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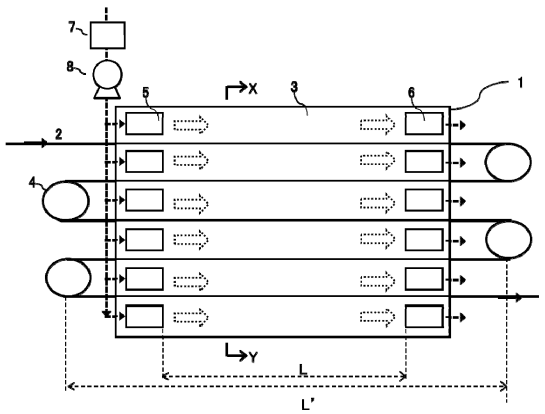
(54) METHOD OF MANUFACTURING STABILIZED FIBER BUNDLE, AND METHOD OF MANUFACTURING CARBON FIBER BUNDLE

(57) A method of manufacturing a stabilized fiber bundle, including travelling an acrylic fiber bundle 2 obtained by adjacently aligning a plurality of bundles, in a hot air heating-type oxidation oven 1, with the acrylic fiber bundle being conveyed by a guide roller 4 placed on each of both sides outside the oxidation oven 1, to thereby subject the acrylic fiber bundle to a heat treatment in an oxidizing atmosphere, wherein a direction of hot air in the oxidation oven 1 is horizontal to a travelling direction of the fiber bundle, and a contact probability P between adjacent fiber bundles, defined by the following expression (1), is 2 to 18%:

$$P = [1 - p(x)\{-t < x < t\}] \times 100 \qquad (1) \quad (1)$$

wherein P represents the contact probability (%) between adjacent fiber bundles, t represents an interspace (mm) between adjacent fiber bundles, p(x) represents a probability density function of a normal distribution $N(0, \sigma^2)$, σ represents a standard deviation of an amplitude of vibration, and x represents a random variable under the assumption that a median amplitude of vibration is zero. A high-quality stabilized fiber bundle and a high-quality carbon fiber bundle can be produced at high production efficiencies without any process troubles.

[Fig. 1]



EP 3 859 060 A1

Description

Technical Field

[0001] The present invention relates to a method of manufacturing a carbon fiber bundle. More specifically, it relates to a method of manufacturing a stabilized fiber bundle, which can produce a high-quality stabilized fiber bundle at a high production efficiency without any process troubles.

Background Art

[0002] Carbon fibers are excellent in specific strength, specific tensile modulus, heat resistance, and chemical resistance, and thus are useful as reinforcing materials of various materials and are used in a wide variety of fields such as aerospace applications, leisure applications, and general industrial applications.

[0003] A commonly known method of manufacturing a carbon fiber bundle from an acrylic fiber bundle is a method involving sending a fiber bundle of several thousands to several tens of thousands of acrylic polymer single fibers bundled, to an oxidation oven, exposing the fiber bundle to hot air in an oxidizing atmosphere, for example, air heated to 200 to 300°C, thereby performing a heating treatment (stabilization treatment), and thereafter sending the resulting stabilized fiber bundle into a carbonization furnace and subjecting the fiber bundle to a heating treatment (precarbonization treatment) in an inert gas atmosphere at 300 to 1000°C and then furthermore a heating treatment (carbonization treatment) in a carbonization furnace filled with an inert gas atmosphere at 1000°C or more. The stabilized fiber bundle as an intermediate material is widely used also as a material for flame-retardant woven fabrics with taking advantage of its flame-retardant properties.

[0004] A stabilization process takes the longest treatment time and consumes the largest amount of energy in a process of manufacturing a carbon fiber bundle. Thus, an enhancement in productivity in the stabilization process is most important for manufacturing a carbon fiber bundle.

[0005] An apparatus for performing stabilization (hereinafter, referred to as "oxidation oven") generally performs a treatment by shuttling an acrylic fiber in a lateral direction many times and thus stabilizing it, with a loop back roller provided outside the oxidation oven, in order to allow for a heat treatment for a long time in the stabilization process. It is effective for an enhancement in productivity in the stabilization process to simultaneously convey a large number of fiber bundles and thus increase the density of fiber bundles in the oxidation oven and increase the travelling speed of fiber bundles.

[0006] However, in a case where the density of fiber bundles in the oxidation oven is increased, the contact frequency between adjacent fiber bundles is increased due to vibration of fiber bundles. This causes yarn gathering of fiber bundles, single fiber break, and/or the like to frequently occur, thereby leading to, for example, deterioration in quality of stabilized fibers.

[0007] In a case where the travelling speed of fiber bundles is increased, the size of the oxidation oven is required to be increased in order to achieve the same amount of heat treating. In particular, in a case where the size in the height direction is increased, there is a need for division of a building floor level into a plurality of levels or a need for an increase in load capacity per floor unit area, thereby leading to an increase in cost of equipment. It is then effective for suppression of such an increase in cost of equipment and an increase in size of the oxidation oven to increase the length per path in the lateral direction (hereinafter, referred to as "oxidation oven length") to thereby decrease the size in the height direction. However, an increase in oxidation oven length results in an increase in amount of suspension of any fiber bundle travelled, and causes the contact between adjacent fiber bundles due to vibration, yarn gathering of fiber bundles, single fiber break, and/or the like to frequently occur as in a case where the density of fiber bundles is increased, thereby leading to, for example, deterioration in quality of stabilized fibers.

Citation List

Patent Literature

[0008] In order to solve the above problems, Patent Literature 1 describes prescription of the surface occupancy of a fiber bundle sheet-like material in a stabilization process, and furthermore optimization of the air velocity in an oxidation oven and the process tension in the stabilization process.

[0009] Patent Literature 2 describes prescription of the surface occupancy of a fiber bundle sheet-like material, the air velocity in an oxidation oven, and the density of fiber bundles in the oxidation oven in a stabilization process, specifically, the fineness per millimeter of a fiber bundle cloth travelled.

[0010] Furthermore, Patent Literature 3 describes optimization of the line speed and the maximum amount of suspension of any fiber bundle in a stabilization process in the case of an increased oxidation oven length.

Patent Literature 1: JP 2000-160435 A
Patent Literature 2: JP 2011-127264 A
Patent Literature 3: JP H11-61574 A

Summary of Invention

Technical Problem

[0011] However, Patent Literature 1 and Patent Literature 2 cannot allow any contact between adjacent fiber bundles to be avoided at a parameter of the surface occupancy prescribed, in the case of an increased oxidation oven length for an enhancement in productivity. Thus, there is a concern that a high-quality stabilized fiber cannot be manufactured. Patent Literature 3 does not mention any density of fiber bundles in the oxidation oven and cannot enhance productivity, although the contact between adjacent fiber bundles in the case of an increased oxidation oven length is considered to be suppressed with prescription of the maximum amount of suspension of any fiber bundle.

[0012] Accordingly, a problem to be solved by the present invention is to produce a high-quality stabilized fiber bundle and a high-quality carbon fiber bundle at high production efficiencies without any process troubles.

