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(54) ULTRAFINE COMPOSITE FIBER, ULTRAFINE FIBER, METHOD FOR MANUFACTURING SAME, AND FIBER STRUCTURE

(57) An ultrafine composite fiber of the present invention is obtained by heating and melting a composite-resin-formed product in front of a supply-side electrode and/or in a space between electrodes and extending the composite-resin-formed product by electrospinning, wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less, and that is exposed on 30 % or more of a surface of the composite-resin-formed product. With this, an ultrafine composite synthetic fiber and an ultrafine synthetic fiber can be obtained by electrospinning, without a solvent being mixed in a supply resin, and further, a method for manufacturing an ultrafine composite fiber, as well as a fiber structure containing an ultrafine composite fiber, are provided

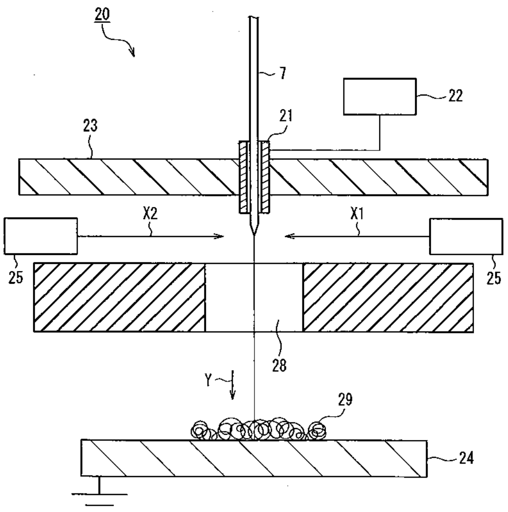

FIG. 2

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Description

Technical Field

[0001] The present invention relates to an ultrafine fiber formed using electrospinning, a method for manufacturing the same, and a fiber structure containing an ultrafine composite fiber obtained by the aforementioned method.

Background Art

[0002] Conventionally, synthetic fibers such as polyethylene terephthalate (PET) fibers, nylon fibers, and polyolefin fibers have been manufactured by melt-spinning in general. With the melt-spinning, however, it is difficult to obtain ultrafine fibers, and particularly it is difficult to obtain fibers having a diameter of not more than 8 μm (single fiber fineness: about 1 decitex) stably.

[0003] On the other hand, the following patent documents 1 to 3 propose electrospinning methods as methods for obtaining ultrafine fibers. Solid-melt-electrospinning is disclosed in Patent Document 1.

Patent Document 1: JP 2007-239114 A
Patent Document 2: JP 2007-197859 A
Patent Document 3: JP 2005-154927 A

[0004] The conventional electrospinning methods, however, have problems as follows. A polymer that cannot be electrified easily is not formed into fine fibers easily even if a voltage is applied thereto, and it is difficult to apply such a polymer to electrospinning. Further, in the techniques disclosed in Patent Documents 1 to 3, a supply resin before spinning has to be dissolved or dispersed in a solvent, which could lead to a problem of components originating from the solvent remaining in an obtained fiber. If a solvent remains in an obtained fiber, components originating from the solvent bleed out therefrom later, which could cause various problems.

Disclosure of Invention

[0005] In order to solve the aforementioned problems in the conventional techniques, the present invention obtains an ultrafine composite synthetic fiber and an ultrafine synthetic fiber by electrospinning, and provides a method for manufacturing an ultrafine composite fiber, and a fiber structure containing an ultrafine composite fiber.

[0006] An ultrafine composite fiber of the present invention is obtained by heating and melting a product formed of a composite resin (hereinafter this product is referred to as "composite-resin-formed product") in front of a supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode and extending the composite-resin-formed product by electrospinning,
wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formed product, and
fiber components composing the ultrafine composite fiber are in a phase separation state.

[0007] An ultrafine fiber of the present invention is obtained by removing any of components composing the ultrafine composite fiber.

[0008] A method for manufacturing an ultrafine composite fiber according to the present invention includes the steps of supplying a composite-resin-formed product to a supply-side electrode, wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formed product;
heating and melting the composste-resin-formed product in front of the supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode; and
extending the molten composite-resin-formed product by electrospinning.

[0009] A fiber structure of the present invention is obtained by heating and melting a composite-resin-formed product in front of a supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode and extending the composite-resin-formed product by electrospinning,
wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formedproduct, and
fiber components composing the ultrafine composite fiber are in a phase separation state.

Brief Description of Drawings

[0010]

[FIG. 1] FIG. 1 is a schematic explanatory view of an electrospinning device according to one example of the present invention.

[FIG. 2] FIG. 2 is a schematic explanatory view of an electrospinning device according to another example of the present invention.

[FIG. 3] FIG. 3 is a scanning electron photomicrograph (SEM, magnification: 20,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 3 of the present invention.

[FIG. 4] FIG. 4 is a schematic cross-sectional view of the fiber shown FIG. 3.

[FIG. 5] FIG. 5 is a scanning electron photomicrograph (SEM, magnification: 10,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 5 of the present invention.

[FIG. 6] FIG. 6 is a schematic cross-sectional view of the fiber shown in FIG. 5.

[FIG. 7] FIG. 7 is a scanning electron photomicrograph (SEM, magnification: 4,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 6 of the present invention.

[FIG. 8] FIG. 8 is a schematic cross-sectional view of the fiber shown in FIG. 7.

[FIG. 9] FIG. 9 is a scanning electron photomicrograph (SEM, magnification: 10,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 10 of the present invention.

[FIG. 10] FIG. 10 is a schematic cross-sectional view of the fiber shown in FIG. 9.

[FIG. 11] FIG. 11 is a schematic explanatory view of an electrospinning device according to another example of the present invention, to perform electrospinning with respect to a plurality of composite fibers as a raw material.

[FIG. 12] FIG. 12A shows an exemplary cross section of a composite fiber as a raw material, which is a composite-resin-formed product, used in Example 2 of the present invention. FIG. 12B shows an exemplary cross section of an ultrafine composite fiber obtained in Example 2 of the present invention.

[FIG. 13] FIG. 13A shows an exemplary cross section of a composite fiber as a raw material, which is a composite-resin-formed product, used in Example 3 of the present invention. FIG. 13B shows an exemplary cross section of an ultrafine composite fiber obtained in Example 3 of the present invention.

[FIG. 14] FIG. 14 is a scanning electron photomicrograph (SEM, magnification: 2,000 times) of an ultrafine fiber obtained in Example 2, Experiment No. 13 of the present invention, in a state before EVOH was removed.

[FIG. 15] FIG. 15 is a scanning electron photomicrograph (SEM, magnification: 2,000 times) of the ultrafine fiber obtained in Example 2, Experiment No. 13 of the present invention, in a state after EVOH was removed.

[FIG. 16] FIG. 16 is a scanning electron photomicrograph (SEM, magnification: 2,000 times) of an ultrafine fiber obtained in Example 2, Experiment No. 14 of the present invention, in a state after EVOH was removed.

[FIG. 17] FIG. 17 is a scanning electron photomicrograph (SEM, magnification: 1,000 times) of an ultrafine fiber obtained in Example 2, Experiment No. 15 of the present invention, in a state after EVOH was removed.

[FIG. 18] FIG. 18 is a scanning electron photomicrograph (SEM, magnification: 5,000 times) of an ultrafine fiber obtained in Example 3, Experiment No. 18 of the present invention, in a state before EVOH was removed.

[FIG. 19] FIG. 19 is a scanning electron photomicrograph (SEM, magnification: 5,000 times) of an ultrafine fiber obtained in Example 3, Experiment No. 18 of the present invention, in a state after EVOH was removed.

[FIG. 20] FIG. 20 is a scanning electron photomicrograph (SEM, magnification: 5,000 times) of an ultrafine fiber obtained in Example 3, Experiment No. 19 of the present invention, in a state after EVOH was removed.

[FIG. 21] FIG. 21 is a scanning electron photomicrograph (SEM, magnification: 5,000 times) of an ultrafine fiber obtained in Example 3, Experiment No. 20 of the present invention, in a state after EVOH was removed.

Description of the Invention

[0011] In the present invention, a composite-resin-formed product in a solid state having two or more phases is used as a raw material, one or more resins in the composite resin have a volume specific resistance of 10^{15} Ω·cm or less, and this resin component is exposed on 30 % or more of a surface of the composite-resin-formed product. This composite-resin-formed product is electrified when passed through a supply-side electrode in a space between electrodes, and is extended by electrospinning, whereby an ultrafine composite fiber and an ultrafine fiber, which were difficult to obtain by a conventional technique, can be obtained without use of an organic solvent. In other words, an organic solvent is not mixed in a supply resin before spinning, and the resin alone can be subjected to spinning. Accordingly, the present invention has an advantage in that no solvent is contained in an obtained fiber.

[0012] The inventors of the present invention examined why specific resins cannot be extended or drawn efficiently in sond-melt-electrospinning. Consequently, they found that some of specific resins such as polypropylene (PP) have high volume specific resistances of 10^{16} to 10^{20} Ω·cm, and such resins are not easily electrified even when a voltage is applied thereto, and it is difficult to form them into ultrafine fibers. Typical resins have volume specific resistance as shown below.

[0013]

[Table 1]

Resin	Volume specific resistance (Ω·cm)
Polyethylene	10^{16}~10^{20}
Polypropylene	10^{16}~10^{20}
Polylactic acid	10^{16}~10^{17}
Polyurethane	10^{13}~10^{15}
Nylon	10^{13}~10^{14}
Polyester	10^{12}~10^{14}
EVOH	10^{7}~10^{9}

[0014]

Note 1: EVOH is an abbreviation for an ethylene-vinyl alcohol copolymer
Note 2: Data shown in Table 1 are based on "Plastic Data Book", edited by Asahi Kasei Amidas Corporation, Plastics Editorial Section, published on December 1, 1999 by Kogyo Chosakai Publishing Inc., page 186.

[0015] Then, the inventors considered forming resin components having low volume specific resistance into a composite-resin-formed product without using a solvent. Various complex methods for composite-resin-formed products are available, and exemplary types of fiber-like composite-resin-formed products include the splittable type, the side-by-side type, the sea-island type, the core-sheath type (this further is classified into various types depending on components selected for the core and the sheath) from the viewpoint of the cross-sectional shape. As a result of various studies, they found that a composite-resin-formed product that contains a resin component having a volume specific resistance of 10^{15} Ω·cm or less as a raw material, wherein the resin component was exposed on 30 % or more of a surface of the composite-resin-formed product, exhibited the greatest extensibility.

[0016] In the present invention, the volume specific resistance is measured according to ASTM D-257.

[0017] In the solid-melt-electrospinning, a resin electrified when the resin is passed through a supply-side electrode is extended toward a collection-side electrode at a high speed by an electric attraction force. Therefore, a resin having a volume specific resistance exceeding 10^{15} Ω·cm is not suitable for electrospinning since it is not easily electrified. In the present invention, however, such a resin having a high volume specific resistance, combined with another resin having a volume specific resistance of not more than 10^{15} Ω·cm upon extension, is made to extend owing to the influences of the another resin. The reason for this is assumed as follows: when a solid composite-resin-formed product is heated and molten in front of a supply-side electrode, and/or in the space between the supply-side electrode and the collection-side electrode, a component having a volume specific resistance of not higher than a predetermined value, exposed on a surface, at an end of a raw material fiber heated and molten, is electrified enough to be electrospun, and with this momentum, the resin having a volume specific resistance exceeding 10^{15} Ω·cm, which is not easily electrified generally, is extended at the same time, thereby being spun.

[0018] In the present invention, a voltage is applied across the supply-side electrode and the collection-side electrode in a space between these electrodes. The voltage preferably is 20 to 100 kV, and more preferably 30 to 50 kV

[0019] When the voltage is in the above-described range, the electrification of resins is easily achieved, whereas sparks or corona discharge hardly occur between electrodes, which does not lead to a problem such as inflammation. If the voltage is less than 20 kV, electrodes have resistance therebetween in a space in the atmosphere (in the space between the electrodes), which could impair flow of electrons, thereby causing resins to be not easily electrified. If the voltage exceeds 100 kV, sparks or corona discharge could occur between electrodes, which could cause burning of the resins.

[0020] A distance between the electrodes may be determined, in view of a fiber diameter of an obtained ultrafine composite fiber, fiber diameter variation, and a property of accumulation of an ultrafine fiber on the collection-side electrode. For example, the distance between the electrodes preferably is 2 to 25 cm, and more preferably 5 to 20 cm. In the case where the distance is in the above-described range, the electrification of a resin is caused easily, sparks or corona discharge hardly occur between the electrodes, and therefore there is no problem of burning or the like. If the distance between the electrodes is less than 2 cm, sparks or corona discharge tend to occur, possibly burning a resin.

If the distance exceeds 25 cm, a resistance between the electrodes increases, interfering with the flow of electrons, so that a resin tends to be not easily electrified.

