-based thermoplastic resin A and a polyesterbased thermoplastic resin B, and satisfies the following requirements (1) to (5):

- (1) A difference ( $M_A$   $M_B$ ) between a weight-average molecular weight  $M_A$  of the polyester-based thermoplastic resin A and a weight-average molecular weight M<sub>B</sub> of the polyester-based thermoplastic resin B is 2000 to 15000.
- (2) An apparent thick-to-thin ratio ( $D_{thick}/D_{thin}$ ) of the composite fiber is 1.00 to 1.04.
- (3) The crimp elongation rate of the composite fiber is 3.0 to 25.0%.
- (4) In a cross-section of the composite fiber, the polyester-based thermoplastic resin B covers the polyester-based thermoplastic resin A, and a ratio  $(t_{min}/D)$  of a minimum value  $t_{min}$  of a thickness t of the polyester-based thermoplastic resin B to a fiber diameter D of the composite fiber is 0.01 to 0.10.
- (5) In the cross-section of the composite fiber, a length Ct of a portion in which a region having the thickness t satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and the circumferential line of the composite fiber are overlapped satisfies  $C_t \ge 0.33C$  with respect to a circumferential length C of the entire composite fiber.

[0012] Hereinafter, the present invention will be described in detail, but the present invention is not limited to the scope described below at all as long as the gist thereof is not exceeded.

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[Polyester-Based Thermoplastic Resin A, Polyester-Based Thermoplastic Resin B]

**[0013]** The composite fiber of the present invention includes the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B.

**[0014]** As the polyester-based resin to be used for the composite fiber of the present invention, it is preferable to use a polyethylene terephthalate-based resin with a main repeat unit of ethylene terephthalate, a polytrimethylene terephthalate-based resin with a main repeat unit of trimethylene terephthalate, or a polybutylene terephthalate-based resin with a main repeat unit of butylene terephthalate. More preferably, both the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B have a main repeat unit of ethylene terephthalate. Here, the phrase "the main repeating unit is ethylene terephthalate" means that the proportion of a structure derived from ethylene terephthalate contained in the repeating unit is 60 mol% or more. The same applies hereinafter.

**[0015]** The polyethylene terephthalate-based resin, the polytrimethylene terephthalate-based resin, and the polybutylene terephthalate-based resin described above may have a small amount (usually less than 30 mol%) of copolymerization component as necessary. When the copolymerization component of the polyester-based thermoplastic resin A is 8 mol% or less, the crimp elongation rate can be increased, and the strength is maintained even after alkali weight reduction, so that softness is easily obtained, which is preferable. Furthermore, when the copolymerization components are 8 mol% or less, a molecular orientation in the composite fiber can be maintained even after dyeing processing, for example, so that dimensional stability is improved. In addition, preferably, the copolymerization components are 5 mol% or less in both the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B, and more preferably, the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B contain no copolymerization component. When no copolymerization component is contained, the boiling water shrinkage rate of the composite fiber can be 10% or less, so that it is easy to make the feelings of the woven or knitted fabric softer.

**[0016]** The polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B in the present invention may contain one kind or two or more kinds of a micropore forming agent, a cationic dyeable agent, a coloring inhibitor, a heat stabilizer, a flame retardant, a fluorescent brightener, a delusterant, a colorant, an antistatic agent, a moisture absorbent, an antibacterial agent, inorganic fine particles, and the like as necessary within a range in which the object of the present invention is not impaired.

**[0017]** In the composite fiber of the present invention, the difference ( $M_A$  -  $M_B$ , hereinafter may be simply referred to as "difference in weight-average molecular weight") between the weight-average molecular weight  $M_A$  of the polyester-based thermoplastic resin A and the weight-average molecular weight  $M_B$  of the polyester-based thermoplastic resin B is 2000 to 15000. When the difference in weight-average molecular weight is less than 2000, the resilience and stretchability of the composite fiber are lowered, and the color development is also lowered because cracks are not formed by alkali treatment. The difference in weight-average molecular weight is preferably 5000 or more. On the other hand, when the difference in weight-average molecular weight is preferably of the raw yarn decreases, and spinning becomes unstable. The difference in weight-average molecular weight is preferably 13000 or less.

**[0018]** In addition, a value of the weight-average molecular weight  $M_A$  of the polyester-based thermoplastic resin A is preferably in a range of 20000 to 28000, and a value of the weight-average molecular weight  $M_B$  of the polyester-based thermoplastic resin B is preferably in a range of 12000 to 20000. Within these ranges, functionality and durability of the composite fiber are improved, and step stability in spinning the composite fiber is also improved.

[0019] The weight-average molecular weight in the present invention is measured by the method described in Examples.

[Composite Fiber or Structural Yarn]

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[0020] In the composite fiber of the present invention, the polyester-based thermoplastic resin B covers the polyester-based thermoplastic resin A. That is, as schematically illustrated in Fig. 1, the composite fiber has a composite cross-section in which the polyester-based thermoplastic resin A1 and the polyester-based thermoplastic resin B2 are present in a state of being substantially joined without being separated in a cross-section substantially perpendicular to a fiber axis of the composite fiber, and the polyester-based thermoplastic resin B2 covers the polyester-based thermoplastic resin A1 on a fiber surface.

**[0021]** At this time, in the cross-section of the composite fiber, the ratio  $(t_{min}/D)$  of the minimum value  $t_{min}$  of the thickness t16 of the polyester-based thermoplastic resin B covering the polyester-based thermoplastic resin A to the fiber diameter D of the composite fiber is 0.01 to 0.10. If  $(t_{min}/D)$  is less than 0.01, fabric quality due to fluff or the like, wear resistance, and color development are deteriorated. The ratio is preferably 0.02 or more. In addition, when  $(t_{min}/D)$  exceeds 0.10, it becomes difficult to obtain bulkiness and softness by sufficient crimp exhibition force. From the viewpoint of further enhancing the bulkiness and softness as well as further improving the stretchability, the  $(t_{min}/D)$  is preferably 0.08 or less. Examples of the method for setting  $(t_{min}/D)$  within the above range include performing a spinning step using a specific distribution plate as described later.

**[0023]** In the cross-section of the composite fiber of the present invention is preferably an eccentric core-sheath type. **[0023]** In the cross-section of the composite fiber of the present invention, a length  $C_t$  of a portion in which a region having the thickness t satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and the circumferential line of the composite fiber are overlapped satisfies  $Ct \ge 0.33C$  with respect to a circumferential length C of the entire composite fiber. Here, when a portion in which a region having the thickness t satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and the circumferential line of the composite fiber are overlapped is discontinuous, a total of individual values is defined as Ct. In this way, as compared with a conventional eccentric coresheath composite fiber having the same ratio of an area  $(S_A)$  of the polyester-based thermoplastic resin A to an area  $(S_B)$  of the polyester-based thermoplastic resin B in its cross-section, the centers of gravity of regions where the respective resins exist are apart from each other, so that the obtained crimping fiber is capable of forming a finer spiral and exhibiting satisfactory crimpiness, and it is possible to obtain woven or knitted fabric excellent in bulkiness and softness. Furthermore, in order to obtain crimpiness suitable for a woven or knitted fabric having a bulkiness and softness,  $C_t \ge 0.40C$  is more preferable. In addition, in principle, Ct < C, and  $C_t \le 0.70C$  is preferable. Examples of the method for setting  $Ct \ge 0.33C$  include performing the spinning step using a specific distribution plate as described later.

**[0024]** Furthermore, in the composite fiber of the present invention, the apparent thick-to-thin ratio  $(D_{thick}/D_{thin})$  is 1.00 to 1.04. In the present invention, the apparent thick-to-thin ratio  $(D_{thick}/D_{thin})$  is a ratio of an average fiber diameter  $(D_{thick})$  of relatively thick portions to an average fiber diameter  $(D_{thin})$  of relatively thin portions after a width in a direction orthogonal to the fiber axis direction is measured for 50 cm of the composite fiber bundle at a load of 0.11 cN/dtex and is classified into relatively thick portions and thin portions by the method described in Examples. An apparent thick-to-thin ratio  $(D_{thick}/D_{thin})$  of the composite fiber is theoretically 1.0 or more. On the other hand, when  $(D_{thick}/D_{thin})$  is more than 1.04, wear resistance is deteriorated, and bulkiness and softness are deteriorated.  $(D_{thick}/D_{thin})$  is preferably 1.02 or less.  $(D_{thick}/D_{thin})$  can be set to the above range by performing pin draw in a range exceeding the natural draw ratio and performing relaxation heat treatment.