Solution to Problem

[0013] In order to solve the above problem, the method of manufacturing a stabilized fiber bundle of the present invention has the following configuration, namely, is a method of manufacturing a stabilized fiber bundle, including travelling an acrylic fiber bundle obtained by adjacently aligning a plurality of bundles, in a hot air heating-type oxidation oven, with the acrylic fiber bundle being conveyed by a guide roller placed on each of both sides outside the oxidation oven, to thereby subject the acrylic fiber bundle to a heat treatment in an oxidizing atmosphere, wherein a direction of hot air in the oxidation oven is horizontal to a travelling direction of the fiber bundle, and a contact probability P between adjacent fiber bundles, defined by the following expression (1), is 2 to 18%.

$$P = [1 - p(x)\{-t < x < t\}] \times 100 \qquad (1)$$

Herein, P represents the contact probability (%) between adjacent fiber bundles, t represents an interspace (mm) between adjacent fiber bundles, p(x) represents a probability density function of a normal distribution $N(0, \sigma^2)$, σ represents a standard deviation of an amplitude of vibration, and x represents a random variable under the assumption that a median amplitude of vibration is zero.

[0014] The "contact probability P between adjacent fiber bundles" in the present invention refers to a probability where, when a plurality of fiber bundles are laid in parallel so as to be adjacent, and are travelled, the interspace between adjacent fiber bundles is zero due to vibration (yarn swinging) in the width direction of fiber bundles. The amplitude of vibration in the width direction of fiber bundles, when the average amplitude of vibration of fiber bundles is 0 and the standard deviation of the amplitude of vibration is σ, is assumed to be according to the normal distribution N, and the contact probability P between adjacent fiber bundles can be determined by the expression (1).

[0015] The method of manufacturing a carbon fiber bundle of the present invention has the following configuration, namely, is a method of manufacturing a carbon fiber bundle, including subjecting a stabilized fiber bundle manufactured by the method of manufacturing a stabilized fiber bundle, to a precarbonization treatment at a maximum temperature of 300 to 1,000°C in an inert gas, to thereby manufacture a precarbonized fiber bundle, and subjecting the precarbonized fiber bundle to a carbonization treatment at a maximum temperature of 1,000 to 2,000°C in an inert gas.

Advantageous Effects of Invention

[0016] According to the method of manufacturing a stabilized fiber of the present invention, a high-quality stabilized fiber can be produced at a high production efficiency without any process troubles.

Brief Description of Drawings

[0017]

Fig. 1 is a schematic side view illustrating an oxidation oven.
Fig. 2 is an X-Y cross-sectional view of the oxidation oven in Fig. 1.

Fig. 3 includes each image diagram for describing the contact probability P between adjacent fiber bundles.

Description of Embodiments

[0018] An acrylic fiber bundle for use as a fiber bundle to be subjected to a heat treatment in the method of manufacturing a stabilized fiber bundle of the present invention suitably includes an acrylic fiber containing 100% of acrylonitrile, or an acrylic copolymer fiber containing 90% by mol or more of acrylonitrile. Examples of a preferable copolymerizable component in the acrylic copolymer fiber include acrylic acid, methacrylic acid, itaconic acid, and any alkali metal salt and any ammonium metal salt thereof, acrylamide, and methyl acrylate, and the acrylic fiber bundle is not particularly limited in terms of, for example, chemical characteristics, physical characteristics, and the dimension.

[0019] The present invention provides a method of subjecting the acrylic fiber bundle to a stabilization treatment in an oxidizing atmosphere, and is carried out in an oxidation oven in which an oxidizing gas flows. As illustrated in Fig. 1, an oxidation oven 1 includes a heat treatment chamber 3 where a stabilization treatment is made by blowing hot air to an acrylic fiber bundle 2 that is traveled with being folded in a multistage travelling region. The acrylic fiber bundle 2 is sent through an opening (not illustrated) located on a side wall of the heat treatment chamber 3 in the oxidation oven 1, into the heat treatment chamber 3, linearly travelled in the heat treatment chamber 3, and thereafter sent out of the heat treatment chamber 3 through an opening located on an opposite side wall. Thereafter, the acrylic fiber bundle is folded by each guide roller 4 provided on a side wall out of the heat treatment chamber 3, and again sent into the heat treatment chamber 3. The acrylic fiber bundle 2 is thus folded multiple times in the travelling direction by such a plurality of guide rollers 4, thus repeatedly sent into and sent out of the heat treatment chamber 3 multiple times, and moved in the heat treatment chamber 3 in a multistage manner as a whole from top to bottom of Fig. 1. The movement direction may be here from bottom to top, and the number of foldings of the acrylic fiber bundle 2 in the heat treatment chamber 3 is not particularly limited and is appropriately designed depending on, for example, the scale of the oxidation oven 1. Such each guide roller 4 may be here provided inside the heat treatment chamber 3.

[0020] The acrylic fiber bundle 2, while is folded and also travelled in the heat treatment chamber 3, is subjected to a stabilization treatment with hot air flowing from a hot air blowoff port 5 toward a hot air discharge port, thereby providing a stabilized fiber bundle. The acrylic fiber bundle 2 here has a wide sheet shape where a plurality of fiber bundles are aligned in a parallel manner in a direction perpendicular to a paper surface, as illustrated in Fig. 2.

[0021] The hot air blowoff port 5 is preferably provided with a resistor such as a porous plate and a rectification member such as a honeycomb (both are not illustrated) on a blowoff surface thereof to thereby have pressure loss. The rectification member can rectify hot air blown into the heat treatment chamber 3 and blow hot air at a more uniform air velocity, into the heat treatment chamber 3.

[0022] A hot air discharge port 6 may be provided with a resistor such as a porous plate on a suction surface thereof to thereby have pressure loss, like the hot air blowoff port 5, and is, if necessary, appropriately determined.

[0023] An oxidizing gas flowing in the heat treatment chamber 3 may be, for example, air, and is heated to a desired temperature by a heater 7, thereafter enters the heat treatment chamber 3, and is controlled in air velocity by a blowing machine 8 and also blown through the hot air blowoff port 5 into the heat treatment chamber 3. An oxidizing gas discharged out of the heat treatment chamber 3 through the hot air discharge port 6 is subjected to a treatment of a toxic substance with an exhaust gas treatment furnace (not illustrated) and then discharged to the atmosphere, or may also pass through a circulation passage (not illustrated) and may be again blown through the hot air blowoff port 5 into the heat treatment chamber 3.

[0024] The heater 7 for use in the oxidation oven 1 is not particularly limited as long as it has a desired function, and, for example, a known heater such as an electric heater may be used therefor. The blower 8 is also not particularly limited as long as it has a desired function, and, for example, a known blower such as an axial fan may be used therefor.

[0025] The rotational speed of each guide roller 4 can be changed to thereby control the travelling speed and the tension of the acrylic fiber bundle 2, which are fixed depending on required physical properties of a stabilized fiber bundle, and the amount of treating per unit time.

[0026] A predetermined number of grooves can be engraved on the surface layer of each guide roller 4 at a predetermined interval, or a predetermined number of comb guides (not illustrated) can be placed immediately close to each guide roller 4 at a predetermined interval, thereby controlling the interval and the number of such a plurality of acrylic fiber bundles 3 traveled in parallel.

[0027] The amount of production may be increased by increasing the number of fiber bundles per unit distance in the width direction of the oxidation oven 1, namely, the yarn density, or increasing the travelling speed of the acrylic fiber bundle 2.

[0028] However, such an increase in yarn density corresponds to a decrease in interval between adjacent fiber bundles, thereby easily causing, for example, deterioration in quality due to yarn gathering of fiber bundles by vibration, as described above.

