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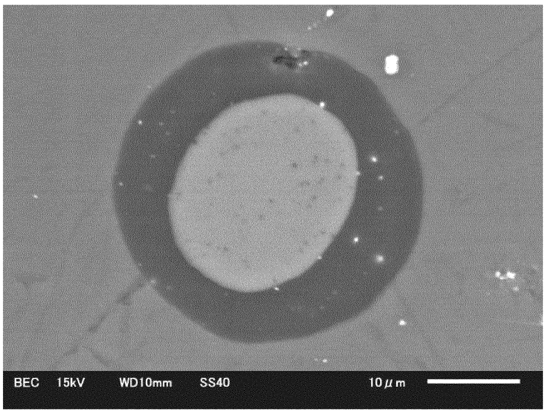
(54) ANTIBACTERIAL FIBER, AND METHOD FOR MANUFACTURING ANTIBACTERIAL FIBER

(57) Provided are an antibacterial fiber in which the amount of incorporation of an antibacterial glass is made sufficient with a small amount by reducing the content of the antibacterial glass in a core portion compared to the content of the antibacterial glass in a sheath portion, and which could exhibit excellent antibacterial properties; and an efficient method for producing such an antibacterial fiber. Disclosed is an antibacterial fiber containing a thermoplastic resin and an antibacterial glass as mixing components, the antibacterial fiber having an average diameter adjusted to a value within the range of 1 to 50 μm, the antibacterial fiber including a core portion and a sheath portion, in which when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1):

$$Q1 < Q2 \quad (1).$$

Fig.1



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Description

TECHNICAL FIELD

[0001] The present invention relates to an antibacterial fiber and a method for producing an antibacterial fiber.

[0002] The invention relates particularly to an antibacterial fiber having a core portion and a sheath portion, in which the amount of incorporation of antibacterial glass is made sufficient with a small amount by reducing the content of the antibacterial glass in the core portion compared to the content of the antibacterial glass in the sheath portion, the antibacterial fiber exhibiting excellent antibacterial properties; and a method for producing an antibacterial fiber.

BACKGROUND ART

[0003] Conventionally, antibacterial fiber products obtained by subjecting fiber products to antibacterial processing have been popularized. Regarding a method for producing such an antibacterial fiber, available are a method of fixating an antibacterial glass composition (glass particles) on the surface of a textile substrate of a synthetic fiber or a natural fiber; and a method of dispersing an antibacterial glass composition into a textile substrate (Patent Document 1).

[0004] Regarding the method of fixating glass particles to the surface of a textile substrate, it is disclosed that antibacterial fibers are obtained by an example in which composite particles are fixated by (a) fixating glass particles in an adhered form by means of an adhesive polymer layer formed on the surface of the textile substrate; (b) further covering the surface side of the fixated glass particles with an overcoat based on a polymer or the like; and (c) having the surface of the glass particles covered in advance by a fixation resin layer, attaching the fixation resin layer to the surface of the textile substrate while softening the fixation resin layer by heating, and then curing the resin layer.

[0005] Furthermore, regarding the method of dispersing glass particles in a textile substrate, it is disclosed that an antibacterial fiber in a dispersed form is obtained by incorporating glass particles into a spinning dope that should become a textile substrate, and spinning this mixture.

[0006] Meanwhile, in Patent Document 2, an antibacterial polyester fiber is disclosed, which is a core-sheath type composite fiber with a core portion containing an antibacterial agent, and in which the proportion of the sheath portion after alkali weight reduction processing is 2% to 20% by weight with respect to the fiber weight, the content of the antibacterial agent in the core portion is 0.1% to 10% by weight with respect to the fiber weight, and the color difference (ΔE) before and after the alkali weight reduction processing is below 2.0.

CITATION LIST

PATENT DOCUMENT

[0007]

Patent Document 1: JP 2001-247333 A
Patent Document 2: JP 11-158730 A

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008] However, in an antibacterial fiber obtainable by the method of fixating glass particles to the surface of a textile substrate as disclosed in Patent Document 1, the glass particles have been fixated with a binder or covered with an overcoat, in order to be fixed to the fiber surface. Therefore, an effort is required to fixate glass particles, and also, there is a problem that it is difficult to obtain sufficient antibacterial properties, the cost is high, and it is economically disadvantageous.

[0009] Furthermore, in an antibacterial fiber obtainable by the method of dispersing antibacterial glass particles in a textile substrate as disclosed in Patent Document 1, while the component that exhibits an antibacterial effect is the antibacterial glass particles fixated to the fiber surface, glass particles are also included in the core portion of the fiber. Therefore, there is a problem that antibacterial glass particles containing highly expensive silver and the like have to be added in large quantities.

[0010] Meanwhile, regarding the antibacterial fiber disclosed in Patent Document 2, oxidation of silver as an antibacterial component occurs due to alkali weight reduction processing, and the antibacterial fiber is discolored (colored). As a result, the antibacterial fiber contains an antibacterial agent only in the core portion, in order to prevent deterioration of antibacterial properties. Therefore, since there is no antibacterial agent existing on the fiber surface, there is a problem that a sufficient antibacterial effect may not be obtained.

[0011] Thus, the inventors of the invention conducted a thorough investigation, and as a result, the inventors found that when an antibacterial fiber containing a thermoplastic resin and an antibacterial glass as mixing components is produced into an antibacterial fiber that has the average diameter adjusted to a value within the range of 1 to 50 μm and includes a core portion and a sheath portion, in which when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy a predetermined relational expression, the antibacterial fiber exhibits excellent antibacterial properties even when the amount of incorporation of the antibacterial glass is a small amount. Thus, the inventors completed the invention.

[0012] That is, an object of the invention is to provide an antibacterial fiber in which the amount of incorporation of antibacterial glass is made sufficient with a small amount by reducing the content of the antibacterial glass in the core portion compared to the content of the antibacterial glass in the sheath portion, and which exhibits excellent antibacterial properties; and an efficient method for producing such an antibacterial fiber.

MEANS FOR SOLVING PROBLEM

[0013] According to the invention, there is provided an antibacterial fiber containing a thermoplastic resin and an antibacterial glass as mixing components, the antibacterial fiber having an average diameter adjusted to a value within the range of 1 to 50 μm, the antibacterial fiber including a core portion and a sheath portion, in which when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1), and thus the above-described problems could be solved.

$$Q1 < Q2 \quad (1)$$

[0014] That is, the content of the antibacterial glass in the core portion could be regulated to be smaller than the content of the antibacterial glass in the sheath portion, and furthermore, even when the amount of incorporation of the antibacterial glass is relatively a small amount with respect to the total amount of the antibacterial fiber, excellent antibacterial properties could be exhibited from an early stage over a long period of time.

[0015] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that Q1 is adjusted to 0 or 0% to below 1% by weight (provided that excluding 0% by weight) .

[0016] When the antibacterial fiber is configured as such, the content of the antibacterial glass in the core portion, which may not easily participate in the exhibition of an antibacterial effect, could be reduced.

[0017] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that Q2 is adjusted to a value within the range of 1% to 10% by weight.

[0018] When the antibacterial fiber is configured as such, antibacterial glass could be incorporated in an amount within a more suitable range with respect to the total amount of the antibacterial fiber.

[0019] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that the antibacterial fiber further contains aggregated silica particles as a mixing component.

[0020] When the antibacterial fiber is configured as such, as silica particles that are richly hydrophilic attach to the periphery of antibacterial glass, the rate of dissolution of the antibacterial glass becomes uniform, and the antibacterial fiber acquires an excellent anti-color-ability.

[0021] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that the volume average particle size of antibacterial glass is adjusted to a value within the range of 0.1 to 5 μm.

[0022] When the antibacterial fiber is configured as such, antibacterial glass could be uniformly dispersed in the resin component, and also, antibacterial glass could be stably processed into the antibacterial fiber.

[0023] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that the thermoplastic resin is selected to be any one or more of a polyester resin, a polyamide resin, and a polyolefin resin.

[0024] When the antibacterial fiber is configured as such, since antibacterial glass could be dispersed more uniformly in the resin component, an excellent antibacterial effect could be obtained.

[0025] On the occasion of configuring the antibacterial fiber of the invention, it is preferable that the antibacterial fiber is in the form of any one of a woven fabric, a nonwoven fabric, and felt.

[0026] That is, since the antibacterial fiber of the invention is an antibacterial fiber having a predetermined shape, even when the amount of incorporation of antibacterial is reduced, a woven fabric, a nonwoven fabric, and felt, all of which exhibit excellent antibacterial properties, could be obtained.

[0027] Furthermore, another embodiment of the invention is a method for producing an antibacterial fiber including a core portion and a sheath portion and containing a thermoplastic resin and an antibacterial glass as mixing components, the method including the following steps (1) to (3) :

(1) a step of preparing antibacterial glass;
(2) a step of dispersing the antibacterial glass thus obtained in a thermoplastic resin such that when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1), and thereby preparing a spinning dope for the core portion and a spinning dope for the sheath portion:

$$Q1 < Q2 \quad (1);$$

and
(3) a step of performing composite spinning using a core-sheath composite spinneret and arranging the spinning dope for the core portion as the core portion and the spinning dope for the sheath portion as the sheath portion, and thereby obtaining an antibacterial fiber having an average diameter of 1 to 50 μm.

[0028] That is, by including steps (1) to (3), the content of the antibacterial glass in the core portion could be reduced compared to the content of the antibacterial glass in the sheath portion.

[0029] Therefore, the amount of incorporation of the antibacterial glass is made sufficient with a relatively small amount with respect to the total amount of the antibacterial fiber, and furthermore, excellent antibacterial properties could be exhibited.

BRIEF DESCRIPTION OF DRAWINGS

[0030]

Fig. 1 is an electron microscopic photograph (SEM image, magnification ratio 2,000) of an antibacterial fiber according to the present embodiment;
Fig. 2 is a schematic diagram of an antibacterial fiber having a core portion and a sheath portion according to the present embodiment;
Fig. 3 is an electron microscopic photograph (SEM image, magnification ratio 2,000) of an antibacterial fiber according to Example 1;
Figs. 4(a) to 4(c) show the results of an EDX mapping analysis of the antibacterial fiber according to Example 1; and
Figs. 5(a) to 5(c) show the results of an EDX mapping analysis of an antibacterial fiber according to Example 2.

MODE(S) FOR CARRYING OUT THE INVENTION

[First embodiment]

[0031] A first embodiment is an antibacterial fiber containing a thermoplastic resin and an antibacterial glass as mixing components, the antibacterial fiber having the average diameter adjusted to a value within the range of 1 to 50 μm, the antibacterial fiber including a core portion and a sheath portion, in which when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1):

$$Q1 < Q2 \quad (1)$$

[0032] In the following description, each of the constituent elements of the antibacterial fiber as the first embodiment will be specifically described.

1. Thermoplastic resin

(1) Main components

(1)-1 Type

[0033] As a main component of a resin that constitutes the antibacterial fiber of the present embodiment, a thermoplastic resin is used.

[0034] The type of such a thermoplastic resin is not particularly limited; however, it is preferable that the thermoplastic resin is at least one of a polyester resin, a polyamide resin, a polyurethane resin, a polyolefin resin (including a polyacrylic resin), a rayon-based resin, a polyvinyl acetate-based resin, a cellulose-based resin, a polyvinyl chloride-based resin, and a polyacetal resin.

[0035] The reason for this is that when a polyester resin is used, an antibacterial fiber having high mechanical strength, durability, and heat resistance and also having excellent flexibility and process-ability could be obtained at relatively low cost.

[0036] Furthermore, it is because when a polyamide resin is used, an antibacterial resin having high mechanical strength, durability, and heat resistance and also having hygroscopic properties could be obtained at relatively low cost.

[0037] Furthermore, it is because when a polyurethane resin is used, an antibacterial fiber having high durability and excellent stretch ability could be obtained.

[0038] Furthermore, it is because when a polyolefin resin (including a polyacrylic resin) is used, an antibacterial fiber having satisfactory transparency and processability could be obtained at low cost.

[0039] Among these thermoplastic resins, more preferred is a polyester resin or a polyolefin resin.

[0040] That is, a suitable polyester resin may be at least one of a polyethylene terephthalate resin, a polypropylene terephthalate resin, a polybutylene terephthalate resin, a polycyclohexanedimethylene terephthalate resin, a polylactic acid resin, a polybutylene succinate resin, a polyglycolic acid resin, and the like, and above all, preferred is a polyethylene terephthalate resin.

[0041] Furthermore, a suitable polyolefin resin may be at least one of a polypropylene resin, polyethylene resins (a high-density polyethylene resin, a linear polyethylene resin, a low-density polyethylene resin, and the like), a polymethylpentene resin, a vinyl acetate copolymer resin, a propylene copolymer resin, and the like, and above all, preferred is a polypropylene resin.

[0042] That is, the reason why a polyethylene terephthalate resin is suitable is that since the polyethylene terephthalate resin has low heat resistance compared to a polybutylene terephthalate resin or the like, the thermoplastic resin composition could be stably processed into an antibacterial fiber, an antibacterial film, or the like, which requires excellent flexibility.

[0043] More specifically, it is because a polyethylene terephthalate resin has a feature that the rate of crystallization is low compared to a polybutylene terephthalate resin, crystallization does not proceed when the temperature is not high, and the strength is increased by heat treatment and stretching treatment.

[0044] Furthermore, when a polyethylene terephthalate resin is used, the antibacterial fiber has high transparency as well as excellent heat resistance and practical strength and also has excellent recyclability, and therefore, it is also advantageous in the economic efficiency.