**[0025]** Specific measurement methods of the thickness t, the fiber diameter D, the thick-to-thin ratio, the circumferential length C, and the like are as described in Examples.

**[0026]** The crimp elongation rate of the composite fiber of the present invention is 3.0 to 25.0%. In the case where the crimp elongation rate is less than 3.0%, bulkiness and wear resistance cannot be obtained. Preferably, the crimp elongation rate is 5.0% or more. On the other hand, when the crimp elongation rate exceeds 25.0%, the crimp becomes too fine, and the bulkiness and softness of the woven or knitted fabric surface are impaired. When the crimp elongation rate is too high, cracks are not formed because the orientation of the thermoplastic resins constituting the composite fiber is high, and the color development is poor. The crimp elongation rate is preferably 15.0% or less. The crimp elongation rate can be measured by the method described in Examples.

**[0027]** The crimp elongation rate can be set within the above range by subjecting the yarn obtained in the spinning step to pin draw and relaxation heat treatment. When only pin draw is performed, the orientation difference of the thermoplastic resins constituting the composite fiber increases, and the crimp elongation rate becomes too large. On the other hand, when only relaxation heat treatment is performed, the orientation difference of the thermoplastic resins constituting the composite fiber becomes too small, and the crimp elongation rate becomes too small.

[0028] In the present invention, by simultaneously satisfying the requirements (1) to (5) described above, it is possible to solve at once the high sensitiveness of carded-wool touch such as softness, deep color development, and bulkiness which are problems of the conventional mixed fiber material, and both properties of the stretchability and the wear resistance.

[0029] In addition, the composite fiber is not limited to a particular cross-sectional shape, and cross-sectional shapes such as a circular shape, an elliptical shape, and a triangular shape can be adopted. The circular shape is more preferable

**[0030]** In the composite fiber of the present invention, when a ratio  $S_A$ :  $S_B$  of the area  $(S_A)$  of the polyester-based thermoplastic resin A to the area  $(S_B)$  of the polyester-based thermoplastic resin B in the cross-section is preferably 70:30 to 30:70, more preferably 60:40 to 40:60, physical properties are improved. In addition, in order to make the crimpiness of the composite fiber finer,  $S_A \ge S_B$  is further preferable.

[0031] An average fiber diameter  $D_{ave}$  of the composite fiber in the present invention is preferably 10  $\mu m$  to 30  $\mu m$ . Within this range, tenseness, stiffness, and stretchability, and a soft touch close to a natural wool material in the case of the woven or knitted fabric can be obtained. In the present invention, the average fiber diameter  $D_{ave}$  is a value calculated from the fineness of the composite fiber.

**[0032]** The composite fiber of the present invention is preferably subjected to twist yarn for a desired purpose. The twist coefficient (K) of twist yarn is preferably set to 6000 to 24000. Within such a range, the stretchability and resilience of the woven or knitted fabric are more easily obtained. Here, the twist coefficient can be calculated by the following formula.

Twist coefficient (K) = Number of twists (T/m)  $\times \sqrt{\text{(fineness (dtex)} \times 0.9)}$ .

because the composite fiber satisfying the requirements (1) to (5) can be stably spun.

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**[0033]** The composite fiber of the present invention usually exhibits a structure such as crimpiness by thermal history. Examples of the thermal history include hot water treatment, alkali weight reduction treatment, and the like performed in a dyeing step and the like described later. In the present invention, a composite fiber exhibiting a structure such as crimpiness is referred to as a structural yarn.

[0034] The structural yarn of the present invention preferably has a crack on the entire circumference of the surface of the structural yarn in at least a portion of the fiber in the fiber length direction. The color development of the woven or knitted fabric can be further enhanced by having a crack on the entire circumference of the surface of the structural yarn. Here, "having a crack on the surface entire periphery" may mean that a crack is formed on the entire circumference of the surface of the structural yarn by one crack, or that cracks are formed over the entire periphery of the surface of the structural yarn by two or more cracks. In addition, it is preferable that cracks are formed over the entire circumference of the surface of the structural yarn by 10 or less cracks. More preferably, the crack is formed in a direction substantially perpendicular to a longitudinal direction of the structural yarn. Still more preferably, the crack in the direction substantially perpendicular to the structural yarn is formed such that its depth changes in a fiber circumferential length direction. In addition, the depth of the crack is preferably 0.5 to 5.0  $\mu$ m. In addition, the frequency of crack formation is preferably in a form in which cracks are formed over the entire circumference of the surface of the structural yarn by 10 or less cracks within a range of 1 cm in the fiber axis direction. In this way, a woven or knitted fabric using the structural yarn can have higher softness and more deep color development.

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[0035] Here, the depth of the crack is measured at the deepest points of the crack. In addition, the direction substantially perpendicular to the longitudinal direction of the structural yarn means that a crack 4 is formed along the circumference substantially perpendicular to the longitudinal direction of a structural yarn 3 as schematically illustrated in Fig. 2. In the present invention, as the depth and length of the crack, average values obtained by observing the crack using an electron microscope and measuring 10 cracks in one structural yarn are used. A specific measurement method is as described in Examples. In addition, when it is difficult to continuously observe the entire circumference of the structural yarn, if cracks are uniformly present in any portion of the multifilament, it can be considered that the cracks cover the entire circumference of the surface.

[Combined Filament Composite Fiber, Woven or knitted fabric, and Clothing Including Composite Fiber or Structural Yarn]

[0036] The composite fiber according to the present invention may be a composite fiber in which at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing. That is, in a combined filament composite fiber of the present invention, at least one type of another thread is mixed with the composite fiber of the present invention. By doing so, the wear resistance in the case of the woven or knitted fabric can be further improved. [0037] The other thread is not particularly limited as long as it is different from the composite fiber of the present invention, but in particular, the thread is preferably constituted of a polyester-based resin because of satisfactory crimpiness and mechanical properties and excellent dimensional stability against humidity and temperature changes. The polyester-based resin, it is preferable to use a polyethylene terephthalate-based resin with a main repeat unit of ethylene terephthalate, a polytrimethylene terephthalate-based resin with a main repeat unit of trimethylene terephthalate, or a polybutylene terephthalate-based resin with a main repeat unit of butylene terephthalate. Note that the polyethylene terephthalate-based resin or the polybutylene terephthalate-based resin described above may have a small amount (usually less than 30 mol% (assuming that total of acid components and diol components is 100 mol%) of copolymerization components as necessary. In addition, from the viewpoint of soft feelings and recycling of the fibers to fibers, all the threads constituting the combined filament composite fiber are more preferably polyethylene terephthalate resins that do not contain a shared synthetic component.

[0038] In addition, the boiling water shrinkage rate of the other thread is more preferably 10% or less, particularly preferably 8% or less. When the boiling water shrinkage rate is 10% or less, the softness of the woven or knitted fabric can be further enhanced. In addition, the boiling water shrinkage rate is preferably 0% or more. When the boiling water shrinkage rate is 0% or more, dimensional stability is excellent. The boiling water shrinkage rate can be determined by dimensions before and after immersion in hot water at 100°C according to JIS L 1013 (2021) 8.18.1a method.
[00391] Furthermore, the other thread is preferably a latent crimping varn. Here, the "latent crimping varn" refers to varn.

**[0039]** Furthermore, the other thread is preferably a latent crimping yarn. Here, the "latent crimping yarn" refers to yarn having a crimp elongation rate of 5.0% or more. When the other thread is latent crimping yarn, stretchability and bulkiness can be improved.

**[0040]** When the other thread is a latent crimping yarn, the crimp elongation rate of the other thread is preferably 10.0 to 30.0% higher than the crimp elongation rate of the composite fiber. When the crimp exhibition rate is set in such a range, crimps having a different coil diameter from that of the composite fiber is mixed in the combined filament composite fiber, so that bulkiness and softness closer to carded wool can be obtained. In the case where the difference in crimp exhibition rate is 10% or more, the bulkiness and softness can be further enhanced. When the difference in crimp exhibition rate is within 30%, the difference in coil diameter from the composite fiber is reduced, and separation of the composite fiber from the

other thread can be prevented.

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**[0041]** Even in such a combined filament composite fiber, the composite fiber in the combined filament composite fiber usually exhibits a structure such as crimpiness by thermal history as described above. Therefore, the structural yarn according to the present invention may be a structural yarn in which at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing. When another thread coexisting with the composite fiber in the combined filament composite fiber is a latent crimping fiber, a structure such as crimpiness is exhibited according to the thermal history described above, and the thread coexists with a structural yarn in which a structure is exhibited from the composite fiber as an explicit crimping fiber.