[0029] In a case where the travelling speed of the acrylic fiber bundle 2 is increased, the residence time in a stabilization

heat treatment chamber is decreased to cause the amount of heat treating to be insufficient, and thus the total length of the heat treatment is required to be increased. Such a need for an increase in total length may be satisfied by increasing the height of the oxidation oven 1 and thus increasing the number of foldings of the acrylic fiber bundle, or increasing the length L per path of the oxidation oven (hereinafter, referred to as "oxidation oven length"), and it is preferable for suppression of the cost of equipment to increase the oxidation oven length L. However, the lateral length L' between the guide rollers 4 is also increased to easily cause any fiber bundle to be suspended, easily causing, for example, deterioration in quality due to the contact between fiber bundles and yarn gathering of fiber bundles by vibration to occur.

[0030] The amplitude of vibration of any fiber bundle causing the contact between fiber bundles is affected by not only the yarn density and the lateral length L' between the guide rollers 4, but also the air velocity of an oxidizing gas flowing through the heat treatment chamber, and the tension of the acrylic fiber bundle travelled. Even in the case of the same amplitude of vibration, the frequency and the degree of yarn gathering are affected by physical properties of the acrylic fiber bundle, namely, for example, chemical characteristics, physical characteristics, and the dimension thereof.

[0031] The method of manufacturing a stabilized fiber bundle of the present invention efficiently produces a high-quality stabilized fiber without any process troubles, regardless of the service specification and running conditions of the oxidation oven, and physical properties of the acrylic fiber bundle.

[0032] Specifically, the method manufacturing a stabilized fiber bundle is a continuous heat treatment method involving subjecting an acrylic fiber bundle 2 obtained by adjacently aligning a plurality of bundles, to a heat treatment, with the acrylic fiber bundle being travelled in a hot air heating-type oxidation oven 1, thereby providing a stabilized fiber bundle, wherein the acrylic fiber bundle 2 is conveyed by each guide roller 4 placed on both sides of a heat treatment chamber 3, the direction of hot air in the oxidation oven 1 is horizontal to each yarn, and the contact probability P between adjacent fiber bundles is 2 to 18% or less. As described above, the contact probability P between adjacent fiber bundles, here mentioned, refers to a probability where, when a plurality of fiber bundles are laid in parallel so as to be adjacent, and are travelled, the interspace between adjacent fiber bundles is zero due to vibration in the width direction of fiber bundles. When the average amplitude of vibration of fiber bundles is 0 and the standard deviation is σ in the vibration in the width direction of fiber bundles, the contact probability P between adjacent fiber bundles can be determined by the following expression (1).

$$P = [1 - p(x)\{-t < x < t\}] \times 100 \qquad (1)$$

Herein, P represents the contact probability (%) between adjacent fiber bundles, t represents the interspace (mm) between adjacent fiber bundles, p(x) represents the probability density function of a normal distribution $N(0, \sigma^2)$, σ represents the standard deviation of the amplitude of vibration, and x represents the random variable under the assumption that the median amplitude of vibration is zero.

[0033] Fig. 3 includes each image diagram of the contact probability P between adjacent fiber bundles, and the upper diagram represents a probability distribution of a plurality of fiber bundles travelled and the lower diagram represents a probability distribution of existence positions with right end portions of fiber bundles at the center of the upper diagram, as the center. The acrylic fiber bundle 2 is vibrated, and the interspace t between adjacent fiber bundles and the standard deviation σ of the amplitude of vibration are always varied depending on such vibration. The interspace t between adjacent fiber bundles can be represented by the following expression.

$$t = (Wp - Wy)/2$$

Herein, Wp represents a pitch interval physically regulated by the guide roller or the like, and Wy represents a width of fiber bundles travelled.

[0034] Fig. 3 includes respective image diagrams at $t < 1\sigma$, $t = 1\sigma$, and $t > 1\sigma$, sequentially from the left. P corresponds to a shaded area of the lower diagram in Fig. 3, the amplitude of vibration of fiber bundles is assumed to be according to a normal distribution, the cumulative probability with respect to positions equal to or less than/equal to or more than the end position of travelling of adjacent fiber bundles (range of t when the position of a fiber bundle as a reference is defined as zero) is represented by P, and Wy and σ can be actually measured for statistical calculation.

[0035] The amplitude of vibration of fiber bundles and the width of fiber bundles travelled can be measured from the upper surface or lower surface of fiber bundles travelled, with, for example, a high-accuracy two-dimensional displacement sensor.

[0036] The contact probability P between adjacent fiber bundles is essentially 2% or more and 18% or less, and is preferably 5 to 16%. In a case where the contact probability P between adjacent fiber bundles is less than 2%, the yarn

density is too low and the production efficiency is reduced. In a case where the contact probability P between adjacent fiber bundles is more than 18%, yarn gathering between adjacent fiber bundles is increased, and a reduction in stabilized fiber quality, such as fuzzing, and operation troubles such as yarn break cannot be suppressed.

[0037] The lateral length between the guide rollers is preferably 14.5 m or more, and in such a case, the production cost can be more advantageously reduced.

[0038] The air velocity of hot air flowing in the oxidation oven is preferably 1.0 to 6.0 m/sec, more preferably 2.0 to 5.0 m/sec. The air velocity of hot air flowing in the oxidation oven is in such a preferable range, and therefore the production cost can be advantageously reduced.

[0039] The guide rollers located on both sides of the oxidation oven preferably each have a control mechanism of the width of fiber bundle. The phrase "guide roller having a mechanism for regulating the width of fiber bundle" means that such a guide roller has a mechanism for regulating the width of fiber bundle on the roller or immediately close to the roller, and the mechanism leads to more excellent quality and process stability of a stabilized fiber bundle. For example, a case where a groove roller with a groove engraved at a regular pitch interval is used as the guide roller (the width of fiber bundle is regulated on the roller) and a case where a comb guide having a regular pitch interval in the width direction is placed at a position of several centimeters in the direction of the oxidation oven from the guide roller (the width of fiber bundle is regulated immediately close to the roller) can allow any fiber bundle to be easily located close to a groove unlike a case where a flat roller not regulated in the width of fiber bundle is used, and thus any adjacent fiber bundle is hardly wound in a treatment of one fiber bundle cut. Even in the case of yarn gathering between adjacent fiber bundles, fiber-separating is again made on a groove section of the roller to hardly cause the subsequent step to be affected, resulting in less deterioration in quality, as long as the degree of yarn gathering is low.

[0040] A single fiber of the acrylic fiber bundle preferably has a surface asperity structure extending for 2.0 μm or more in the longitudinal direction of the fiber in a square range of 2.0 μm in the circumferential direction of the surface of the single fiber and 2.0 μm in the fiber axis direction, and preferably exhibits a longer diameter/shorter diameter ratio in a cross section of the single fiber, of 1.01 to 1.10, and in such a case, quality and process stability of a stabilized fiber bundle are more excellent. In general, pseudo adhesion may occur between single fibers which are each one fiber constituting the acrylic fiber bundle, due to, for example, a rapid rise of temperature in a stabilization process. Similarly, pseudo adhesion may probably occur between single fibers of adjacent fiber bundles, also in the contact between fiber bundles. Herein, a fine asperity can be present on the surface of a single fiber to thereby allow the pseudo adhesion to be suppressed, and tangling hardly occurs even at the same contact probability P between adjacent fiber bundles, thereby hardly causing yarn gathering to be largely spread. A cross section of a single fiber, having a shape close to an ellipse, causes a short fiber to be biased in a fiber bundle, easily resulting in tangling in the contact between fiber bundles. On the contrary, a cross section of a single fiber, having a shape close to a true circle, can allow yarn gathering between fiber bundles to be suppressed, and thus the longer diameter/shorter diameter ratio in a cross section of the single fiber is preferably 1.01 to 1.10, more preferably 1.01 to 1.05.