[0021] A composite-resin-formed product supplied to the supply-side electrode preferably is supplied in a solid state. When the product passes through the supply-side electrode, the composite-resin-formed product may be heated to be in a molten or semi-molten (soften) state. The product preferably is supplied in a fiber state. When the composite-resin-formed product is in a fiber state, a shape of a cross section of the ultrafine composite fiber tends to be analogous to a shape of a cross section of the fiber-state composite-resin-formed product. Thus, this makes it possible to control easily a cross-sectional shape of an ultrafine composite fiber obtained by electrospinning. The composite-resin-formed product (composite fiber) preferably is a monofilament, a multifilament composed of a plurality of monofilaments bundled, or a tow. In the foregoing, the "multifilament" refers to that composed of 2 to 100 filaments, and the "tow" refers to that composed of more than 100 filaments. Among these, from the viewpoint of electrospinning properties, the composite-resin-formed product preferably is a multifilament or a tow composed of 2 to 1,000 monofilaments bundled.

[0022] A composite-resin-formed product (e.g., a solid composite fiber) is irradiated with a laser beam immediately after the beam passes the supply-side electrode, whereby the composite-resin-formed product is heated and melted. Even in the case where the composite-resin-formed product is molten or semi-molten preliminarily, the composite-resin-formed product is made to have a low viscosity by additional heating and melting in the space between the electrodes, whereby extensibility can be improved. Examples of the laser beam include a laser beam emitted from light sources such as a YAG laser, a carbon dioxide gas (CO_2) laser, an argon laser, an excimer laser, and a helium-cadmium laser. Among these, the laser beam emitted from a carbon dioxide gas laser is preferred, from the viewpoint of a high heat absorptivity with respect to a polymer resin, a high power source efficiency, and a high composite fiber melting property. The laser beam has a wavelength of, for example, 200 nm to 20 μm, preferably 500 nm to 18 μm, more preferably 1 to 16 μm (particularly 5 to 15 μm) approximately As another means for heating and melting the composite-resin-formed product, a known means such as a means of near infrared radiation in a wavelength range of 780 nm to 2.5 μm may be used.

[0023] The method for irradiation with a laser beam is not limited particularly, but the method of irradiation with a laser beam in a spotlight form is preferred, since the composite fiber is irradiated with a beam locally. Abeam diameter of the laser beam irradiating a composite fiber can be selected according to the shape of the composite fiber. A specific beam diameter may be, in the case of a linear-form resin for example (e.g., monofilament, multifilament, tow, etc), greater than an average diameter of the linear-form resin, and is in a range of, for example, 0.5 to 30 mm, preferably 1 to 20 mm, more preferably 2 to 15 mm (particularly 3 to 10 mm). The beam diameter may be such that a ratio of the beam diameter to the average diameter of the linear-form resin is 1:1 to 100:1, preferably 1:2 to 1:50, and more preferably 1:3 to 1:30 (particularly 1:5 to 1:20).

[0024] In the case where the composite-resin-formed product is irradiated with a laser beam after the beam passes through the supply-side electrode, whereby the product is heated and melted, a distance between an end on a side of the supply-side electrode from which the composite-resin-formed product comes out and a portion of the product irradiated with the laser beam is 1 to 6 mm preferably. More preferably the distance is 2 to 4 mm. If the distance is less than 1 mm, the laser-irradiated portion is very close to the electrode, thereby causing the temperature of the electrode to rise. As a result, the resin-formed product is heated longer in time, which could cause the resin to be decomposed. If the distance exceeds 6 mm, the amount of electric charges in the resin-formed product electrified when the product passes through the supply-side electrode decreases, and even if such a portion of the product is heated and molten by the laser beam, the resin in the molten state is not easily extended uneasily toward the collection-side electrode.

[0025] An output power of the laser beam necessary for melting the composite-resin-formed product may be controlled so that the product can be heated to a temperature that is not lower than a melting point of a resin having the highest melting point among resins composing the composite-resin-formed product, and at which none of the resins composing the composite-resin-formed product is ignited or decomposed In short, the composite-resin-formed product may assume a viscous state. The temperature at which the composite-resin-formed product assumes a viscous state varies with the rate of supply of the composite-resin-formed product, the output power of the laser beam, the distance between the laser and the composite-resin-formed product, and the fineness of the composite-resin-formed product. In the case of a laser beam, the heating temperature preferably is 160°C to 1200°C, and more preferably 600°C to 800°C. If the temperature is lower than 160°C, the amount of heat for heating the product is insufficient, whereby melting failures occur. This causes the product to fail to assume a viscous state, making it difficult to form the product into an ultrafine fiber. If the temperature is over 1,200°C, the resin might be burned or decomposed, which makes it impossible to form the resin into fibers. The specific output power of the laser beam may be selected appropriately depending on the physical property (melting point), shape, fineness, and supply rate of the composite-resin-formed product used. The output power thereof may be, for example, 3 to 100 mA, preferably 3 to 50 mA, and more preferably 6 to 40 mA If the output power of the laser beam is less than 3 mA, the power is not enough to melt the resin. Irradiation conditions of the laser beam may be controlled by the melting point of the composite-resin-formed product. In the case where, however, the composite-resin-formed product is a filament having a small diameter and a high voltage is applied thereto, the control of the conditions is performed by the control of the output power of the laser beam from the viewpoint of conveniences. One or a plurality of points around the composite-resin-formed product is irradiated with the laser beam.

[0026] The composite-resin-formed product molten is extended toward the collection-side electrode in accordance with the electric attraction force. Here, the extension ratio is 100 to 1000 times, preferably 200 to 800 times, and more preferably 300 to 500 times. The product is extended at such a ratio, thereby being formed into ultrafine fibers. Here, hyperextension possibly could occur. As a result, the diameter of the ultrafine composite fiber containing a resin having a volume specific resistance exceeding 10^{15} Ω·cm can be decreased to 5 μm or less. Under preferable conditions, the diameter can be decreased to 3 μm or less, and under more preferable conditions, the diameter can be decreased to 1 μm or less.

[0027] In the present invention, the composite-resin-formed product preferably is of a sea-island type, a splittable type, or a core-sheath type as viewed in a cross section thereof. When the product has such a cross section, a resin that easily is electrified upon passing through the supply-side electrode can be arranged selectively.

[0028] It should be noted that the fiber diameter is derived from a diameter of the fiber when the fiber has a round cross section. The fiber diameter (diameter) is determined from a fiber cross section or a fiber side face.

[0029] In the case where the fiber has a cross section in an irregular shape (polygonal, elliptic, hollow, "C"-shaped, "Y"-shaped, "X'-shaped, or indefinite-shaped cross section, etc.), a circular shape having the same area as that of the cross section of the fiber is given and the diameter of the round shape is determined, which is assumed to be the diameter of the fiber. Therefore, in the case of an oddly-shaped fiber, the fiber diameter cannot be derived from the side face of the fiber.

[0030] The resin exposed on 30 % or more of the surface of the part of the composite-resin-formed product that is passed through the supply-side electrode preferably has a volume specific resistance of 10^{6} to 10^{14} Ω·cm. More preferably, the resistivity is 10^{7} to 10^{14} Ω·cm. With this configuration, the composite-resin-formed fiber is electrified easily when it is passed through the supply-side electrode.

[0031] Further, even a resin having a volume specific resistance of more than 10^{15} Ω·cm could possibly be made suitable for electrospinning, by decreasing an apparent volume specific resistance using one of the following techniques alone or a plurality of the same in combination by the time when it is electrospun: processing techniques for decreasing a resistivity of a resin, such as kneading a master batch that causes a volume specific resistance of a resin to decrease (e.g., a master batch containing a filler such as carbon or a metal salt), corona processing, fluorine processing, and electret processing; and processing techniques of coating the composite-resin-formed product with an oil agent that allows a volume specific resistance to decrease (e.g., an anionic surfactant, a cationic surfactant, or a nonionic surfactant) or immersing the composite-resin-formed product with such an oil agent.

[0032] It should be noted that the "apparent volume specific resistance" refers to a value obtained by determining a volume specific resistance (ASTM D-257) of a sample obtained by subjecting a resin portion of the sample to the aforementioned processing technique, the volume specific resistance (ASTM D-257) being determined usually with respect to a resin.

[0033] In other words, the volume specific resistance is not a volume specific resistance of a resin itself, but a value indicative of a volume specific resin of a processed resin.

[0034] A configuration in which a resin having a volume specific resistance of 10^{15} Ω·cm or less is exposed on 30 % or more of a surface of a composite-resin-formed product has the following advantage: even if a resin having a volume specific resistance of more than 10^{15} Ω·cm and therefore becoming electrified uneasily is included in the configuration, the resin having a volume specific resistance of 10^{15} Ω·cm or less is sufficiently electrified and electrospun, and the influences of the same cause even the resin having a volume specific resistance of more than 10^{15} Ω·cm to be electrospun and extended at the same time.

[0035] It is essential only that a resin having a volume specific resistance of 10^{15} Ω·cm or less is exposed on 30 % or more of a surface of a composite-resin-formed product, which makes it possible to form an ultrafine composite fiber even with a combination of a resin having a high volume specific resistance and a resin having a low volume specific resistance, and under preferable conditions. This could make it possible to obtain an ultrafine composite fiber having a diameter of 3 μm or less.

[0036] Needless to say, there is no problem in the combination of resins having volume specific resistances of 10^{15} Ω·cm or less.

[0037] In the present invention, a proportion of a resin having a volume specific resistance of 10^{15} Ω·cm or less is 10 percent by mass (mass%) or more, preferably 30 mass% or more, and more preferably 50 mass% or more in a composite-resin-formed product. When the proportion of the above-described resin is in this range, an ultrafine composite fiber can be obtained stably. When the proportion of the resin is less than 10 mass%, even the provision of the resin on the surface of the composite-resin-formed product is not effective for achieving ultrafineness, since an uneasily-electrified resin having a volume specific resistance of more than 10^{15} Ω·cm, which is in a large part due to the small total amount of resins in the composite-resin-formed product, has to be extended toward the collection-side electrode upon electrospinning, which makes it difficult to form an ultrafine fiber.

[0038] Even in the case where an uneasily electrified resin having a volume specific resistance of 10^{16} Ω·cm or more, such as olefin (e.g., polypropylene, or polyethylene) is provided, excellent electrospinning can be performed if there is 10 mass% or more of a resin having a volume specific resistance of 10^{15} Ω·cm or less. If a resin having a volume specific resistance of 10^{16} Ω·cm or more, such as olefin, and a resin having a volume specific resistance of 10^{15} Ω·cm or less are used, a preferable proportion of the resin having a volume specific resistance of 10^{15} Ω·cm or less is 10 mass% to 70 mass%. More preferably, the proportion is 35 mass% to 60 mass%. If the resin having a volume specific resistance of 10^{15} Ω·cm or less accounts for less than 10 mass%, the ultrafineness is not easily achieved, and if the resin accounts for more than 70 mass%, there is no problem in electrospinning, but it is difficult to stably obtain a composite-resin-formed product as a raw material, since an olefin portion is extremely small when the composite-resin-formed product is produced.

[0039] Further, it is preferable that the component exposed on 30 % or more of the surface of the composite-resin-formed product is at least one selected from ethylene-vinyl alcohol copolymers, polyesters, nylons, and polyurethanes, and that a component of the other phase is at least one selected from polyolefins, polyesters, nylons, and polylactic acids.

[0040] The component exposed on 30 % or more of the surface of the composite-resin-formed product particularly preferably is an ethylene-vinyl alcohol copolymer, from the viewpoint that an ethylene-vinyl alcohol copolymer can be highly electrified and has a great extensibility upon electrospinning and has excellent biocompatibility. The ethylene-vinyl alcohol copolymer has a volume specific resistance of, preferably, 10^6 to 10^{15} Ω·cm, more preferably 10^7 to 10^9 Ω·cm, and further more preferably $10^{7.5}$ to $10^{8.5}$ Ω·cm.

[0041] The ethylene-vinyl alcohol copolymer is obtained by saponification of an ethylene-vinyl acetate copolymer The content of ethylene in the ethylene-vinyl alcohol copolymer is not limited particularly, but preferably is 25 to 70 percent by mole (mol%), and more preferably 30 to 65 mol%. Commercially available examples of the same include "EUAL" (trade name) produced by Kuraray Co., Ltd., "Soarnol" (trade name) produced by Nippon Synthetic Chemical Industry Co., Ltd., and such commercially available products can be used in the present invention. The melting point of an ethylene-vinyl alcohol copolymer varies with the content of ethylene and vinyl alcohol contained therein, and for example, an ethylene-vinyl alcohol copolymer containing 38 % of ethylene has a melting point of 171°C, and an ethylene-vinyl alcohol copolymer containing 55 % of ethylene has a melting point of 142°C. The ethylene-vinyl alcohol copolymer used may be an ethylene-vinyl alcohol copolymer of a single type, or alternatively, a mixture of two or more types of ethylene-vinyl alcohol copolymers that are different in the content of ethylene.

[0042] The ethylene-vinyl alcohol copolymer preferably has a melting point of 100°C to 190°C, more preferably 120°C to 180°C, and further preferably 140°C to 175°C. When the melting point of ethylene-vinyl alcohol copolymer is 100°C or higher, the composite-resin-formed product is easily formed into fibers, and when the melting point of ethylene-vinyl alcohol copolymer is 190°C or lower, the thermal bonding of intersection points of fibers can be performed at a relatively low temperature.