[0045] More specifically, for example, as in the case of PET bottles, plastic products formed from a polyethylene terephthalate resin are currently distributed in large quantities and are very cheap compared to other resin materials.

[0046] Furthermore, when a polyethylene terephthalate resin is used, as is obvious from the current situation of actively implementing recycling, reutilization is easy compared to other resin materials. Therefore, this makes the polyethylene terephthalate resin as a cheaper resin material.

[0047] The polyethylene terephthalate resin may also be a copolymerized polyester containing other copolymerized components.

[0048] Furthermore, when the thermoplastic resin is a polypropylene resin, the thermoplastic resin has excellent mechanical strength such as tensile strength, impact strength, and compression strength, and the mechanical strength could be adjusted according to the use application.

[0049] Since a polypropylene resin has excellent abrasion resistance and chemical resistance and has excellent quick dry ability and warming performance, it is thought that a polypropylene resin could be suitably used for antibacterial fibers.

[0050] Therefore, by using a polyethylene terephthalate resin or a polypropylene resin as a main component, crystallization of the thermoplastic resin composition in the course of producing and molding an antibacterial fiber could be suppressed effectively, and the thermoplastic resin composition could be stably processed into an antibacterial fiber, an antibacterial film, or the like.

(1)-2 Number average molecular weight

[0051] When the thermoplastic resin that serves as a main component is a polyethylene terephthalate resin, a polypropylene resin, or the like, it is preferable that the number average molecular weight thereof is adjusted to a value within the range of 5,000 to 80,000.

[0052] The reason for this is that when the number average molecular weight of the polyethylene terephthalate resin, the polypropylene resin, or the like is adjusted to a value within such a range, the compatibility with a resin that serves as a sub-component of the thermoplastic resin that will be described below could be enhanced, hydrolysis of the resin could be effectively suppressed, and the antibacterial glass could be dispersed more uniformly.

[0053] Therefore, it is more preferable that the number average molecular weight of the thermoplastic resin is adjusted to a value within the range of 10,000 to 60,000, and even more preferably to a value within the range of 20,000 to 50,000.

(1)-3 Melting point

[0054] Furthermore, it is preferable that the melting point of the thermoplastic resin that serves as a main component is adjusted to a value within the range of 150°C to 350°C.

[0055] The reason for this is that when the melting point is 150°C or higher, the mechanical characteristics such as tensile strength and tear strength of the thermoplastic resin composition could be sufficiently secured, and since appropriate viscosity is obtained when the thermoplastic resin composition is heated and melted, appropriate processability is obtained.

[0056] On the other hand, it is because when the melting point is 350°C or lower, moldability of the thermoplastic resin composition is satisfactory, and the thermoplastic resin could be easily mixed with resin components other than the thermoplastic resin that will be described below.

[0057] Therefore, it is more preferable that the melting point of the thermoplastic resin as a main component is adjusted to a value within the range of 200°C to 300°, and even more preferably to a value within the range of 230°C to 270°C.

[0058] Meanwhile, the melting point of the resin could be measured according to ISO 3146.

[0059] Furthermore, in a case in which the melting point is not observed, it is preferable that the glass transition point is adjusted to a value within the range of 150°C to 350°C.

(1)-4 Amount of incorporation

[0060] Furthermore, it is preferable that the amount of incorporation of the polyethylene terephthalate resin or polypropylene resin is adjusted to a value within the range of 80 to 99.4 parts by weight in a case in which the total amount of the thermoplastic resin composition is designated as 100 parts by weight.

[0061] The reason for this is that when the amount of incorporation of the polyethylene terephthalate resin or polypropylene resin is adjusted to a value within such a range, hydrolysis of the resin could be effectively suppressed, and the thermoplastic resin composition could be easily processed into an antibacterial fiber or an antibacterial film.

[0062] Therefore, it is more preferable that the amount of incorporation of the polyethylene terephthalate resin or polypropylene resin is adjusted to a value within the range of 85 to 99 parts by weight, and even more preferably to a value within the range of 90 to 98 parts by weight, when the total amount of the antibacterial resin composition is designated as 100 parts by weight.

(1)-5 Tensile force

[0063] Furthermore, the tensile strength of the resin that serves as a main component is adjusted to a value within the range of 20 to 100 MPa, in a case in which the tensile strength is measured according to JIS L 1015.

[0064] The reason for this is that when the tensile strength of the resin is below 20 MPa, cutting of the fiber may occur at the time of stretching, or a manufactured product produced using an antibacterial fiber may break open at the time of washing the manufactured product.

[0065] On the other hand, it is because when the tensile strength of the resin is above 100 MPa, the flexibility as an antibacterial fiber may not be sufficient, and the use applications may be excessively restricted.

[0066] Therefore, it is more preferable that the tensile strength of the resin is adjusted to a value within the range of 25 to 95 MPa, and even more preferably to a value within the range of 30 to 90 MPa.

(2) Mixing resin

(2)-1 Type

[0067] In a case in which a polyethylene terephthalate resin is used as a main component, it is preferable that the thermoplastic resin according to the present embodiment is prepared as a mixing resin including a polybutylene terephthalate resin as another resin component.

[0068] The reason for this is that when a polybutylene terephthalate resin having excellent hydrolysis resistance compared to a polyethylene terephthalate resin is included, a polyethylene terephthalate being hydrolyzed due to the moisture included in the antibacterial glass could be effectively suppressed at the time of heating and melting of the thermoplastic resin during production and molding of an antibacterial fiber.

[0069] More specifically, since a polybutylene terephthalate resin has high oleophilic compared to a polyethylene terephthalate resin and a smaller number of ester bonds contained per unit weight, it is thought that the polybutylene terephthalate resin does not easily undergo hydrolysis.

[0070] Therefore, when a polybutylene terephthalate resin is included, hydrolysis of the polyethylene terephthalate resin as a main component could be effectively suppressed, dispersibility of the antibacterial glass is excellent, and an inexpensive thermoplastic resin could be obtained.

[0071] That is, when a predetermined amount of antibacterial glass is first mixed with a polybutylene terephthalate resin, thereby a masterbatch including antibacterial glass at a relatively high concentration is obtained, and then a polyethylene terephthalate resin is mixed thereinto, an antibacterial resin composition having a predetermined mixing ratio could be finally obtained while hydrolysis of the polyethylene terephthalate resin is suppressed.

[0072] Furthermore, the polybutylene terephthalate resin according to the present embodiment basically refers to a polymer obtainable by a polycondensation reaction between terephthalic acid or an ester-forming derivative thereof as an acid component and 1,4-butanediol or an ester-forming derivative thereof as a glycol component.

[0073] However, in a case in which the total amount of acid components is designated as 100 mol%, another acid component may also be included as long as the amount has a value within the range of 20 mol% or less.

(2)-3 Amount of incorporation

[0074] Furthermore, it is preferable that the amount of incorporation of a polybutylene terephthalate resin is adjusted to a value within the range of 0.5 to 25 parts by weight with respect to 100 parts by weight of the polyethylene terephthalate resin.

[0075] The reason for this is that when the amount of incorporation of the polybutylene terephthalate resin is adjusted to a value within such a range, a thermoplastic resin having hydrolysis resistance and having excellent dispersing properties for the antibacterial glass could be obtained, while a polyethylene terephthalate resin that could be processed into an antibacterial fiber or an antibacterial film is used as a main component.

[0076] Therefore, more specifically, it is more preferable that the amount of incorporation of the polybutylene terephthalate resin is adjusted to a value within the range of 2 to 15 parts by weight, and even more preferably to a value within the range of 3 to 10 parts by weight, with respect to 100 parts by weight of the polyethylene terephthalate resin.

(3) Other resin component

[0077] Furthermore, in the invention, the types of the thermoplastic resins used in the core portion and the sheath portion may be identical to each other or different from each other. When the types of the thermoplastic resins used in the core portion and the sheath portion are identical, the core portion and the sheath portion have high compatibility, and an antibacterial fiber could be stably obtained.

[0078] On the other hand, in a case in which the types of the thermoplastic resins used in the core portion and the sheath portion are different, the mechanical characteristics such as tensile strength and tear strength of the antibacterial fiber thus obtainable could be enhanced by using a resin having higher mechanical strength in the core portion.

2. Antibacterial glass

[0079] It is preferable that the antibacterial fiber according to the present embodiment contains antibacterial glass, and the antibacterial glass contains silver ions as an antibacterial active ingredient.

[0080] The reason for this is that when such an antibacterial glass is used, the antibacterial glass is highly safe and maintains antibacterial action for a long period of time, and since the antibacterial glass also has high heat resistance, the antibacterial glass has excellent adaptability as an antibacterial agent that is to be incorporated into the antibacterial fiber.

(1) Composition

[0081] Furthermore, it is preferable that the type of the antibacterial glass is produced from both or either of a phosphate-based antibacterial glass and a borosilicate-based glass.

[0082] The reason for this is that when a phosphate-based antibacterial glass or a borosilicate-based glass is used, since the glass releases an antibacterial active ingredient while absorbing water in the surroundings in the form of moisture and in the form of water and then being dissolved in the water, the amount of elution of an antibacterial active ingredient such as silver ions in the antibacterial fiber could be regulated to a suitable range, while discoloration of the thermoplastic resin is prevented.

(1)-1 Glass composition 1

[0083] Furthermore, it is preferable that the glass composition of the phosphate-based antibacterial glass includes Ag_2O, ZnO, CaO, B_2O_3, and P_2O_5, and that when the total amount is designated as 100% by weight, the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.2% to 5% by weight, the amount of incorporation of ZnO is adjusted to a value within the range of 2% to 60% by weight, the amount of incorporation of CaO is adjusted to a value within the range of 0.1% to 15% by weight, the amount of incorporation of B_2O_3 is adjusted to a value within the range of 0.1% to 15% by weight, the amount of incorporation of P_2O_5 is adjusted to a value within the range of 30% to 80% by weight, and the weight ratio of ZnO/CaO is adjusted to a value within the range of 1.1 to 15.

[0084] Here, Ag_2O is an essential constituent component as an antibacterial ion-releasing substance in glass composition 1, and since the glass composition includes Ag_2O, when glass components are melted, silver ions could be slowly eluted at a predetermined rate, and thus excellent antibacterial properties could be exhibited for a long period of time.

[0085] It is also preferable that the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.2% to 5% by weight.

[0086] The reason for this is that when the amount of incorporation of Ag_2O has a value of 0.2% by weight or more, sufficient antibacterial properties could be exhibited.

[0087] On the other hand, it is because when the amount of incorporation of Ag_2O is 5% by weight or less, the antibacterial glass may not be easily discolored, and since the cost could be suppressed, it is economically advantageous.

[0088] Therefore, it is more preferable that the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.5% to 4% by weight, and it is even more preferable that the amount of incorporation is adjusted to a value within the range of 0.8% to 3.5% by weight.

[0089] Furthermore, P_2O_5 is an essential constituent component in glass composition 1 and basically functions as a network-forming oxide; however, in addition to that, in the invention, P_2O_5 is also involved in a function of improving the transparency of the antibacterial glass or uniform release properties for silver ions.

[0090] Regarding the amount of incorporation of P_2O_5, it is preferable that the amount of incorporation is adjusted to a value within the range of 30% to 80% by weight.

[0091] The reason for this is that when the amount of incorporation of P_2O_5 as such is 30% by weight or more, the transparency of the antibacterial glass is not easily lowered, and uniform release properties for silver ions and physical strength could be easily secured.

[0092] On the other hand, it is because when the amount of incorporation of P_2O_5 as such is 80% by weight or less, the antibacterial glass does not easily undergo yellowing, and since curability is improved, physical strength could be easily secured.

[0093] Therefore, it is more preferable that the amount of incorporation of P_2O_5 is adjusted to a value within the range of 35% by 75% by weight, and it is even more preferable that the amount of incorporation is adjusted to a value within the range of 40% to 70% by weight.

[0094] Furthermore, ZnO is an essential constituent component in the glass composition 1, has a function as a network-modifying oxide for the antibacterial glass, prevents yellowing, and also has a function of enhancing the antibacterial properties.

[0095] Regarding the amount of incorporation of ZnO, it is preferable that the amount of incorporation is adjusted to a value within the range of 2% to 60% by weight with respect to the total amount.

[0096] The reason for this is that when the amount of incorporation of ZnO as such has a value of 2% by weight or more, a yellowing preventing effect and an effect of enhancing the antibacterial properties are easily exhibited. On the other hand, it is because when the amount of incorporation of ZnO as such has a value of 60% by weight or less, the transparency of the antibacterial glass is not easily lowered, and mechanical strength could be easily secured.

[0097] Therefore, it is more preferable that the amount of incorporation of ZnO is adjusted to a value within the range of 5% to 50% by weight, and it is even more preferable that the amount of incorporation is adjusted to a value within the range of 10% to 40% by weight.

[0098] Furthermore, it is preferable that the amount of incorporation of ZnO is determined by taking the amount of incorporation of CaO that will be described below into consideration.

[0099] Specifically, it is preferable that the weight ratio represented by ZnO/CaO is adjusted to a value within the range of 1.1 to 15.

[0100] The reason for this is that when such a weight ratio has a value of 1.1 or more, yellowing of the antibacterial glass could be efficiently prevented. On the other hand, it is because when the weight ratio is 15 or less, the antibacterial glass does not easily undergo clouding or yellowing.

[0101] Therefore, it is more preferable that the weight ratio represented by ZnO/CaO is adjusted to a value within the range of 2.0 to 12, and it is even more preferable that the weight ratio is adjusted to a value within the range of 3.0 to 10.

