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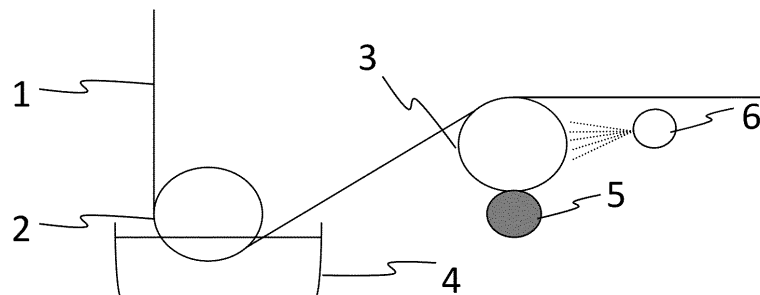
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(54) **METHOD FOR MANUFACTURING CARBON FIBER BUNDLES WITH SIZING AGENT APPLIED**

(57) In a method for producing sizing agent-applied carbon fiber bundles, the method including a sizing agent application process of immersing a plurality of carbon fiber bundles running side by side in a sizing agent bath, followed by a dry process performed to obtain sizing agent-applied carbon fiber bundles, in order to solve a

problem of wrapping of a carbon fiber bundle caused by sticking of a sizing agent solution to a guide roller, the first guide roller for the carbon fiber bundles after being immersed in the sizing agent bath and coming out of a liquid surface of the sizing agent bath is set to have a surface adhesive force of 0.2 N/cm² or less.

Fig. 4



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method for producing sizing agent-applied carbon fiber bundles having a sizing agent applied thereto.

BACKGROUND ART

10 **[0002]** A carbon fiber bundle is characterized to have excellent mechanical properties, particularly high specific strength and a high specific modulus of elasticity, so that the carbon fiber bundle is widely used for, for example, aerial or cosmic application, sport and leisure application, and general industrial application such as automobiles and windmills. In recent years, consumers who use carbon fiber bundles strongly require high-quality and cost-cutting of the carbon fiber bundles.

15 **[0003]** The carbon fiber bundle generally has low elongation and a brittle property, and easily generates fuzz and sometimes breakage by, for example, contacting with a roller or rubbing with a guide in a high-order process. A general countermeasure against these problems is applying various sizing agents to the carbon fiber bundle to impart better handling ability, improve the convergence and the rubbing resistance of the carbon fiber bundle, and suppress the generation of fuzz of the carbon fiber bundle, so that the grade of the carbon fiber bundle is maintained.

20 **[0004]** There are various methods for applying a sizing agent to the carbon fiber bundle, such as spray jetting, dripping, kiss-roller coating, and so on. In view of efficiency of simultaneous and easy application of a sizing agent to multiple carbon fiber bundles, dipping is preferable in which the carbon fiber bundles are immersed in a sizing agent bath. A process for multiple carbon fiber bundles or high-speed production for cost cutting, however, increases the amount of a sizing agent solution attached to the carbon fiber bundles and taken out from the sizing agent bath and also increases the amount of the sizing agent solution attached to a guide roller for guiding the carbon fiber bundles to a dry process following the sizing agent application process. Then, the sizing agent solution is dried on a surface of the guide roller resulting in generation of a resin rich area and thus increase the viscosity of the surface. A carbon fiber bundle brought into contact with the resin rich area generates fuzz and sometimes wraps around the guide roller, causing a problem of decreasing the process stability. Further, when the pitch between adjacent carbon fiber bundles is decreased to perform the process for multiple carbon fiber bundles, a coating layer formed by the sizing agent solution is easily generated between the adjacent carbon fiber bundles. Then, this liquid coating layer is directly dried resulting in unevenness of the sizing agent solution attached thereto. Further, the carbon fiber bundles that adjacently run stick to each other due to the surface tension of the sizing agent solution and easily cause a problem of poor yarn separation.

25 **[0005]** As an improvement technique, Patent Documents 1 and 2 disclose a method for removing a liquid coating layer, which is formed of a sizing agent generated between carbon fiber bundles, by spraying a pressurized gas toward the carbon fiber bundles that have come out of a liquid surface of a sizing agent bath.

30 **[0006]** Patent Document 3 discloses a method for holding carbon fiber bundles with at least a pair of nip rollers to remove an excessive sizing agent solution that has been impregnated into the carbon fiber bundles and applying a sizing agent solution to a surface(s) of the nip roller(s) to prevent drying of the sizing agent solution on the nip rollers. Further, Patent Document 4 discloses a method for producing carbon fiber bundles having excellent spreadability, the method including sizing never-twisted carbon fiber bundles and then drying the carbon fiber bundles with a hot roller, in which wipe cloth is pressed against the hot roller to remove an excessive sizing agent solution from the hot roller.

PRIOR ART DOCUMENTS

45 PATENT DOCUMENTS

[0007]

50 Patent Document 1: Japanese Patent Laid-open Publication No. 2013-23785
 Patent Document 2: Japanese Patent Laid-open Publication No. 07-145549
 Patent Document 3: Japanese Patent Laid-open Publication No. 2011-256486
 Patent Document 4: Japanese Patent Laid-open Publication No. 01-292038

SUMMARY OF THE INVENTION

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PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] With the methods of Patent Documents 1 and 2, even though it is possible to remove the liquid coating layer

between the carbon fiber bundles, the carbon fiber bundles still have a sizing agent solution attached thereto to transfer to a surface of a guide roller, causing a problem of generating a resin rich area. In the method of Patent Document 3, the brittle carbon fiber bundles are held by the nip rollers resulting in generation of fuzz, causing a problem of decreasing the process stability. In the method of Patent Document 4, the excessive sizing agent solution attached onto the hot roller is removed with the wipe cloth to suppress a resin rich area formed by drying of the sizing agent solution on the hot roller itself, but the sizing agent solution is easily dried on a guide roller located before the hot roller but first after the sizing agent application process, and a filament of the carbon fiber bundles is stuck in a resin rich area generated during the drying of the sizing agent solution, causing a problem of generating fuzz or wrapping.