[0043] The component of the other phase is not limited particularly, and, for example, one of the following, or a mixture of two or more of the following, may be used as the component: polyolefins such as polyethylene, polypropylene, polybutene, polymethylpentene, polytrimethylene terephthalate, ethylene-propylene copolymer; polyesters such as polyethylene terephthalate, and polybutylene terephthalate; polyamides such as nylon 6, and nylon 66; and polystyrene. The component of the other phase preferably has a melting point in a range of 150°c to 300°C, from the viewpoint of obtaining a fiber strength. It should be noted that examples of a polymer having a melting point in a range of 150°C to 300°C include polypropylene (160°C to 175°C), polymethyl pentene (230°C to 240°C), polyethylene terephthalate (212°C to 265°C), polybutylene terephthalate (220°C to 267°C), nylon 6 (210°C to 220°C), and nylon 66 (255°C to 265°C) ("Plastic Data Book", edited by Asahi Kasei Amidas Corporation, Plastics Editorial Section, published on December 1, 1999 by Kogyo Chosakai Publishing Inc., pages 7 to 11).

[0044] Particularly a composite fiber such as a core-sheath-type composite fiber, a sea-island-type composite fiber, or a splittable-type composite fiber in which a component that is exposed on 30 % or more of a surface is an ethylene-vinyl alcohol copolymer and a composite of the other phase is a polylactic acid can be used in the following materials to be embedded in a living body, since both components are highly biocompatible and such a composite fiber does not contain a solvent in the fiber. The exemplary materials in which the foregoing composite fiber can be used include materials to be embedded in a living body such as surgical sutures, stents, and artificial joints; medical materials such as hematostatic materials, cell culture substrates, masks, and body fluid absorbing pads; and cosmetics such as face masks, and interpersonal wipes.

[0045] The ultrafine composite fibers preferably do not contain solvents in the fiber itself. More preferably, the resin composing the ultrafine composite fiber does not contain an organic solvent or a component originating from an organic solvent. In the case where the ultrafine composite fiber does not contain a solvent in the fiber itself, it can be applied to a field of products brought into contact with humans and a medical field, since a solvent or a component originating from such a solvent, which are generally toxic with respect to humans and animals, never is eluted from such a fiber. It should be noted that the "component originating from an organic solvent" refers to a component such as a solvent chemically changed by heat or electric charges.

[0046] In order to obtain a configuration in which the ultrafine composite fiber does not contain any solvent in the fiber itself, the composite-resin-formed product in a solid state may contain no solvent. The composite-resin-formed product not containing a solvent is obtained by, for example, spinning a resin by a conventional melt-spinning method, in the case where the composite-resin-formed product is in a fiber form.

[0047] The "solvent" refers to that which can dissolve or disperse a resin therein and exhibits toxicity with respect to humans and animals. Examples of the solvent include hexane, benzene, toluene, diethyl ether, chloroform, ethyl acetate, tetrahydrofuran, methylene chloride, acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, acetic acid, 1-butanol, 1-propanol, 2-propanol, methanol, ethanol, and formic acid. As described above, the ultrafine composite fiber preferably does not contain a solvent in the fiber itself.

[0048] The ultrafine composite fiber preferably has a diameter of 20 μm or less, more preferably a diameter in a range of 0.2 to 17 μm, and particularly preferably a diameter in a range of 0.5 to 5μm. The ultrafine fiber having a diameter in such a range is difficult to obtain by a normal melt-spinning technique.

[0049] A composite fiber obtained by electrospinning preferably has phase separation of two components, that is, one component that is exposed on 30 % of or more a surface of the fiber, and another component having the other phase. The phase separation causes the components to easily separate from each other, whereby an ultrafine fiber can be obtained easily.

[0050] The ultrafine composite fiber preferably is of a sea-island type, a splittable type, or a core-sheath type as viewed in its cross-section. In the case where the composite-resin-formed product is a multifilament or a tow, an ultrafine fiber obtained has such a cross-sectional shape that the multifilament or the two becomes one fiber in some cases. An exemplary case is as follows: in the case where a tow composed of 600 core-sheath-type composite fibers bundled is used as a composite-resin-formed product, an ultrafine composite fiber obtained by extension through electrospinning is of a sea-island type in which the number of segments of an island component is 1 to 600 apparently. An ultrafine fiber having such a cross-sectional shape is also included in examples of the sea-island type and/or core-sheath type composite fiber in the present invention.

[0051] The composite fiber preferably contains 30 to 90% of the component exposed on 30% or more of the surface, and 70 to 10 % of the component of the other phase. More preferably, the ratio of the former fiber to the latter fiber is 35:65 to 60:40. When the ratio is in the foregoing range, the product is easily electrified in the space between the electrodes, whereby excellent spinning properties are achieved.

[0052] It also is possible to remove any of the components that compose the ultrafine composite fiber obtained in the present invention, so as to obtain an ultrafine fiber composed of the remaining components. This makes it possible to obtain a further finer fiber. Still further, this also makes it possible to obtain an ultrafine fiber containing only a specific polymer that is intended to remain.

[0053] In the sea-island structure or the splittable structure that can be split into a multiplicity of components, the segment unit of each individual resin component is small (as viewed in a cross-section, the structure is a group of very small units). Therefore, it is considered that the structure is influenced easily by the electrification of the resins at the supply-side electrode, and by the heating and melting of the resins by a laser beam, and therefore, which allows the entire segments to be homogeneously influenced.

[0054] A finer fiber may be taken out from the obtained ultrafine composite fiber by further removing either one of the resin components. The removing method is not limited particularly, and a known method using an acid, an alkali, an organic solvent, or the like may be used. The removing method may be selected appropriately, according to a solubility product of a resin with respect to a solvent.

[0055] Particularly in the case of a core-sheath-type composite fiber in which the sheath and the core are formed with an ethylene-vinyl alcohol copolymer and a polylactic acid, respectively, water at 80°C to 100°C, or an alkaline aqueous solution obtained by dissolving potassium hydroxide, sodium hydroxide, or sodium hydrogencarbonate in water may be used, in order to remove the polylactic acid. In order to remove the ethylene-vinyl alcohol copolymer, dimethyl sulfoxide (DMSO) at normal temperature (20°C to 30°C), isopropyl alcohol heated to 60°C, 2-propanol or the like may be used.

[0056] The extended ultrafine composite fiber is allowed to have various shapes depending on the method for heating the composite-resin-formed product as a raw material. For example, homogeneous heating allows a fiber having a cross-section in a shape analogous to that of the composite-resin-formed product to be obtained. Heating the composite-resin-formed product from one side causes bias in a molten state as viewed in the cross-section, thereby allowing a fiber having an unsymmetrical cross-section shape to be obtained. The reason for this is considered as follows: one resin side face is molten sufficiently thereby being extended, while an opposite side face has a greater melting viscosity as compared with the other side and is not extended sufficiently, which results in that an ultrafine composite fiber obtained has a shape different from that of the composite-resin-formed product. Specifically the circular cross-section of the composite-resin-formed product is turned into a C-letter-shaped cross-section of the obtained ultrafine composite fiber, or the core component is split into two or more, whereby a further finer fiber could be obtained

[0057] The ultrafine composite fibers are accumulated on the collection-side electrode, whereby a fiber structure can be obtained. The fiber structure in its accumulated state may be collected directly from the collection electrode. Alternatively, the collection-side electrode may be formed in a conveyer form, and the position at which fibers are accumulated may be shifted continuously so that a sheet-form fiber structure can be produced continuously. Further alternatively, another method of collecting a fiber structure is as follows: a metal mesh, a woven fabric, a nonwoven fabric, or a sheet of paper is arranged on the collection-side electrode, and ultrafine composite fibers are accumulated on such a sheet-form material, whereby a laminate-like fiber structure can be obtained. Further, fibers may be accumulated in a non-sheet shape, such as an article having a certain thickness such as a cartridge-type filter. In the present invention, the "fiber structure" refers to a fiber accumulation such as an article having a certain thickness, for example, a fiber sheet, a filter, and the like.

[0058] A physical object to be accumulated preferably is grounded so as to have no potential difference from the collection-side electrode. If no problem arises in the production, however, they do not have to be grounded intentionally, and may be held slightly afloat on the collection-side electrode.

[0059] In the present invention, a combination of EVOH and PP also is a preferable example. From an ultrafine composite fiber obtained, the ethylene-vinyl alcohol copolymer (EVOH) may be removed further, so that a polypropylene (PP) fiber alone can be obtained. The removal of ethylene-vinyl alcohol copolymer (EVOH) is achieved by, for example, immersing the obtained fiber in an aqueous solution containing 2-propanol, or dimethyl sulfoxide (DMSO). The polypropylene ultrafine fiber thus obtained as a result of the removing of EVOH possibly could be further finer than the foregoing ultrafine composite fiber. The polypropylene ultrafine fiber preferably has a fiber diameter of 13 μm or less, and more preferably, 5 μm or less. For example, an ultrafine composite fiber formed to have a diameter of about 1.2 μm and a core-sheath ratio of 50:50 under preferable conditions may be subjected to removal of ethylene-vinyl alcohol copolymer, whereby a further finer polypropylene ultrafine fiber having a diameter of 0.3 μm can be obtained.

[0060] The extended ultrafine composite fiber and/or polypropylene as a core component is allowed to have various shapes depending on the method for heating the composite-resin-formed product as a raw material. For example, homogeneous heating allows a fiber having a cross-section in a shape analogous to that of the composite-resin-formed product to be obtained. Heating the composite-resin-formed product from one side causes bias in a molten state as viewed in the cross-section, thereby allowing a fiber having an unanalogous cross-section shape to be obtained. The reason for this is considered as follows: one resin side face is sufficiently melted thereby being extended, while an opposite side face has a greater melting viscosity as compared with the other side, which results in that an ultrafine composite fiber has a shape different from that of the composite-resin-formed product. Specifically, the circular cross-section of the composite-resin-formed product is turned into a C-letter-shaped cross-section of the obtained ultrafine composite fiber, or the core component is split into two or more, whereby a further finer fiber could be obtained

[0061] The following will describe a manufacturing method, referring to the drawings. FIG. 1 specifically illustrates an electrospinning device according to an example of the present invention. In this electrospinning device 11 a voltage generator 3 applies a voltage across the supply-side electrode 1 and the collection-side electrode 2, and a laser irradiation equipment 4 emits a laser beam in a direction indicated by an arrow X toward a position immediately under the supply-side electrode 1. A distance between the supply-side electrode and the collection-side electrode preferably is 2 to 25 cm. The distance is more preferably 5 to 20 cm. If the distance between the electrodes is smaller than 2 cm, sparks or corona discharge occur due to the application of a high voltage. If the distance is greater than 25 cm, the effect of electric attraction force decreases, and there is a possibility that a molten fiber is not extended toward the collection-side electrode. A composite fiber 7 as a raw material is taken out of housed fibers 6 contained in a container 5, passes via guides 8 and 9, and a supply roller 10, and thereafter is supplied to the electrospinning device 11. The composite fiber as a raw material may be supplied from a bobbin around which the material is wound. The composite fiber 7 is electrified when passing the supply-side electrode. The composite fiber 7, in this electrified state, is irradiated with the laser beam emitted from the laser irradiation equipment 4 in the arrow X direction, so as to be heated and melted, immediately under the supply-side electrode 1, and is extended toward the collection-side electrode by the electric attraction force. Here, the composite fiber is extended in a direction indicated by an arrow Y, becoming ultrafine. "12" denotes a fiber structure (sheet) obtained from accumulation of the composite fibers that have been made ultrafine.

[0062] In FIG. 1, in the case where a plurality of composite fibers as raw materials are used, for example, six composite fibers 7a to 7f as shown in FIG. 11, a position immediately under the supply-side electrode 1 may be irradiated by the laser irradiation equipment 4 via a reflection plate mirror 13. Here, by operating the reflection plate mirror 13, the laser beam is swung by an angle θ between a direction indicated by an arrow X1 and a direction indicated by an arrow X2. This allows all of the composite fibers 7a to 7f as raw materials to be irradiated with a laser beam. This makes spinning possible even if a plurality of composite fibers or a nonwoven fabric is used as the composite-resin-formed product.