[0102] CaO is an essential constituent component for glass composition 1, and CaO basically accomplishes a function as a network-modifying oxide, and could lower the heating temperature at the time of producing the antibacterial glass or exhibit a yellowing preventing function together with ZnO.

[0103] It is preferable that the amount of incorporation of CaO is adjusted to a value within the range of 0.1% to 15% by weight with respect to the total amount.

[0104] The reason for this is that when the amount of incorporation of CaO as such is 0.1% by weight or more, a yellowing preventing function and an effect of lowering the melting temperature are easily exhibited. On the other hand, it is because when the amount of incorporation of CaO as such is 15% by weight or less, deterioration of the transparency of the antibacterial glass could be easily suppressed.

[0105] Therefore, it is preferable that the amount of incorporation of CaO is adjusted to a value within the range of 1.0% to 12% by weight, and it is more preferable that the amount of incorporation is adjusted to a value within the range of 3.0% to 10% by weight.

[0106] Furthermore, B_2O_3 is an essential constituent component for glass composition 1, and basically accomplishes a function as a network-forming oxide. However, in addition to that, in the invention, B_2O_3 is a component that is involved in the transparency-improving function of the antibacterial glass as well as uniform release properties for silver ions.

[0107] It is preferable that the amount of incorporation of B_2O_3 is adjusted to a value within the range of 0.1% to 15% by weight with respect to the total amount.

[0108] The reason for this is that when the amount of incorporation of B_2O_3 as such is 0.1% by weight or more, transparency of the antibacterial glass could be sufficiently secured, and uniform release properties for silver ions and mechanical strength could be secured easily.

[0109] On the other hand, it is because when the amount of incorporation of B_2O_3 as such is 15% by weight or less, yellowing of the antibacterial glass is easily suppressed, curability is improved, and mechanical strength could be easily secured.

[0110] Therefore, it is preferable that the amount of incorporation of B_2O_3 is adjusted to a value within the range of 1.0% to 12% by weight, and it is more preferable that the amount of incorporation is adjusted to a value within the range of 3.0% to 10% by weight.

[0111] Meanwhile, it is also preferable that CeO_2, MgO, Na_2O, Al_2O_3, K_2O, SiO_2, BaO, and the like as optional constituent components for glass composition 1 are added in predetermined amounts within the scope of the object of the invention.

(1)-2 Glass composition 2

[0112] Furthermore, it is preferable that the glass composition of the phosphate-based antibacterial glass includes Ag_2O, CaO, B_2O_3, and P_2O_5, while ZnO is not substantially included therein, and when the total amount is designated as 100% by weight, the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.2% to 5% by weight, the amount of incorporation of CaO is adjusted to a value within the range of 15% to 50% by weight, the amount of incorporation of B_2O_3 is adjusted to a value within the range of 0.1% to 15% by weight, the amount of incorporation of P_2O_5 is adjusted to a value within the range of 30% to 80% by weight, and the weight ratio of CaO/Ag_2O is adjusted to a value within the range of 5 to 15.

[0113] Here, with regard to Ag_2O, matters similar to those for glass composition 1 could be applied.

[0114] Therefore, it is preferable that the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.2% to 5% by weight, more preferably to a value within the range of 0.5% to 4.0% by weight, and even more preferably to a value within the range of 0.8% to 3.5% by weight.

[0115] Furthermore, by using CaO for the antibacterial glass, the antibacterial glass could basically accomplish a function as a network-modifying oxide and could also lower the heating temperature at the time of producing antibacterial glass or exhibit a yellowing preventing function.

[0116] That is, it is preferable that the amount of incorporation of CaO is adjusted to a value within the range of 15% to 50% by weight with respect to the total amount.

[0117] The reason for this is that when the amount of incorporation of such CaO is 15% by weight or more, even though the antibacterial glass substantially does not contain ZnO, a yellowing preventing function and an effect of lowering the melting temperature are exhibited. On the other hand, it is because when the amount of incorporation of CaO as such is 50% by weight or less, transparency of the antibacterial glass could be sufficiently secured.

[0118] Therefore, it is more preferable that the amount of incorporation of CaO is adjusted to a value within the range of 20% to 45% by weight, and it is even more preferable that the amount of incorporation is adjusted to a value within the range of 25% to 40% by weight.

[0119] Meanwhile, it is preferable that the amount of incorporation of CaO is determined by taking the amount of incorporation of Ag_2O into consideration, and specifically, it is preferable that the weight ratio represented by CaO/Ag_2O is adjusted to a value within the range of 5 to 15.

[0120] More specifically, it is more preferable that the weight ratio represented by CaO/Ag_2O is adjusted to a value within the range of 6 to 13, and it is even more preferable that the weight ratio is adjusted to a value within the range of 8 to 11.

[0121] Furthermore, with regard to B_2O_3 and P_2O_5, matters similar to those for glass composition 1 could be applied.

[0122] Also, it is preferable that components such as CeO_2, MgO, Na_2O, Al_2O_3, K_2O, SiO_2, and BaO are added in predetermined amounts as optional constituent components similarly to glass composition 1, within the scope of the purpose of the invention.

(1)-3 Glass composition 3

[0123] Furthermore, it is preferable that the glass composition of borosilicate glass includes B_2O_3, SiO_2, Ag_2O, and alkali metal oxides, and when the total amount is designated as 100% by weight, the amount of incorporation of B_2O_3 is adjusted to a value within the range of 30% to 60% by weight, the amount of incorporation of SiO_2 is adjusted to a value within the range of 30% to 60% by weight, the amount of incorporation of Ag_2O is adjusted to a value within the range of 0.2% to 5% by weight, the amount of incorporation of the alkali metal oxides is adjusted to a value within the range of 5% to 20% by weight, the amount of incorporation of Al_2O_3 is adjusted to a value within the range of 0.1% to 2% by weight, and in a case in which the total amount is below 100% by weight, other glass components (alkaline earth metal oxides, CeO_2, CoO, and the like) are included as balance components at a value within the range of 0.1% to 33% by weight.

[0124] Here, in the mixing composition of an alkaline antibacterial glass, B_2O_3 basically accomplishes a function as a network-forming oxide; however, in addition to that, B_2O_3 is also involved in a function of improving transparency and uniform release properties for silver ions.

[0125] Furthermore, SiO_2 accomplishes a function as a network-forming oxide in an antibacterial glass and also has a function of preventing yellowing.

[0126] Furthermore, Ag_2O is an essential constituent component for an antibacterial glass, and as the glass components are melted and thereby silver ions are eluted, excellent antibacterial properties could be exhibited for a long period of time.

[0127] Alkali metal oxides, for example, Na_2O and K_2O, basically accomplish a function as network-modifying oxides, also exhibit a function of adjusting the melt characteristics of antibacterial glass, reduce the water-resistance of antibacterial glass, and could thereby adjust the amount of elution of silver ions from an antibacterial glass.

[0128] Regarding alkaline earth metal oxides, for example, when MgO or CaO is added, a function as network-modifying oxides could be accomplished, and similarly to alkali metal oxides, a function of improving the transparency of the antibacterial glass and a function of adjusting the melting temperature could be exhibited.

[0129] In addition to that, when CeO_2, Al_2O_3, and the like are separately added, discoloration properties against electron beams and transparency, or mechanical strength could also be enhanced.

(2) Elution rate

[0130] Furthermore, it is preferable that the elution rate of antibacterial ions from the antibacterial glass is adjusted to a value within the range of 1×10^2 to 1×10^5 mg/Kg/24 Hr.

[0131] The reason for this is that when such an elution rate of antibacterial ions has a value of below 1×10^2 mg/Kg/24 Hrs, the antibacterial properties may be significantly deteriorated, and when such an elution rate of antibacterial ions is above 1×10^5 mg/Kg/24 Hrs, it may be difficult to exhibit an antibacterial effect over a long period of time, or the transparency of an antibacterial fiber thus obtainable may be deteriorated. Therefore, from the viewpoint that the balance between such antibacterial properties and transparency and the like is more preferable, it is more preferable that the elution rate of antibacterial ions from the antibacterial glass is adjusted to a value within the range of 1×10^3 to 5×10^4 mg/Kg/24 Hrs, and even more preferably to a value within the range of 3×10^3 to 1×10^4 mg/Kg/24 Hr. Meanwhile, such an elution rate of antibacterial ions could be measured under the following measurement conditions.

(Measurement conditions)

[0132] 100 g of antibacterial glass is immersed in 500 ml of distilled water (20°C), and the antibacterial glass is shaken for 24 hours using a shaker. Next, an Ag ion eluate is separated using a centrifuge and then is further filtered through a filter paper (5C), and thereby a measurement sample is obtained. Then, Ag ions in the measurement sample are measured by an ICP emission spectral analysis method, and the amount of Ag ion elution (mg/Kg/24 Hrs) is calculated.

(3) Volume average particle size

[0133] Furthermore, it is preferable that the volume average particle size (volume average primary particle size, D50) of the antibacterial glass is adjusted to a value within the range of 0.1 to 5.0 μm.

[0134] The reason for this is that when the volume average particle size of the antibacterial glass is adjusted to a value within such a range, the antibacterial glass could be dispersed more uniformly, and it is because a thermoplastic resin containing antibacterial glass could be processed into an antibacterial fiber or an antibacterial film more stably.

[0135] That is, it is because when the volume average particle size of the antibacterial glass is 0.1 μm or greater, mixing and dispersing of the antibacterial glass into the resin component are easily achieved, light scattering is suppressed, or transparency could be easily secured.

[0136] On the other hand, it is because when the volume average particle size of the antibacterial glass is 5.0 μm or less, since the antibacterial glass is uniformly dispersed in the resin component, the mechanical strength of the antibacterial fiber could be easily secured.

[0137] Therefore, more specifically, it is more preferable that the volume average particle size of the antibacterial glass is adjusted to a value within the range of 0.5 to 4.0 μm, and even more preferably to a value within the range of 1.0 to 3.0 μm.

[0138] Meanwhile, the volume average particle size (D50) of the antibacterial glass could be calculated from the particle size distribution obtainable using a laser type particle counter (according to JIS Z 8852-1) or a sedimentation type particle size distribution meter, or from the particle size distribution obtainable by performing image processing based on electron microscopic photographs of the antibacterial glass.

(4) Specific surface area

[0139] Furthermore, it is preferable that the specific surface area of the antibacterial glass is adjusted to a value within the range of 10,000 to 300,000 cm^2/cm^3.

[0140] The reason for this is that when such a specific surface area has a value of 10,000 cm^2/cm^3 or greater, mixing and dispersing into the resin component or handling is facilitated, and in the case of producing an antibacterial fiber, surface smoothness and mechanical strength could be easily secured.

[0141] On the other hand, it is because when such a specific surface area is 300,000 cm^2/cm^3 or less, mixing and dispersing into the resin component is facilitated, light scattering is not likely to occur, and deterioration of the transparency could be suppressed.

[0142] More specifically, it is more preferable that the specific surface area of the antibacterial glass is adjusted to a value within the range of 15,000 to 200,000 cm^2/cm^3, and it is even more preferable that the specific surface area is adjusted to a value within the range of 18,000 to 150,000 cm^2/cm^3.

[0143] Meanwhile, the specific surface area (cm^2/cm^3) of the antibacterial glass could be determined from the results of particle size distribution measurement, and under an assumption that the antibacterial glass has a spherical shape, the specific surface area could be calculated as a surface area (cm^2) per unit volume (cm^3) from the actually measured data of the particle size distribution.

(5) Shape

[0144] Furthermore, it is preferable that the shape of the antibacterial glass is made into a polyhedron, that is, a polyhedron configured to have a plurality of corners and faces, for example, a polyhedron configured to have 6 to 20 faces.

[0145] The reason for this is that when the shape of the antibacterial glass is made into a polyhedron as described above, unlike spherical-shaped antibacterial glass, light could easily advance in-plane in a fixed direction. It is also because since light scattering attributed to the antibacterial glass could be effectively prevented, transparency of the antibacterial glass could be enhanced.

[0146] Furthermore, when the antibacterial glass is made into a polyhedron as such, mixing and dispersing into the resin component is facilitated, and particularly in a case in which an antibacterial fiber is produced using a spinning apparatus or the like, the antibacterial fiber has a feature that the antibacterial glass is easily oriented in a fixed direction.

[0147] Therefore, the antibacterial glass could be easily dispersed uniformly in the resin component, and at the same time, scattering of light by the antibacterial glass in the resin component is effectively prevented so that excellent transparency could be exhibited.

[0148] Furthermore, when the shape of the antibacterial glass is a polyhedron as such, external additives that will be described below could easily adhere thereto, and the antibacterial glass may not easily reaggregate during production or during use or the like. Therefore, control of the average particle size and the variation during the production of the antibacterial glass is facilitated.

(6) Surface treatment

[0149] It is preferable that the surface of the antibacterial glass is treated with a polyorganosiloxane-silicone resin, a silane coupling agent, a titanate coupling agent, an aluminate coupling agent, or the like.

[0150] Thereby, the adhesive force between the antibacterial glass and the thermoplastic resin could be adjusted.

(7) External additives

[0151] Furthermore, it is also preferable that aggregated silica particles (dry silica or wet silica) are externally added to the antibacterial glass.

[0152] As long as aggregated silica particles constitute a main component, combination thereof with one of titanium oxide, zinc oxide, aluminum oxide, zirconium oxide, calcium carbonate, shirasu balloons, quartz particles, glass balloons, and the like, or with two or more kinds thereof is also preferable.