[0009] An object of the present invention is to attempt to solve the above conventional technical problems, and is to provide a method for producing sizing agent-applied carbon fiber bundles that is capable of solving the problems of wrapping and fuzz of a carbon fiber bundle caused by the drying or the resin rich area of the sizing agent solution on the guide roller.

SOLUTIONS TO THE PROBLEMS

[0010] In order to achieve the above object, the present invention has a following configuration. That is, provided is a method for producing sizing agent-applied carbon fiber bundles, the method including a sizing agent application process of immersing a plurality of carbon fiber bundles running side by side in a sizing agent bath, followed by a dry process performed to obtain sizing agent-applied carbon fiber bundles, wherein the first guide roller for the carbon fiber bundles after being immersed in the sizing agent bath and coming out of a liquid surface of the sizing agent bath has a surface adhesive force of 0.2 N/cm² or less.

EFFECTS OF THE INVENTION

[0011] According to the present invention, the method for producing sizing agent-applied carbon fiber bundles having a sizing agent solution applied thereto prevents drying and a resin rich area of the sizing agent solution on a guide roller and is thus capable of obtaining high grade carbon fiber bundles with less fuzz. The method is also capable of suppressing wrapping of a carbon fiber bundle on the guide roller and is excellent in process stability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Fig. 1 shows a schematic configuration diagram illustrating one example of a sizing process in the present invention.

Fig. 2 shows a schematic configuration diagram illustrating another example of the sizing process in the present invention.

Fig. 3 shows a schematic configuration diagram illustrating another example of the sizing process in the present invention.

Fig. 4 shows a schematic configuration diagram illustrating another example of the sizing process in the present invention.

Fig. 5 shows a diagram illustrating a method for calculating force with which a carbon fiber bundle starts to move.

Fig. 6 shows a schematic configuration diagram illustrating one example of a conventional sizing process.

EMBODIMENTS OF THE INVENTION

[0013] A method for producing sizing agent-applied carbon fiber bundles according to the present invention is to obtain sizing agent-applied carbon fiber bundles through a sizing agent application process of immersing a plurality of carbon fiber bundles running side by side in a sizing agent bath, and a dry process provided after the sizing agent application process. In the method, the first guide roller for the carbon fiber bundles after being immersed in the sizing agent bath and coming out of a liquid surface of the sizing agent bath has a surface adhesive force of 0.2 N/cm² or less.

[0014] Hereinafter, described in detail is the method for producing sizing agent-applied carbon fiber bundles according to the present invention.

[0015] A carbon fiber bundle used in the present invention may be one made of any of, for example, a pitch-based raw material, a rayon-based raw material, and a polyacrylonitrile-based raw material, but a polyacrylonitrile-based carbon fiber bundle is preferable from viewpoints of quality and productivity. The form of the carbon fiber bundle used in the present invention is not also particularly limited, and it is possible to use, for example, a carbon fiber bundle having a filament diameter of 3 μm or more and 10 μm or less. The number of carbon fiber filaments constituting the carbon fiber bundle is not also particularly limited, and can be set at, for example, 1000 to 100000. The effects of the present invention,

however, are easily achieved when the carbon fiber bundle includes a relatively large number of filaments, 3000 filaments or more that take a large amount of a sizing agent solution from the sizing agent bath.

[0016] The polyacrylonitrile-based carbon fiber bundle preferably used in the present invention can be obtained by a known method that includes oxidizing, pre-carbonizing, and carbonizing a polyacrylonitrile-based precursor fiber bundle, and the polyacrylonitrile-based carbon fiber bundle is not particularly limited. The oxidation can be performed at 200 to 300°C in an oxidizing atmosphere. As an oxidizing gas in the oxidation, air is preferable from an economical viewpoint. Subsequently, the pre-carbonization can be performed in an inert atmosphere and in a pre-carbonization furnace at a maximum temperature of 300 to 1000°C. Further, the pre-carbonized fiber bundle is carbonized at a maximum temperature of 1200 to 2000°C to obtain a carbon fiber bundle. The carbon fiber bundle may further be graphitized at a temperature of 2000 to 3000°C as necessary. The pre-carbonization, the carbonization, and the graphitization are performed in an inert atmosphere. A used inert gas is, for example, nitrogen, argon, or xenon, and nitrogen is preferably used from the economical viewpoint.

[0017] When the carbon fiber bundle is made into carbon fiber reinforced composites, the carbon fiber bundle is preferably subjected to a surface treatment such as an electrolytic oxidation treatment performed in an electrolyte, or an oxidation treatment in a gas phase or a liquid phase, to easily improve the affinity or the adhesive property between the carbon fiber bundle and a matrix resin. As the electrolyte, both an acidic aqueous solution and an alkaline aqueous solution are usable. As the acidic aqueous solution, sulfuric acid or nitric acid having strong acidity is preferable. As the alkaline aqueous solution, preferably used is an aqueous solution of an inorganic alkali such as ammonium carbonate, ammonium hydrogen carbonate, or ammonium bicarbonate.

[0018] As the sizing agent solution used in the present invention, it is possible to use one obtained by dispersing or dissolving a sizing agent in water or an organic solvent such as acetone. From viewpoints of uniform application to the carbon fiber bundles and safety, an aqueous dispersion or an aqueous solution is preferable that is obtained by dispersing or dissolving a sizing agent in water. As the sizing agent, it is possible to use one of sizing agents known in a field of a carbon fiber, according to the matrix resin used in a high-order process. The sizing agent can contain a main agent and various additives described later, and can be formed of, for example, the main agent and an emulsifier. It is possible to obtain sizing agent-applied carbon fiber bundles having the sizing agent applied to surfaces thereof by drying carbon fiber bundles impregnated with this sizing agent solution.