[0063] FIG. 2 schematically illustrates another electrospinning device according to another example of the present invention. This electrospinning device 20 applies a voltage from a high-voltage terminal 22 to a supply-side electrode 21 attached to a polyimide resin plate 23. The supply-side electrode preferably is in a needle shape. In such a needle electrode, the needle length preferably is 5 to 30 mm, and more preferably 10 to 20 mm. If the needle length is less than 5 mm, the direction in which the composite fiber as a raw material is to be extruded is not set, which makes it difficult to guide the composite fiber to the laser beam irradiation position. If the needle length is more than 30 mm, a resistance is applied to the raw material fiber when it passes through the needle, and the raw material fiber cannot be extruded smoothly. The needle preferably has an inner diameter of 10 to 2000 μm, and more preferably 20 to 1650 μm. If the inner diameter is less than 20 μm, the number of fibers to be processed decreases, and also it is difficult to pass the raw material fibers therethrough since it is narrow. If the inner diameter exceeds 2000 μm, there could be a difficulty in electrifying the fibers sufficiently, particularly inward parts thereof. The needle electrode does not have to be one in number. In the case where a large amount of a material is to be electrospun at one time, a bundle of a plurality of thin needles, rather than one thick needle, is advantageous regarding the guiding property for guiding raw material fibers toward the laser beam irradiation position. The number of needles preferably is 1 to 1,000, and more preferably 1 to 300. The collection-side electrode 24 is earthed. Aposition immediately under the supply-side electrode 21 is irradiated with laser beams in directions indicated by arrows X1 and X2 from a plurality of laser irradiation equipment 25. Composite fibers 7 as a raw material are electrified when passing the supply-side electrode 21. When the composite fibers 7 in this electrified state are irradiated, at a position immediately under the supply-side electrode 21, with laser beams emitted by the laser irradiation equipment 25 in the directions indicated by arrows X1 and X2, the composite fibers 7 are heated and molten, and extended toward the collection-side electrode 24 by an electric attraction force. Here, the composite fibers 7 are extended several hundred times in length, for example, in a direction indicated by the arrow Y, thereby being made ultrafine. "29" denotes an accumulation of composite fibers that have been made ultrafine. In a heating-extending region 28, if the temperature decreases with the increasing proximity from the laser beam irradiation position to the collection-side electrode, the resin starts crystallizing while the composite fibers are being extended, which makes it difficult to draw the resin to make finer fibers. Therefore, the heating-extending region 28 preferably is heated by transmitting heat from a heating means such as a heater or an oil tank, so that the fibers are not cooled rapidly. The temperature of the heating-extending region depends on the type of the fiber, but the region may be heated to a temperature in a range from a glass-transition point to a melting point of a synthetic fiber. Specifically, the temperature in the heating-extending region preferably is 50 to 300°C, and more preferably 100 to 200°C. The heating preferably is performed by a method using electricity, since minute temperature adjustment is performed easily by such a method.

[0064] FIG. 12A is a cross-sectional view of a composite fiber as a composite-resin-formed product as a raw material used in one example of the present invention. This composite fiber 70 is a monofilament that has a core-sheath structure having a core 71 made of polypropylene (PP) and a sheath 72 made of an ethylene-vinyl alcohol polymer (EVOH). FIG. 12B is a cross-sectional view of an ultrafine composite fiber obtained in one example of the present invention. This composite fiber 73 has a core-sheath structure having a polypropylene (PP)-made core 74 that is made ultrafine, and an ethylene-vinyl alcohol copolymer (EVOH)-made sheath 75 that is made ultrafine.

[0065] FIG. 13A is a cross-sectional view of a composite fiber that is a composite-resin-formed product as a raw material used in another example of the present invention. In this example, a composite fiber 76 is a multifilament obtained by temporarily fixing a plurality of core-sheath-type filaments into a bundle, each filament having a core 77 made of polypropylene (PP) and a sheath 78 made of an ethylene-vinyl alcohol copolymer (EVOH). The filaments can be fixed temporarily to be bundled, for example, by pouring boiled water over a plurality of composite fibers. FIG. 13B is a cross-sectional view of an ultrafine composite fiber obtained in another example of the present invention. The composite fiber 80 has a core-sheath structure having polypropylene (PP)-made cores 81 that are made ultrafine and ethylene-vinyl alcohol copolymer (EVOH)-made sheaths 82 that are made ultrafine.

Example

[0066] The following describes the present invention in more detail, while referring to Examples. It should be noted that the present invention is not limited to Examples shown below.

1. Raw material resin

[0067] The following resins are used:

(1) Polyethylene terephthalate (PET): "T200E" (trade name) produced by Toray Industries, Inc. having a melting point of 255°C and an intrinsic viscosity (IV) of 0.64.
(2) Polypropylene (PP): "SA03" (trade name) produced by Japan Polypropylene Corporation, having a melting point of 161°C, and a melt flow rate of 30 determined according to JIS-K-7210 (MFR; temperature upon determination: 230°C, load: 21.18 N (2.16 kgf))
(3) Nylon 6 (Ny): "1015B" (trade name) produced by Ube Industries, Ltd., having a molecular weight of 15000
(4) High-density polyethylene (PE): "HE481" (grade name) produced by Japan Polyethylene Corporation, having a melting point of 130°C, and a melt flow rate of 12 determined according to JIS-K-7210 (MFR; temperature upon determination: 190°C, load: 21.18 N (2.16 kgf))
(5) Ethylene-vinyl alcohol copolymer (EVOH) used in Experiment No. 10: "K3835BN" produced by Nippon Synthetic

Chemical Industry Co., having a melting point of 171°C, and a melt flow rate of 35 determined according to JIS-K-7210 (AIM; temperature upon determination: 230°C, load: 21.18 N (2.16 kgf).

(6) Ethylene-vinyl alcohol copolymer (EVOH) used in Experiments Nos. 11 and 12: "SG544" produced by Nippon Synthetic Chemical Industry Co., having a melting point of 170°C and a melt flow rate of 45 determined according to JIS-K-7210 (MFR; temperature upon determination: 230°C, load: 21.18N (2.16 kgf)).

(7) Polylactic acid (PLA) used in Experiments Nos. 11 and 12: "U'z S-32" produced by Toyota Motor Corp., having a melting point of 179°C and a volume specific resistance of 9×10^{16} (Ω.cm).

2. Production of Raw-Material Composite-Resin-Formed Product

[0068] A raw-material composite-resin-formed product was obtained as follows: an unextended fiber was obtained by conventional melt-spinning, and was used as a composite-resin-formed product (composite fiber) as a raw material.

3. Electrospinning

[0069] As an electrospinning device, the device shown in FIG. 2 was used under the conditions as shown in Table 2.
Laser device: PIN-30R manufactured by Onizca Glass Co., Ltd. (rated output: 30 W, wavelength: 10.6 μm, beam diameter: 6 mm)
Voltage applied across electrodes: 35 kV
Distance between electrodes: 8 cm
Raw material fiber feeding rate: 6.0 mm/min
Ambient temperature: 28°C
Laser intensity: 100 V, 8mA
Distance between supply-side electrode and laser irradiation position: 4 mm
Supply-side electrode: UN series, 20G×15 (as one unit), manufactured by Unicontrols Co., Ltd.

4. Method for Measuring Fiber Diameter

[0070] Side faces of fibers were observed using a scanning electron microscope (SEM, "S-3500" (trade name) manufactured by Hitachi, Ltd., magnification: 1500 times), and an average was determined based on measurement results of arbitrarily selected 30 fibers.

Example 1

[0071] A first component, a second component, a cross-sectional structure, a resin ratio, and a fiber diameter of a raw-material composite-resin-formed product of each of Experiments Nos. 1 to 12 are as shown in Table 2.

[0072] Ultrafine fibers were produced by the electrospinning method shown in FIG. 2, with use of these raw-material composite-resin-forined products. The electrospinning conditions and the fiber diameters of the obtained ultrafine fibers are shown collectively in Table 2.

[0073]

[Table 2]

Experiment No.	Raw-material fiber					Spinning condition					Fiber diameter after electrospinning (µm)	Removed Component	Removal Ratio (%)	Fineness after removal (µm)
	Core component	Sheath component	Cross-sectional structure	Resin ratio	Fiber diameter (µm)	Electric field intensity (kV)	Distance between Electrodes (cm)	Laser intensity (mA)	Spinning rate (mm/min)	Heating-extending region temperature °C)				
1	PET	Ny	Core-sheath	50/50	360	32.5	20	20	5.41	160	4.70	–	–	–
2	Ny	PET	Core-sheath	30/70	410	32.5	20	40	5.41	160	–	–	–	–
3	Ny	PET	Core-sheath	50/50	410	32.5	20	40	5.41	160	0.56	–	–	–
4	Ny	PET	Core-sheath	70/30	410	32.5	20	40	5.41	160	–	–	–	–
5	PET	PE	16-part split	50/50	120	32.5	20	40	20.3	160	1.93	–	–	–
6	PET	PE	16-part split	50/50	220	32.5	5	16	5.41	160	1.08	–	–	–
7 (Comp. Ex.)	PET	PE	Core-sheath	50/50	420	32.5	5	20	5.41	160	Unspinnable	–	–	–
8	PE	PET	Core-sheath	50/50	420	32.5	5	20	5.41	160	2.15	–	–	–
9 (Comp. Ex.)	PP	PE	Core-sheath	50/50	220	32.5	20	10	5.41	160	Unspinnable	–	–	–
10	PP	EVOH	Sea-island 37 islands	50/50	360	32.5	20	20	5.41	160	2.21	–	–	–
11	PLA	EVOH	16-part split	50/50	350	32.5	20	20	5.41	None (Normal Temp.)	1.21	PLA	100	0.78
12	PLA	EVOH	Core-sheath	50/50	400	32.5	20	20	5.41	None (Normal Temp.)	1.85	EVOH	100	1.12

[0074] Solvent removal conditions of Experiments Nos. 11 and 12 in Table 2 are as follows:

A Removal of EVOH
1 g of a composite fiber obtained by electrospinning was placed in 20 ml of dimethyl sulfoxide, and was stirred at normal temperature (20 to 30°C) for 15 hours. Thereafter, suction filtration of a solvent and substitution cleaning with methanol were performed, followed by drying at normal temperature for one hour, whereby a PLA fiber was obtained.
B. Removal of PLA
1 g of a composite fiber obtained by electrospinning was placed in 200 ml of 5 mass% aqueous solution of potassium hydroxide, and was stirred at 80°C for 15 hours. Thereafter, suction filtration of a solvent and substitution cleaning with pure water were performed, followed by drying at 60°C for one hour, whereby an EVOH fiber was obtained.

[0075] As is clear from Table 2, in each of Experiments Nos. 1 to 6, 8, and 10 to 12, a part of the composite-resin-formed product that passed through the supply-side electrode had a resin having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less on 50 % or 100 % of a surface of the foregoing part, which resulted in that excellent spinning properties were achieved, and ultrafine fibers were obtained. No solvent was present in the obtained composite fibers.

[0076] In contrast, in each of Experiments Nos. 7 and 9, the sheath component of the composite fiber was polyolefin, and therefore, the resin having a volume specific resistance of 10^{15} $\Omega\cdot$cm or more and not easily electrified was present on 100 % of the surface of the composite fiber. As a result, it was impossible to perform spinning.

[0077] A scanning electron photomicrograph (SEM, magnification: 20,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 3 is shown in FIG. 3, and a specific cross-sectional view of the fiber is shown in FIG. 4. In FIG. 4, "30" denotes an ultrafine composite fiber of a core-sheath structure, "31" denotes Ny, and "32" denotes PET. Since it was a core-sheath type composite fiber in which PET having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less was the sheath component and hence was exposed on 100 % of a surface of the fiber, excellent spinning properties were obtained, and the extended fiber was in a phase separation state. In the present case under these conditions, since the composite-resin formed product having a core-sheath structure was used as a raw material, an ultrafine composite fiber having an analogous shape was obtained.

[0078] A scanning electron photomicrograph (SEM, magnification: 10,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 5 was shown in FIG. 5, and a schematic cross-sectional view of the fiber is shown in FIG. 6. In FIG. 6, "40" denotes an ultrafine composite fiber having a 16-part-split structure, "41" denotes PET, and "42" denotes PE. Since the fiber was a splittable-type composite fiber in which Ny having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less was used and the resin having a low volume specific resistance was exposed on 50 % of the surface, excellent spinning properties were exhibited, and the extended fiber was in a phase separation state. In the present case, since the splittable-type composite-resin-formed product was used as a raw material, a splittable-type ultrafine composite fiber having an analogous shape was obtained.

[0079] A scanning electron photomicrograph (SEM, magnification: 4,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 6 of the present invention was shown in FIG. 7, and a cross-sectional view of the fiber is shown in FIG. 8. In FIG. 8, "50" denotes an ultrafine composite fiber having a 16-part-split structure, "51" denotes PET, and "52" denotes PE. Since the fiber was a splittable-type composite fiber in which Ny having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less was used and the resin having a low volume specific resistance was exposed on 50 % of the surface, excellent spinning properties were exhibited, and the extended fiber was in a phase separation state.

[0080] A scanning electron photomicrograph (SEM, magnification: 10,000 times) of a cross section of an ultrafine fiber obtained in Experiment No. 10 was shown in FIG. 9, and a schematic cross-sectional view of the fiber is shown in FIG. 10. In FIG. 10, "60" denotes an ultrafine composite fiber having a sea-island structure, "61" denotes PP, and "62" denotes EVOH. It is a sea-island-type composite fiber in which EVOH having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less was used and the resin having a low volume specific resistance was exposed on 100 % of the surface, excellent spinning properties were exhibited, and the extended fiber was in a phase separation state. In the present case under these conditions, since a sea-island-type composite-resin-formed product was used as a raw material, a sea-island-type ultrafine composite fiber having an analogous shape was obtained.

[0081] The ultrafine fiber obtained in Experiment No. 11 was substantially identical to those of FIGS. 5 and 6. In FIG. 6, "40" denotes an ultrafine composite fiber having a 16-part-split structure, "41" denotes PLA, and "42" denotes EVOH. Since the fiber was a splittable-type composite fiber in which EVOH having a volume specific resistance of 10^{15} $\Omega\cdot$cm or less was used and the resin having a low volume specific resistance was exposed on 50 % of the surface, excellent spinning properties were exhibited, and the extended fiber was in a phase separation state. In the present case under these conditions, since the splittable-type composite-resin-formed product was used as a raw material, a splittable-type ultrafine composite fiber having an analogous shape was obtained. In Experiment No. 11, PLA was removed, whereby an ultrafine fiber composed of a single component of EVOH was obtained.