**[0042]** A woven or knitted fabric of the present invention includes the composite fiber and/or the combined filament composite fiber of the present invention in at least a portion of the woven or knitted fabric. A composite fiber or a combined filament composite fiber alone can constitute a woven or knitted fabric.

[0043] That is, the woven or knitted fabric of the present invention can be formed into a woven or knitted fabric by being subjected to weaving or knitting using the composite fiber of the present invention in at least a portion of the woven or knitted fabric. After the weaving or knitting, by the dyeing step and an alkali weight reduction step carried out as necessary, the composite fiber in the woven or knitted fabric may be formed into a structural yarn in which a structure is exhibited. The weaving or knitting may be performed after the composite fiber is formed into a structural yarn in which a structure is exhibited in advance, but the former method is preferable. Such a woven or knitted fabric is a woven or knitted fabric including a structural yarn in at least a portion of the woven or knitted fabric. In addition, the composite fiber or the structural yarn to be subjected to the weaving or knitting may be in the form of composite mixed fibers mixed with the other thread.

[0044] The combined filament composite fiber may be a mixed yarn, a composite false twist yarn, or a combined twist yarn of the composite fiber and another thread, and further bulkiness and softness are obtained by constituting a woven or knitted fabric in the form of interlacing, interweaving, or the like of the combined filament composite fiber and another thread.

**[0045]** In the woven or knitted fabric of the present invention, a usage rate of the composite fiber and/or the combined filament composite fiber of the present invention is preferably 30 mass% or more, more preferably 40 mass% or more, with respect to the mass of the woven or knitted fabric. In another preferable aspect, all the fibers constituting the woven or knitted fabric are the composite fibers and/or the combined filament composite fibers of the present invention.

**[0046]** The woven or knitted fabric of the present invention has a fabric structure as a woven fabric or a knitted fabric. A woven fabric texture is selected from plain weave, twill weave, satin weave, and derivative weave thereof according to feelings and design properties. Furthermore, a multiple weave texture such as double weave may be employed. A knitted fabric texture may be selected according to desired feelings and design properties, and examples of weft knitting include Jersey stitch, rubber stitch, pearl stitch, tuck stitch, float stitch, lace stitch, and derivative texture thereof, and examples of warp knitting include single denbigh stitch, single van dyke stich, single cord stitch, Berlin stitch, double denbigh stitch, atlas stitch, cord stitch, half tricot stitch, satin stitch, sharkskin stitch, and derivative texture thereof. Among them, it is more preferable to use a relatively simple woven or knitted structure such as plain weave or derivative texture thereof, twill weave or derivative texture thereof, and satin weave in order to have a delicate worsted-wool feeling and a deep natural appearance.

[0047] A clothing of the present invention includes the composite fiber (including a structural yarn in which the structure of the composite fiber is exhibited) or the combined filament composite fiber, or the woven or knitted fabric of the present invention in at least a portion of the clothing. In this manner, it is possible to obtain clothing that satisfies both properties of the stretchability and the wear resistance that the composite fiber (including the structural yarn in which the structure of the composite fiber is exhibited) or the combined filament composite fiber, or the woven or knitted fabric of the present invention, and exhibits softness, deep color development, and bulkiness. The clothing of the present invention includes an item in the field of outerwear worn as a women's or men's garment, sportswear, and outdoor wear particularly a jacket, a suit, lower garment, and clothing including a part thereof, for example, a front main panel, a back main panel, a collar, a sleeve, a chest pocket, and a side pocket, innerwear, socks, hats, and the like.

[Method for Producing Composite Fiber, Structural Yarn in Which Structure Thereof is Exhibited, Combined Filament Composite Fiber, and Woven or knitted fabric]

[0048] Next, an example of a preferred method for producing the composite fiber, the structural yarn in which the structure thereof is exhibited, the combined filament composite fiber, and the woven or knitted fabric of the present invention will be described.

**[0049]** The composite fiber of the present invention can be produced in a step of winding ejected thermoplastic resins as an undrawn yarn or a half drawn yarn, then, once drawing, and performing relaxation heat treatment. In particular, the composite fiber obtained by including the step of drawing after being wound as a half drawn yarn is preferable because the composite fiber is particularly excellent in stretchability when formed into the woven or knitted fabric and processed with dyeing processing because of an orientation difference between the polyester-based thermoplastic resin A and the

polyester-based thermoplastic resin B, and is also excellent in resistance to embrittlement due to alkali weight reduction because of an increase in orientation of the polyester resin A.

#### [Spinning Step]

**[0050]** In the method for producing the composite fiber of the present invention, first, the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B are individually melted, and ejected from a spinneret, and wound up as the undrawn yarn or the half drawn yarn at a spinning speed of preferably 1,400 m/min to 3,800 m/min. In the present invention, the yarn is preferably wound as a half drawn yarn at a spinning speed of 2,500 to 3,800 m/min.

**[0051]** A composite fiber formed from a half drawn yarn is preferable because the composite fiber is excellent in wear resistance after alkali weight reduction. Since the half drawn yarn is more crystallized than the undrawn yarn, a local fiber cutting due to alkali weight reduction can be inhibited.

**[0052]** A spinning temperature is preferably  $+20^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  higher than melting points ( $T_{mA}$ ,  $T_{mB}$ ) of the polyester-based thermoplastic resin B. When the temperature is  $+20^{\circ}\text{C}$  or more higher than ( $T_{mA}$ ,  $T_{mB}$ ), it is possible to prevent the melted polyester-based thermoplastic resin A and polyester-based thermoplastic resin B from solidifying in pipelines of a spinning machine and clogging the pipelines. On the other hand, when the temperature is  $+50^{\circ}\text{C}$  or less higher than ( $T_{mA}$ ,  $T_{mB}$ ), it is possible to inhibit thermal deterioration of the melted polyester-based thermoplastic resin A and polyester-based thermoplastic resin B.

**[0053]** The spinneret used in the method for producing the composite fiber of the present invention may have any of common internal structures so long as the spinneret renders stable spinning with respect to quality and operation.

**[0054]** Here, in the composite fiber of the present invention, the polyester-based thermoplastic resin A is completely covered by the polyester-based thermoplastic resin B in the cross-section of the composite fiber as described above. By forming such a cross-section of the composite fiber, it is also possible to inhibit ejected-filament bending occurring due to a difference in flow rate between the two types of thermoplastic resins ejected from the spinneret, which has been a problem in production of the composite fiber.

[0055] In the composite fiber of the present invention, it is preferable to precisely control the minimum value  $t_{min}$  of the thickness t of the polyester-based thermoplastic resin B covering the polyester-based thermoplastic resin A, and a length  $C_t$  of a portion in which a region having the thickness t in the cross-section of the composite fiber satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and the circumferential line of the composite fiber are overlapped, and a spinning method using distribution plates as exemplified in Japanese Patent Laid-open Publication No. 2011-174215, Japanese Patent Laid-open Publication No. 2011-174215, Japanese Patent Laid-open Publication No. 2011-208313, and Japanese Patent Laid-open Publication No. 2012-136804 is suitably used. By using such distribution plates,  $t_{min}$  can be set within the above-described range, exposure of the polyester-based thermoplastic resin A generated as a result of an excessive decrease in  $t_{min}$  can be inhibited, and whitening and fluffing of the woven or knitted fabric can be further inhibited. Alternatively, an excessive increase in  $t_{min}$  can be inhibited, and the crimpiness of the composite fiber can be exhibited in a suitable range to improve the stretchability of the woven or knitted fabric. In the method using such distribution plates, a cross-sectional form of single yarn can be controlled by disposition of distribution holes in a final distribution plate installed most downstream among the plurality of distribution plates.

## [Draw and Relaxation Heat Treatment Step]

**[0056]** Next, the yarn produced through the above-described spinning step is drawn using a draw and relaxation heat treatment device as illustrated in Fig. 3 at a draw ratio within a range exceeding a natural draw ratio of the yarn to form a drawn yarn, and then the relaxation heat treatment is performed to form a relaxation heat treatment yarn. By this step, a desired composite fiber can be obtained.