[0019] The type of the sizing agent used in the present invention is not particularly limited, but the present invention is effective against a sizing agent solution that is dried on the guide roller resulting in generation of a resin rich area and thus easily form adhesive attached substances. When the sizing agent contains a thermoset resin as a component, possibly used as the main component of the sizing agent is, for example, an epoxy resin, an epoxy-modified polyurethane resin, a polyester resin, a phenolic resin, a polyamide resin, a polyurethane resin, a polycarbonate resin, a polyetherimide resin, a polyamide imide resin, a polyimide resin, a bismaleimide resin, a urethane-modified epoxy resin, a polyvinyl alcohol resin, a polyvinyl pyrrolidone resin, a polyethersulfone resin, or a combination of two or more of these resins. Alternatively, when the sizing agent contains a thermoplastic resin as a component, possibly used as the main component of the sizing is one containing at least a single component or a plurality of components selected from the group of polycarbonate, polypropylene, polyethylene, polystyrene, polyethylene terephthalate, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol, polyethylene imine, polyacrylamide, polyphenylene ether, polyacetal, polybutylene terephthalate, polyphenylene sulfide, polyether ether ketone, an elastomer cellulose compound, an acrylic resin, a polyurethane resin, a polyamide resin, a fluorine resin, an ABS resin, a liquid crystal polymer, and a styrene-maleic anhydride copolymer (partially) neutralized with sodium hydroxide.

[0020] These organic compounds are mostly insoluble in water, and therefore, may be formed into an emulsion by adding a surfactant to these organic compounds. The type of the surfactant is not particularly limited, but a nonionic surfactant is preferably used. Examples of the nonionic surfactant include ether compounds such as polyoxyethylene alkyl ether, single chain polyoxyethylene alkyl ether, polyoxyethylene secondary alcohol ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene sterol ether, polyoxyethylene sterol ether, a polyoxyethylene lanolin derivative, an ethylene oxide derivative of an alkyl phenol formalin condensate, and polyoxyethylene polyoxypropylene alkyl ether; ether ester compounds such as polyoxyethylene glycerin fatty acid ester, polyoxyethylene castor oil or hydrogenated castor oil, polyoxyethylene sorbitan fatty acid ester, and polyoxyethylene sorbitol fatty acid ester; and ester compounds such as polyethylene glycol fatty acid ester and polyglycerin fatty acid ester. From among these compounds, one or several compounds in combination are used.

[0021] Dilution to form the sizing agent solution is preferably performed using economical and safe water. When the sizing agent solution is arranged as an aqueous dispersion, adjustment is made so that the sizing agent is in a concentration range allowing water to be present as a continuous phase. A general method includes diluting the sizing agent to give a sizing agent concentration of about 0.1 to 10 mass% in the sizing agent bath so that the amount of the sizing agent attached to the carbon fiber bundles becomes a desired amount, and impregnating the carbon fiber bundles with the sizing agent solution. When water is added to dilute the sizing agent solution for adjustment of the concentration in the sizing agent bath to a desired concentration, the dilution may be performed once or a plurality of times depending

on the composition concentration of, for example, the main component other than water in the sizing agent solution. The sizing agent solution may also contain, in addition to the main component, various additives such as a surfactant, a smoothing agent, and an emulsifier.

[0022] As regards a resin rich area of the sizing agent solution that is generated on the guide roller along a running course of the carbon fiber bundles after the carbon fiber bundles pass the sizing agent application process, the resin rich area is generated as follows: the sizing agent solution taken out by the carbon fiber bundles from the sizing agent bath is transferred, retained, and dried on the guide roller. The generation of the resin rich area due to the drying of the resin of the sizing agent solution on the guide roller brings a running carbon fiber bundle into contact with the resin rich area on the guide roller resulting in the adhesiveness at the time of separation of the carbon fiber bundle from the resin rich area increased, and thus generate, for example, fuzz or wrapping. The method for producing carbon fiber bundles according to the present invention is capable of preventing the drying of the sizing agent solution on the guide roller and preventing the resin rich area of the sizing agent by making the first guide roller for the carbon fiber bundles after being immersed in the sizing agent bath and coming out of a liquid surface of the sizing agent bath to have a surface adhesive force of 0.2 N/cm² or less, preferably 0.1 N/cm² or less. The guide roller having a surface adhesive force of more than 0.2 N/cm² allows a carbon fiber bundle to generate fuzz, sometimes causing the problem of wrapping. The guide roller retains a surface adhesive force of preferably 0.20 N/cm² or less, further preferably 0.10 N/cm² or less. With the guide roller having a lower surface adhesive force, the carbon fiber bundles have a higher grade, and an object of the present invention is to obtain high grade carbon fiber bundles with less fuzz by preventing the drying and the resin rich area of the sizing agent solution on the guide roller, whereas it is necessary to apply the sizing agent to the carbon fiber bundles. Then, not a little amount of the sizing agent solution is dried and forms the resin rich area on the guide roller to make the guide roller adhesive. Therefore, the guide roller does not substantially have a surface adhesive force of zero, and the guide roller preferably has a surface adhesive force of 0.01 N/cm² as a lower limit.

[0023] Here, the surface adhesive force of the guide roller is calculated by the following equation.

$$\begin{aligned} &\text{Surface adhesive force of guide roller (N/cm}^2\text{)} = \\ &\quad \text{force with which carbon fiber bundle starts to move /} \\ &\quad \text{contacting surface area of carbon fiber bundle with guide} \\ &\quad \text{roller} \end{aligned}$$

[0024] A method for calculating the force with which the carbon fiber bundle starts to move is described with reference to Fig. 5. The force with which the carbon fiber starts to move is measured as follows within 10 minutes after a stop of a facility for producing carbon fiber bundles at the time of long-term stable production, and the measured value is regarded as a value during the production.