[0082] The ultrafine fiber obtained in Experiment No. 12 had a cross section substantially identical to those of FIGS.

3 and 4. In FIG. 4, "30" denotes an ultrafine composite fiber having a core-sheath structure, "31" denotes PLA, and "32" denotes EVOH. Since the fiber was a core-sheath-type composite fiber in which the sheath component was EVOH having a volume specific resistance of 10^{15} Ω·cm or less and was exposed on 100 % of the surface, excellent spinning properties were exhibited, and the extended fiber was in a phase separation state. In the present case under these conditions, since the core-sheath-type composite-resin-formed product was used as a raw material, an ultrafine composite fiber having an analogous shape was obtained. In Experiment No. 12, EVOH was removed, whereby an ultrafine fiber composed of a single component of PLA was obtained.

Example 2

[0083] In Experiments Nos. 13 to 15, fibers having a cross-sectional structure shown in FIG. 12A were used as raw-material fibers that were composite-resin-formed products. Cross-sectional structures of Experiments Nos. 16 and 17 (Comparative Examples) are shown in Table 3. Additionally, core and sheath components, resin ratios, and fiber diameters of Experiments Nos. 13 to 17 are shown in Table 3.

[0084] Ultrafine fibers were produced by the above-described electrospinning method, with the use of these raw-material fibers. A scanning electron photomicrograph (SEM, magnification: 2,000 times) of an ultrafine fiber obtained in Experiment No. 13 is shown in FIG. 14. The fibers obtained in Experiments Nos. 14 and 15 also had similar appearances.

[0085] The ultrafine fibers obtained were immersed sufficiently in a mixed solution at 90°C composed of 70 g of 2-propanol and 30 g of distilled water until ethylene-vinyl alcohol copolymer (EVOH) was dissolved completely therein, so that the ethylene-vinyl alcohol copolymer (EVOH) was removed from the fibers. The scanning electron photomicrographs (SEM, magnification: 2,000 times) of the ultrafine fibers of Experiments Nos. 1 to 3 after EVOH was removed are shown in FIGS. 15 to 17. The obtained results are shown in Table 3.

[0086]

[Table 3]

Experiment No.	Raw-material fiber					Fiber diameter after electrospinning (µm) Standard deviation shown in ()	Fiber diameter after removal of sheath component (µm) Standard deviation shown in ()
	Core component	Sheath component	Cross-sectional structure	Resin ratio	Fiber diameter µm		
13	PP	EVOH	Core-sheath	30/70	452	1.85(1.60)	
14	PP	EVOH	Core-sheath	50/50	438	3.46(0.76)	
15	PP	EVOH	Core-sheath	70/30	472	16.34(3.32)	12.74(4.59)
16 (Comp. Ex.)	PP	—	Homogeneous	—	600	Unspinnable	—
17 (Comp. Ex.)	EVOH	PP	Core-sheath	50/50	450	Unspinnable	—

[0087] As is clear from Table 3, in Experiments Nos. 13 to 15, composite fibers each of which had a core of polypropylene (PP) and a sheath of ethylene-vinyl alcohol copolymer (EVOH) were used as raw materials, and as a result, fiber diameters of 1.85 µm to 16.34 µm after spinning were achieved. As the proportion of ethylene-vinyl alcohol copolymer (EVOH) was greater, better spinning properties were achieved and the obtained fibers were finer, but the fiber diameter variation was significant.

[0088] Further, after ethylene-vinyl alcohol copolymer (EVOH) was removed, an ultrafine fiber made of polypropylene (PP) alone was obtained.

Example 3

[0089] In Experiments Nos. 18 to 20, fibers having a cross-sectional structure shown in FIG. 13A were used as raw-material fibers that are composite-resin-formed products. Core and sheath components, resin ratios, and fiber diameters in these experiments are shown in Table 4. 60 of these fibers were bundled. The bundling was performed by fixing ends on one side of these 60 fibers with use of a clip, aligning the fibers by slightly pulling the other ends so as to make them tense, temporarily fixing them by pouring boiled water, and drying the same. For example, in Experiment No. 18, 60 filament fibers having a fiber diameter of 120 μm were bundled, as shown in FIG. 13A.

[0090] Using these raw-material fibers, ultrafine fibers were produced by the above-described electrospinning method. A scanning electron photomicrograph (SEM, magnification: 5,000 times) of an ultrafine fiber obtained in Experiment No. 18 is shown in FIG. 18. The fibers obtained in Experiments Nos. 19 and 20 also had similar appearances.

[0091] The ultrafine fibers obtained were immersed sufficiently in a mixed solution at 90°C composed of 70 g of 2-propanol and 30 g of distilled water until ethylene-vinyl alcohol copolymer (EVOH) was dissolved completely therein, so that the ethylene-vinyl alcohol copolymer (EVOH) was removed from the fibers. The scanning electron photomicrographs (SEM, magnification: 5,000 times) of the ultrafine fibers of Experiments Nos. 18 to 20 after EVOH was removed are shown in FIGS. 19 to 21. The obtained results are shown in Table 4.

[0092]

[Table 4]

Exp. No.	Raw-material fiber					Fiber diameter after electrospinning (μm) Standard deviation shown in ()	Fiber diameter after removal of sheath component (μm) Standard deviation shown in ()
	Core component	Sheath component	Cross-sectional structure	Resin ratio	Fiber diameter μm		
18	PP	EVOH	Core-sheath	30/70	120	1.53(0.55)	0.43(0.19)
19	PP	EVOH	Core-sheath	50/50	121	1.21(0.30)	0.70(0.09)
20	PP	EVOH	Core-sheath	70/30	115	1.38(0.31)	1.28(0.42)

[0093] As is clear from Table 4, in Experiments Nos. 18 to 20, composite fibers each of which had a core of polypropylene (PP) and a sheath of ethylene-vinyl alcohol copolymer (EVOH) were used as raw materials, and as a result, fiber diameters of 1.21 μm to 1.53 μm after spinning were achieved. Spinning properties were excellent, ultrafineness was achieved more stably even as compared with Example 3, and the variation of the fiber diameter variation was small as well. Ultrafine composite fibers having analogous shapes to those of core-sheath composite fibers as raw materials were obtained.

[0094] Further, polypropylene (PP) fibers obtained after removal of ethylene-vinyl alcohol copolymer (EVOH) had fiber diameters of 0.43 to 1.28 μm.

Industrial Applicability

[0095] Ultrafine composite fibers and fiber structures obtained in the present invention are useful in filters, battery separators (separators for lithium ion batteries in particular), paper, nonwoven fabrics, skin layers for synthetic leather substitute, and the like. Further, such fibers also are useful in materials to be embedded in a living body such as surgical sutures, stents, and artificial joints; medical materials such as hematostatic materials, cell culture substrates, masks, and bodily fluid absorbing pads; and cosmetics such as face masks, and interpersonal wipes.

Claims

1. An ultrafine composite fiber obtained by heating and melting a composite-resin-formed product in front of a supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode and extending the composite-resin-formed product by electrospinning,
wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formed product, and
fiber components composing the ultrafine composite fiber are in a phase separation state.

2. The ultrafine composite fiber according to claim 1, containing no solvent therein.

3. The ultrafine composite fiber according to claim 1, wherein the composite-resin-formed product is a fiber having a phase structure of a sea-island type, a splittable type, or a core-sheath type.

4. The ultrafine composite fiber according to claim 1 or 3, wherein the composite-resin-formed product is a monofilament, a multifilament composed of a plurality of monofilaments bundled, or a tow.

5. The ultrafine composite fiber according to claim 1, wherein the resin component exposed on 30 % or more of the surface of the composite-resin-formed product is at least one selected from ethylene-vinyl alcohol copolymers, polyesters, nylons, and polyurethanes, and a resin component of another phase is at least one selected from polyolefins, polyesters, nylons, and polylactic acids.

6. An ultrafine fiber obtained by removing any of the components composing the ultrafine composite fiber according to any one of claims 1 to 5.

7. A method for manufacturing an ultrafine composite fiber, the method comprising the steps of:

supplying a composite-resin-formed product to a supply-side electrode, wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formed product;
heating and melting the composite-resin-formed product in front of the supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode; and
extending the molten composite-resin-formed product by electrospinning.

8. The method for manufacturing an ultrafine composite fiber according to claim 7, wherein a heating-extending region is provided between the collection electrode and a position where the composite-resin-formed product is heated and molten.

9. A fiber structure obtained by heating and melting a composite-resin-formed product in front of a supply-side electrode and/or in a space between the supply-side electrode and a collection-side electrode, and extending the composite-resin-formed product by electrospinning,
wherein the composite-resin-formed product is a solid-state composite-resin-formed product having two or more phases and including a resin that has a volume specific resistance of 10^{15} Ω·cm or less and that is exposed on 30 % or more of a surface of the composite-resin-formed product, and
fiber components composing the ultrafine composite fiber are in a phase separation state.