[0041] The acrylic fiber bundle preferably has a length of hook drop of 300 mm or less, and in such a case, quality and process stability of a stabilized fiber bundle are more excellent. As the length of hook drop is shorter, entanglement between single fibers in a fiber bundle is larger. In a case where such entanglement between single fibers is large, a force of a single fiber trying to return into the same fiber bundle is large even in yarn gathering of adjacent fiber bundles, and thus such yarn gathering of fiber bundles is easily eliminated.

[0042] The amount of attachment of a silicon based oil agent to the acrylic fiber bundle is preferably 0.1 to 3.0% by mass, more preferably 0.1 to 1.5% by mass. The amount of attachment of a silicon based oil agent to the acrylic fiber bundle is in such a preferable range, and thus quality and process stability of a stabilized fiber bundle are more excellent. In general, a silicon based oil agent having certain heat resistance is provided to a single fiber of the acrylic fiber bundle to thereby suppress adhesion between single fibers.

[0043] The single fiber fineness in the acrylic fiber bundle is preferably 0.05 to 0.22 tex, more preferably 0.05 to 0.17 tex. The single fiber fineness in the acrylic fiber bundle is in such a preferable range, and thus quality and process stability of a stabilized fiber bundle are more excellent. In a case where the single fiber fineness is in a proper range, the single fiber surface area in the same volume and mass of a single fiber is not too large, and a single fiber hardly tangles even in the contact between adjacent fiber bundles.

[0044] A stabilized fiber bundle manufactured by the above method is subjected to a precarbonization treatment at a maximum temperature of 300 to 1000°C in an inert gas, thereby manufacturing a precarbonized fiber bundle, and the precarbonized fiber bundle is subjected to a carbonization treatment at a maximum temperature of 1,000 to 2,000°C in an inert gas, thereby manufacturing a carbon fiber bundle.

[0045] The maximum temperature in the inert gas in the precarbonization treatment is preferably 550 to 800°C. Any known inert gas such as nitrogen, argon, or helium can be adopted as the inert gas with which a precarbonization furnace is filled, and nitrogen is preferable in terms of economic efficiency.

[0046] A precarbonized fiber obtained by the precarbonization treatment is then sent into a carbonization furnace and subjected to a carbonization treatment. The carbonization treatment is preferably performed at a maximum temperature

of 1,200 to 2,000°C in an inert gas in order to enhance mechanical properties of a carbon fiber.

[0047] Any known inert gas such as nitrogen, argon, or helium can be adopted as the inert gas with which the carbonization furnace is filled, and nitrogen is preferable in terms of economic efficiency.

[0048] A sizing agent may be given to a carbon fiber bundle thus obtained, in order to enhance handleability, and affinity with a matrix resin. The type of the sizing agent is not particularly limited as long as desired characteristics can be obtained, and examples include any sizing agent containing an epoxy resin, a polyether resin, an epoxy-modified polyurethane resin, or a polyester resin, as a main component. A known method can be used for providing the sizing agent.

[0049] The carbon fiber bundle may be, if necessary, subjected to an electrolytic oxidation treatment or an oxidation treatment for the purpose of enhancements in affinity with and adhesiveness to a fiber-reinforced composite material matrix resin.

[0050] As described above, the present invention can produce a high-quality stabilized fiber at a high production efficiency without any process troubles, according to a method of manufacturing a stabilized fiber bundle, including travelling an acrylic fiber bundle obtained by adjacently aligning a plurality of bundles, in a hot air heating-type oxidation oven, with the acrylic fiber bundle being conveyed by a guide roller placed on each of both sides outside the oxidation oven, to thereby subject the acrylic fiber bundle to a heat treatment in an oxidizing atmosphere, wherein a direction of hot air in the oxidation oven is horizontal to a travelling direction of the fiber bundle, and a contact probability P between adjacent fiber bundles is 2 to 18%.

Examples

[0051] Hereinafter, the present invention will be more specifically described by Examples, but the present invention is not limited thereto. Evaluation methods/measurement methods of respective characteristics were according to methods described below.

<Method of measuring of single fiber fineness of acrylic fiber bundle>

[0052] Measurement was performed according to JIS L 1013.

<Measurement of surface asperity structure of single fiber of acrylic fiber bundle>

[0053] Both ends of a single fiber of an acrylic fiber bundle were secured, with a carbon paste, to a metallic sample stage (20 mm in diameter) for SPA400, attached to a scanning probe microscope, "item number: K-Y10200167 manufactured by Epolead Service Inc.", and measurement was performed in the following conditions.

(Measurement conditions with scanning probe microscope)

[0054] Apparatus: "SPI4000 Probe Station, SPA400 (unit)" manufactured by SII NanoTechnology Inc.
Scanning mode: Dynamic Force Mode (DFM) (measurement of shape image)
Probe: "SI-DF-20" manufactured by SII NanoTechnology Inc.
Scanning range: 2.0 μm $\times$ 2.0 μm and 600 nm $\times$ 600 nm
Rotation: 90° (scanning in direction perpendicular to fiber axis direction)
Scanning speed: 1.0 Hz
Number of pixels: 512 $\times$ 512

Measurement environment: room temperature, in the air

[0055] One image was obtained with respect to one single fiber in the above conditions, and the resulting image was analyzed in the following conditions by use of image analysis software (SPIWin) attached to the scanning probe microscope.

(Image analysis conditions)

[0056] The resulting shape image was subjected to "flat treatment", "median 8 treatment" and "cubic slope correction", thereby obtaining an image where a curved surface was corrected to a flat surface by fitting. Such an image where correction to a flat surface was made was analyzed about the surface roughness, and thus the average surface roughness (Ra) and the maximum in-plane difference in height (R_{max}) were determined. The average surface roughness (Ra) and the maximum in-plane difference in height (R_{max}), according to such surface roughness analysis, were obtained with any data in a scanning range of a circumferential length of 600 nm $\times$ a length in the fiber axis direction, of 600 nm. Ra

was calculated by the following expression.

[Math. 1]

$$R_a = \{1/(L_x \times L_y)\} \int_0^{L_y} \int_0^{L_x} |f(x,y)|\, dxdy$$

[0057] Central surface: flat surface which was horizontal to flat surface minimum in deviation of height from actual surface and which divided actual surface into two so that equal volumes were obtained
f(x, y): difference in height between actual surface and central surface
L_x, L_y: size of XY flat surface
Ten single fibers with respect to one sample were subjected to shape measurement with a scanning probe microscope, the average surface roughness (Ra) and the maximum difference in height (R_{max}) were determined with respect to each measurement image, and the respective average values were defined as the average surface roughness (Ra) and the maximum difference in height (R_{max}) with respect to such a sample. The presence of a surface asperity structure extending for 2 μm or more in the longitudinal direction of a single fiber, in the surface of the fiber, was determined from a measurement image obtained by repeatedly scanning with displacement little by little over a length in the fiber axis direction, of 2.0 μm, in a range of 2.0 μm in the circumferential direction of a single fiber in an AFM (atomic force microscope) mode.