[0153] Particularly, among these, aggregated silica particles (dry silica or wet silica) or colloidal silica, which is an aqueous dispersion of the aggregated silica particles, is a preferred external additive because these materials have a small number average primary particle size and highly excellent dispersibility in the antibacterial glass.

[0154] That is, it is because since such aggregated silica particles are dispersed while the aggregated state becomes loose, silica particles adhere to the periphery of the antibacterial glass and could uniformly disperse the antibacterial glass even in the resin component. As the result, the antibacterial glass could be uniformly dispersed evenly within the antibacterial fiber.

[0155] Furthermore, it is preferable that the number average secondary particle size of the aggregated silica as an external additive is adjusted to a value within the range of 1 to 15 μm.

[0156] The reason for this is that when the number average secondary particle size of such an external additive has a value of 1 μm or more, dispersibility of the antibacterial glass 10 is improved, light scattering is suppressed, and transparency could be secured.

[0157] On the other hand, it is because when the number average secondary particle size of such an external additive is 15 μm or less, mixing and dispersing into the resin component or handling is facilitated, and in a case in which an antibacterial fiber or an antibacterial film is produced, surface smoothness, transparency, and mechanical strength could be easily secured.

[0158] Therefore, it is more preferable that the number average secondary particle size of the external additive is adjusted to a value within the range of 5 to 12 μm, and it is even more preferable that the number average secondary particle size is adjusted to a value within the range of 6 to 10 μm.

[0159] Meanwhile, the number average secondary particle size of the external additive could be measured using a laser type particle counter (according to JIS Z 8852-1) or a sedimentation type particle size distribution meter.

[0160] Furthermore, the number average secondary particle size of the external additive could be calculated by subjecting an electron microscopic photograph of these particles to image processing.

[0161] Further, in a case in which the external additive is basically aggregated, it is preferable that the number average primary particle size in a state in which the aggregates are loosened is adjusted to a value within the range of 0.005 to 0.5 μm.

[0162] The reason for this is that when the number average primary particle size of the external additive has a value of 0.005 μm or greater, an effect of enhancing the dispersibility of the antibacterial glass could be easily obtained, light scattering is suppressed, and deterioration of transparency could be suppressed.

[0163] On the other hand, it is because when the number average primary particle size of the external additive is 0.5 μm or less, similarly, an effect of enhancing the dispersibility of the antibacterial glass could be easily obtained, mixing and dispersing into the resin component or handling is similarly facilitated when an antibacterial fiber or an antibacterial film is produced, and the surface smoothness, transparency, and mechanical strength could be sufficiently secured.

[0164] Therefore, it is more preferable that the number average primary particle size of the external additive is adjusted to a value within the range of 0.01 to 0.2 μm, and it is even more preferable that the number average primary particle size is adjusted to a value within the range of 0.02 to 0.1 μm.

[0165] Meanwhile, the number average primary particle size of the external additive could be measured by a method similar to that used for the number average secondary particle size.

[0166] Furthermore, it is preferable that the amount of addition of aggregated silica as an external additive is adjusted to a value within the range of 0.1 to 50 parts by weight with respect to 100 parts by weight of the antibacterial glass.

[0167] The reason for this is that when the amount of addition of the external additive as such has a value of 0.1 parts by weight or more, dispersibility of the antibacterial glass is improved.

[0168] On the other hand, it is because when the amount of addition of the external additive as such has a value of 50 parts by weight or less, the external additive could be uniformly mixed with the antibacterial glass, and the transparency of the antibacterial resin composition thus obtainable is not easily deteriorated.

[0169] Therefore, it is more preferable that the amount of addition of the external additive is adjusted to a value within the range of 0.5 to 30 parts by weight, and even more preferably to a value within the range of 1 to 10 parts by weight, with respect to 100 parts by weight of the antibacterial glass.

(8) Moisture content

[0170] Furthermore, even in a case in which the antibacterial glass contains moisture, it is preferable that the content of the moisture is adjusted to a value within the range of 1×10^{-4} to 5 parts by weight with respect to 100 parts by weight of the solid components of the antibacterial glass.

[0171] The reason for this is that when the moisture content is adjusted to a value within such a range, at the time of producing a thermoplastic resin composition, hydrolysis of the thermoplastic resin is effectively suppressed even in a case in which a step of drying the antibacterial glass is omitted, and the antibacterial glass could be uniformly dispersed.

[0172] That is, it is because when such moisture content has a value of 1×10^{-4} parts by weight or more, excessively large-scaled facilities are not used as the drying facility for the antibacterial glass, the time required for the drying step is not likely to become excessively lengthened, and the economic efficiency is not impaired noticeably.

[0173] On the other hand, it is because when such moisture content has a value of 5 parts by weight or less, hydrolysis of the thermoplastic resin mentioned above could be stably suppressed.

[0174] Therefore, it is more preferable that the moisture content of the antibacterial glass is adjusted to a value within the range of 1×10^{-3} to 1 parts by weight, and even more preferably to a value within the range of 1×10^{-2} to 1×10^{-1} parts by weight, with respect to 100 parts by weight of the solid components of the antibacterial glass.

[0175] Meanwhile, the measurement of the moisture content in the antibacterial glass could be carried out by, for example, a weight loss on heating method at 105°C with an electronic moisture meter, or could also be carried out using a Karl-Fischer method.

(9) Amount of incorporation

[0176] Furthermore, the amount of incorporation of the antibacterial glass is preferably such that when the content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and the content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 is adjusted to 0 or 0% to below 1% by weight (provided that 0% by weight is excluded), and Q2 is adjusted to a value within the range of 1% to 10% by weight.

[0177] The reason for this is that when the amount of incorporation of the antibacterial glass is adjusted to a value within such a range, hydrolysis of the thermoplastic resin is effectively suppressed, the antibacterial glass is uniformly dispersed in the resin component, and an excellent antibacterial effect could be obtained.

[0178] Furthermore, it is because when the antibacterial fiber is configured as such, the content of the antibacterial glass in the core portion could be regulated to be smaller than the content of the antibacterial glass in the sheath portion, and excellent antibacterial properties could be exhibited even when a small amount of incorporation is used with respect to the total amount of the antibacterial fiber.

[0179] That is, it is because when Q1 has a value of 0% or below 1% by weight, the antibacterial glass is not included in excess in the core portion of the antibacterial portion, and since the absolute amount is sufficient, sufficient antibacterial properties could be imparted to the antibacterial fiber.

[0180] On the other hand, it is because when Q2 has a value within the range of 1% to 10% by weight, the amount of moisture included in the antibacterial glass also increases along with the amount of incorporation of the antibacterial glass; however, hydrolysis of the thermoplastic resin could be sufficiently suppressed. Furthermore, it is because the thermoplastic resin could be easily processed into an antibacterial fiber or an antibacterial film.

[0181] Therefore, more specifically, it is more preferable that Q1 is adjusted to 0 or below 0.5% by weight, and it is more preferable that Q2 is adjusted to a value within the range of 1.5% to 9% by weight. Furthermore, it is even more preferable that Q1 is adjusted to 0 or below 0.1% by weight, and it is even more preferable that Q2 is adjusted to a value within the range of 2% to 8% by weight.

3. Antibacterial fiber

(1) Form

[0182] Antibacterial fiber 1 according to the present embodiment includes, as shown in the electron microscopic photograph (SEM image) of Fig. 1 and the schematic diagram of Fig. 2, a core portion 20 and a sheath portion 30, in which the content of the antibacterial glass 10 in the core portion 20 is smaller than the content of the antibacterial glass 10 in the sheath portion 30.

[0183] Furthermore, it is preferable that the average diameter of the antibacterial fiber is adjusted to a value within the range of 1 to 50 μm.

[0184] The reason for this is that when the average diameter of the antibacterial fiber has a value of 1 μm or greater, the mechanical strength of the antibacterial fiber could be easily secured, and the antibacterial fiber could be stably produced.

[0185] On the other hand, it is because when the average diameter of such an antibacterial fiber has a value of 50 μm or less, flexibility of the antibacterial fiber could be secured, and the antibacterial fiber could be applied to a wide variety of use applications.

[0186] Therefore, it is more preferable that the average diameter of the antibacterial fiber is adjusted to a value within the range of 2 to 49 μm, and even more preferably to a value within the range of 3 to 48 μm.

[0187] Meanwhile, regarding the average diameter of the antibacterial fiber, the diameter could be actually measured at several points (for example, five points) using an electron microscope, a micrometer, or vernier calipers, and an average value thereof could be adopted. Furthermore, the average diameter could also be determined as an equivalent circle diameter.

(2) Core portion

(2)-1 Type of thermoplastic resin

[0188] Regarding the type of the thermoplastic resin used in the core portion, the above-mentioned thermoplastic resin could be used. Furthermore, it is also preferable that the number average molecular weight and the melting point of the thermoplastic resin are adjusted to values within the above-mentioned ranges.

(2)-2 Average diameter

[0189] Furthermore, it is preferable that the average diameter Φ of the core portion of the antibacterial fiber 1 according to the present embodiment is adjusted to a value within the range of 0.3 to 40 μm.

[0190] The reason for this is that when the average diameter of the core portion is adjusted to a value within such a range, mechanical characteristics such as tensile strength and tear strength could be sufficiently secured.

[0191] Therefore, it is more preferable that the average diameter of the core portion is adjusted to a value within the range of 0.5 to 35 μm, and even more preferably to a value within the range of 0.7 to 30 μm.

[0192] Meanwhile, regarding the average diameter of the core portion, the diameter could be actually measured at several points (for example, five points) using an electron microscope or a micrometer, and an average value thereof could be adopted.

(3) Sheath portion

(3)-1 Type of thermoplastic resin

[0193] Regarding the type of the thermoplastic resin used in the sheath portion, the above-mentioned thermoplastic resin could be used. Furthermore, it is also preferable that the number average molecular weight and melting point of the thermoplastic resin are adjusted to values within the above-mentioned ranges.

(3)-2 Thickness of sheath portion

[0194] Furthermore, it is preferable that the thickness t of the sheath portion of the antibacterial fiber 1 according to the present embodiment is adjusted to a value within the range of 0.7 to 49.7 μm.

[0195] The reason for this is that when the thickness of the sheath portion is adjusted to a value within such a range, sufficient antibacterial properties could be maintained from an early stage over a long period of time.

[0196] Therefore, it is more preferable that the thickness of the sheath portion is adjusted to a value within the range of 1 to 45 μm, and even more preferably to a value within the range of 5 to 40 μm.

[0197] Meanwhile, regarding the thickness of the sheath portion, t is actually measured at several points (for example, five points) using an electron microscope or a micrometer, and an average value thereof could be adopted.

(4) Relational expression Q1 < Q2

[0198] With regard to the antibacterial fiber according to the present embodiment, when the content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and the content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1):

$$Q1 < Q2 \quad (1)$$

[0199] Thereby, since the content of the antibacterial glass in the core portion could be reduced compared to the content of the antibacterial glass in the sheath portion, the antibacterial fiber could have a concentration distribution of the antibacterial glass and could exhibit excellent antibacterial properties.

[0200] Furthermore, it is more preferable that Q1 and Q2 satisfy the following relational expression (2):

$$0 < Q2 - Q1 \leq 10 \quad (2)$$

[0201] It is because the concentration distribution of the antibacterial glass in the antibacterial fiber could be thereby adjusted to be in an optimal range.

[0202] Therefore, regarding Q1 and Q2 that satisfy such a relational expression, it is preferable that Q1 is adjusted to 0 or below 1% by weight (provided that 0% by weight is excluded), and it is preferable that Q2 is adjusted to a value within the range of 1% to 10% by weight.

Furthermore, it is more preferable that Q1 is adjusted to 0 or below 0.5% by weight, and it is more preferable that Q2 is adjusted to a value within the range of 1.5% to 9% by weight. Furthermore, it is even more preferable that Q1 is adjusted to 0 or below 0.1% by weight, and it is even more preferable that Q2 is adjusted to a value within the range of 2% to 8% by weight.

[0203] The reason for this is that when the value of Q1 is a value within this range, even in a case in which the average diameter of the antibacterial fiber is small, an antibacterial effect of the antibacterial glass could be effectively obtained. On the other hand, it is because Q2 has a value within this range, the content of the antibacterial glass with respect to the total amount of the antibacterial fiber could be adjusted to an appropriate range.

(5) Tensile strength

[0204] Furthermore, regarding the antibacterial fiber according to the present embodiment, from the viewpoint of imparting sufficient strength to a manufactured product when the antibacterial fiber is processed into a woven fabric or the like, it is preferable that the tensile strength (cN/dtex) measured according to JIS L 1015 is adjusted to a value within the range of 3 to 50 cN/dtex.

[0205] The reason for this is that when the tensile strength (cN/dtex) of the antibacterial fiber is below 3 cN/dtex, cutting of the fiber may occur at the time of stretching, or a manufactured product that uses the antibacterial fiber may break open at the time of washing of the manufactured product or the like.

[0206] On the other hand, it is because when the tensile strength (cN/dtex) of the antibacterial fiber is above 50 cN/dtex, the antibacterial fiber may not have sufficient flexibility, and the use application may be excessively limited.

[0207] Therefore, it is more preferable that the tensile strength (cN/dtex) of the antibacterial fiber is adjusted to a value within the range of 3.5 to 30 cN/dtex, and even more preferably to a value within the range of 4.5 to 20 cN/dtex.

(6) Others

[0208] The apparent degree of weaving and the number of windings of the antibacterial fiber are not particularly limited and could be adjusted as appropriate according to the use application of the antibacterial fiber.