[0025] First, a guide roller 3 having a sizing agent solution attached thereto is fixed so as not to be rotated, and then a carbon fiber bundle 1 that is about to be subjected to application of a sizing agent and is absolutely dry is hung, with a contact angle of 180°, from a most upper point of the guide roller 3. Next, a ring is made at one end of the carbon fiber bundle 1 hung around the circumference of the guide roller 3, a hook is attached to a tip of a load measuring apparatus 7, and the hook is hooked to the ring of the carbon fiber bundle. The load measuring apparatus is not particularly limited, but preferred is a push-pull gauge capable of measuring an instantaneous maximum load. The carbon fiber bundle is slowly pulled with the load measuring apparatus, and the maximum force right before the carbon fiber bundle 1 starts to move on the surface of the guide roller 3 is defined as the force with which the carbon fiber starts to move (the unit is Newton).

[0026] In the meantime, the "at the time of long-term stable production" refers to period during which the carbon fiber bundles are continuously produced industrially stably for a long period (24 hours or longer) without fuzz and wrapping. The "stop of the facility for producing carbon fiber bundles" refers to a moment of stopping the facility for producing carbon fiber bundles that serves the process from the sizing agent bath to the guide roller. It is possible to measure the force with which the carbon fiber bundle starts to move only by fixing the guide roller through stopping the facility for producing carbon fiber bundles.

[0027] The force with which the carbon fiber bundle starts to move is adjustable by adjusting the dryness of the sizing agent solution attached to the surface of the guide roller or by changing the material for the guide roller.

[0028] The contacting surface area of the carbon fiber bundle with the guide roller is calculated by a product of the circumferential length along the circumference of the surface of the guide roller between a point at which the carbon fiber bundle starts to be brought into contact with the guide roller and a point at which the carbon fiber bundle is separated from the guide roller and the width of the carbon fiber bundle. It is possible to change the contacting surface area by

changing, for example, the circumferential length on the guide roller in contact with the carbon fiber or the number of filaments in the carbon fiber bundle.

[0029] Next, the present invention is described in further detail with reference to drawings.

[0030] Fig. 1 shows a schematic configuration diagram illustrating one example of a sizing process in the present invention. In the aspect illustrated in Fig. 1, carbon fiber bundles 1 pass a dipping roller 2 to be immersed in a sizing agent bath 4, is taken out from a liquid surface by a guide roller 3, and is lead to a next process, or a dry process following the sizing process. In such an aspect, the carbon fiber bundles 1 having a sizing agent solution applied thereto pass the guide roller 3 to attach the sizing agent solution to the guide roller 3. Here, in order to prevent sticking of the sizing agent solution attached to the guide roller 3, at least one contacting object 5 selected from cloth and elastic materials such as a resin and rubber is brought into contact with the guide roller 3. The contacting object 5 wipes the sizing agent solution attached to the guide roller to adjust the surface adhesive force of the guide roller, enabling the guide roller to have a surface adhesive force of 0.2 N/cm² or less.

[0031] Here, a method for bringing the contacting object into contact with the guide roller is not particularly limited, and is, for example, a method for uniformly pressing the contacting object against the guide roller. The contacting object to be pressed is made of any material such as cloth, flannel, an elastic material such as a resin or rubber, or a metal, as long as the material is capable of removing the sizing agent solution attached to the guide roller and enables the guide roller to have a surface adhesive force of 0.2 N/cm² or less. Particularly, in terms of a property of being less likely to generate static electricity, toughness, and water absorbability, thick flat-woven cotton cloth represented by calico, or flannel such as long-pile cotton flannel or wool fabric is optimal in respect of the effect of removing the sizing agent solution.

[0032] The pressure applied to the contacting object is not particularly limited as long as the contacting object is capable of removing the sizing agent solution attached to the guide roller, and the disposition state of the contacting object can be either fixation or rotation. When the applied pressure is low, the removal of the sizing agent solution is insufficient and so the effect decreases, whereas when the applied pressure is excessively high, the guide roller is not rotated and thus a lot of fuzz of a running carbon fiber bundle is generated by rubbing, allowing wrapping of the carbon fiber bundle on the guide roller to decrease the process stability. Therefore, a cloth contacting object is preferably rotatable while wrapped around the guide roller. Further, a position of the contacting object to which the guide roller is pressed is not particularly limited, but the contacting object is preferably pressed on a surface of the guide roller in no contact with the running carbon fiber bundles, in terms of preventing the generation of fuzz and breakage of a running carbon fiber bundle caused by contact between the contacting object and the carbon fiber bundles.

[0033] Further, when an elastic material or a metal is pressed against the guide roller, the elastic material or the metal is preferably formed into a sharp shape, such as a scraper, which is, however, not too sharp to damage the guide roller, in terms of removal efficiency of the sizing agent solution. When the scraper is used, the scraper is set to be capable of holding back, during rotation of the guide roller, the sizing agent solution transferred onto the surface of the guide roller, with a sharp tip portion of the scraper that is in contact with the guide roller. Further, in order to hold back, with the scraper, the sizing agent solution efficiently against the whole surface of the guide roller, the scraper is preferably set to allow the sharp tip portion of the scraper to be in linear contact with the guide roller in parallel with a shaft direction of the guide roller. The sharp portion of the scraper is preferably a hard scraper blade made of a metal or plastic, and such a sharp portion is capable of uniformly removing solid attached substances or adhesive attached substances, such as the resin rich area, generated on the guide roller during the drying of the sizing agent solution. Further, in order to remove, with the scraper, the sizing agent solution across the full width direction of the guide roller, the scraper may be set along the shaft direction of the guide roller, with guide means, such as a guide rail for the scraper blade, provided in parallel with the shaft of the guide roller. This configuration enables efficient removal of the solid attached substances or the adhesive attached substances on the guide roller.