(Flat treatment)

[0058] The treatment corresponded to a treatment for removal of distortion and undulation in the Z-axis direction, appearing in the image data by, for example, lift, vibration, or creep of a scanner, and a treatment for removal of data stains due to an apparatus upon SPM (scanning probe microscope) measurement.

(Median 8 treatment)

[0059] The treatment was to obtain a filter effect including smoothing and noise removal, by performing calculation to be performed between S and D1 to D8 (matrices at 8 points surrounding S as a center) in a window (matrix) of 3 × 3 around a data point S to be treated, and replacing the Z (height direction) data of S.
[0060] The median 8 treatment was to determine the median value of Z data at 9 points of S and D1 to D8, and replace S.

(Cubic slope correction)

[0061] Slop correction corrected any slop by determining a curved surface from all data of an image to be treated, by least squares approximation, followed by fitting. The terms (linear) (quadric) and (cubic) represented respective dimensions of the curved surface to be fitted, and fitting of a cubic curved surface was performed in the cubic correction. Such a cubic slope correction treatment allowed the curvature of a fiber of the data to be eliminated, thereby providing a flat image.

<Evaluation of cross-sectional shape of single fiber of acrylic fiber bundle>

[0062] The ratio of the longer diameter and the shorter diameter (longer diameter/shorter diameter) in a fiber cross section of a single fiber constituting a fiber bundle was determined as follows.
[0063] A fiber bundle for measurement was allowed to pass through a vinyl chloride resin tube having an inner diameter of 1 mm, and thereafter sliced in rounds by a knife to prepare a sample. Next, the sample was bonded onto a SEM sample stage so that a fiber cross section turned up, furthermore Au was sputtered at a thickness of about 10 nm, thereafter the fiber cross section was observed in conditions of an acceleration voltage of 7.00 kV and a working distance of 31 mm with XL20 scanning electron microscope manufactured by Philips N.V., the longer diameter and the shorter diameter in the fiber cross section of the single fiber were measured, and the ratio of longer diameter/shorter diameter was evaluated.

<Method of measuring length of hook drop of acrylic fiber bundle>

[0064] An acrylic fiber bundle was drawn by 120 mm and mounted to an upper section of a hanging apparatus, twisting was taken out, and thereafter a weight of 200 g was hung on a lower section of the fiber bundle. A hook (made of a stainless wire of φ1 mm, R of hook = 5 mm) was inserted into a spot of 1 cm from an upper section to a lower section of the fiber bundle so that the fiber bundle was divided into three, and the hook was descended. The total mass of the hook was adjusted by a weight so as to be 10 g. The distance of the hook descended was determined until the hook was stopped due to entanglement of the fiber bundle. The number of tests was set to N = 50, and the average value was defined as the length of hook drop.

<Method of measuring of air velocity in oxidation oven>

[0065] An air speedometer for use at high temperatures, an anemomaster Model 6162 manufactured by KANOMAX JAPAN INC., was used, and the average value of measurement values at 30 points with respect to one second was adopted. A measurement probe was inserted through a measurement hole (not illustrated) on a side surface of a heat treatment chamber 3, located at a position corresponding to the center of a guide roller 4 on each of both sides of an oxidation oven 1, and the air velocity of an oxidizing gas flowing in the lateral direction was measured. Such measurement was made at 5 points in the width direction, and the average value was adopted.

<Method of measuring of width of fiber bundle and amplitude of vibration of fiber bundles travelled>

[0066] Measurement was performed at a position corresponding to the center of a guide roller 4 on each of both sides of an oxidation oven 1, where the maximum amplitude of vibration of fiber bundles travelled was obtained. Specifically, a laser displacement meter LJ-G200 manufactured by KEYENCE CORPORATION was placed on an upper or lower portion of fiber bundles travelled, and a specified fiber bundle was irradiated with laser. The distance between both ends in the width direction of such a fiber bundle was defined as the width of the fiber bundle, and the amount of variation in the width direction at one end in the width direction was defined as the amplitude of vibration. These were each measured at a frequency of once/60 seconds or more and an accuracy of 0.01 mm or less for 5 minutes, the width Wy of fiber bundles (average value) and the standard deviation σ of the amplitude of vibration were acquired, and the contact probability P between adjacent fiber bundles was calculated.

[0067] The results of process stability, quality and productivity in Examples and Comparative Examples were qualitatively shown in Table 1. Ratings of excellent, good, and unacceptable were according to the criteria.

(Process stability)

[0068] Excellent: troubles such as yarn gathering and fiber bundle break occurred zero times per day on average, and process stability was at an extremely favorable level.

[0069] Good: troubles such as yarn gathering and fiber bundle break occurred about several times per day on average, and process stability was at a level where continuous running could be sufficiently continued.

[0070] Unacceptable: troubles such as yarn gathering and fiber bundle break occurred several ten times per day on average, and process stability was at a level where continuous running could not be continued.

(Quality)

[0071] Excellent: the number of pieces of fuzz of 10 mm or more on fiber bundles, which could be visually confirmed after the stabilization process, was several pieces/m or less on average, and was at a level where fuzz quality did not have any effect on process passability and high-order processability of a product, at all.

[0072] Good: the number of pieces of fuzz of 10 mm or more on fiber bundles, which could be visually confirmed after the stabilization process, was 10 pieces/m or less on average, and was at a level where fuzz quality did almost not have any effect on process passability and high-order processability of a product.

[0073] Unacceptable: the number of pieces of fuzz of 10 mm or more on fiber bundles, which could be visually confirmed after the stabilization process, was several ten pieces/m or more on average, and was at a level where fuzz quality had any adverse effect on process passability and high-order processability of a product.

(Productivity)

[0074] Excellent: the manufacturing cost was at a sufficiently low level (80% or less relative to "Good") and the amount of production per unit time was at a sufficiently large level (120% or more relative to "Good").

[0075] Good: the manufacturing cost was at a relatively low level and the amount of production per unit time was at a relatively large level.

[0076] Unacceptable: the manufacturing cost was at a high level (150% or more relative to "Good") or the amount of production per unit time was at a small level (60% or less relative to "Good").

(Example 1)

[0077] A stabilized fiber bundle was obtained by aligning 100 to 200 acrylic fiber bundles 2 each made of 20,000 single fibers each having a single fiber fineness of 0.11 tex, having a surface asperity structure extending for 2.5 μm in the longitudinal direction of such each fiber in a square range of 2.0 μm in the circumferential direction of the surface of such each single fiber and 2.0 μm in the fiber axis direction, and exhibiting a ratio of longer diameter/shorter diameter in a cross section of such each single fiber, of 1.04, and subjecting the resultant to a heat treatment in an oxidation oven 1. The amount of attachment of a silicon based oil agent to the acrylic fiber bundles was 0.5% and the length of hook drop of the acrylic fiber bundles was 250 mm. The lateral length L' between guide rollers 4 on both sides of a heat treatment chamber 3 of an oxidation oven 1 was 20 m, and each of the guide rollers 4 was a groove roller with a groove engraved at a predetermined interval (pitch interval to be physically regulated) Wp ranging from 3 to 15 mm. The temperature of an oxidizing gas in the heat treatment chamber 3 of the oxidation oven 1 was here 240 to 280°C, and the air velocity in the lateral direction of the oxidizing gas was 3 m/sec. The yarn travelling speed was adjusted in the range from 1 to 15 m/minute according to the oxidation oven length L so that the stabilization treatment time was sufficiently taken, and the process tension was adjusted in the range from 0.5 to 2.5 g/tex.