[0209] The apparent degree of weaving of the antibacterial fiber could be adjusted as appropriate according to the use application; however, for example, it is preferable that the apparent degree of weaving is adjusted to a value within the range of 0.1 to 50 dtex, more preferably to a value within the range of 0.5 to 30 dtex, and even more preferably to a value within the range of 1 to 10 dtex.

[0210] Furthermore, the number of windings of the antibacterial fiber could be adjusted according to the use application from the viewpoints of imparting elastic force, tactile sensation, and the like, and as the number of windings is larger, the antibacterial fiber becomes richer in elastic force.

[0211] The number of windings of the antibacterial fiber may be usually adjusted to 5 to 90 windings per 25 mm of the fiber, and for a use application that requires elasticity, it is preferable that the number of windings is adjusted to 50 to 90.

4. Dispersion aid

[0212] Furthermore, it is preferable that the antibacterial fiber according to the present embodiment includes a dispersion aid for the antibacterial glass.

[0213] The reason for this is that when the antibacterial fiber includes a dispersion aid, the antibacterial glass could be dispersed more uniformly.

(1) Type

[0214] The type of the dispersion aid is not particularly limited, and for example, an aliphatic amide-based dispersion aid, a hydrocarbon-based dispersion aid, a fatty acid-based dispersion aid, a higher alcohol-based dispersion aid, a metal soap-based dispersion aid, an ester-based dispersion aid, or the like could be used. However, above all, an aliphatic amide-based dispersion aid is particularly preferred.

[0215] Aliphatic amide-based dispersion aids are roughly classified into fatty acid amides such as stearic acid amide, oleic acid amide, and erucic acid amide; and alkylene fatty acid amides such as methylenebisstearic acid amide and ethylenebisstearic acid amide. However, it is more preferable to use an alkylene fatty acid amide.

[0216] The reason for this is that when an alkylene fatty acid amide is used, the dispersibility of the antibacterial glass could be enhanced without lowering the thermal stability of the antibacterial resin composition, compared to fatty acid amides.

[0217] Furthermore, from the viewpoint of having a melting point of 141.5°C to 146.5°C and having an excellent stability during molding of the antibacterial fiber, it is particularly preferable to use ethylenebisstearic acid amide among the alkylene fatty acid amides.

(2) Amount of incorporation

[0218] It is preferable that the amount of incorporation of the dispersion aid is adjusted to a value within the range of 1 to 20 parts by weight with respect to 100 parts by weight of the antibacterial glass.

[0219] The reason for this is that when the amount of incorporation of the dispersion aid has a value of 1 part by weight or more, the dispersibility of the antibacterial glass in the antibacterial fiber could be sufficiently enhanced.

[0220] On the other hand, it is because when the amount of incorporation of the dispersion aid is 20 parts by weight or less, mechanical characteristics such as tensile strength and tear strength of the antibacterial resin composition could be sufficiently secured, and bleed-out of the dispersion aid from the antibacterial resin composition does not easily occur.

[0221] Therefore, it is more preferable that the amount of incorporation of the dispersion aid is adjusted to a value within the range of 3 to 12 parts by weight, and even more preferably to a value within the range of 5 to 8 parts by weight, with respect to 100 parts by weight of the antibacterial glass.

5. Other mixing components

[0222] Regarding the antibacterial fiber according to the present embodiment, it is preferable to add additives such as a stabilizer, a mold release agent, a nucleating agent, a filler, a dye, a pigment, an antistatic agent, an oil solution, a lubricating agent, a plasticizer, a sizing agent, an ultraviolet absorber, an antifungal agent, an antiviral agent, a flame retardant, and a flame retardant aid; another resin; an elastomer, and the like as optional components to the antibacterial fiber as necessary, to the extent that does not impair the original purpose.

[0223] The method of adding these optional components into the antibacterial fiber is not particularly limited, and for example, it is also preferable to perform the addition by melt kneading the optional components into a thermoplastic resin together with antibacterial glass.

6. Form

[0224] It is preferable that the antibacterial fiber according to the present embodiment is processed into a cotton form or a sheet-like molded article such as a woven fabric, nonwoven fabric, a textile fabric, a felt, or a web.

[0225] Furthermore, when the antibacterial fiber according to the present embodiment is processed into cotton, a woven fabric, nonwoven fabric, a knit fabric, a felt, a web, or the like, processing may be carried out using only the antibacterial fiber of the present embodiment; however, it is also preferable that a fiber of another kind and the antibacterial fiber of the present embodiment are subjected to yarn mixing and mixed spinning to be processed into a plied yarn, a covering yarn, or a braided cord.

[0226] Examples of the other kind of fiber include synthetic fibers of nylon, polyester, polyurethane, or the like; natural fibers of cotton yarn, silk yarn, or the like; carbon fibers; and glass fibers.

[0227] A product obtained by subjecting the antibacterial fiber and another type of fiber to yarn mixing and mixed spinning, and processing the resultant into a plied yarn, a covering yarn, or a braided cord, also has antibacterial properties that are equivalent to those of the antibacterial fiber of the present embodiment, and has an excellent feature that such a product maintains antibacterial properties even when washed repeatedly.

[0228] Furthermore, it is also preferable that the antibacterial fiber according to the present embodiment or a processed product such as cotton, a woven fabric, or a knit fabric, which is obtained by processing the antibacterial fiber according to the use application, is further subjected to dyeing or various finish processing (crease resistance, anti-fouling, flame retardance, insect-proofing, mildew-proofing, deodorization, moisture absorption, water repellency, calendaring, anti-pilling, and the like).

[0229] Thereby, functions other than antibacterial properties could be imparted.

7. Use applications

[0230] Among the above-described forms, the use application of the sheet-like molded article is not particularly limited; however, examples include clothes, bedding, interior tools, absorption cloth, packaging materials, miscellaneous goods, and filtration media.

[0231] Examples of the clothes include underwear, a shirt, sportswear, an apron, socks, insoles, stockings, tights, tabi socks, kimono items, a necktie, a handkerchief, a scarf, a muffler, a hat, gloves, and a mask for domestic or medical use.

[0232] Examples of the bedding include a futon cover, padding in a futon, a pillowcase, padding in a pillow, a towelket, a sheet, and external cladding of a mattress. Particularly, the sheet-like molded article is appropriate for the use in bedding that is difficult to wash, such as a down quilt or a down pillow.

[0233] Examples of the interior tools include a curtain, a mat, a carpet, a rug, a floor cushion, a cushion, a tapestry, wall cladding, tablecloth, and moquette.

[0234] Examples of the absorption cloth include a towel, dishcloth, a handkerchief, a mop, a diaper, a tampon, a sanitary napkin, and adult incontinence articles.

[0235] Examples of the packaging materials include a wrapping cloth, wrapping paper, and a food package.

[0236] Examples of the miscellaneous goods include various brushes such as a toothbrush, a dish scrubber, and a brush; a carrier bag, a luncheon mat, a pen case, a purse, an eyeglasses case, an eyeglasses wiper, a shop curtain, a coaster, a mouse pad, inner cotton for stuffed toys, and a pet bed.

[0237] Examples of the filtration media include filters for use in an air conditioner, a ventilating fan, an air hatch, and an air cleaner, and filters for water purification, and these could be applied to filters for domestic use, industrial use, automobile use, and the like.

[0238] Examples of other uses include artificial hair, a tent, a light-shielding sheet such as a weed preventing sheet, a soundproof material, an acoustic material, and a buffer material.

[Second embodiment]

[0239] A second embodiment is a method for producing the antibacterial fiber described in the first embodiment and is a method for producing an antibacterial fiber having a core portion and a sheath portion and containing a thermoplastic resin and an antibacterial glass as mixing components, and it is a method for producing an antibacterial fiber, the method including the following steps (1) to (3):

(1) a step of preparing an antibacterial glass;
(2) a step of dispersing the antibacterial glass thus obtained in a thermoplastic resin such that
when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and
a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber,
Q1 and Q2 satisfy the following relational expression (1):

$$Q1 < Q2 \quad (1)$$

and thereby preparing a spinning dope for the core portion and the spinning dope for the sheath portion; and

(3) a step of performing composite spinning using a core-sheath composite spinneret and arranging the spinning dope for the core portion as the core portion and the spinning dope for the sheath portion as the sheath portion, and thereby obtaining an antibacterial fiber having an average diameter of 10 to 30 μm.

[0240] Hereinafter, the method for producing an antibacterial fiber as the second embodiment will be specifically described, mainly on the basis of differences from the first embodiment.

[0241] Meanwhile, the antibacterial fiber according to the present embodiment could be produced by a production method having at least the steps (1) to (3) described above, and if necessary, the following steps (4) to (6) may be added.

1. Step (1): Step of preparing antibacterial glass

[0242] Step (1) is a step of producing an antibacterial glass from glass raw materials including an antibacterial active ingredient.

[0243] That is, the antibacterial glass could be produced by a conventionally known method, and for example, it is preferable to produce the antibacterial glass by a method including the following (1)-1 to (1)-3.

(1)-1 Melting step

[0244] In the melting step, it is preferable that glass raw materials are accurately weighed and then uniformly mixed, subsequently the mixture is melted using, for example, a glass melting furnace, and thus a glass melt is produced.

[0245] Upon mixing of the glass raw materials, it is preferable to use a mixing machine (mixer) such as a universal stirrer (planetary mixer), an alumina porcelain crusher, a ball mill, or a propeller mixer, and for example, in the case of using a universal stirrer, it is preferable that the glass raw materials are stirred and mixed by setting the speed of revolution to 100 rpm and the speed of rotation to 250 rpm, under the conditions of 10 minutes to 3 hours.

[0246] Regarding the glass melting conditions, for example, it is preferable that the melting temperature is adjusted to 1,100°C to 1,500°C and the melting time is adjusted to a value within the range of 1 to 8 hours.

[0247] The reason for this is that under such melting conditions, the production efficiency of the glass melt is increased, and at the same time, yellowing of the antibacterial glass during production could be reduced as much as possible.

[0248] Meanwhile, after such a glass melt is obtained, it is preferable that the glass melt is injected into flowing water and cooled, and water pulverization is combined to obtain a glass body.

(1)-2 Pulverization step

[0249] Next, as the pulverization step, it is preferable that the glass body thus obtained is pulverized, and an antibacterial glass that is composed of polyhedrons and has a predetermined volume average particle size is produced.

[0250] Specifically, it is preferable to perform crude pulverization, intermediate pulverization, and fine pulverization as described below.

[0251] By performing as such, an antibacterial glass having a uniform volume average particle size could be efficiently obtained.

[0252] However, in order to control the volume average particle size more finely according to the use application, classification is further carried out after pulverization, and it is also preferable to perform sieve treatment or the like.

[0253] In the crude pulverization, it is preferable to pulverize the glass body so as to obtain a volume average particle size of about 10 mm.

[0254] More specifically, it is preferable to obtain a predetermined volume average particle size by performing water granulation when a glass melt in a molten state is converted into a glass body, or performing pulverization an amorphous glass body with bare hands or using a hammer or the like.

[0255] Meanwhile, it has been verified from electron microscopic photographs that the antibacterial glass after crude pulverization is usually in a lump-like state without corners.

[0256] In the intermediate pulverization, it is preferable that the antibacterial glass obtained after crude pulverization is pulverized so as to obtain a volume average particle size of about 1 mm.

[0257] More specifically, for example, it is preferable that the antibacterial glass having a volume average particle size of about 10 mm is produced into an antibacterial glass having a volume average particle size of about 5 mm using a ball mill, and subsequently, an antibacterial glass having a volume average particle size of about 1 mm is obtained using a rotary mortar or a rotating roll (roll pulverizer).

[0258] The reason for this is that when intermediate pulverization is carried out in multiple stages as such, an antibacterial glass having a predetermined particle size could be effectively obtained without having an antibacterial glass having excessively small particle sizes produced therein.

[0259] Meanwhile, it has been verified from electron microscopic photographs that the antibacterial glass obtained after intermediate pulverization includes polyhedrons having corners.

[0260] In the fine pulverization, it is preferable that the antibacterial glass obtained after intermediate pulverization is pulverized so as to obtain a volume average particle size of 1.0 to 5.0 μm, in a state in which aggregated silica particles have been added as an external additive having a volume average particle size of 1 to 15 μm.

[0261] More specifically, for example, it is preferable to pulverize the antibacterial glass using a rotary mortar, a rotating roll (roll pulverizer), a vibrating mill, a vertical mill, a dry ball mill, a planetary mill, a sand mill, or a jet mill.

[0262] Among these dry pulverizing machines, it is more preferable to use a vertical mill, a dry ball mill, a planetary mill, and a jet mill in particular.

[0263] The reason for this is that appropriately shear force could be exerted by using a vertical mill, a planetary mill, or the like, and a polyhedral antibacterial glass having a predetermined particle size could be effectively obtained without having an antibacterial glass having excessively small particle sizes produced therein.

[0264] In the case of performing fine pulverization using a vertical mill, a dry ball mill, a planetary mill, or the like, it is preferable that a vessel is rotated at a rate of 30 to 100 rpm using zirconia balls or alumina balls as pulverizing media, and the antibacterial glass obtained after intermediate pulverization is subjected to a pulverization treatment for 5 to 50 hours.

[0265] Furthermore, in the case of using a jet mill, it is preferable that acceleration is achieved in a vessel, and antibacterial glass particles obtained after intermediate pulverization are caused to collide with one another at a pressure of 0.61 to 1.22 MPa (6 to 12 Kgf/cm^2).