[0034] Fig. 2 shows a schematic configuration diagram illustrating another example of the sizing process in the present invention. In the aspect illustrated in Fig. 2, carbon fiber bundles 1 pass a dipping roller 2 to be immersed in a sizing agent bath 4, are taken out from a liquid surface by a guide roller 3, and are lead to a next process, or a dry process following the sizing process. Also in this aspect, the carbon fiber bundles 1 having a sizing agent solution applied thereto pass the guide roller 3 to attach the sizing agent solution to the guide roller 3. Therefore, in order to prevent sticking of the sizing agent attached to the guide roller 3, a sizing agent solution different from the sizing agent solution in the sizing agent bath 4 is applied to the guide roller 3 with use of, for example, sizing agent solution spray means 6. A method for applying the sizing agent solution is not particularly limited to the sizing agent solution spray means 6, and is, for example, a method for dripping or spraying the sizing agent solution to the whole surface of the guide roller, or a method for immersing the guide roller in the sizing agent solution. In such an aspect, there is no problem as long as the sizing agent solution is applied so that the guide roller is not dried and the guide roller is allowed to have a surface adhesive force of 0.2 N/cm² or less, and no particular limitation is provided unless the sizing agent solution is retained and dried on the surface of the guide roller resulting in generation of the resin rich area.

[0035] For example, as illustrated in Fig. 2, the disposition of the sizing agent solution spray means 6 above the guide roller 3 and the spray of the sizing agent solution from the sizing agent solution spray means 6 are capable of sufficiently

suppressing the drying of the sizing agent solution on the guide roller 3. An upper limit of the spraying amount of the sizing agent solution per one hour sprayed from the sizing agent solution spray means 6 is not particularly limited because the guide roller 3 only has to be wet, but the upper limit is in a preferable range of 50 to 130 mg/cm²/hr, in a more preferable range of 80 to 100 mg/cm²/hr. The sizing agent solution in a spraying amount per one hour of less than 50

mg/cm²/hr is sometimes evaporated on the guide roller 3, generating the resin rich area and resulting in generating fuzz or wrapping of a carbon fiber bundle. The sizing agent solution in a spraying amount per one hour of more than 130 mg/cm²/hr means use of an excessive amount of the sizing agent solution and thus is disadvantageous in terms of costs.

[0036] Further, as illustrated in Fig. 3, immersing of the guide roller 3 in a sizing agent bath 8 different from the sizing agent bath used in the sizing process is also capable of sufficiently suppressing the drying of the sizing agent solution on the guide roller 3.

[0037] The sizing agent solution separately applied to the guide roller as in the aspects illustrated in Figs. 2 and 3 is not particularly limited, but preferably cause no change to the composition and the amount of the sizing agent applied to the carbon fiber bundles obtained and is preferably identical with the sizing agent solution for immersing the carbon fiber bundles.

[0038] In the meantime, more effect is exerted by combining the method for bringing the contacting object into contact with the guide roller and the method for applying a sizing agent solution separately from the sizing agent bath 4. For example, as illustrated in Fig. 4, the spray of the sizing agent solution from the sizing agent solution spray means 6 to the guide roller 3, followed by the pressing the contacting object against the guide roller prevents sticking of the sizing agent solution and removes an excessive sizing agent solution to be capable of adjusting the surface adhesive force of the guide roller to the prescribed range, more securely than employing only the method for pressing the contacting object against the guide roller.

[0039] Further, in the present invention, when the carbon fiber bundles 1 pass the dipping roller 2 to be immersed in the sizing agent bath 4, are taken out from the liquid surface by the guide roller 3, and are lead to the next process, or the dry process following the sizing process, a water-resistant guide roller is preferably used as the guide roller 3 so as not to allow the generation of the resin rich area on the guide roller 3 caused by the sizing agent solution. Specific examples of the water-resistant guide roller include a fluororesin and stainless steel (SUS). Particularly, stainless steel (SUS) that is less likely to cause rust is more preferable, because the carbon fiber bundles having the sizing agent solution applied thereto run on the guide roller to always make the surface of the guide roller wet. Examples of the type of stainless steel include SUS304, SUS304L, SUS316, and SUS316L.

[0040] In the production method according to the present invention, a sizing agent liquid coating layer between adjacent carbon fiber bundles is easily formed in a place between a position where the carbon fiber bundles come out of the liquid surface after immersed in the sizing agent solution and a guide roller with which the carbon fiber bundles is firstly brought into contact, and in a place between the guide roller and before the dry process. The sizing agent liquid coating layer can be formed by an excessive sizing agent solution that is taken out by the carbon fiber bundles immersed in the sizing agent bath or by the above-described sizing agent solution applied to the guide roller separately from the sizing agent solution in the sizing agent bath. The formation of the sizing agent liquid coating layer between adjacent carbon fiber bundles brings the adjacent carbon fiber bundles into contact with each other due to the surface tension of the sizing agent liquid coating layer resulting in generation of fuzz or increase of unevenness in sizing agent amount, dryness, or in color of the carbon fiber bundles obtained. Therefore, the sizing agent liquid coating layer is preferably removed in each of the places. A method for removing the sizing agent liquid coating layer is not particularly limited, and is, for example, spraying a pressurized gas, application of vibration, application of ultrasonic waves, or physical contact by disposing a guide. Among these methods, a non-contact method is preferable that is capable of easily preventing the generation of fuzz of a carbon fiber bundle, and further, spraying a pressurized gas is more preferable from a viewpoint of reducing facility costs.

[0041] In the production method according to the present invention, the tension of the carbon fiber bundles in the sizing agent application process is preferably set at 3.5 to 8.5 cN/tex. With the tension set at 3.5 cN/tex or more, it is possible to prevent a decrease in convergence of the carbon fiber bundles. On the other hand, with the tension set at 8.5 cN/tex or less, it is possible to easily prevent the generation of fuzz and breakage of a carbon fiber bundle caused by tension application. From the above viewpoints, the tension of the carbon fiber bundles in the sizing agent application process is preferably set at 3.5 to 8.5 cN/tex, more preferably 4.0 to 8.0 cN/tex, further preferably 4.5 to 7.5 cN/tex. The tension of the carbon fiber bundles in the sizing agent application process may be singly controlled only in the sizing agent application process or may be controlled together with the tension in the dry process by an identical mechanism. A method for controlling the tension is not particularly limited, and is, for example, a method including adjusting a ratio of driving speed between before and after the sizing agent application process. It is possible to know the process tension by measuring the tension of a running filament right before the application of the sizing agent solution with, for example, a tension meter, and to adjust the tension by, for example, rotary torque of a roller before and after the application of the sizing agent solution.