[0078] The stabilized fiber bundle was thereafter carbonized in a precarbonization furnace at a maximum temperature of 700°C, thereafter carbonized in a carbonization furnace at a maximum temperature of 1,400°C, and subjected to an electrochemical treatment of fiber surface and coated with a sizing, thereby providing a carbon fiber bundle.

[0079] The width Wy and the standard deviation σ of the amplitude of vibration, of fiber bundles travelled in the uppermost stage in the heat treatment chamber 3 of the oxidation oven 1, were actually measured at the center of the heat treatment chamber, and the contact probability P between adjacent fiber bundles, statistically calculated, was 6%.

[0080] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

[Table 1]

	Properties of Acyric Fiber Bundle				Equipment Spec			Calculation from Measured Values	Results		
	Single Fiber Fineness tex	Longer Diameter/ Shorter Diameter of Single Fiber	Amount of Attachment of Oil %	Length of Hook Drop mm	Lateral Length between the Guid Rollers m	Shape of Guid Roller	Air Velocity m/s	Contact Probability between Adjacent Fiber Bundles P %	Product Stability (Yarn Break etc.)	Product Quality (Result of Visual Check)	Productivity Cost
Example 1	0.11	1.04	0.5	250	20	groove	3	6	excellent	excellent	excellent
Example 2	0.11	1.04	0.5	250	15	groove	3	10	excellent	excellent	good
Example 3	0.11	1.04	0.5	250	30	groove	3	15	excellent	excellent	excellent
Example 4	0.11	1.04	0.5	250	20	groove	5	7	excellent	excellent	excellent
Example 5	0.11	1.04	0.5	250	10	groove	3	5	excellent	excellent	good
Example 6	0.11	1.04	0.5	250	20	groove	8	14	excellent	excellent	good
Example 7	0.11	1.04	0.5	250	20	flat	3	14	good	good	excellent
Example 8	0.11	1.50	0.5	250	20	groove	3	14	good	good	excellent
Example 9	0.11	1.04	4.0	250	20	groove	3	6	good	good	excellent
Example 10	0.11	1.04	0	250	20	groove	3	6	good	good	excellent
Example 11	0.11	1.04	0.5	350	20	groove	3	14	good	good	excellent
Example 12	0.18	1.04	0.5	250	20	groove	3	14	good	good	excellent
Example 13	0.11	1.04	0.5	250	20	flat + comb-like	3	14	excellent	excellent	excellent
Comparative Example 1	0.11	1.04	0.5	250	20	groove	3	24	failure	failure	good
Comparative Example 2	0.11	1.04	0.5	250	20	groove	3	1	good	good	failure
Comparative Example 3	0.11	1.04	0.5	250	30	groove	3	28	failure	failure	good

(continued)

	Properties of Acyric Fiber Bundle				Equipment Spec			Calculation from Measured Values	Results		
	Single Fiber Fineness tex	Longer Diameter/ Shorter Diameter of Single Fiber	Amount of Attachment of Oil %	Length of Hook Drop mm	Lateral Length between the Guid Rollers m	Shape of Guid Roller	Air Velocity m/s	Contact Probability between Adjacent Fiber Bundles P %	Product Stability (Yarn Break etc.)	Product Quality (Result of Visual Check)	Productivity Cost
Comparative Example 4	0.11	1.04	0.5	250	30	groove	8	19	failure	failure	failure

(Example 2)

[0081] The same manner as in Example 1 was performed except that the lateral length L' between the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1 was 15 m and the contact probability P between adjacent fiber bundles was 10%.

[0082] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Example 3)

[0083] The same manner as in Example 1 was performed except that the lateral length L' between the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1 was 30 m and the contact probability P between adjacent fiber bundles was 15%.

[0084] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Example 4)

[0085] The same manner as in Example 1 was performed except that the air velocity in the lateral direction of the oxidizing gas in the heat treatment chamber 3 of the oxidation oven 1 was 5 m/sec and the contact probability P between adjacent fiber bundles was 7%.

[0086] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Example 5)

[0087] The same manner as in Example 1 was performed except that the lateral length L' between the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1 was 10 m and the contact probability P between adjacent fiber bundles was 5%.

[0088] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Example 6)

[0089] The same manner as in Example 1 was performed except that the air velocity in the lateral direction of the oxidizing gas in the heat treatment chamber 3 of the oxidation oven 1 was 8 m/sec and the contact probability P between adjacent fiber bundles was 14%.

[0090] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Example 7)

[0091] The same manner as in Example 1 was performed except that the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1 were each a flat roller and the contact probability P between adjacent fiber bundles was 14%.

[0092] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles

in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 8)

[0093] The same manner as in Example 1 was performed except that the longer diameter/shorter diameter in a cross section of any single fiber of the acrylic fiber bundle used was 1.50 and the contact probability P between adjacent fiber bundles was 14%.

[0094] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 9)

[0095] The same manner as in Example 1 was performed except that the amount of attachment of the silicon based oil agent in the acrylic fiber bundle used was 4.0% and the contact probability P between adjacent fiber bundles was 6%.

[0096] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 10)

[0097] The same manner as in Example 1 was performed except that no silicon based oil agent was provided to the acrylic fiber bundle used and the contact probability P between adjacent fiber bundles was 6%.

[0098] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 11)

[0099] The same manner as in Example 1 was performed except that the length of hook drop of the acrylic fiber bundle used was 350 mm and the contact probability P between adjacent fiber bundles was 14%.

[0100] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 12)

[0101] The same manner as in Example 1 was performed except that the single fiber fineness in the acrylic fiber bundle used was 0.18 tex and the contact probability P between adjacent fiber bundles was 14%.

[0102] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality.

(Example 13)

[0103] The same manner as in Example 1 was performed except that the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1 were each a flat roller, furthermore a comb guide was placed at a position of 30 mm from such each flat roller in the direction of the oxidation oven and the comb guide had a gap at a regular interval ranging from 3 to 15 mm in the width direction, the pitch interval of fiber bundles physically regulated by allowing fiber bundles to pass through the gas was a predetermined interval Wp ranging from 3 to 15 mm, and the contact probability P between adjacent fiber bundles was 14%.

[0104] There were not caused any yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles at all, in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at extremely favorable process stability and a higher production efficiency. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had no fuzz and the like and were extremely favorable in quality.

(Comparative Example 1)

[0105] The same manner as in Example 1 was performed except that the contact probability P between adjacent fiber bundles was 24% by, for example, decreasing the groove interval in the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1.

[0106] The amount of production by itself could be increased by enhancing the yarn density in the above conditions, but there were considerably caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundle, thereby making it difficult to continue any process. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, considerably had fuzz and the like and were inferior in quality.

(Comparative Example 2)

[0107] The same manner as in Example 1 was performed except that the contact probability P between adjacent fiber bundles was 1% by, for example, increasing the groove interval in the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1.