[0266] Meanwhile, it has been verified from electron microscopic photographs and particle size distribution measurement that the antibacterial glass obtained after performing fine pulverization using a dry ball mill, a jet mill, or the like is composed of polyhedrons having more numerous corners than the antibacterial glass obtained after intermediate pulverization, and the volume average particle size (D50) and the specific surface area could be easily adjusted to predetermined ranges.

[0267] Furthermore, in a case in which fine pulverization is performed using a planetary mill or the like, it is preferable to perform fine pulverization substantially in a dry state (for example, the relative humidity is 20%RH or less).

[0268] The reason for this is that a classification apparatus such as a cyclone could be attached to a planetary mill or the like, and the antibacterial glass could be circulated without causing the antibacterial glass to aggregate.

[0269] Therefore, the volume average particle size and the particle size distribution for the antibacterial glass could be easily adjusted to desired ranges by controlling the number of times of circulation, and at the same time, a drying step after fine pulverization could be omitted.

[0270] On the other hand, regarding antibacterial glass that is smaller than or equal to a predetermined range, when the antibacterial glass is in a dry state, the antibacterial glass could be easily removed using a bag filter.

[0271] Therefore, adjustment of the volume average particle size and the particle size distribution for the antibacterial glass becomes even easier.

(1)-3 Drying step

[0272] Next, it is preferable that the antibacterial glass obtained in the pulverization step is dried in a drying step.

[0273] The reason for this is that as the antibacterial glass is dried, when the antibacterial glass is mixed with a thermoplastic resin in the step described below, the possibility that the thermoplastic resin may cause hydrolysis could be reduced.

[0274] Meanwhile, in the drying step, it is preferable to also perform a drying treatment after performing a solid-liquid separation treatment, and the facilities used for these treatments are not particularly limited. However, a centrifuge or the like could be used for the solid-liquid separation, and a dryer, an oven, or the like could be used for drying.

[0275] Furthermore, after the drying step of the antibacterial glass, some of the antibacterial glass is aggregated. Therefore, it is preferable that the aggregated antibacterial glass is disintegrated using a disintegrator.

2. Step (2): Step of preparing spinning dopes

[0276] Step (2) is a step of producing spinning dopes using the antibacterial glass obtained in step (1).

[0277] In Step (2), it is preferable that a spinning dope is produced by melting and kneading antibacterial glass or a masterbatch obtained by dispersing antibacterial glass in a thermoplastic resin with resin pellets or regenerated resin flakes.

[0278] Furthermore, in step (2), it is also preferable to further add additives such as a colored masterbatch, an oxidation inhibitor, an internal lubricating agent, and a crystallizing agent.

[0279] In step (2), the antibacterial glass thus obtained is mixed and dispersed such that when the content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and the content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber, Q1 and Q2 satisfy the following relational expression (1), and a spinning dope for the core portion and the spinning dope for the sheath portion are prepared.

$$Q1 < Q2 \quad (1)$$

[0280] Here, it is preferable that Q1 is adjusted to 0 or below 1% by weight (provided that 0% by weight is excluded), and Q2 is adjusted to a value within the range of 1% to 10% by weight.

[0281] Furthermore, regarding the thermoplastic resin, in the case of using a polyethylene terephthalate resin as a main component, it is preferable that a polybutylene terephthalate resin is mixed and dispersed therein.

[0282] This is because hydrolysis of the polyethylene terephthalate resin as a main component is effectively suppressed, and a spinning dope in which the antibacterial glass at the final concentration is uniformly dispersed could be obtained.

3. Step (3): Step of producing antibacterial fiber

[0283] The antibacterial fiber according to the invention could be produced by a method similar to a conventionally known method applicable to composite fibers. Examples of spinning include melt spinning and solution spinning; however, the method is selected depending on the resin to be used.

[0284] In step (3), it is preferable that a core-sheath composite spinneret is used, a molten spinning dope for the core portion is introduced into the core portion, while a molten spinning dope for the sheath portion is introduced as the sheath portion, and the spinning dopes are discharged through the spinneret and then produced into fibers by thermal stretching.

[0285] Here, the spinning dope for the core portion and the spinning dope for the sheath portion refer, in the case of melt spinning, to molten resins obtained by melting resins by heating, and in the case of solution spinning, to dopes in a state in which resins have been dissolved in solvents.

[0286] The yarn lines discharged through the spinneret are usually cooled; however, the cooling method is not particularly limited, and a method of blowing cold air against the spun yarn lines could be preferably mentioned as an example.

[0287] Regarding the spun yarn, it is also preferable that a two-step method of first winding the yarn and canning yarn in a can is employed as necessary, and then the yarn is subjected to a stretching treatment.

[0288] Regarding the apparatus used upon spinning, any conventionally known apparatus could be used.

[0289] For example, it is preferable to use a pressure melter type spinning machine, or a single-screw or twin-screw extruder type spinning machine.

[0290] The reason for this is that when such an apparatus is used, an antibacterial fiber having excellent surface smoothness could be efficiently obtained.

[0291] The shape of the spun yarn is not particularly limited; however, the shape may be a circular shape or a flat shape, or may be a polygonal shape such as a hexagonal shape or a star shape.

[0292] The spinning temperature is preferably, for instance, from 240°C to 320°C, and the winding speed is preferably from 100 m/min to 6,000 m/min.

[0293] Next, the fiber obtained by spinning is stretched.

[0294] The stretching step could be carried out using conventionally known methods and apparatuses, and for example, it is preferable to employ a direct spinning and stretching method or a roller stretching method. In a case in which spinning and stretching are performed separately, it is preferable to use a warm water bath.

[0295] The direct spinning and stretching method is carried out by first cooling the fibers to a temperature lower than or equal to the glass transition point after spinning, subsequently causing the fibers to travel inside a tubular heating apparatus at a temperature ranging from the glass transition temperature to the melting point, and winding the fibers.

[0296] The roller stretching method is carried out by taking over the spun yarn by winding around a take-over roller that rotates at a predetermined speed, an stretching the yarn thus taken over in one stage or in multiple stages such as two or more stages, by means of a group of rollers set to a temperature ranging from the glass transition temperature to the melting point of the thermoplastic resin.

[0297] The warm water bath is carried out by immersing the fibers in warm water at 60°C to 90°C, and preferably around 80°C.

[0298] Meanwhile, regarding the stretch ratio, it is preferable that the stretch ratio is 1.2 times or higher from the viewpoint of increasing the mechanical strength.

[0299] The upper limit of the stretch ratio is not particularly limited; however, from the viewpoint of preventing breakage of the yarn caused by excessive stretching, it is preferable that the stretch ratio is 7 times or less.

4. Step (4): Crimping step

[0300] The crimping step of step (4) is an optional process and is a step of guiding the stretched yarn obtained in step (3) into a crimping apparatus, subjecting the yarn to false twisting, and imparting bulkiness and stretch-ability to the yarn.

[0301] In the crimping step, conventionally known methods and apparatuses could be used, and for example, it is preferable to use a heated fluid crimping apparatus that subjects a yarn to false twisting by bringing the yarn into contact with a heated fluid.

[0302] The heated fluid crimping apparatus is an apparatus that gives crimps to yarn lines by spraying a heated fluid such as, for example, vapor, to the yarn lines and forcing in the yarn lines together with the heated fluid into a compression adjustment unit.

[0303] Here, it is preferable that the temperature of the heated fluid is adjusted to a value within the range of 100°C to 150°C.

[0304] The reason for this is that when the temperature is within the above-described range, fusion between fibers could be avoided while sufficient crimping is achieved.

[0305] Therefore, more specifically, it is more preferable that the temperature of the heated fluid is adjusted to a value within the range of 110°C to 145°C, and it is even more preferable that the temperature is adjusted to a value within the range of 115°C to 140°C.

5. Step (5): Post-treatment step

[0306] The post-treatment step of step (5) is also an optional process and is a step of applying an oil agent to the crimped yarn obtained in step (4), drying the crimped yarn with a dryer, subsequently guiding the crimped yarn to a thermosetting roller, and adjusting the degree of elongation by means of the heating temperature.

[0307] It is preferable that the temperature of the thermosetting roller is a temperature within the range of 130°C to 160°C, from the viewpoint of preventing troubles between winding rolls or defective shrinkage at the time of processing the fibers or in the case of producing base cloth.

[0308] More specifically, it is more preferable that the temperature of the thermosetting roller is adjusted to a value within the range of 135°C to 155°C, and it is even more preferable that the temperature is adjusted to a value within the range of 140°C to 150°C.

6. Step (6): Dyeing step

[0309] The dyeing step of step (6) is also an optional process and is a step of dyeing the antibacterial fibers that have been stretched and then subjected to crimping and/or thermosetting as necessary, under alkaline conditions or acidic conditions.

[0310] In such a dyeing step, conventionally known methods and apparatuses could be used, and it is preferable to use, for example, manual dyeing, package dyeing, spray dyeing, rotating bag dyeing, Obermaier dyeing, or cheese dyeing.

[0311] It is also preferable that the dyeing solution includes, along with a dye, dyeing aids such as a level dyeing agent, a dye accelerant aid, and a metal sequestering agent, a dye-fixing agent, and a fluorescent brightening agent, as necessary.

[0312] In the case of performing dyeing under alkaline conditions, the pH could be adjusted to 7.5 to 10.5, and it is preferable to use a carbonic acid salt such as calcium carbonate, sodium hydroxide, or the like for the adjustment of pH.

[0313] In the case of performing dyeing under acidic conditions, the pH could be adjusted to 3.5 to 6.5, and it is preferable to use an organic acid such as acetic acid, citric acid, malic acid, fumaric acid, or succinic acid, and salts thereof for the adjustment of pH.

[0314] After dyeing, it is preferable to perform batch washing, and it is also preferable to perform reduction washing or soaping.

[0315] For the washing conditions, the conditions that are implemented for conventional polyester fibers could be employed, and in the case of reduction washing, a reducing agent, an alkali, and sodium hydrosulfite could be used respectively in an amount of 0.5 to 3 g/L. It is preferable to treat the fibers at 60°C to 80°C for 10 to 30 minutes.

EXAMPLES

[0316] Hereinafter, the invention will be described more specifically using Examples.

[0317] However, unless particularly stated otherwise, the invention is not intended to be limited to the following description of Examples.

[Example 1]

1. Production of antibacterial glass

(1) Melting step

[0318] The respective glass raw materials were stirred until the components were uniformly mixed, using a universal mixing machine under the conditions of a speed of rotation of 250 rpm and 30 minutes, such that when the total amount of the antibacterial glass was designated as 100% by weight, the composition ratio of P_2O_5 would be 50% by weight, the composition ratio of CaO would be 5% by weight, the composition ratio of Na_2O would be 1.5% by weight, the composition ratio of B_2O_3 would be 10% by weight, the composition ratio of Ag_2O would be 3% by weight, the composition ratio of CeO_2 would be 0.5% by weight, and the composition ratio of ZnO would be 30% by weight.

[0319] Next, the glass raw materials were heated using a melting furnace under the conditions of 1,280°C and 3.5 hours, and thereby a glass melt was produced.

(2) Crude pulverization step

[0320] The glass melt taken out from the glass melting furnace was water-granulated by causing the glass melt to flow into still water at 25°C, and crude pulverized glass having a volume average particle size of about 10 mm was obtained.

[0321] Meanwhile, the crude pulverized glass in this stage was observed with an optical microscope, and as a result, it was confirmed that the crude pulverized glass was in a lump-like state without any corners or faces.

(3) Intermediate pulverization step

[0322] Next, primary intermediate pulverization (volume average particle size about 1,000 μm) was performed using a pair of rotating rolls made of alumina (manufactured by TOKYO ATOMIZER M.F.G. CO., LTD., roll pulverizer) under the conditions of a gap of 1 mm and a speed of rotation of 150 rpm, while the crude pulverized glass was supplied from a hopper by utilizing the weight of the glass itself.

[0323] Furthermore, the crude pulverized glass that had been treated by primary intermediate pulverization was subjected to secondary intermediate pulverization using a rotary mortar made of alumina (manufactured by CHUO KAKOHKI CO., LTD., PREMAX) under the conditions of a gap of 400 μm and a speed of rotation of 700 rpm, and an intermediate pulverized glass having a volume average particle size of about 400 μm was obtained.

[0324] This intermediate pulverized glass was observed with an electron microscope, and as a result, it was confirmed that at least 50% by weight or more was polyhedrons having corners or faces.

(4) Fine pulverization step

[0325] Next, 210 kg of alumina spheres having a diameter of 10 mm as media, 20 kg of the intermediate pulverized glass that had been subjected to secondary intermediate pulverization, 14 kg of isopropanol, and 0.2 kg of silane coupling agent A-1230 (manufactured by NUC Corporation) were respectively accommodated in a vibrating ball mill having an internal capacity of 105 liters (manufactured by CHUO KAKOHKI CO., LTD.), and then a fine pulverization treatment was performed for 7 hours under the conditions of a speed of rotation of 1,000 rpm and a vibration width of 9 mm. Thus, a fine pulverized glass was obtained.

[0326] Meanwhile, this fine pulverized glass was observed with an electron microscope, and as a result, it was confirmed that at least 70% by weight or more was polyhedrons having corners or faces.

(5) Solid-liquid separation and drying step

[0327] The fine pulverized glass obtained in the previous step and isopropanol were subjected to solid-liquid separation using a centrifuge (manufactured by KOKUSAN Co., Ltd.) under the conditions of a speed of rotation of 3,000 rpm and 3 minutes.

[0328] Next, the fine pulverized glass was dried using an oven under the conditions of 105° and 3 hours.