**[0057]** Fig. 3 is a schematic view of a draw and relaxation heat treatment device used in production of the composite fiber of the present invention. That is, after passing through the guide 6, the half drawn yarn 5 is heated and drawn by a hot pin 8 between a first feed roller 7 and a second feed roller 9, further subjected to relaxation heat treatment by a heater 10 between the second feed roller 9 and a third feed roller 11 to become a composite fiber 12, and wound up by a winding section 13.

**[0058]** For example, a half drawn yarn obtained by composite spinning at a spinning speed of 2500 to 3800 m/min is subjected to pin draw at a draw ratio of 1.5 to 2.2 times, a hot pin temperature of 70 to 150°C, and a yarn speed of 200 to 800 m/min, and then subjected to relaxation heat treatment at a heater temperature of 130 to 180°C and an overfeed rate +25 to 55% (as an example, a half drawn yarn obtained by composite spinning at a spinning speed of 2600 m/min is subjected to pin draw at a draw ratio of 1.8 times, a hot pin temperature of 95°C, and a yarn speed of 300 m/min, and then subjected to relaxation heat treatment at a heater temperature of 140°C and an overfeed rate +10%), whereby a composite fiber having an apparent thick-to-thin ratio of 1.00 or more and 1.04 or less and a crimp elongation rate of 3.0 to 25.0% can be obtained. In addition, it is preferable that the draw is draw in a region in which the natural draw ratio is the upper limit or more, and that the overfeed rate of relaxation heat treatment is 50% or less of the draw ratio. By drawing within the above range, the

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degree of reduction of the fiber by the alkali treatment becomes easier to be controlled, and both softness and wear resistance can be achieved.

**[0059]** In addition, before or after winding the composite fiber subjected to the draw, another thread may be combined by mixing or the like to form the combined filament composite fiber. The mixing method is not particularly limited, and typical methods such as interlaced fiber mixing and Taslan fiber mixing have no problem.

[Step of Forming Woven or knitted fabric]

**[0060]** The composite fiber obtained at the drawing step is formed into the woven fabric or the knitted fabric. In the case of the woven fabric, weaving is performed using an air-jet loom, a water-jet loom, a rapier loom, a projectile loom, a shuttle loom, or the like. In the case of the knitted fabric, knitting is performed using a weft knitting machine such as a flat knitting machine, a full-fashion knitting machine, a circular knitting machine, a computer jacquard knitting machine, a socks knitting machine, and a cylindrical knitting machine, or a warp knitting machine such as a tricot knitting machine, a raschel knitting machine, an air-jet loom, and a milanese knitting machine.

[Alkali Weight Reduction Step]

**[0061]** Furthermore, the woven or knitted fabric obtained at the above-described step of forming the woven or knitted fabric is subjected to an alkali weight reduction treatment as necessary so that an alkali weight reduction rate is 5 to 20%, more preferably 10 to 15%. Through this step, the entire surface of the above-described composite fiber can have cracks. In addition, a continuous weight reduction process is preferable in order to avoid embrittlement due to selective weight reduction.

[Dyeing Step]

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**[0062]** Furthermore, if necessary, before and/or after the above-described alkali weight reduction step, or simultaneously, conventional scouring, relaxation treatment, intermediate thermal setting, dyeing processing, and finishing thermal setting may be performed (in the present invention, these processes may be collectively referred to as "dyeing step"). In order to obtain the bulkiness and softness of the present invention, feed and tension management of each step are appropriately performed. For example, in the axis direction of the composite fiber of the present invention, it is desirable that overfeed is within 10% in a feed amount and a facility of, for example, a roll-to-roll system capable of controlling, and that a liquid amount and a flow rate are controlled so that an excessive tension is not applied to a travel direction in a batch-type jet dyeing machine or the like. Dyeing is preferably performed in a dyeing solution at 110 to 130°C using a disperse dye or a cationic dye, though depending on the dyeability of the thermoplastic resins constituting the composite fiber or another

**[0063]** The composite fiber of the present invention usually performs a structural exhibition and a crimp exhibition due to a thermal history in the dyeing step or the alkali weight reduction step. Then, cracks are formed on the surface of the composite fiber by the alkali weight reduction step.

40 EXAMPLES

**[0064]** Next, the present invention is described in detail on the basis of the Examples. However, the present invention is not limited only to these Examples. Unless otherwise described, physical properties are measured on the basis of the methods described above.

[Measurement Method]

thread to be combined.

- (1) Measurement of Weight-Average Molecular Weight of Thermoplastic Resin
- [0065] The weight-average molecular weights of the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B used in the composite fiber were measured using "TOSO GMHHR-H (S) HT" manufactured by Tosoh Corporation as a gel permeation chromatography (GPC) tester.

  [0066]

Detector: Differential refractive index detector RI (Waters-2414, Sensitivity 128x)

Column: ShodexHFIP806M (two columns connected) manufactured by Showa Denko K.K.

Solvent: Tetrohydrofuran (25cm<sup>3</sup>)

Flow rate: 1.0 mL/min

Column temperature: 30°C Injection volume: 0.10 mL Standard substance: Polystyrene

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5 (2) Measurement of Average Fiber Diameter D<sub>ave</sub>

**[0067]** The fineness and the number of filaments of the composite fibers were measured in accordance with JIS L 1013 (2010) 8.3.1B method and JIS L 1013 (2010) 8.4, respectively, and a single yarn fineness was obtained from the fineness/number of filaments. From the obtained single yarn fineness, an average fiber diameter was calculated by the following formula.

[Mathematical Formula 1]

$$D_{ave}(\mu m) = \sqrt{\frac{\text{Single Yarn Fineness}}{10000 \times \pi \times \rho}} \times 10^6 \times 2$$

 $\rho$  density (g/m³) 1.38  $\times$  106 g/m³ in the case of polyethylene terephthalate.

25 (3) Measurement of Fiber Diameter D, Thickness t of Polyester-Based Thermoplastic Resin B Covering Polyester-Based Thermoplastic Resin A, and Circumferential Length C of Fiber

[0068] A multifilament including composite fibers, embedded in an embedding material such as an epoxy resin continuously at 10 locations at intervals of 1 cm in the fiber axis direction was used as a sample, and each sample was photographed with a transmission electron microscope (TEM) to obtain an image thereof at such a magnification that 10 or more fibers can be observed. At this time, metal dyeing was performed to render the contrast of a joint portion between the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B clear. By using "WinROOF 2015" manufactured by Mitani Corporation as image analysis software, the fiber diameter D was measured from all the single yarns in the observation image, and the circumferential length C, the thickness t of the polyester-based thermoplastic resin B, and the area Sa of the polyester-based thermoplastic resin A were individually measured therefrom. The fiber diameter D is a circle equivalent diameter. The fiber diameter D, the circumferential length C, the thickness t, and the area ratio Sa of the polyester-based thermoplastic resin A were obtained by preparing and averaging 10 sets. The fiber diameter D was obtained with three significant digits, the circumferential length C, the thickness t, and the area ratio Sa were obtained with two significant digits, as the fiber diameter D, the circumferential length C, the thickness t, and the area ratio Sa of the present invention. The thickness t was measured at 360 points every 1° in the fiber circumferential direction, the smallest thickness was  $t_{min}$ , and the length of a portion in which a region having the thickness t satisfying 1.00 $t_{min} \le t \le t$  $1.05t_{min}$  and the circumferential line of the composite fiber are overlapped was  $C_t$ . The area ratio Sa of the polyester-based thermoplastic resin A was subtracted from the total area S of the cross section to obtain the area ratio Sb of the polyesterbased thermoplastic resin B.

(4) Crimp Elongation Rate

[0069] The crimp elongation rate of the composite fiber was determined by the following formula.

Crimp elongation rate (%) = 
$$\{(L1 - L0)/L0\} \times 100$$

**[0070]** L0: Length after 30 seconds when, after 50 cm of the composite fiber was wrapped in gauze in a free state and left to stand for 24 hours, the composite fiber was treated with hot water at  $100^{\circ}$ C  $\times$  15 minutes in a no-load state, dried at  $20^{\circ}$ C  $\times$  65RH% for 24 hours, and then suspended with a load of  $1.1 \times 10^{-3}$  cN/dtex

[0071] L1: Length after 30 seconds when a load of 0.22 cN/dtex is suspended after L0 is measured

**[0072]** The measurement was performed 10 times, and the result was obtained by rounding off the second decimal place of the average value to one decimal place. In the case of a combined filament composite fiber, the composite fiber was

separated and measured before L0 measurement.