[0108] There were less caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, and a stabilized fiber bundle was obtained at favorable process stability. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, had less fuzz and the like and were favorable in quality. However, the number of fiber bundles that could be loaded to the oxidation oven 1 was consequently decreased, resulting in a significant reduction in productivity.

(Comparative Example 3)

[0109] The same manner as in Example 3 was performed except that the contact probability P between adjacent fiber bundles was 28% by, for example, decreasing the groove interval in the guide rollers 4 on both sides of the heat treatment chamber 3 of the oxidation oven 1.

[0110] The amount of production by itself could be increased by enhancing the yarn density in the above conditions, but there were considerably caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundle, thereby making it difficult to continue any process. The resulting stabilized fiber bundle and carbon fiber bundle were visually confirmed, and as a result, considerably had fuzz and the like and were inferior in quality.

(Comparative Example 4)

[0111] The same manner as in Example 3 was performed except that the air velocity in the lateral direction of the oxidizing gas in the heat treatment chamber 3 of the oxidation oven 1 was 8 m/sec and the contact probability P between adjacent fiber bundles was 19%.

[0112] There were considerably caused yarn gathering, fiber bundle break, and the like due to the contact between fiber bundles in the stabilization treatment of the acrylic fiber bundles in the above conditions, thereby making it difficult to continue any process. The resulting stabilized fiber and carbon fiber were visually confirmed, and as a result, considerably had fuzz and the like and were inferior in quality. Furthermore, the air velocity was 8 m/sec, thereby causing the cost of equipment of the blower 8 for enabling the air velocity, to be increased, resulting in significant deterioration in production cost.

Industrial Applicability

[0113] The present invention relates to a method of manufacturing a stabilized fiber bundle and a method of manufacturing a carbon fiber bundle, and can be applied in aerospace applications, industrial applications such as pressure containers and windmills, sports applications such as golf shafts, and/or the like, but the application scope thereof is not limited thereto.

Reference Signs List

[0114]

1	oxidation oven
2	acrylic fiber bundle
3	heat treatment chamber
4	guide roller
5	hot air blowoff port
6	hot air discharge port
7	heater
8	blower
L	oxidation oven length (effective length of stabilization in one path)
L'	lateral length between guide rollers
Wp	pitch interval physically regulated
Wy	width of fiber bundles travelled
t	interspace between adjacent fiber bundles

Claims

1. A method of manufacturing a stabilized fiber bundle, comprising travelling an acrylic fiber bundle obtained by adjacently aligning a plurality of bundles, in a hot air heating-type oxidation oven, with the acrylic fiber bundle being conveyed by a guide roller placed on each of both sides outside the oxidation oven, to thereby subject the acrylic fiber bundle to a heat treatment in an oxidizing atmosphere, wherein a direction of hot air in the oxidation oven is horizontal to a travelling direction of the fiber bundle, and a contact probability P between adjacent fiber bundles, defined by the following expression (1), is 2 to 18%:

$$P = [1 - p(x)\{-t < x < t\}] \times 100 \qquad (1)$$

wherein P represents the contact probability (%) between adjacent fiber bundles, t represents an interspace (mm) between adjacent fiber bundles, p(x) represents a probability density function of a normal distribution $N(0, \sigma^2)$, σ represents a standard deviation of an amplitude of vibration, and x represents a random variable under the assumption that a median amplitude of vibration is zero.

2. The method of manufacturing a stabilized fiber bundle according to claim 1, wherein a lateral length between the guide rollers is 14.5 m or more.

3. The method of manufacturing a stabilized fiber bundle according to any of claim 1 or 2, wherein an air velocity of hot air flowing in the oxidation oven is 1.0 to 6.0 m/sec.

4. The method of manufacturing a stabilized fiber bundle according to any of claims 1 to 3, wherein the guide roller has a control mechanism of a width of fiber bundle.

5. The method of manufacturing a stabilized fiber bundle according to any of claims 1 to 4, wherein a surface of a single fiber of the acrylic fiber bundle has a surface asperity structure extending for 2.0 μm or more in a longitudinal direction of the fiber in a square range of 2.0 μm in a circumferential direction and 2.0 μm in a fiber axis direction, and a longer diameter/shorter diameter ratio in a cross section of the single fiber is 1.01 to 1.10.

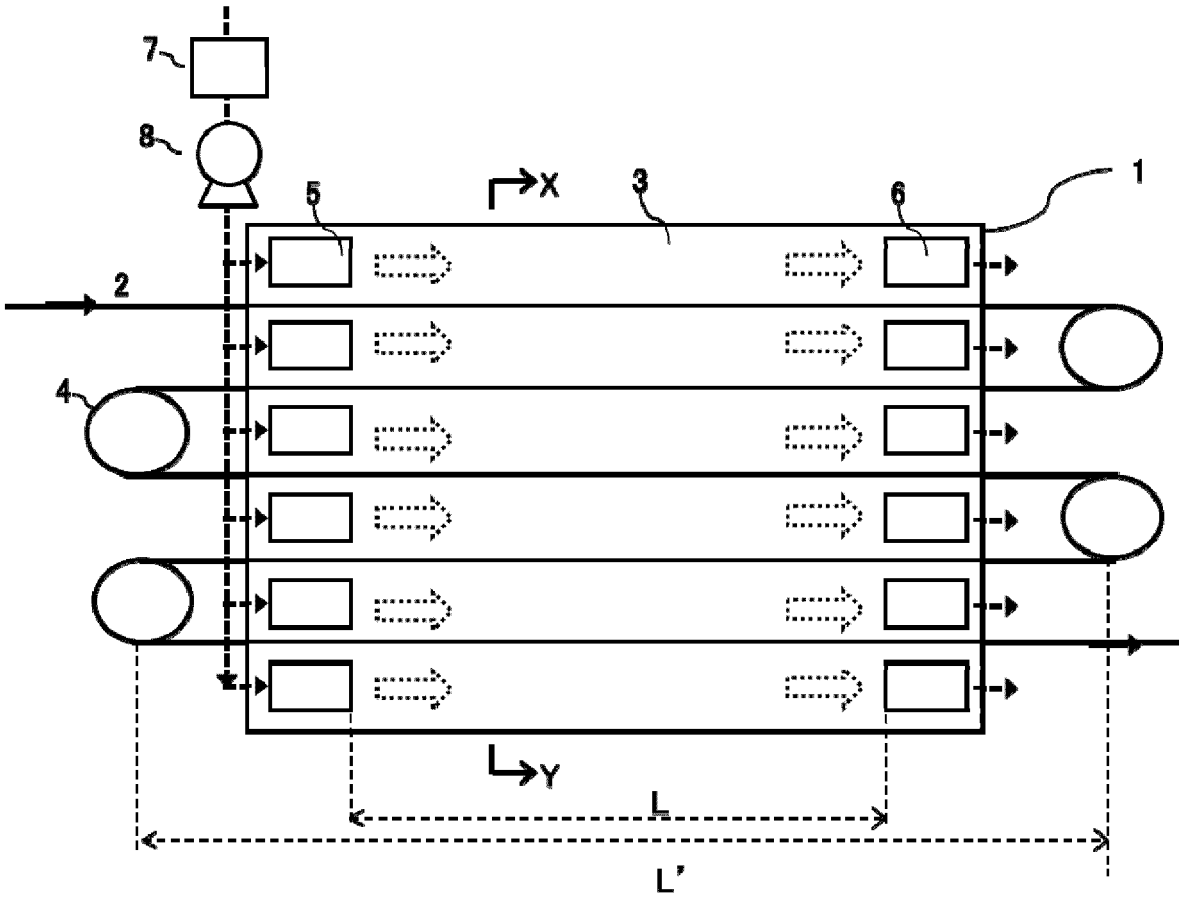
6. The method of manufacturing a stabilized fiber bundle according to any of claims 1 to 5, wherein the acrylic fiber bundle has a length of hook drop of 300 mm or less.