(6) Crushing step

[0329] The fine pulverized glass that had been dried and thereby partially agglomerated was crushed using a gear type crusher (manufactured by CHUO KAKOHKI CO., LTD.), and an antibacterial glass (polyhedral glass) having a volume average particle size of 1.0 μm was obtained.

[0330] Meanwhile, the antibacterial glass in this stage was observed with an electron microscope, and as a result, it was confirmed that at least 90% by weight or more was polyhedrons having corners or faces.

2. Production of antibacterial fiber

(1) Spinning step

(1)-1 Preparation of spinning dope for core portion

[0331] 100 parts by weight of a polyethylene terephthalate resin having a number average molecular weight of 34,000 was mixed and dispersed using a bulk molding compound (BMC) injection molding apparatus at a cylinder temperature of 250°C and a speed of screw rotation of 30 rpm, and thus a spinning dope for the core portion was obtained.

(1)-2 Preparation of spinning dope for sheath portion

[0332] 7 parts by weight of the antibacterial glass, 95 parts by weight of a polyethylene terephthalate resin having a number average molecular weight of 34,000, and 5 parts by weight of a polybutylene terephthalate resin having a number average molecular weight of 26,000 were mixed and dispersed using a bulk molding compound (BMC) injection molding apparatus at a cylinder temperature of 250°C and a speed of screw rotation of 30 rpm, and thereby a spinning dope for the sheath portion was obtained.

[0333] Meanwhile, a predetermined amount of the antibacterial glass was mixed with the polybutylene terephthalate resin to obtain a masterbatch, and then the polyethylene terephthalate resin was mixed therein. Thereby, while hydrolysis of the polyethylene terephthalate resin was suppressed, an antibacterial resin composition finally having the above-described mixing ratio was obtained.

(1)-3 Composite spinning

[0334] The spinning dope for the core portion was used for the core portion and the spinning dope for the sheath portion was used for the sheath portion at a core-sheath weight ratio of 50/50, and using a core-sheath composite spinneret having 24 circular composite spinning holes having a nozzle diameter of 0.3 mm, antibacterial fibers were discharged through the spinneret at a spinning temperature of 285°C and a winding speed of 3,000 m/min.

(2) Stretching step

[0335] Next, the antibacterial fibers were stretched to three times by stretching while heating the antibacterial fibers to 90°C by passing the fibers through a tubular heating apparatus, and thereby antibacterial fibers having an average diameter of 40 μm were obtained. Furthermore, the average diameter of the core portion was 30 μm.

3. Evaluation of antibacterial fiber

(1) Observation with electron microscope

[0336] The antibacterial fibers thus obtained were observed using a scouldning electron microscope (manufactured by JEOL Ltd., JSM-6610LA), and it was confirmed that the antibacterial glass was dispersed as white spots, only in the sheath portion of the antibacterial fibers. Furthermore, black spots are air bubbles. The results are shown in Fig. 3.

[0337] Furthermore, the presence or absence of metal ions could also be determined by scouldning electron microscopic images and elemental mapping. That is, EDX measurement was performed (manufactured by JEOL Ltd., JED-2300), and the distribution state of constituent elements was qualitatively analyzed by a mapping analysis. The results are shown in Figs. 4(a) to 4(c).

[0338] Here, Figs. 4(a) to 4(c) show EDX mapping images obtained using characteristic X-radiation of the K-line of elemental P (phosphorus) (Fig. 4(a)), the K-line of elemental C (carbon) (Fig. 4(b)), and the K-line of elemental 0 (oxygen) (Fig. 4(c)).

[0339] Judging from Fig. 4(a), it could be seen from EDX mapping images obtained using characteristic X-radiation of the K-line of elemental P, that the antibacterial glass related to the antibacterial fiber of the invention is not distributed homogeneously in the entirety of the antibacterial fibers, but a plurality of regions in which the antibacterial glass is locally distributed at high concentrations exist in the sheath portion. Furthermore, from Fig. 4(b), it could be seen that elemental C is not distributed at the sites where the antibacterial fibers are distributed. Furthermore, it could be seen from Fig. 4(c) that elemental 0 is uniformly distributed.

(2) Chemical fiber staple test

[0340] For the antibacterial fibers obtained in Example 1, the tensile strength was measured according to JIS L 1015, and the tensile strength was evaluated according to the following criteria.

[0341] The initial weighting at the time of measuring the tensile strength was set to 5.88 mN/1 tex, the tensile rate to 20 mm/min, and the length of the specimen between grips to 10 mm. The results thus obtained are presented in Table 1.

⊙ (Very good): The tensile strength is higher than or equal to 3 cN/dtex and below 8 cN/dtex.
○ (Good): The tensile strength is higher than or equal to 2 cN/dtex and below 10 cN/dtex (provided that the range of higher than or equal to 3 cN/dtex and below 8 cN/dtex is excluded).
Δ (Fair): The tensile strength is higher than or equal to 1 cN/dtex and below 12 cN/dtex (provided that the range of higher than or equal to 2 cN/dtex and below 10 cN/dtex is excluded).
×(Bad): The tensile strength is below 1 cN/dtex and higher than or equal to 12 cN/dtex.

(3) Evaluation of antibacterial properties 1 to 2

[0342] 10 g of antibacterial fibers were used as a specimen for the evaluation of antibacterial properties. Meanwhile, testing bacteria were cultured at 35°C for 24 hours in an agar plate medium of Trypticase Soy Agar (BBL), the growth colonies were suspended in a common broth medium (manufactured by EIKEN CHEMICAL CO., LTD.) at a 1/500 concentration, and thereby the cell count was adjusted to a concentration of about 1×10^6 CFU/ml.

[0343] Next, the antibacterial fibers as specimens were brought into uniform contact with 0.5 ml of a suspension of Staphylococcus aureus (IFO#12732) and 0.5 ml of a suspension of Escherichia coli (ATCC#8739), respectively. A polyethylene film (sterilization) was mounted thereon, and each of the samples was used as a measurement sample for a film covering method.

[0344] Next, a measurement sample was placed in a constant temperature chamber under the conditions of a humidity of 95%, a temperature of 35°C and 24 hours, and the number of bacterial cells (growth colonies) before test and the number of bacterial cells (growth colonies) after test were respectively measured. Antibacterial property 1 (Staphylococcus aureus) and antibacterial property 2 (Escherichia coli) were evaluated according to the following criteria.

[0345] Meanwhile, the number of bacterial cells (growth colonies) before test was 2.6×10^5 (cells/specimen) for both Staphylococcus aureus and Escherichia coli. The results thus obtained are presented in Table 1.

⊙ (Very good): The number of bacterial cells after test is below 1/10,000 of the number of bacterial cells before test.
○ (Good): The number of bacterial cells after test is larger than or equal to 1/10,000 and below 1/1,000 of the number of bacterial cells before test.
Δ (Fair): The number of bacterial cells after test is larger than or equal to 1/1,000 and below 1/100 of the number of bacterial cells before test.
× (Bad): The number of bacterial cells after test is larger than or equal to 1/100 of the number of bacterial cells before test.

[Example 2]

[0346] In Example 2, antibacterial fibers were produced in the same manner as in Example 1, except that the amount of the antibacterial glass in the sheath portion was changed to 10 parts by weight, and the thermoplastic resin was changed to 100 parts by weight of a polypropylene resin having a number average molecular weight of 60,000, and evaluation of the fibers and evaluation of antibacterial properties were carried out in the same manner as in Example 1. The results thus obtained are presented in Table 1.

[0347] Meanwhile, the antibacterial fibers obtained in Example 2 were observed with a scouldning electron microscope, and similarly to Example 1, antibacterial glass dispersed only in the sheath portion of the antibacterial fibers could be recognized. The results are presented in Fig. 1.

[0348] Furthermore, EDX measurement was performed by a method similar to that of Example 1, and the distribution state of constituent elements was qualitatively analyzed by a mapping analysis. The results are shown in Figs. 5(a) to 5(c).

[0349] Here, Figs. 5(a) to 5(c) represent EDX mapping images obtained using characteristic X-radiation of the K-line of elemental P (phosphorus) (Fig. 5(a)), the K-line of elemental C (carbon) (Fig. 5(b)), and the K-line of elemental 0 (oxygen) (Fig. 5(c)).

[0350] Judging from Fig. 5(a), it could be seen that the antibacterial glass is not distributed in the entirety of the antibacterial fibers, but a plurality of regions in which the antibacterial glass is locally distributed at high concentrations exist in the sheath portion. Furthermore, from Fig. 5(b), the sheath portion is brighter, and it could be seen that elemental C is distributed more therein. Furthermore, from Fig. 5(c), the core portion is brighter; however, this is because of elemental 0 of polyethylene terephthalate or polybutylene terephthalate contained in the core portion.

[Example 3]

[0351] In Example 3, antibacterial fibers were produced in the same manner as in Example 1, except that the spinning dope for the sheath portion was formed from 3 parts by weight of the antibacterial glass, 95 parts by weight of a polyethylene terephthalate resin having a number average molecular weight of 34,000, and 5 parts by weight of a polybutylene terephthalate resin having a number average molecular weight of 26,000, and evaluation of fibers and evaluation of the antibacterial properties were carried out in the same manner as in Example 1. The results thus obtained are presented in Table 1.

[0352] Meanwhile, the antibacterial fibers obtained in Example 3 were observed with a scouldning electron microscope, and similarly to Example 1, antibacterial glass dispersed only in the sheath portion of the antibacterial fibers could be confirmed.

[Example 4]

[0353] In Example 4, antibacterial fibers were produced in the same manner as in Example 1, except that the spinning dope for the core portion was formed from 0.5 parts by weight of the antibacterial glass, 95 parts by weight of a polyethylene terephthalate resin having a number average molecular weight of 34,000, and 5 parts by weight of a polybutylene terephthalate resin having a number average molecular weight of 26,000, and evaluation of fibers and evaluation of the antibacterial properties were carried out in the same manner as in Example 1. The results thus obtained are presented in Table 1.

[0354] Meanwhile, the antibacterial fibers obtained in Example 4 were observed with a scouldning electron microscope, and it was confirmed that antibacterial glass was distributed more in the sheath portion of the antibacterial fibers.

[Comparative Example 1]

[0355] In Comparative Example 1, antibacterial fibers were produced in the same manner as in Example 1, except that the spinning dope for the sheath portion was made the same as the spinning dope for the core portion, that is, antibacterial glass was not incorporated into both the core portion and the sheath portion, and evaluation of fibers and evaluation of the antibacterial properties were carried out in the same manner as in Example 1. The results thus obtained are represented in Table 1.

[Table 1]

	Average diameter (μm)	Tensile strength	Antibacterial property 1 (Staphylococcus aureus)	Antibacterial property 2 (Escherichia coli)
Example 1	40	⊙	○	⊙
Example 2	33	⊙	○	⊙
Example 3	20	⊙	Δ	⊙
Example 4	15	○	Δ	○
Comparative Example 1	12	Δ	×	×

INDUSTRIAL APPLICABILITY

[0356] As described above, according to the invention, an antibacterial fiber in which the amount of incorporation of antibacterial glass is made sufficient with a small amount by reducing the content of antibacterial glass in the core portion compared to the content of antibacterial glass in the sheath portion, and which could exhibit excellent antibacterial properties; and an efficient method for producing such an antibacterial fiber, could be obtained.

[0357] Therefore, the invention is expected to contribute noticeably to product quality improvement of antibacterial articles, particularly woven fabrics and nonwoven fabrics, which are molded using antibacterial fibers.

Claims

1. An antibacterial fiber comprising a thermoplastic resin and an antibacterial glass as mixing components,
   the antibacterial fiber having an average diameter adjusted to a value within the range of 1 to 50 μm, and
   the antibacterial fiber including a core portion and a sheath portion,
   wherein when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber,
   Q1 and Q2 satisfy the following relational expression (1) .

$$Q1 < Q2 \quad (1).$$

2. The antibacterial fiber according to claim 1, wherein Q1 is 0 or below 1% by weight (provided that 0% by weight is excluded).

3. The antibacterial fiber according to claim 1 or 2, wherein Q2 has a value within the range of 1% to 10% by weight.

4. The antibacterial fiber according to any one of claims 1 to 3, further comprising aggregated silica particles as a mixing component.

5. The antibacterial fiber according to any one of claims 1 to 4, wherein a volume average particle size of the antibacterial glass is adjusted to a value within the range of 0.1 to 5 μm.

6. The antibacterial fiber according to any one of claims 1 to 5, wherein the thermoplastic resin is any one or more of a polyester resin, a polyamide resin, and a polyolefin resin.

7. The antibacterial fiber according to any one of claims 1 to 6, wherein the antibacterial fiber is in the form of any one of a woven fabric, a nonwoven fabric, and a felt.

8. A method for producing an antibacterial fiber including a core portion and a sheath portion and containing a thermoplastic resin and an antibacterial glass as mixing components, the method comprising the following steps (1) to (3);

   (1) a step of preparing antibacterial glass;
   (2) a step of dispersing the antibacterial glass thus obtained in a thermoplastic resin such that
   when a content of the antibacterial glass in the core portion is designated as Q1 (weight%) with respect to the total amount of the antibacterial fiber, and a content of the antibacterial glass in the sheath portion is designated as Q2 (weight%) with respect to the total amount of the antibacterial fiber,
   Q1 and Q2 satisfy the following relational expression (1) :

$$Q1 < Q2 \quad (1)$$

   and thereby preparing a spinning dope for the core portion and a spinning dope for the sheath portion; and
   (3) performing composite spinning using a core-sheath composite spinneret by arranging the spinning dope for the core portion as the core portion and the spinning dope for the sheath portion as the sheath portion, and thereby obtaining an antibacterial fiber having an average diameter of 1 to 50 μm.