- (5) Measurement of Apparent Thick-to-Thin Ratio (D<sub>thick</sub>/D<sub>thin</sub>)
- 5 [0073] Both ends of the composite fiber were fixed while a load of 0.11 cN/dtex was applied to the composite fiber. In an image obtained by photographing a side surface of the fixed sample with a digital microscope "VHX 2000" manufactured by Keyence Corporation at a magnification of 200 times, the diameter of a fiber bundle was continuously measured at 500 locations at intervals of 1.0 mm in the fiber axis direction. The fiber diameter (D<sub>thick</sub>) of the thick portion and the fiber diameter (D<sub>thin</sub>) of the thin portion were determined by defining a portion thinner than an average value of all the measurement data as the thin portion (thin portion < average value) and defining a portion thicker than the average value of all the measurement data as the thick portion (thick portion > average value), and an average value of the thick portion and the thin portion was obtained to calculate an apparent thick-to-thin ratio. The apparent thick-to-thin ratio was obtained by rounding off the third decimal place to two decimal places.

**[0074]** In addition, for structural yarn obtained by extracting and collecting structural yarn from the woven or knitted fabric after the dyeing step (finishing thermal setting), the apparent thick-to-thin ratio was determined in the same manner.

- (6) Measurement of Presence or Absence and Depth of Crack
- **[0075]** An arbitrary portion of the structural yarn from the woven or knitted fabric after the dyeing processing was observed using a scanning electron microscope "S-3400N" manufactured by Hitachi, Ltd. as an electron microscope. The composite fiber was pulled out from the woven or knitted fabric after the finishing thermal setting without applying an external force, and the presence or absence of a crack and the crack form were confirmed. In the case of the presence of a crack, a side surface in a direction substantially orthogonal to the crack was observed at a magnification of 2000 times. The largest depths and lengths of the crack were measured, and an average value obtained by measuring 10 cracks in one composite fiber was defined as the crack depth.

[0076] The crack form was judged according to the following criteria.

- A. A form is that cracks are formed over the entire circumference of the surface of the structural yarn by 10 or less cracks within a range of 1 cm in the fiber axis direction.
- B. Cracks are formed over the entire circumference of the surface of the structural yarn by 10 or less cracks.
- C. A crack is formed, but it is in the middle of B and C.
- D. Cracks are formed, but in a degree that only over half the circumference of the surface of the structural yarn.
- E. A degree that is the middle of D and F.
- F. No crack is formed.

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- (7) Stretchability of Woven or knitted fabric
- [0077] An elongation rate in a direction along the composite fiber of the present invention was measured in accordance with JIS L 1096 (2010) 8.16.1, method B. In a case where the composite fiber of the present invention was used for both the warp and the weft, the elongation rate of each of the warp and the weft was measured, and an average value thereof was used as the result.
- (8) Wear Resistance
- 45 [0078] The woven or knitted fabric was dyed black, and the woven or knitted fabric after being dyed was cut into a circle having a diameter of 10 cm, wetted with distilled water, and attached to a disk. Furthermore, the woven or knitted fabric cut into 30 cm square was fixed on a horizontal plate while being dried. The disc, on which the woven or knitted fabric wetted with distilled water was attached, was brought into horizontal contact with a woven fabric fixed on a horizontal plate, and the disc was circularly moved at a speed of 50 rpm for 10 minutes so that the center of the disc draws a circle having a diameter of 10 cm, and the two woven or knitted fabrics were rubbed. After the end of the rubbing, the woven or knitted fabric was left to stand for 4 hours, and the degree of discoloration and fading of the woven or knitted fabric attached to the disk was judged to be grades 1 to 5 in increments of grade 0.5 using a gray scale for discoloration.
  - (9) Evaluation of Color Development, Bulkiness, and Softness of Woven or knitted fabric Using Composite Fiber and Combined Filament Composite Fiber

**[0079]** Samples of the woven or knitted fabric formed using the composite fiber in the present invention were subjected to sensory evaluation in five stages of very good (5 points), good (4 points), normal (3 points), not very good (2 points), and

bad (1 point) by using 10 healthy adults (five men and five women) as evaluators to evaluate color development of the woven or knitted fabric by a visual judgment, and bulkiness and softness thereof by a touch, and the result was obtained by rounding off the second decimal place of the average value of the inspectors to one decimal place. For comparison, a woven fabric made of a false-twist textured yarn of polyethylene terephthalate having the same total fineness and the same number of filaments as those in Examples and Comparative Examples was defined as normal (three points).

[Example 1]

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[0080] Polyethylene terephthalate having a weight-average molecular weight of 25000 was used as the polyester-based thermoplastic resin A, polyethylene terephthalate having a weight-average molecular weight of 15000 was used as the polyester-based thermoplastic resin B were caused to flow into a composite fiber spinneret having 12 ejection holes so as to have a mass composition ratio of 50 : 50 at a spinning temperature of 290°C, assuming that disposition of distribution holes in a final distribution plate installed most downstream among the plurality of distribution plates is in a shape illustrated in Fig. 4. Fig. 4 shows a state in which a group of distribution holes 15 of the polyester-based thermoplastic resin B is arranged around a group of distribution holes 14 of the polyester-based thermoplastic resin A in the final distribution plate. In this way, a composite cross section of an eccentric core-sheath type (Fig. 1) in which the polyester-based thermoplastic resin A was contained in the polyester-based thermoplastic resin B was formed. Threads ejected from the spinneret were cooled by an air-cooling device, oiled, and wound up with a winder at a speed of 2600 m/min, to be stably wound up as a half drawn yarn having a total fineness of 100 dtex and 12 single yarn filaments.

**[0081]** Subsequently, the obtained half drawn yarn was fed to a drawing device at a speed of 300 m/min, subjected to pin draw at a draw ratio of 1.80 times, and a hot pin temperature of 95°C using the drawing device as shown in Fig. 3, and then subjected to relaxation heat treatment at heater temperature 140°C and overfeed rate +20%, to obtain a composite fiber having an apparent thick-to-thin ratio ( $D_{thick}/D_{thin}$ ) of 1.02. For this composite fiber, the above-described ( $t_{min}/D$ ) was 0.020, and the relationship between Ct and C was Ct = 0.40C (Ct/C = 0.40). In addition,  $S_A$ :  $S_B$  = 50: 50.

**[0082]** Next, a yarn obtained by imparting twist of 1200T/m to the above-described composite fiber was used as the warp and the weft, and a 3/1 twill texture woven fabric having a warp density of 115 yarns/2.54 cm and a weft density of 105 yarns/2.54 cm was produced.

**[0083]** The woven fabric was further subjected to scouring, relaxation treatment, and intermediate thermal setting. Thereafter, as the dyeing step, dyeing was performed at a concentration of 1.0 owf% and a temperature of 130°C for 30 minutes using a disperse dye "Dystar Navy BlueS-GL", and finishing thermal setting was performed at 160°C. The results are shown in Table 1.

[Example 2]

**[0084]** A composite fiber and a woven fabric were obtained in the same manner as in Example 1 except that in the dyeing processing, alkali weight reduction processing (reduction rate: 10%) was performed after intermediate setting to form cracks on the single yarn surface of the composite fiber. The results are shown in Table 1.

40 [Example 3]

[0085] A woven fabric was obtained in the same manner as in Example 2 except that a polyethylene terephthalate fiber (56 dtex-24f, boiling water shrinkage rate of 8%, crimp elongation rate of 0.0%) was entangled and mixed as another thread to the composite fiber produced in Example 1 with an interlacing nozzle to form a combined filament composite fiber in which the mixing rate of the composite fiber is 54%, and the warp density was 88 yarns/inch, and the weft density was 79 yarns/inch (2.54 cm). The results are shown in Table 1. The boiling water shrinkage rate was obtained by measuring changes in dimensions before and after immersion in hot water at 100°C according to JIS L 1013 (2021) 8.18.1a method.

[Example 4]

**[0086]** A woven fabric was obtained in the same manner as in Example 3 except that the following drawn yarn was used as the other thread. The results are shown in Table 1.

**[0087]** Drawn yarn: A polyethylene terephthalate having a weight-average molecular weight of 25000 and a polyethylene terephthalate having a weight-average molecular weight of 15000 were flowed into a spinneret for a side-by-side type composite fiber having a discharge hole number of 12 so that a spinning temperature was 290°C and a mass composite ratio of the polyethylene terephthalates was 50:50. The thread discharged from the spinneret was cooled by an air cooling device, applied with an oil agent, then taken up at 1500 m/min, drawn 2.67 times between a preheating roller at 80°C and a roller at 4000 m/min, subjected to thermal setting at 130°C, and then wound by a winder, and stably wound as a

drawn yarn having a total fineness of 56 dtex and 12 single yarn filaments and a crimp elongation rate of 32.0%.