7. The method of manufacturing a stabilized fiber bundle according to any of claims 1 to 6, wherein an amount of attachment of a silicon based oil agent to the acrylic fiber bundle is 0.1 to 3.0% by mass.

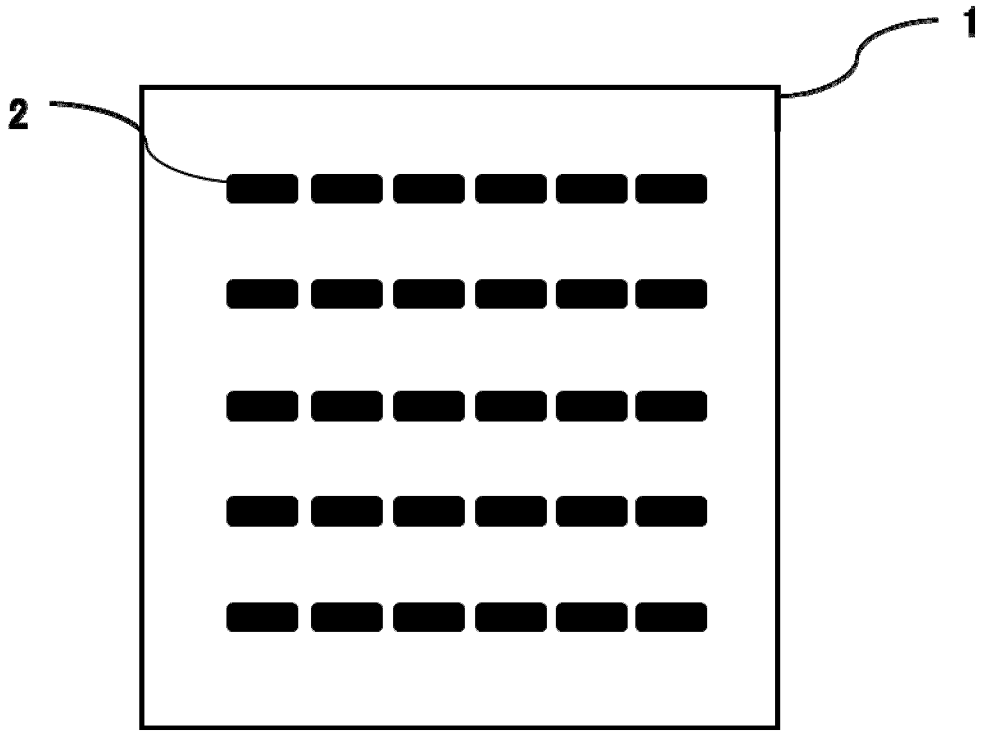
8. The method of manufacturing a stabilized fiber bundle according to any of claims 1 to 7, wherein a single fiber fineness in the acrylic fiber bundle is 0.05 to 0.22 tex.

9. A method of manufacturing a carbon fiber bundle, comprising subjecting a stabilized fiber bundle manufactured by the method of manufacturing a stabilized fiber bundle according to any of claims 1 to 8, to a precarbonization treatment at a maximum temperature of 300 to 1,000°C in an inert gas, to thereby manufacture a precarbonized fiber bundle, and subjecting the precarbonized fiber bundle to a carbonization treatment at a maximum temperature of 1000 to 2000°C in an inert gas.

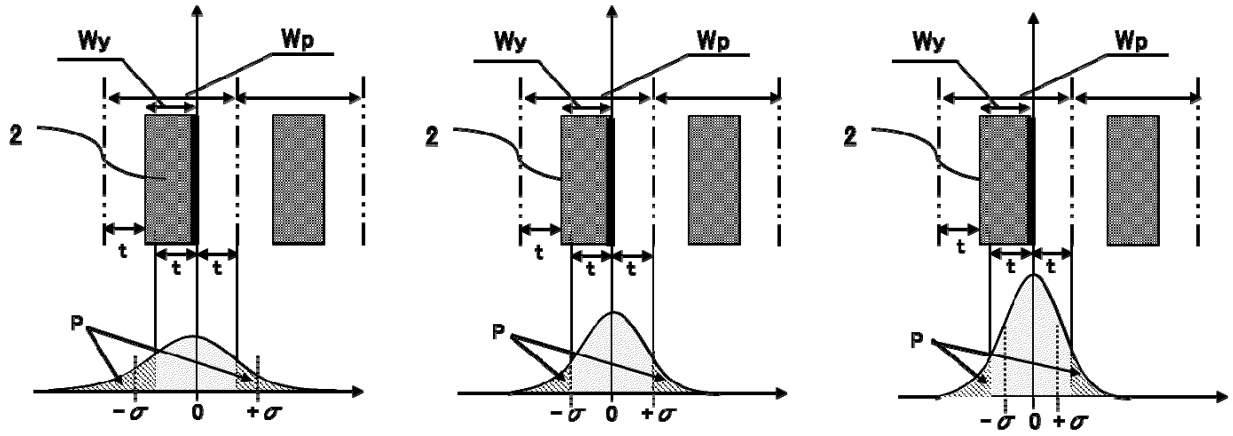
[Fig. 1]



[Fig. 2]



[Fig. 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/035858

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D01F9/22(2006.01)i, D01F9/32(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. D01F9/22, D01F9/32

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.
X Y	JP 2000-160435 A (MITSUBISHI RAYON CO., LTD.) 13 June 2000, claim 2, examples 4, 5, fig. 1-5, paragraphs [0004]-[0011] (Family: none)	1-4, 8, 9 5-7
X Y	JP 2011-127264 A (MITSUBISHI RAYON CO., LTD.) 30 June 2011, claims, examples, paragraphs [0009]-[0011], [0022] (Family: none)	1-4, 8, 9 5-7

☒ 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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Date of the actual completion of the international search	Date of mailing of the international search report
20 November 2019 (20.11.2019)	03 December 2019 (03.12.2019)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/035858

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 11-61574 A (MITSUBISHI RAYON CO., LTD.) 05 March 1999, claims, examples, paragraphs [0009], [0027] (Family: none)	1-4, 8, 9 5-7
Y	JP 2016-160560 A (MITSUBISHI RAYON CO., LTD.) 05 September 2016, claims (Family: none)	5
Y	JP 2016-216883 A (MITSUBISHI RAYON CO., LTD.) 22 December 2016, paragraph [0009] (Family: none)	5
Y	JP 2000-160436 A (TORAY INDUSTRIES, INC.) 13 June 2000, claim 7, paragraph [0039] (Family: none)	6, 7
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A	JP 10-266023 A (TOHO RAYON CO., LTD.) 06 October 1998, abstract (Family: none)	1-9
A	JP 2008-19526 A (MITSUBISHI RAYON CO., LTD.) 31 January 2008, abstract (Family: none)	1-9

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2011127264 A **[0010]**
- JP H1161574 A **[0010]**