[0042] The carbon fiber bundles having the sizing agent solution applied thereto in the sizing agent application process

is dried at about 200 to 300°C in the dry process and wound up around a paper tube. As a dry method, it is possible to use a contact-type dryer such as a drum dryer, and a non-contact-type hot air dryer singly or in combination, and the method is not particularly limited.

EXAMPLES

[0043] The present invention is further specifically described by way of examples and a comparative example. Evaluation items for the examples and the comparative example were checked by the following evaluation methods.

[Surface adhesive force of guide roller]

[0044] The surface adhesive force of the guide roller was calculated by the following equation.

$$\text{Surface adhesive force of roller (N/cm}^2\text{)} = \text{force with which carbon fiber bundle starts to move} / \text{contacting surface area of carbon fiber bundle with guide roller}$$

[0045] The force with which a carbon fiber bundle starts to move was measured as follows in 5 minutes after a stop of a facility for producing carbon fiber bundles at the time of long-term stable production. That is, as illustrated in Fig. 5, a stainless steel guide roller 3 having a sizing agent solution attached thereto was fixed so as not to be rotated, and then a carbon fiber bundle 1 that was about to be subjected to application of a sizing agent solution and was absolutely dry was hung, with a contact angle of 180°, from a most upper point of the guide roller 3. Thereafter, a ring was made at one end of the carbon fiber bundle 1. As a load measuring apparatus 7, a digital push-pull gauge (RX series, item No. RX-10) manufactured by Aikoh Engineering Co., Ltd. was used. A gauge attachment (item No. 011B), or a hook was attached to a tip of the digital push-pull gauge, and the carbon fiber bundle 1 was slowly pulled along the circumference of the guide roller 3 while the hook was kept hooked to the ring of the carbon fiber bundle 1. The maximum force right before the carbon fiber bundle 1 started to move on the surface of the guide roller 3, that is, the force with which the carbon fiber bundle started to move was measured with the push-pull gauge.

[0046] The contacting surface area of the carbon fiber bundle with the guide roller was calculated by a product of the circumferential length of the guide roller in contact with the carbon fiber bundle and the width of the carbon fiber bundle.

[Grade]

[0047] As a grade of a sizing agent-applied carbon fiber bundle, visual fuzz on a side surface of a carbon fiber bundle packaged bobbin was observed and evaluated according to the following criteria.

- = fuzz of less than 5 fibers/100 mm²
- = fuzz of 5 fibers/100 mm² or more and less than 10 fibers/100 mm²
- × = fuzz of 10 fibers/100 mm² or more

[Example 1]

[0048] A sizing agent was applied to a plurality of carbon fiber bundles running side by side in a facility having the configuration illustrated in Fig. 1, and the carbon fiber bundles were allowed to undergo a dry process to obtain sizing agent-applied carbon fiber bundles.

[0049] Specifically, carbon fiber bundles that were formed from polyacrylonitrile-based precursor fiber bundles and each included 3000 filaments were immersed in a sizing agent bath filled with a sizing agent solution containing, as a main component, an aromatic epoxy compound, or a bisphenol A epoxy resin at a concentration of 3 mass%, and were subsequently subjected to the dry process to obtain sizing agent-applied carbon fiber bundles. As the guide roller 3 with which the carbon fiber bundles were firstly brought into contact after coming out of a liquid surface of the sizing agent, a guide roller made of stainless steel (SUS) was used, and long-pile cotton flannel cloth was, as a contacting object 5, pressed on a lowermost portion of the guide roller 3.

[0050] The guide roller 3 had a surface adhesive force of 0.05 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was very good. Table 1 shows the results.

[Example 2]

[0051] Sizing agent-applied carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 1 except that a scraper made of plastic was used as the contacting object 5, in place of the long-pile cotton flannel cloth. The guide roller 3 had a surface adhesive force of 0.07 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was very good. Table 1 shows the results.

[Example 3]

[0052] Sizing agent-applied carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 1 except that the process illustrated in Fig. 2 was employed as the sizing agent application process. That is, all the procedures were performed similarly to in Example 1 except that a sizing agent solution was sprayed from above the guide roller 3 with which the carbon fiber bundles were firstly brought into contact after coming out of a liquid surface of the sizing agent and that the contacting object was removed. The spraying amount of the sizing agent solution per one hour at this time was set at 100 mg/cm²/hr. The guide roller 3 had a surface adhesive force of 0.04 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was very good. Table 1 shows the results.

[Example 4]

[0053] Carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 3 except that the spraying amount of the sizing agent solution per one hour was changed to 80 mg/cm²/hr. The guide roller 3 had a surface adhesive force of 0.13 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was good. Table 1 shows the results.

[Example 5]

[0054] Sizing agent-applied carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 1 except that the process illustrated in Fig. 3 was employed as the sizing agent application process. That is, all the procedures were performed similarly to in Example 1 except that the guide roller 3 with which the carbon fiber bundles were firstly brought into contact after coming out of the liquid surface of the sizing agent in Example 1 was immersed in another independent sizing agent bath 8 and that the contacting object was removed. The guide roller 3 had a surface adhesive force of 0.08 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was good. Table 1 shows the results.

[Example 6]

[0055] Sizing agent-applied carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 1 except that the process illustrated in Fig. 4 was employed as the sizing agent application process. That is, the procedures were performed similarly to in Example 1 except that a sizing agent solution was sprayed to the carbon fiber bundles sent out from the guide roller 3 at a spraying amount per one hour of 80 mg/cm²/hr. The guide roller 3 had a surface adhesive force of 0.02 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was very good. Table 1 shows the results.