[Example 5]

[0088] A woven fabric was obtained in the same manner as in Example 2 except that the polyester-based thermoplastic resin A was polyester having a weight-average molecular weight of 19000 and the polyester-based thermoplastic resin B was polyester having a weight-average molecular weight of 15000. The results are shown in Table 1.

[Example 6]

**[0089]** A woven fabric was obtained in the same manner as in Example 2 except that polyester having a weight-average molecular weight of 25000 obtained by copolymerizing isophthalic acid (IPA) with respect to an acid component in an amount of 10 mol% was used as the polyester-based thermoplastic resin A. The results are shown in Table 1.

15 [Example 7]

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**[0090]** A woven fabric was obtained in the same manner as in Example 4 except that the thermal setting temperature of the other thread was 125°C and the boiling water shrinkage rate was 10%. The results are shown in Table 1.

20 [Example 8]

**[0091]** A woven fabric was obtained in the same manner as in Example 3 except that the following drawn yarn was used as the other thread. The results are shown in Table 1.

**[0092]** Drawn yarn: A polyethylene terephthalate having a weight-average molecular weight of 25000 obtained by copolymerizing isophthalic acid (IPA) with respect to an acid component in an amount of 10 mol% and a polyethylene terephthalate having a weight-average molecular weight of 15000 were flowed into a spinneret for a side-by-side type composite fiber having a discharge hole number of 12 so that a spinning temperature was 290°C and a mass composite ratio of the polyethylene terephthalates was 50:50. The thread discharged from the spinneret was cooled by an air cooling device, applied with an oil agent, then taken up at 1500 m/min, drawn 2.67 times between a preheating roller at 80°C and a roller at 4000 m/min, subjected to thermal setting at 130°C, and then wound by a winder, and stably wound as a drawn yarn having a total fineness of 56 dtex and 12 single yarn filaments.

[Comparative Example 1]

35 [0093] A woven fabric were obtained in the same manner as in Example 4 except that the spinneret used in Example 4, which was the spinneret of the distribution plate type, was replaced with a spinneret of the type described in Japanese Patent Laid-open Publication No. H09-157941, to obtain a side-by-side type composite fiber including the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B. The obtained woven fabric had low wear resistance due to peeling of the composite cross section on the side by side due to abrasion, and was poor in color development because high molecular weight polyethylene terephthalate having low color development was exposed. The results are shown in Table 2.

[Comparative Example 2]

- 45 [0094] A woven fabric was obtained in the same manner as in Example 4 except that relaxation heat treatment was performed without performing pin draw. The obtained woven fabric had low wear resistance due to local cutting of fibers by alkali treatment, and was poor in bulkiness because the crimp elongation rate of the composite fiber was low. The results are shown in Table 2.
- <sup>50</sup> [Comparative Example 3]

**[0095]** A woven fabric was obtained in the same manner as in Example 4 except that pin draw was performed and relaxation heat treatment was not performed. The obtained woven fabric had low color development due to high orientation of the composite fiber, and also had poor bulkiness and softness due to too high crimp elongation rate. The results are shown in Table 2

#### [Comparative Example 4]

**[0096]** A woven fabric was obtained in the same manner as in Example 4 except that a composite fiber having an apparent thick-to-thin ratio of 1.22 and a crimp elongation rate of 27.0% was used with the pin draw ratio being 1.50 times and the heat treatment overfeed rate being 0%. The obtained woven fabric had low wear resistance of the thick portion and a high crimp elongation rate, and thus had poor softness. The results are shown in Table 2.

[Comparative Example 5]

10 [0097] A woven fabric was obtained in the same manner as in Example 4 except that a composite fiber having an apparent thick-to-thin ratio of 1.22 was used with the pin draw ratio being 1.50 times. The obtained woven fabric had low wear resistance of the thick portion and a low crimp elongation rate, and thus had poor bulkiness and softness. The results are shown in Table 2.

#### 15 [Comparative Example 6]

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**[0098]** A woven fabric was obtained in the same manner as in Example 4 except that the disposition of the distribution holes of the final distribution plate of the spinneret used so that the value of the minimum value  $t_{min}$  of the thickness t of the polyester-based thermoplastic resin B covering the polyester-based thermoplastic resin A would increase by 10 times in Example 4 was changed from that in Fig. 4 to Fig. 5, to obtain a core-sheath type composite fiber including the polyester-based thermoplastic resin A and the polyester-based thermoplastic resin B and having  $(t_{min}/D)$  of 0.20. The results are shown in Table 2.

#### [Comparative Example 7]

**[0099]** A woven fabric was obtained in the same manner as in Example 2 except that the polyester-based thermoplastic resin A was polyethylene terephthalate having a weight-average molecular weight of 20000 and the polyester-based thermoplastic resin B was polyethylene terephthalate having a weight-average molecular weight of 19000. The results are shown in Table 2.

# [Table 1-1]

		T 1	T 1	F 1	B 1
		Example 1	Example 2	Example 3	Example 4
	Weight-average molecular weight $(M_{\mathtt{A}})$ of polyester-based thermoplastic resin A	25000	25000	25000	25000
	Weight-average molecular weight $(M_{\rm B})$ of polyester-based thermoplastic resin B	15000	15000	15000	15000
	$M_A$ - $M_B$	10000	10000	10000	10000
	Copolymerization component of thermoplastic resin A				
	Fiber cross-section	Eccentric core-sheath type	Eccentric core-sheath type	Eccentric core-sheath type	Eccentric core-sheath type
Composi	Spinning speed (m/min)	2600	2600	2600	2600
fibe		1.80	1.80	1.80	1.80
	Heat treatment overfeed rate (%)	20	20	20	20
	Fineness (dtex)	66.7	66.7	66.7	66.7
	Number of filaments	12	12	12	12
	Average fiber diameter Dave (μm)	22.6	22.6	22.6	22.6
	Crimp elongation rate (%)	7.0	7.0	7.0	7.0
	Apparent thick-to-thin ratio $(D_{thick}/D_{thin})$	1.02	1.02	1.02	1.02
	t <sub>min</sub> /D	0.02	0.02	0.02	0.02
	C <sub>t</sub> /C	0.40	0.40	0.40	0.40
	Apparent thick-to-thin ratio $(D_{thick}/D_{thin})$	1.02	1.02	1.02	1.02
Structur yarn		Absent	Present over entire circumference	Present over entire circumference	Present over entire circumference
		F	А	А	A
	Crack depth (µm)	-	2.1	2.1	2.1
Yarn mix with	Materials			PET	PET/PET
composi fiber	Roiling water chrinkage rate (%)	<u></u>		8	8
	Stretchability (elongation rate (%))	8.0	8.0	7.0	30.0
Woven o	Wear Resistance	4.5	4.5	5.0	5.0
knitte		3.5	5.0	5.0	5.0
fabri	c Bulkiness	3.0	3.0	3.0	5.0
	Softness	4.5	5.0	5.0	5.0

# [Table 1-2]

			Example	Example	Example	Example
			5	6	7	8
5		Weight-average molecular weight $(M_{\underline{\lambda}})$ of polyester-based thermoplastic resin A	19000	25000	25000	25000
		Weight-average molecular weight $(M_{\scriptscriptstyle B})$ of polyester-based thermoplastic resin B	15000	15000	15000	15000
		$M_{A}-M_{B}$	4000	10000	10000	10000
10		Copolymerization component of thermoplastic resin A		IPA 10 mol%		
		Fiber cross-section	Eccentric core-sheath type	Eccentric core-sheath type	Eccentric core-sheath type	Eccentric core-sheath type
	Composite	Spinning speed (m/min)	2600	2600	2600	2600
45	fiber	Draw ratio	1.80	1.80	1.80	1.80
15		Heat treatment overfeed rate (%)	20	20	20	20
		Fineness (dtex)	66.7	66.7	66.7	66.7
		Number of filaments	13	12	12	12
		Average fiber diameter Dave (µm)	21.8	22.6	22.6	22.6
		Crimp elongation rate (%)	4.0	4.0	7.0	7.0
20		Apparent thick-to-thin ratio (D thick/D thin)	1.02	1.02	1.02	1.02
		t min/D	0.02	0.02	0.02	0.02
		C <sub>e</sub> /C	0.40	0.40	0.40	0.40
25	Structural yarn	Apparent thick-to-thin ratio (D thick/D thin)	1.02	1.02	1.02	1.02
		Crack form	Present over entire circumference	Present over entire circumference	Present over entire circumference	Present over entire circumference
			В	A	A	A
		Crack depth (µm)	1.5	5.6	2.1	2.1
30	Yarn mixed with	Materials			PET/PET	Copolymerized PET/PET
	composite fiber	Boiling water shrinkage rate (%)			10	15
	Woven or knitted fabric	Stretchability (elongation rate (%))	5.0	15.0	30.0	30.0
		Wear Resistance	4.5	4.0	5.0	5.0
35		Color development (orientation, crack)	4.0	5.0	5.0	5.0
		Bulkiness	3.0	3.5	5.0	4.0
		Softness	5.0	3.0	4.5	3.0