Fig.1

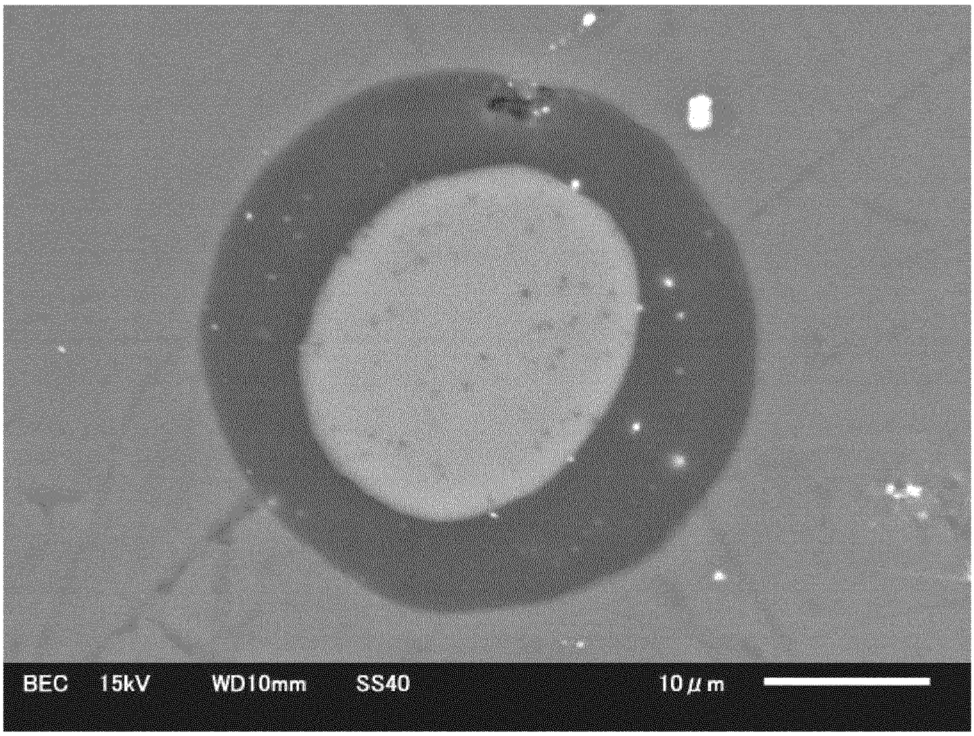


Fig.2

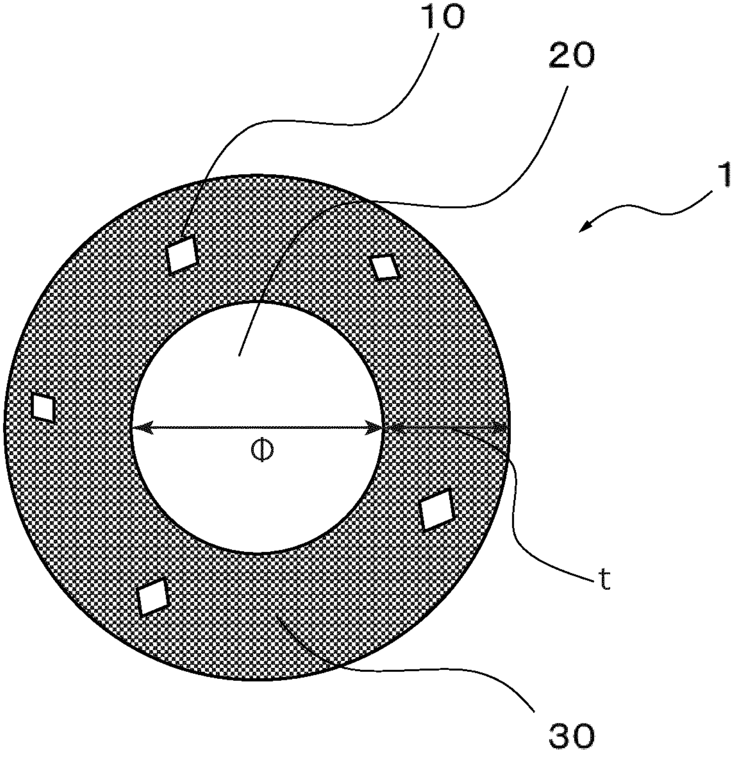


Fig.3

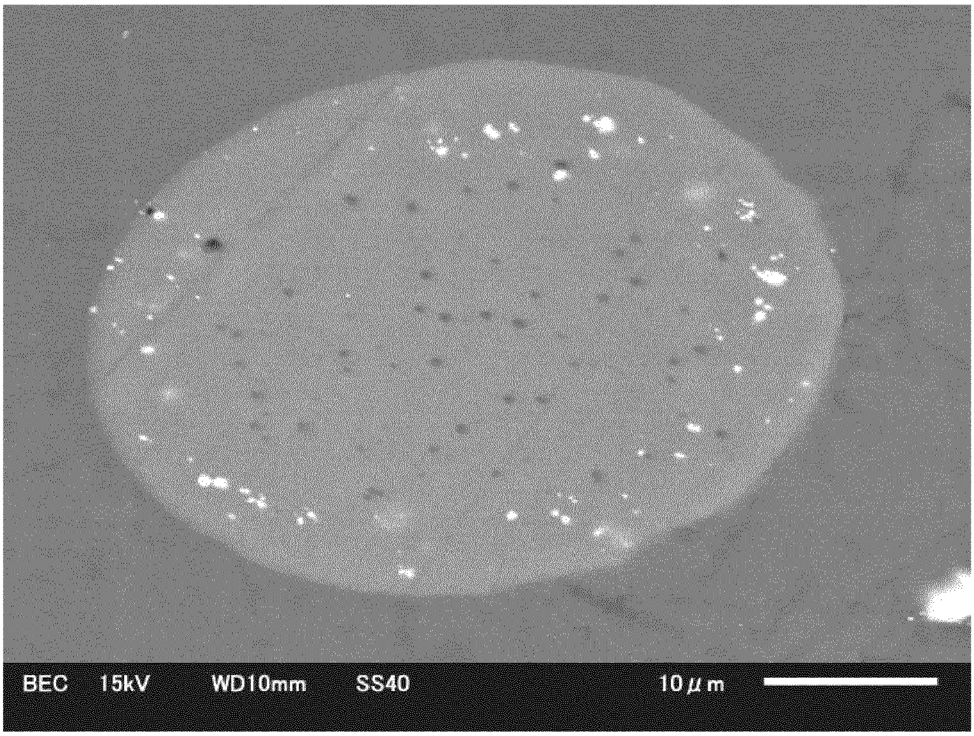


Fig.4(a)

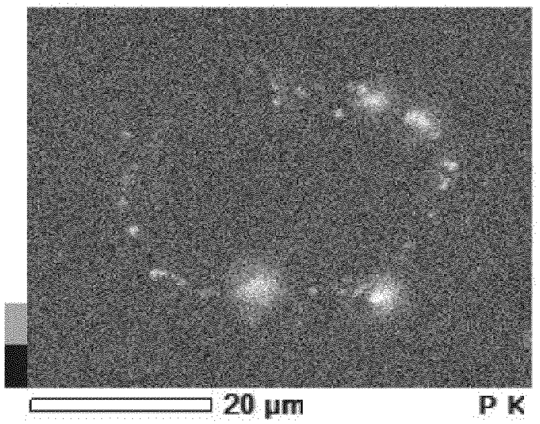


Fig.4(b)

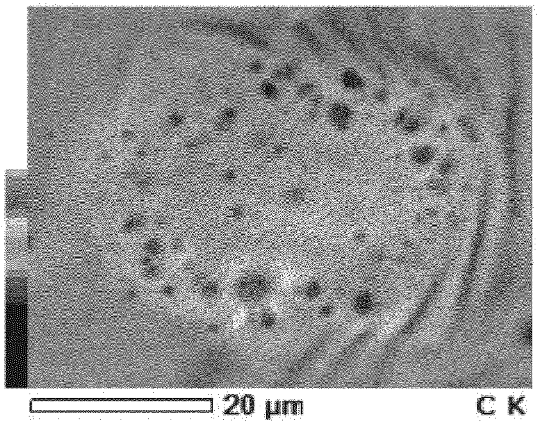


Fig.4(c)

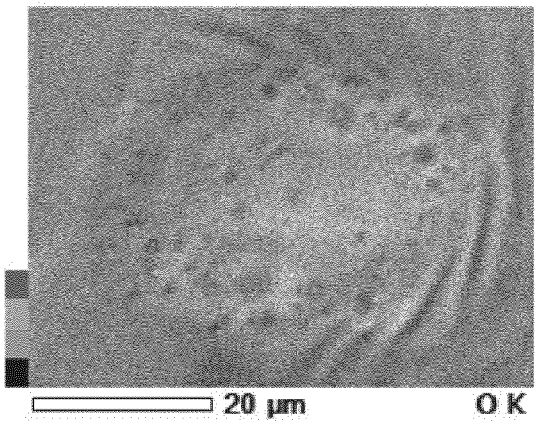


Fig.5(a)

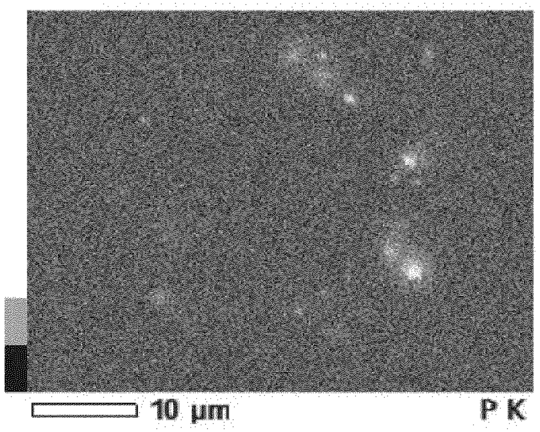


Fig.5(b)

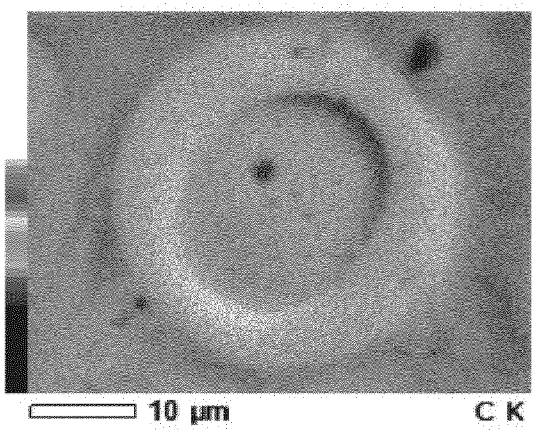
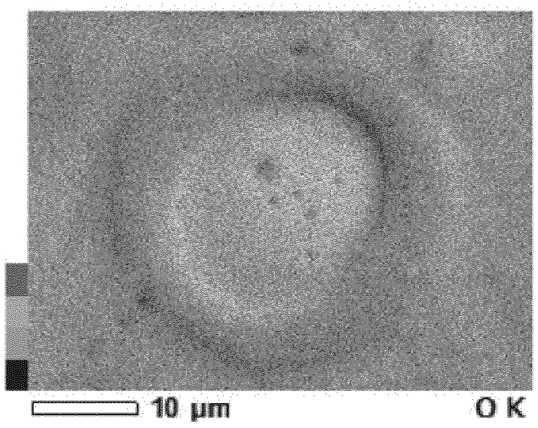


Fig.5(c)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/021950

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D01F8/04(2006.01)i, A01N25/10(2006.01)i, C03C3/14(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)
Int.Cl. D01F8/04, A01N25/10, C03C3/14

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
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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2008-133583 A (KOA GLASS KK) 12 June 2008, claims 1-8 & US 2009/0060967 A1, claims 1-10 & WO 2006/120772 A1 & CN 101151405 A & KR 10-2007-0112482 A	1-8
Y	WO 2012/098742 A1 (KOA GLASS KK) 26 July 2012, examples & US 2012/0321689 A1, examples & EP 2530120 A1 & CN 102933654 A & KR 10-2013-0086278 A & TW 201231550 A & ES 2453992 T	1-8
Y	JP 2004-190197 A (TEIJIN FIBERS LTD.) 08 July 2004, claims 1-8, paragraphs [0026], [0036] (Family: none)	1-8

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

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
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"P"	document published prior to the international filing date but later than the priority date claimed
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Date of the actual completion of the international search 21.08.2019	Date of mailing of the international search report 03.09.2019
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/021950

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 11-158728 A (UNITIKA LTD.) 15 June 1999, paragraphs [0013], [0014], examples (Family: none)	1-8
Y	JP 11-124729 A (KURARAY CO., LTD.) 11 May 1999, example 7 (Family: none)	1-8
Y	JP 9-33069 A (DYNIC CORPORATION) 07 February 1997, claims 1-4, paragraphs [0003], [0011] (Family: none)	1-8
Y	JP 2002-503770 A (E. I. DU PONT DE NEMOURS AND COMPANY) 05 February 2002, claims 1-10 & US 6037057 A, claims & WO 1999/041438 A1 & EP 1053361 A1 & AU 2481799 A & CA 2320034 A & TW 593814 B & CN 1297496 A & TR 200002364 T & MX PA00007883 A	1-8

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- JP 2001247333 A **[0007]**
- JP 11158730 A **[0007]**