[Example 7]

[0056] Sizing agent-applied carbon fiber bundles were obtained, with all the procedures performed similarly to in Example 1 except that the sizing agent bath was filled with a sizing agent solution containing, as a main component, polyurethane at a concentration of 2 mass%. The guide roller 3 had a surface adhesive force of 0.06 N/cm², and the visual fuzz on the side surface of the carbon fiber bobbin was very good. Table 1 shows the results.

[Comparative Example 1]

[0057] Sizing agent-applied carbon fiber bundles were obtained similarly to in Example 1 except that the process illustrated in Fig. 6 was employed as the sizing agent application process. That is, the procedures were performed similarly to in Example 1 except that the cotton flannel cloth as the contacting object was not pressed against the guide roller. As a result, the sizing agent was dried on the guide roller resulting in generation of a resin rich area and thus increase the surface adhesive force of the guide roller 3 to as high as 0.25 N/cm², generating fuzz of a running carbon fiber bundle and thus remarkably deteriorating the visual fuzz on the side surface of the carbon fiber bobbin. Table 1

shows the results.

[0058] [Table 1]

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Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1
Material for guide roller	SUS	SUS	SUS	SUS	SUS	SUS	SUS	SUS
Contacting object	Cotton flannel cloth	Scraper	None	None	None	Cotton flannel cloth	Cotton flannel cloth	None
Main component of sizing agent solution	Bisphenol A epoxy	Bisphenol A epoxy	Bisphenol A epoxy	Bisphenol A epoxy	Bisphenol A epoxy	Bisphenol A epoxy	Polyurethane	Bisphenol A epoxy
Spraying amount of sizing agent solution per one hour [mg/cm ² /hr]	None	None	100	80	None	80	None	None
Immersion of guide roller in sizing agent solution	None	None	None	None	Performed	None	None	None
Surface adhesive force of guide roller [N/cm ²]	0.05	0.07	0.04	0.13	0.08	0.02	0.06	0.25
Fuzz grade*	⊙	⊙	⊙	○	○	⊙	⊙	×

* Fuzz grade

⊙ = fuzz of less than 5 fibers/100 mm²○ = fuzz of 5 fibers/100 mm² or more and less than 10 fibers/100 mm²× = fuzz of 10 fibers/100 mm² or more

DESCRIPTION OF REFERENCE SIGNS

[0059]

- 5 1: Carbon fiber bundle
- 2: Dipping roller
- 3: Guide roller
- 10 4: Sizing agent bath
- 5: Contacting object
- 15 6: Sizing agent solution spray means
- 7: Load measuring apparatus
- 20 8: Sizing agent bath different from sizing agent bath 4

Claims

- 25 1. A method for producing sizing agent-applied carbon fiber bundles, the method comprising a sizing agent application process of immersing a plurality of carbon fiber bundles running side by side in a sizing agent bath, followed by a dry process performed to obtain sizing agent-applied carbon fiber bundles, wherein the first guide roller for the carbon fiber bundles after being immersed in the sizing agent bath and coming out of a liquid surface of the sizing agent bath has a surface adhesive force of 0.2 N/cm² or less.
- 30 2. The method for producing sizing agent-applied carbon fiber bundles according to claim 1, wherein a contacting object is brought into contact with the guide roller to allow the guide roller to have a surface adhesive force of 0.2 N/cm² or less.
- 35 3. The method for producing sizing agent-applied carbon fiber bundles according to claim 1, wherein a sizing agent solution is further applied to the guide roller after the sizing agent application process to allow the guide roller to have a surface adhesive force of 0.2 N/cm² or less.