# [Table 2-1]

Comparative   Example   Comparative   Example   Exampl							
1				Comparative	-	_	Comparative
Weight-average molecular weight (N <sub>6</sub> ) of polyester-based thermoplastic resin A   25000   25				Example	Example	Example	
Weight-average molecular weight (Ng) of polysater-based thermoplastic resin B   15000   1500	5			1	2	3	4
Polyester-based thermoplastic resin B	Ü			25000	25000	25000	25000
Copolymerization component of thermoplastic resin A   Side-by-side type type type type type type type typ				15000	15000	15000	15000
Composite   Fiber cross-section			$M_{\lambda}$ – $M_{B}$	10000	10000	10000	10000
Fiber cross-section	10						
Transmixed   Structural yarn   Structural yarn   Crack depth (µm)   Structural yarn   Crack depth (µm)   Structural yarn   Stretchability (elongation rate (\$)   8   8   8   8   8   8   8   8   8			Fiber cross-section	_	core-sheath	core-sheath	core-sheath
Tiber			Spinning speed (m/min)	2600	2600	2600	2600
Fineness (dtex)   66.7   83.3   55.6   66.7     Number of filaments   12   12   12   12   12     Average fiber diameter Dave (µm)   22.6   25.3   20.7   22.6     Crimp elongation rate (%)   6.0   2.0   32.0   27.0     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.02   1.22     C_t/C   - 0.40   0.40   0.40     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.22     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D takes/D takes)   1.02   1.02   1.02     C_t/C	15		Draw ratio	1.80		1.80	1.50
Number of filaments   12	15		Heat treatment overfeed rate (%)	20	20		0
Average fiber diameter Dave (µm)   22.6   25.3   20.7   22.6     Crimp elongation rate (%)   6.0   2.0   32.0   27.0     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02   1.02   1.22     Cy/C   - 0.40   0.40   0.40   0.40     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02   1.02   1.02     Apparent thick-to-thin ratio (D thick/D this)   1.02     Apparent thick-to-thin ratio (D this)   1.02     Appare			Fineness (dtex)	66.7	83.3	55.6	66.7
Crack depth (µm)   Crack depth			Number of filaments	12	12	12	12
### Apparent thick-to-thin ratio     (D thick/D thin)			Average fiber diameter Dave (µm)	22.6	25.3	20.7	22.6
Apparent thick-to-thin ratio	20		Crimp elongation rate (%)	6.0	2.0	32.0	27.0
25    C_t/C	20			1.02	1.02	1.02	1.22
Apparent thick-to-thin ratio			t man/D	-	0.02	0.02	0.02
Structural yarn   Structural yarn   Crack form   Present around only half circumference   D			•	-	0.40	0.40	0.40
Structural yarn   Crack form   only half circumference   Absent   entire circumference	25			1.02	1.02	1.02	1.22
30			Crack form	only half	entire	Absent	entire
30  Yarn mixed with composite fiber  Boiling water shrinkage rate (%)  Stretchability (elongation rate (%))  Wowen or knitted fabric  Bulkiness  Materials  PET/PET				D	A	F	В
Materials			Crack depth (µm)	2.1	5.7	-	5.2
## Stretchability (elongation rate (%)	30	1	Materials	PET/PET	PET/PET	PET/PET	PET/PET
Woven or knitted fabric   Wear Resistance   2.0   1.0   5.0   3.0		_	Boiling water shrinkage rate (%)	8	8	8	8
Worken or   knitted   Color development (orientation, crack)   2.5   5.0   2.0   3.0		knitted	Stretchability (elongation rate (%))	27.0	25.0	30.0	26.0
fabric Bulkiness 4.0 1.0 2.0 3.0	0.5		Wear Resistance	2.0	1.0	5.0	3.0
Bulkiness 4.0 1.0 2.0 3.0	35		Color development (orientation, crack)	2.5	5.0	2.0	3.0
Softness 4.0 3.0 2.0 2.0			Bulkiness	4.0	1.0	2.0	3.0
	Ĺ		Softness	4.0	3.0	2.0	2.0

## [Table 2-2]

					G
_			Comparative Example	Comparative Example	Comparative Example
5			5	Example 6	7
		Weight-average molecular weight $(M_{\lambda})$ of polyester-based thermoplastic resin A	25000	25000	20000
10		Weight-average molecular weight $(M_{B})$ of polyester-based thermoplastic resin B	15000	15000	19000
70		M <sub>A</sub> -M <sub>B</sub>	10000	10000	1000
		Copolymerization component of thermoplastic resin A			
15		Fiber cross-section	Eccentric core-sheath type	Eccentric core-sheath type	Eccentric core-sheath type
	Composite	Spinning speed (m/min)	2600	2600	2600
	fiber	Draw ratio	1.50	1.80	1.80
		Heat treatment overfeed rate (%)	20	20	20
20		Fineness (dtex)	80.0	66.7	66.7
20		Number of filaments	12	12	12
		Average fiber diameter Dave (µm)	24.8	22.6 22.6	22.6
		Crimp elongation rate (%)	3.0	3.0	1.0
25		Apparent thick-to-thin ratio (D <sub>thick</sub> /D <sub>thin</sub> )	1.22	1.02	1.02
		t min/D	0.02	0.20	0.02
		C <sub>t</sub> /C	0.40	0.20	0.40
		Apparent thick-to-thin ratio (D thick/D thin)	1.22	1.02	1.02
30	Structural yarn	Crack form	Present over entire circumference	Present over entire circumference	Absent
			A	A	E
		Crack depth (µm)	5.8	0.4	-
35	Yarn mixed with	Materials	PET/PET	PET/PET	
	composite fiber	Boiling water shrinkage rate (%)	8	8	
		Stretchability (elongation rate (%))	25.0	25.0	1.0
40	Woven or	Wear Resistance	3.0	5.0	5.0
	knitted fabric	Color development (orientation, crack)	5.0	5.0	2.0
		Bulkiness	2.0	1.0	1.0

## DESCRIPTION OF REFERENCE SIGNS

## [0100]

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1: Polyester-based thermoplastic resin A

2: Polyester-based thermoplastic resin B

Softness

- 3: Composite fiber
- 4: Crack
- 5: Half drawn yarn
- 6: Guide
  - 7: First feed roller
  - 8: Hot pin
  - 9: Second feed roller

2.0

2.0

2.0

- 10: Heater
- 11: Third feed roller
- 12: Composite fiber
- 13: Winding unit
- 14: Distribution hole of polyester-based thermoplastic resin A
- 15: Distribution hole of polyester-based thermoplastic resin B
- 16: Thickness t of polyester-based thermoplastic resin B covering polyester-based thermoplastic resin A