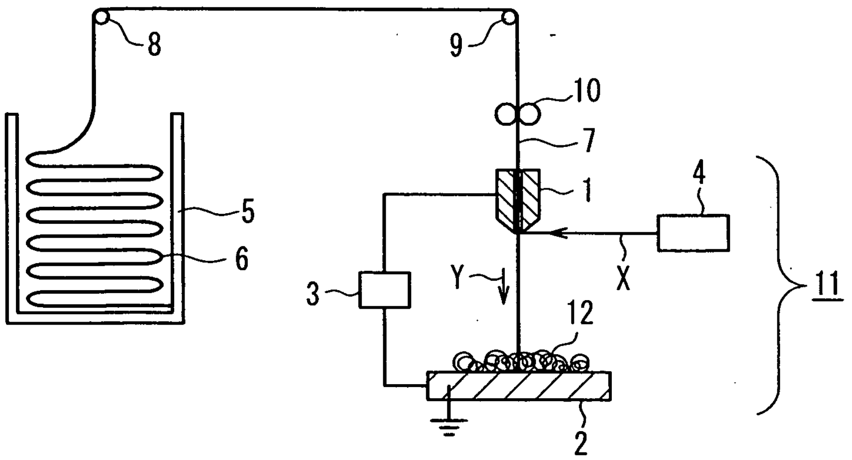

FIG. 1

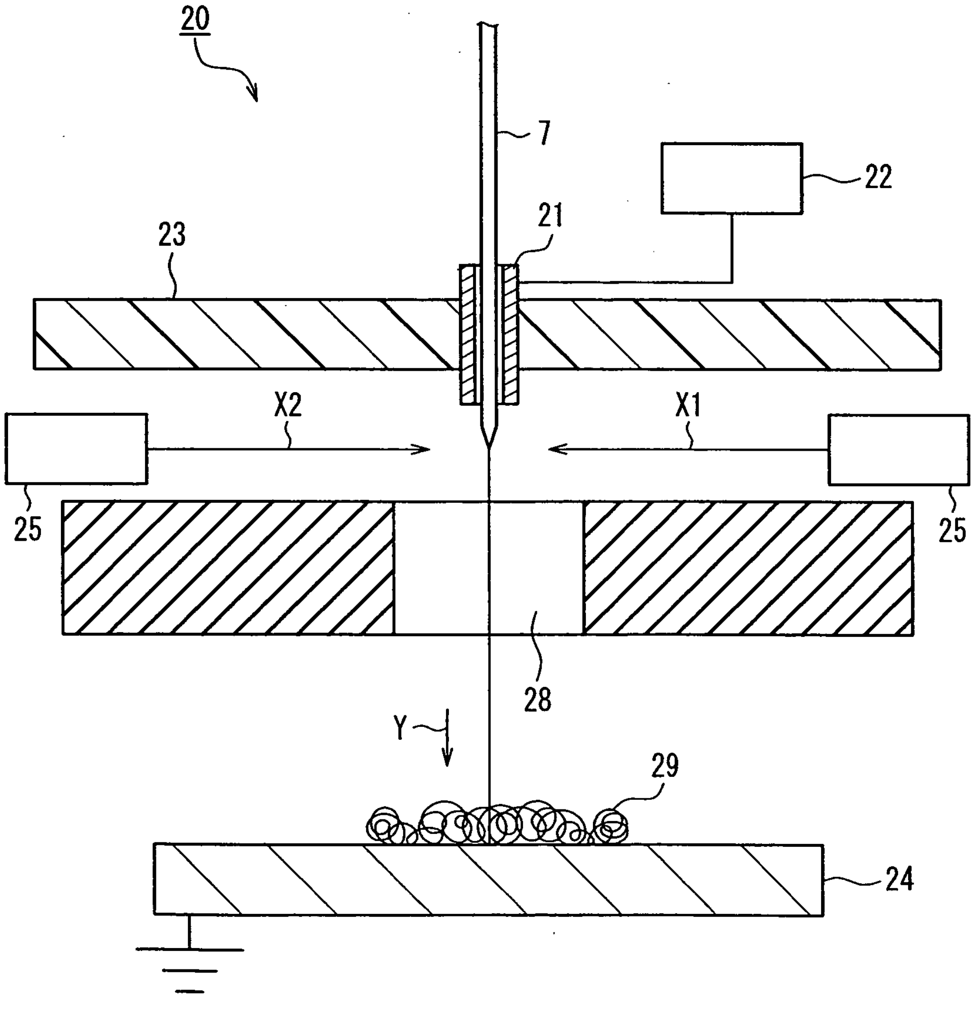

FIG. 2

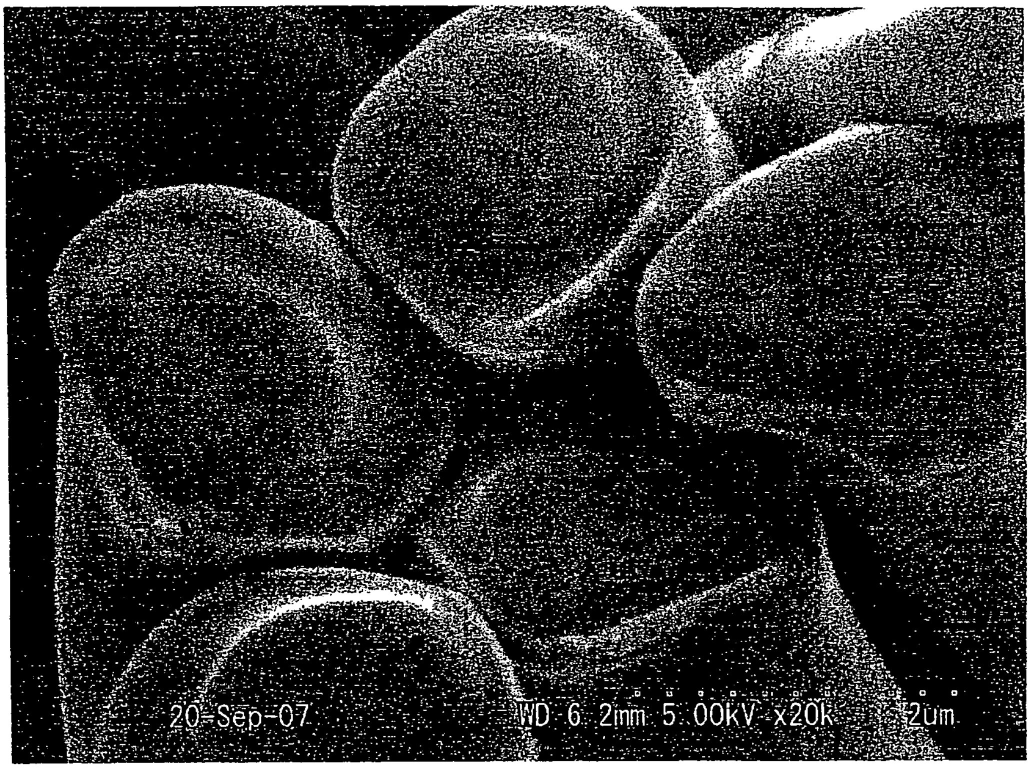

FIG. 3

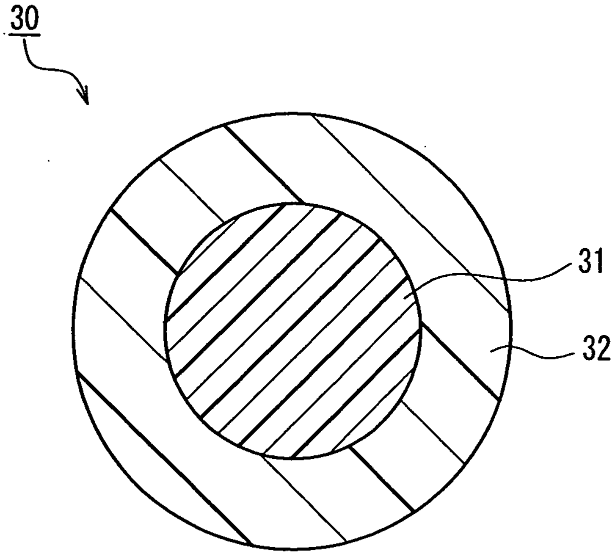

FIG. 4

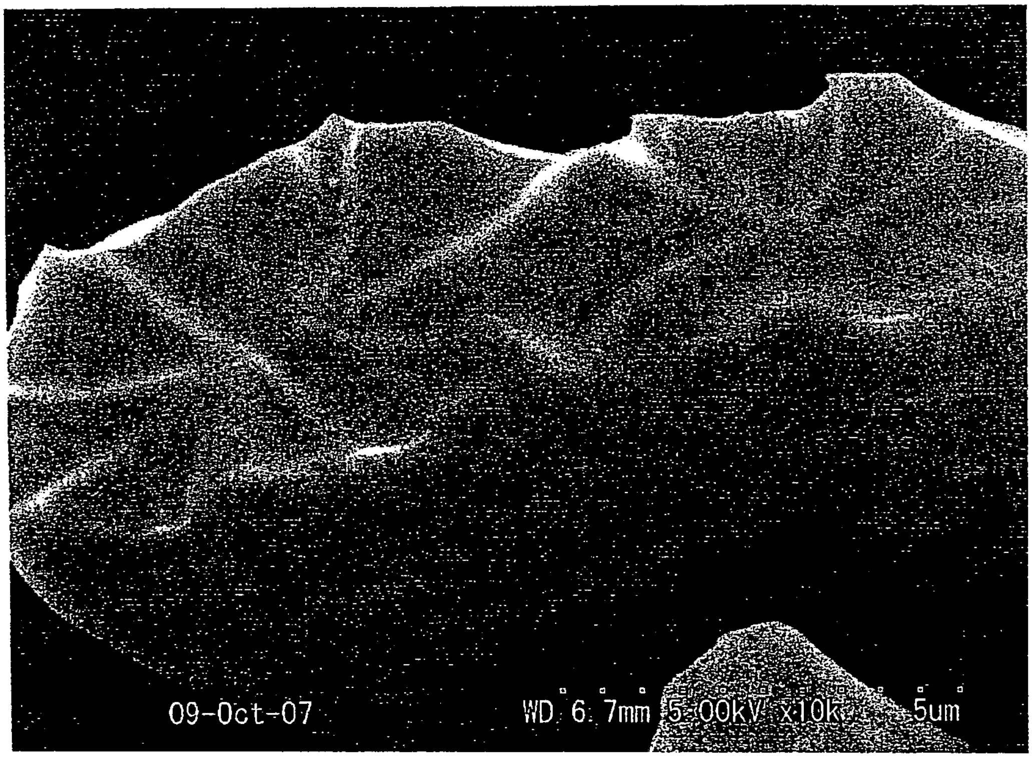

FIG. 5

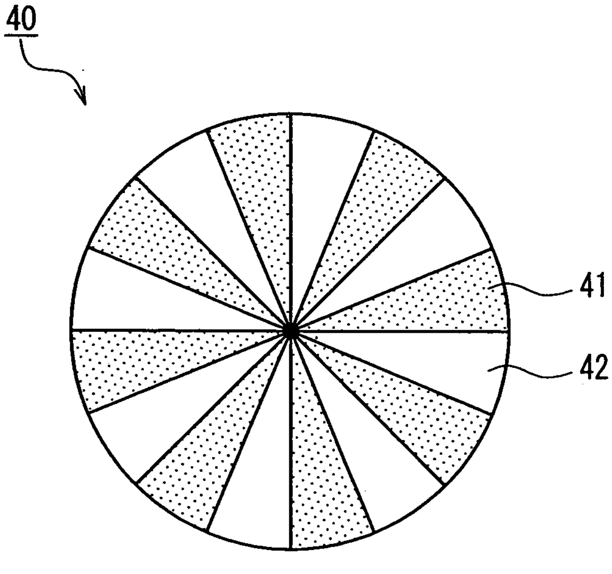

FIG. 6

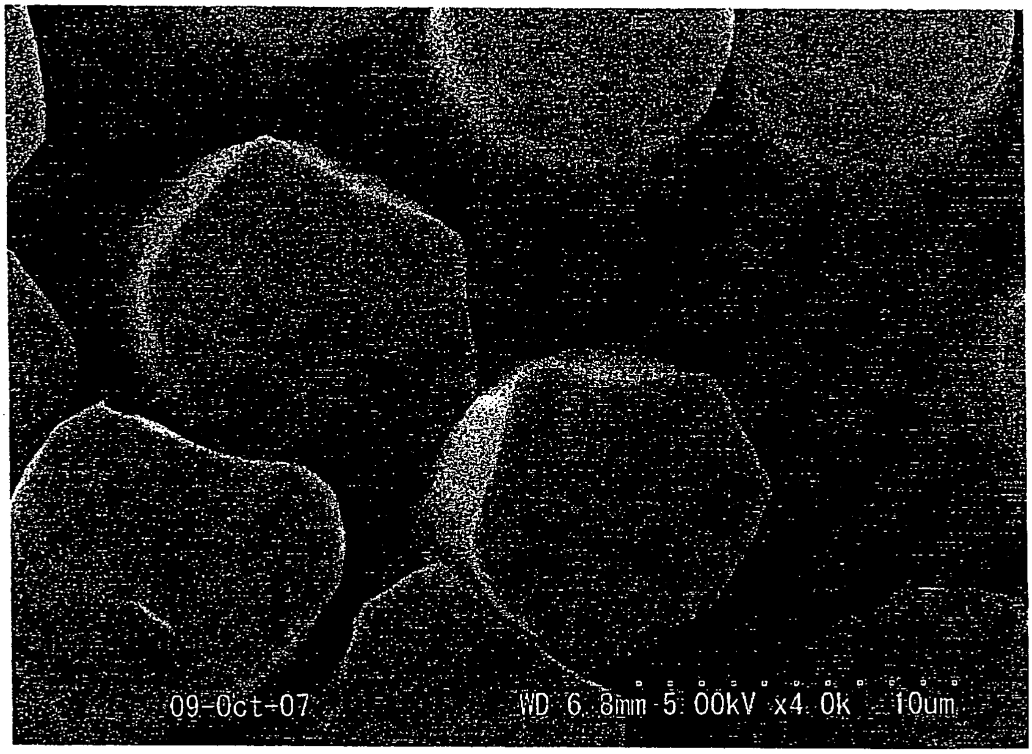

FIG. 7

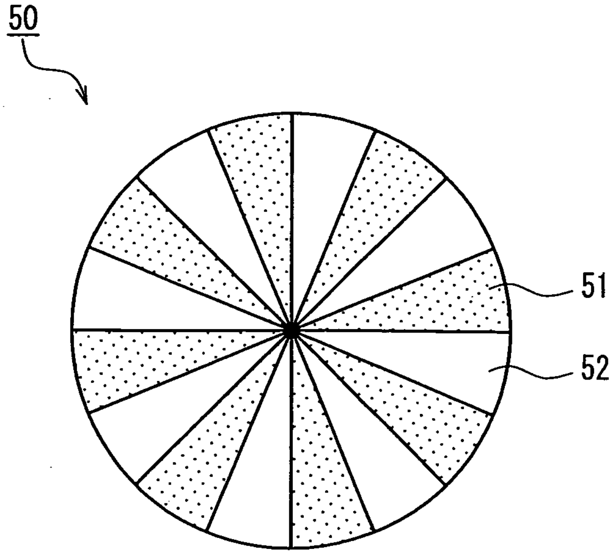

FIG. 8

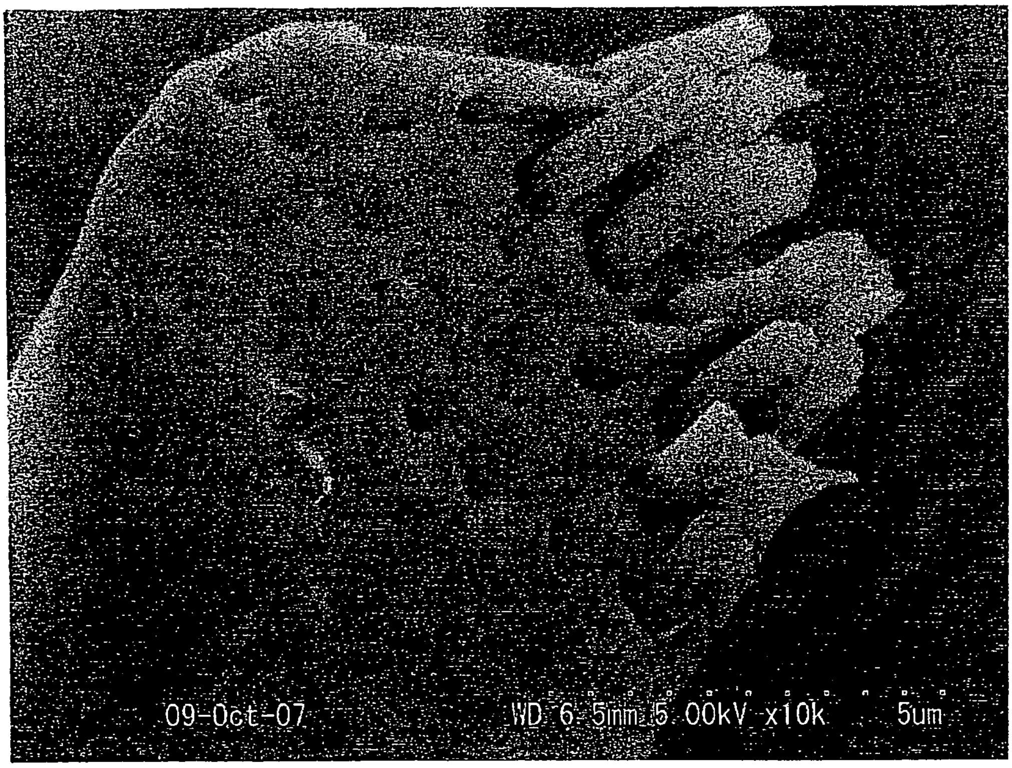

FIG. 9

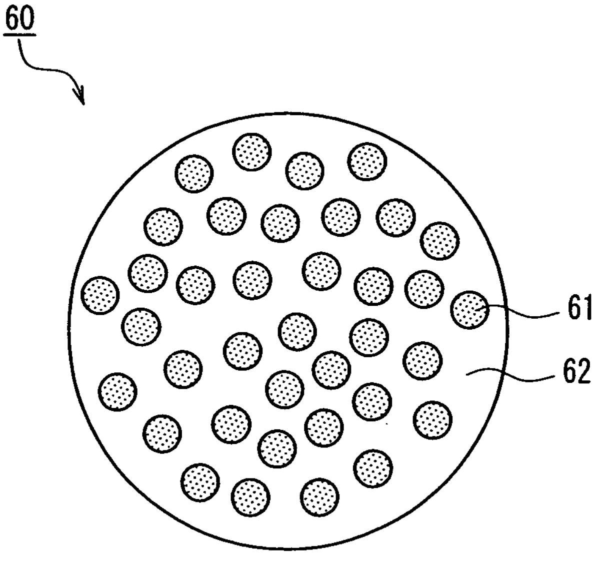

FIG. 10

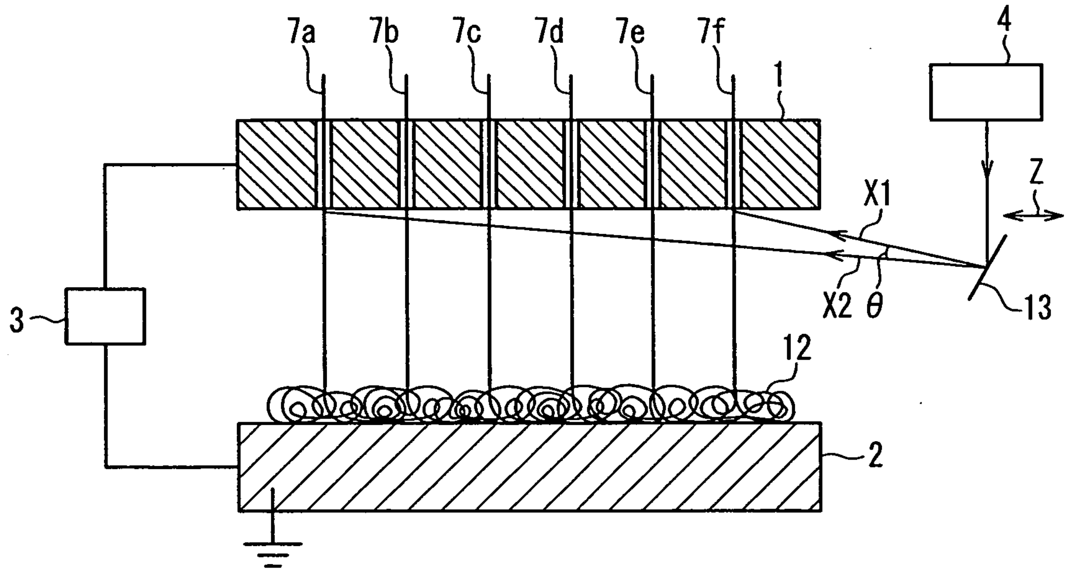

FIG. 11

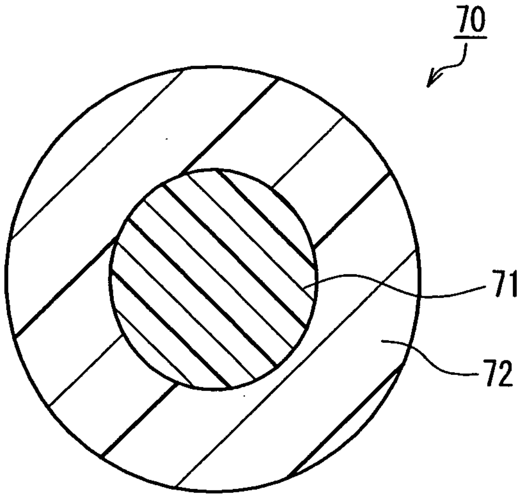

FIG. 12A