Fig. 1

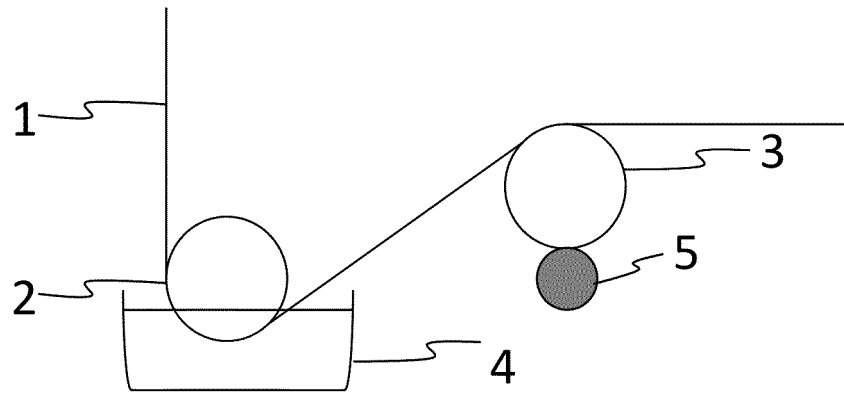


Fig. 2

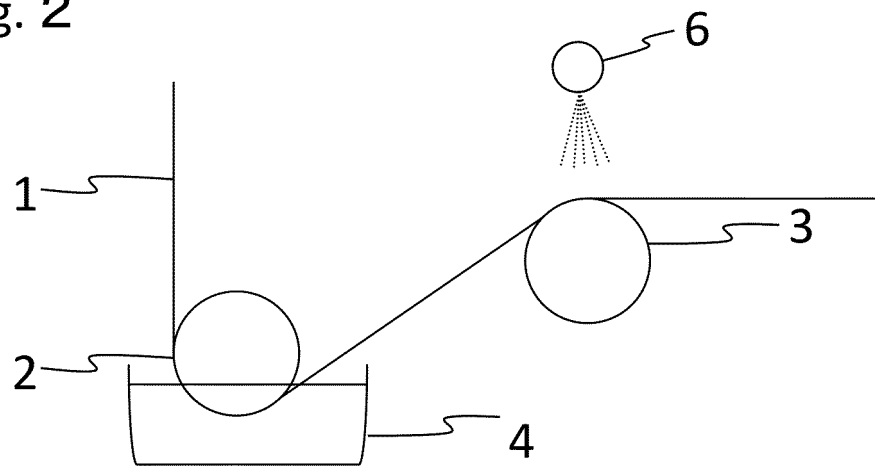


Fig. 3

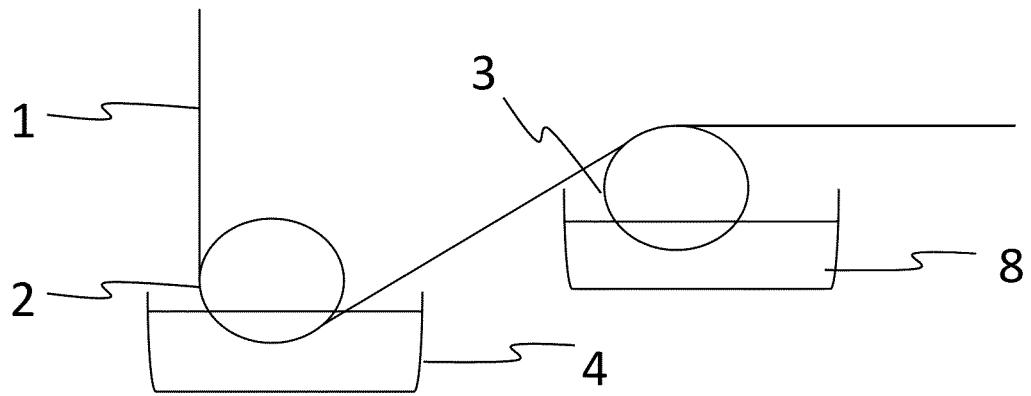


Fig. 4

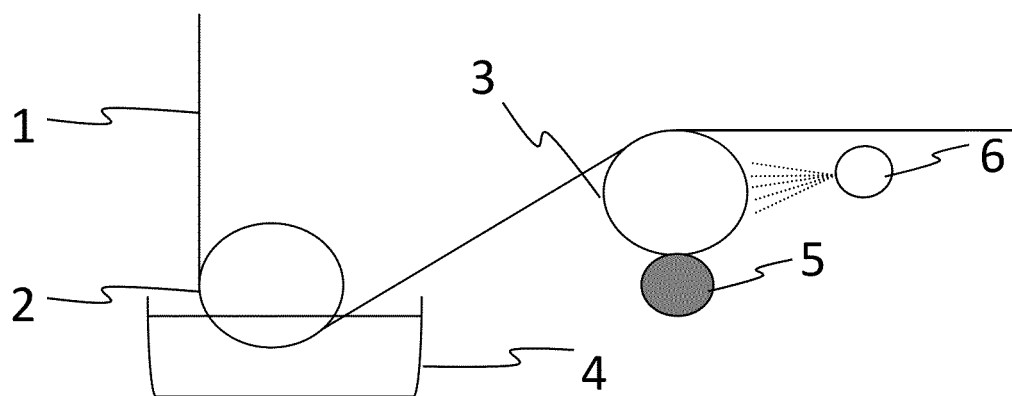


Fig. 5

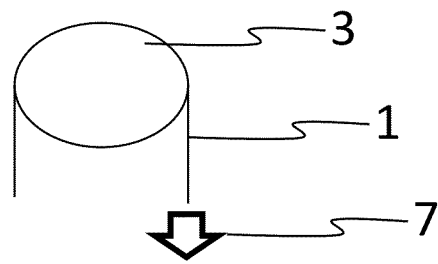
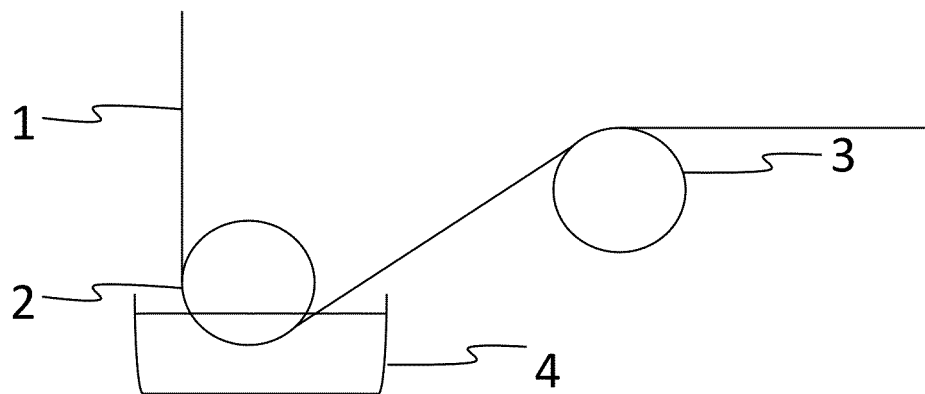


Fig. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/021342

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D06B3/04 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. D06B1/00-23/30 D06C3/00-29/00, D06G1/00-5/00, D06H1/00-7/24,
D06J1/00-1/12, D06M15/55, D06M23/00-23/18

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-256486 A (MITSUBISHI RAYON CO., LTD.) 22 December 2011, claims 1, 3, fig. 1-3 (Family: none)	1-3
A	JP 1-292038 A (TORAY INDUSTRIES, INC.) 24 November 1989, claim 1, page 3, lower left column, lines 3-13, fig. 1 (Family: none)	1-3
A	JP 39-7160 Y1 (KAWAMOTO SEIKI KK) 24 March 1964, claims, page 1, left column, lines 12-17, fig. 1, 2 (Family: none)	1-3



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

26 July 2018 (26.07.2018)

Date of mailing of the international search report

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Name and mailing address of the ISA/

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku,

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2013023785 A [0007]
- JP 7145549 A [0007]
- JP 2011256486 A [0007]
- JP 1292038 A [0007]