#### 10 Claims

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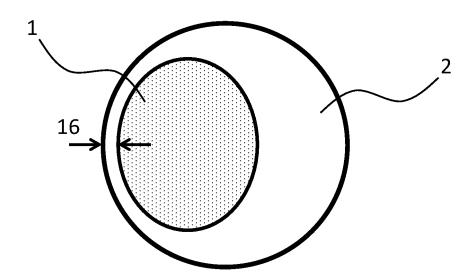
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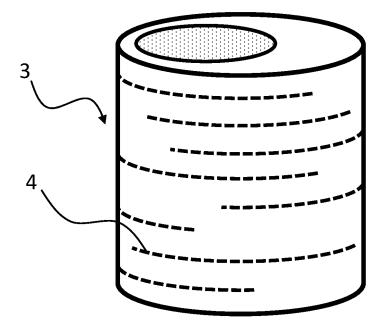
- 1. A composite fiber comprising a polyester-based thermoplastic resin A and a polyester-based thermoplastic resin B, wherein the composite fiber satisfying following requirements:
  - (1) a difference ( $M_A$   $M_B$ ) between a weight-average molecular weight  $M_A$  of the polyester-based thermoplastic resin A and a weight-average molecular weight  $M_B$  of the polyester-based thermoplastic resin B is 2000 to 15000;
  - (2) an apparent thick-to-thin ratio ( $D_{thick}/D_{thin}$ ) of the composite fiber is 1.00 to 1.04;
  - (3) a crimp elongation rate of the composite fiber is 3.0 to 25.0%;
  - (4) in a cross-section of the composite fiber, the polyester-based thermoplastic resin B covers the polyester-based thermoplastic resin A, and a ratio  $(t_{min}/D)$  of a minimum value  $t_{min}$  of a thickness t of the polyester-based thermoplastic resin B to a fiber diameter D of the composite fiber is 0.01 to 0.10; and
  - (5) in the cross-section of the composite fiber, a length  $C_t$  of a portion in which a region having the thickness t satisfying  $1.00t_{min} \le t \le 1.05t_{min}$  and a circumferential line of the composite fiber are overlapped satisfies  $Ct \ge 0.33C$  with respect to a circumferential length C of the entire composite fiber.
- 2. The composite fiber according to claim 1, wherein at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing.
- 3. The composite fiber according to claim 2, wherein the other thread is a latent crimping yarn.
- **4.** A structural yarn wherein cracks are made on an entire circumference of the surface of the composite fiber according to claim 1.
- 5. The structural yarn according to claim 4, wherein at least one type of another thread coexists in a form of a combined filament composite fiber subjected to mixing.
  - **6.** The structural yarn according to claim 5, wherein the other thread is an explicit crimping yarn.
- 7. A woven or knitted fabric made by weaving or knitting, using the composite fiber according to any one of claims 1 to 3 in at least a portion of the woven or knitted fabric.
  - 8. A woven or knitted fabric comprising the structural yarn according to any one of claims 4 to 6 in at least a portion of the woven or knitted fabric.
- 9. Clothing comprising the woven or knitted fabric according to claim 7 or 8 in at least a portion of the clothing.

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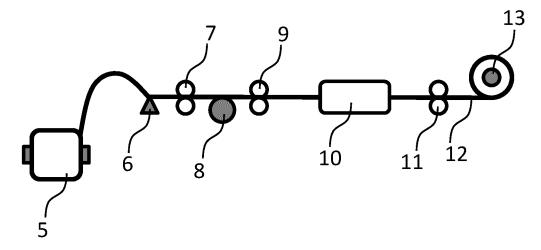
[Fig. 1]



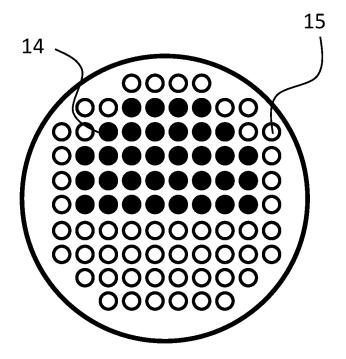
[Fig. 2]



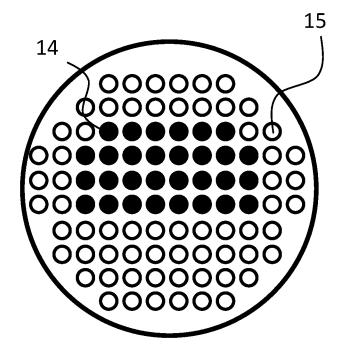
[Fig. 3]



[Fig. 4]



[Fig. 5]



## INTERNATIONAL SEARCH REPORT

International application No.

## PCT/JP2023/023193

	A. CLA	SSIFICATION OF SUBJECT MATTER						
	<b>D01F 8/14</b> (2006.01)i FI: D01F8/14 B							
	According to International Patent Classification (IPC) or to both national classification and IPC							
	B. FIELDS SEARCHED							
	Minimum d	ocumentation searched (classification system followed	by classification symbols)					
	D01F	8/00-8/18						
	Documenta	tion searched other than minimum documentation to the	e extent that such documents are included in	n the fields searched				
	Publi Regis	Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2023 Registered utility model specifications of Japan 1996-2023 Published registered utility model applications of Japan 1994-2023						
	Electronic d	ata base consulted during the international search (nam	e of data base and, where practicable, searc	ch terms used)				
ŀ	C. DOO	CUMENTS CONSIDERED TO BE RELEVANT						
	Category*	Citation of document, with indication, where a	appropriate, of the relevant passages	Relevant to claim No.				
	Y	WO 2018/110523 A1 (TORAY INDUSTRIES, INC claims 1-4, 9, paragraphs [0032], [0036], [0039] examples		1-9				
	Y	JP 2005-273116 A (HYOSUNG CORP) 06 October claims 1-4, paragraph [0009]		1-9				
	Y	JP 2006-507421 A (KOLON INDUSTRIES, INC) 0 claims 1, 2, 4, paragraph [0022], examples	2 March 2006 (2006-03-02)	1-9				
	Y	JP 2003-293226 A (NIPPON ESTER CO LTD) 15 0 claims 1, 2, paragraphs [0013], [0018], example:		1-9				
	Y	JP 2001-123336 A (TORAY INDUSTRIES, INC.) (claim 1, paragraphs [0001], [0015], [0019], exar		1-9				
	Y	JP 2000-212837 A (KURARAY CO LTD.) 02 Auguclaims 1, 4, paragraphs [0001], [0026], [0036], e	ust 2000 (2000-08-02)	1-9				
	<b>✓</b> Further	documents are listed in the continuation of Box C.	See patent family annex.					
	"A" docume to be of "E" earlier a	categories of cited documents: nt defining the general state of the art which is not considered particular relevance pplication or patent but published on or after the international	"T" later document published after the intern date and not in conflict with the application principle or theory underlying the invent document of particular relevance; the document of particular relevance; the document of particular relevance is the considered povel or cannot be considered to the considered povel or cannot be considered.	on but cited to understand the ion elaimed invention cannot be				
	filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means							
	"P" docume	nt published prior to the international filing date but later than rity date claimed	"&" document member of the same patent far					
ļ	Date of the ac	ctual completion of the international search	Date of mailing of the international search	report				
		16 August 2023	05 September 20	23				
ļ	Name and ma	uiling address of the ISA/JP	Authorized officer					
		atent Office (ISA/JP) sumigaseki, Chiyoda-ku, Tokyo 100-8915						
	Telephone No.							

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## INTERNATIONAL SEARCH REPORT

International application No.

5	C. DOCUMENTS CONSIDERED TO BE RELEVANT					
· ·	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.			
	Y	JP 8-269868 A (TORAY INDUSTRIES, INC.) 15 October 1996 (1996-10-15) claim 1, paragraphs [0006], [0025], examples and comparative examples, fig. 5, 7	4-6, 8, 9			
10	Y	WO 92/00408 A1 (KANEBO LTD) 09 January 1992 (1992-01-09) claims 1, 3, p. 10, upper left column, lines 12-14, fig. 2a, 2b, 3a, 3b	4-6, 8, 9			
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#### INTERNATIONAL SEARCH REPORT International application No. Information on patent family members PCT/JP2023/023193 Patent document Publication date Publication date 5 Patent family member(s) cited in search report (day/month/year) (day/month/year) WO 2018/110523 21 June 2018 2020/0087820 A1 US claims 10-13, 21, paragraphs [0033]-[0035], [0055]-[0059], [0083], [0120], [0187], [0251],10 examples ΕP 3556915 A1CN 110088365KR 10-2019-0087462 JP 2005-273116 06 October 2005 KR 10-2005-0095207 15 CN1673426 US 2006/0051575 JP 2006-507421 Α 02 March 2006 **A**1 claims 1, 2, 4, paragraph [0023], examples ΕP 1565601 **A**1 KR 10-2004-0047600 Α 20 1717510CN JP 2003-293226 15 October 2003 (Family: none) JP 08 May 2001 2001-123336 (Family: none) JP 2000-212837 02 August 2000 (Family: none) A 25 (Family: none) 15 October 1996 JP 8-269868 Α wo 92/00408 A1 09 January 1992 5352518 claims 1, 2, column 14, lines 37-41, fig. 2a, 2b, 3a, 3b ΕP 496888 A130 KR 10-1992-0702445 35 40 45 50 55

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#### REFERENCES CITED IN THE DESCRIPTION

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