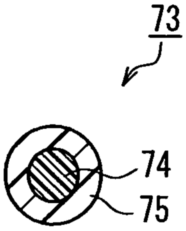

FIG. 12B

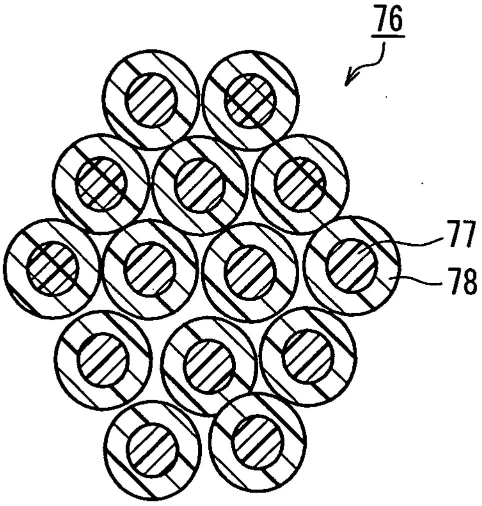

FIG. 13A

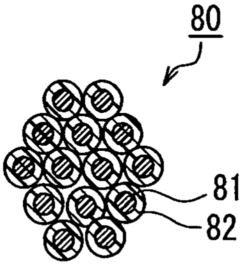

FIG. 13B

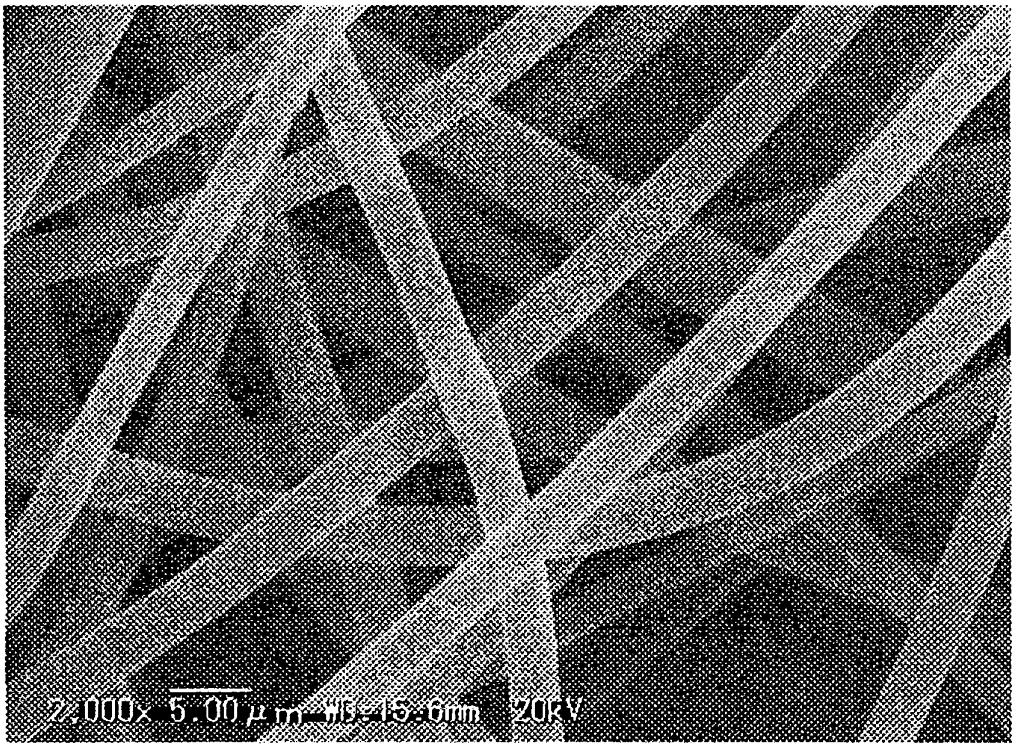

FIG. 14

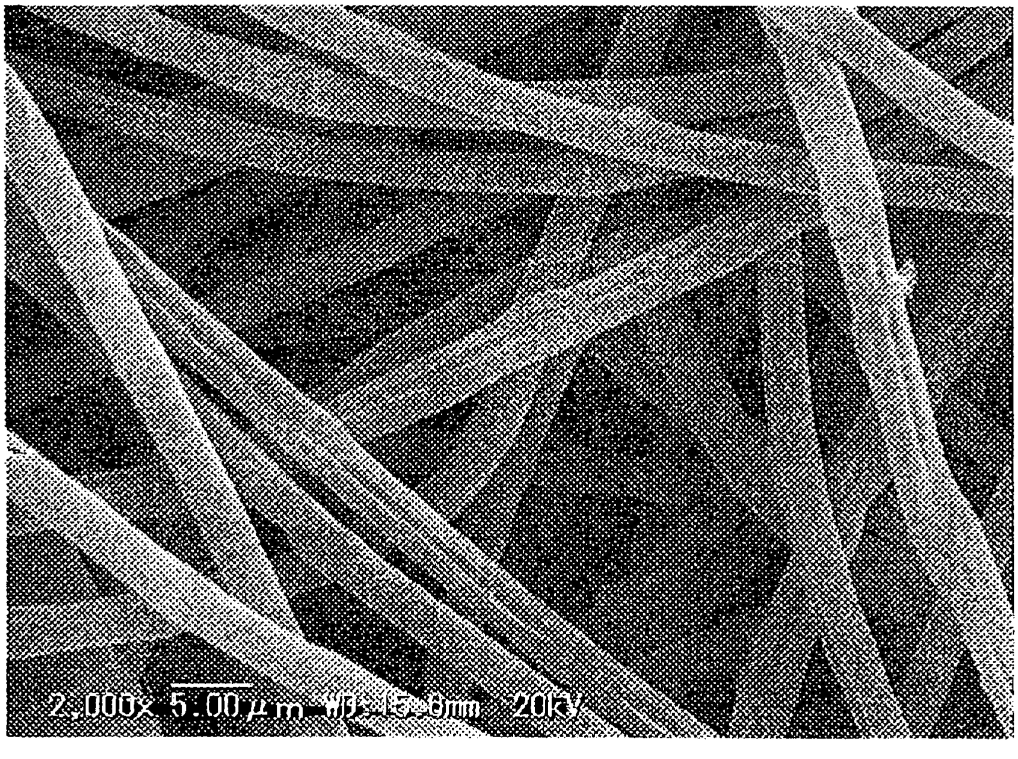

FIG. 15

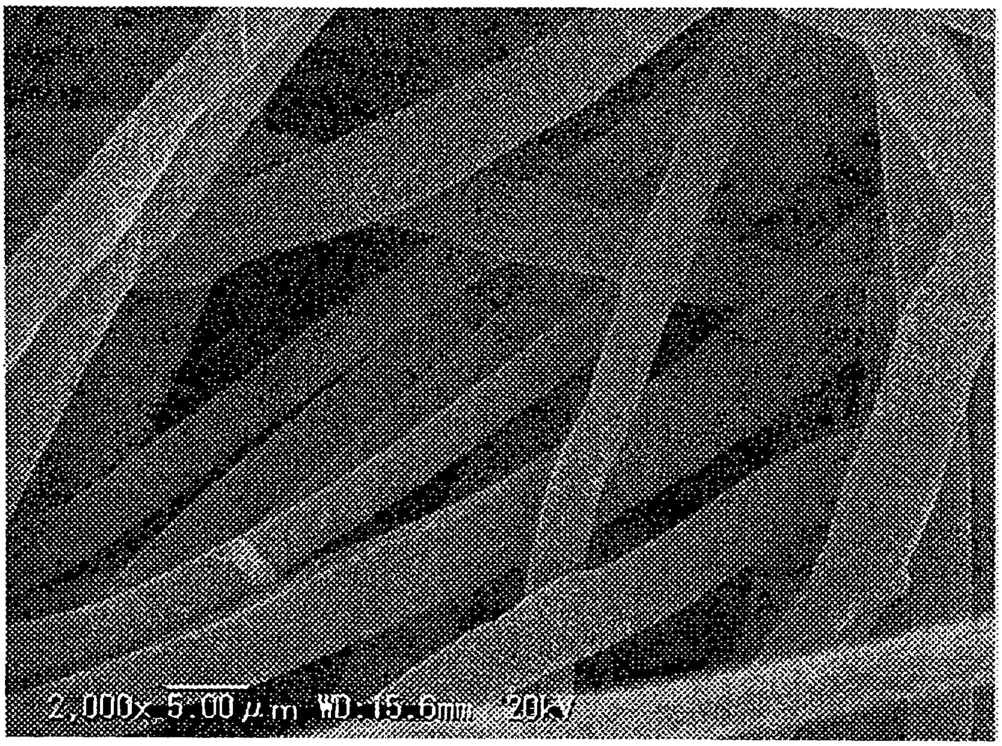

FIG. 16

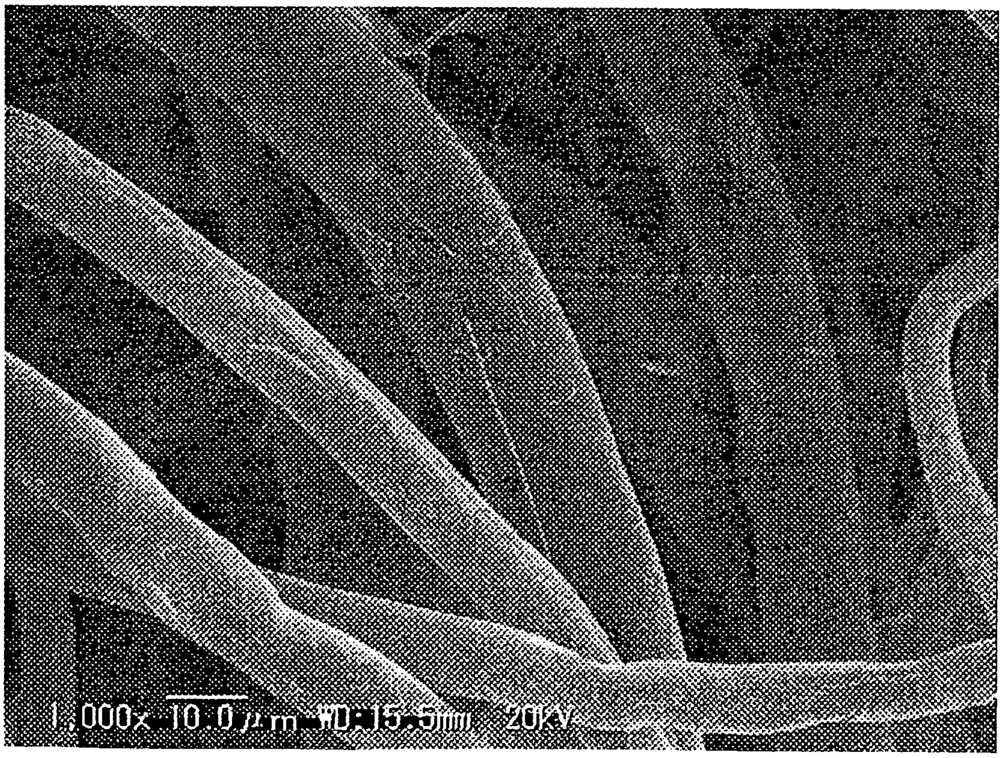

FIG. 17

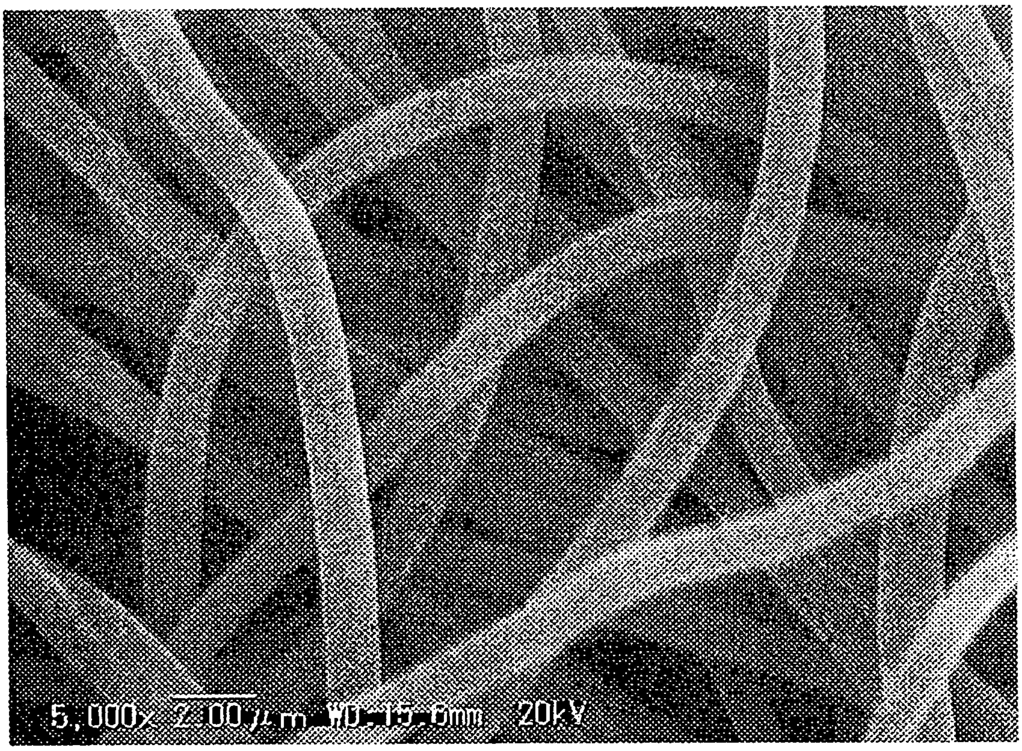

FIG. 18

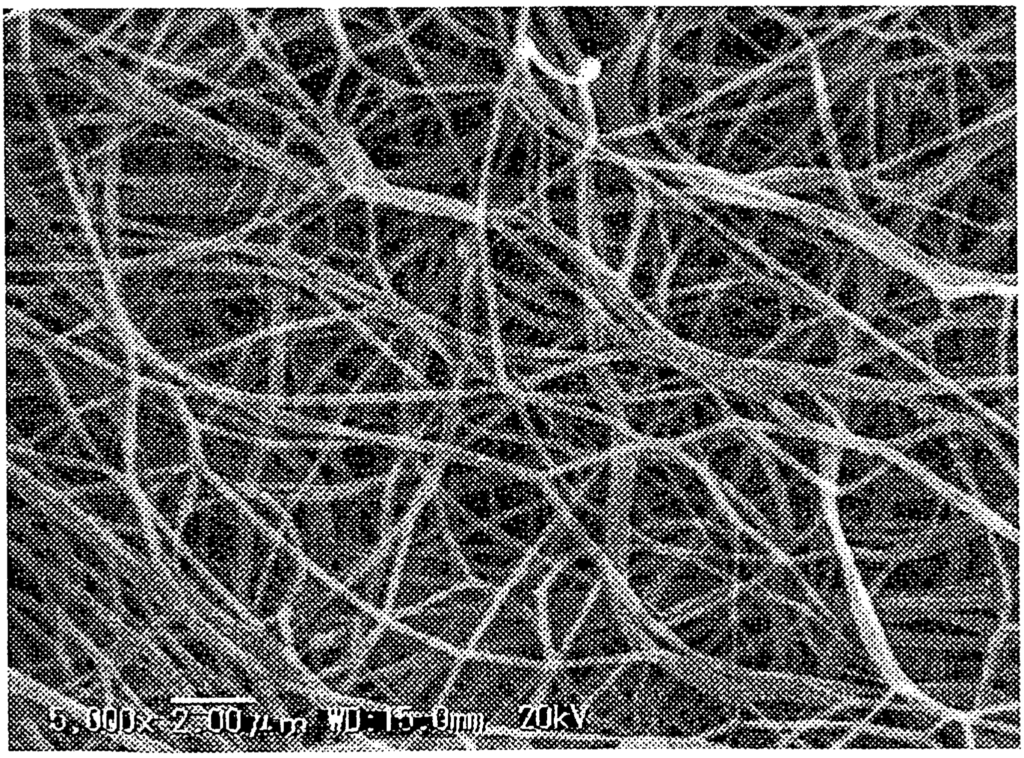

FIG. 19

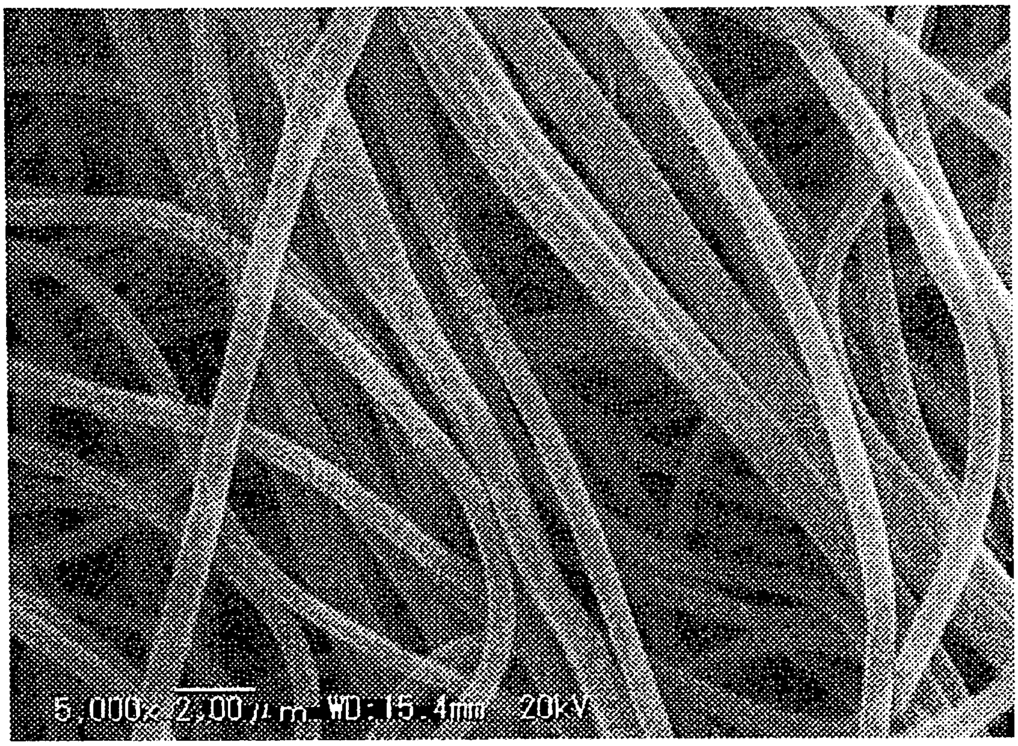

FIG. 20

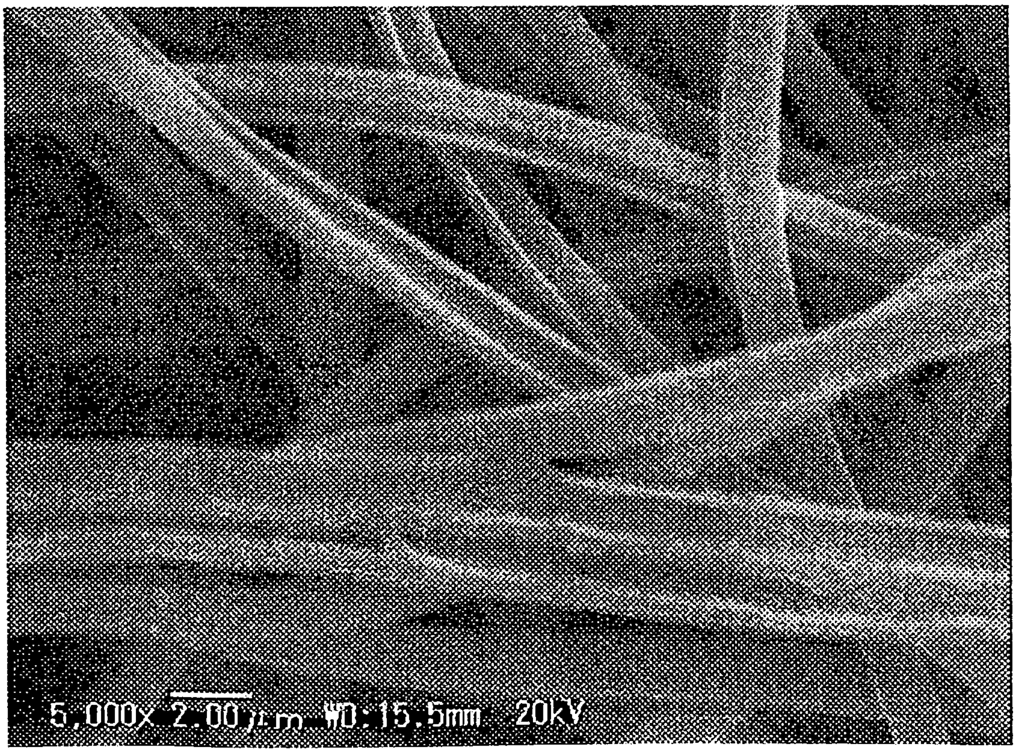

FIG. 21

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/071677

A. CLASSIFICATION OF SUBJECT MATTER
D01F8/04(2006.01)i, *D01D5/08*(2006.01)i, *D02J1/22*(2006.01)i, *D04H1/72*
(2006.01)n

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)
D01F8/04, D01D5/08, D02J1/22, D04H1/72

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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	WO 2006/099107 A2 (MASSACHUSETTS INSTITUTE OF TECHNOLOGY), 21 September, 2006 (21.09.06), Whole document & US 2006/0292369 A1 & EP 1856314 A & CA 2601992 A & KR 10-2007-0110024 A & CN 101137779 A	1-9
A	JP 2007-154336 A (SNT Co.), 21 June, 2007 (21.06.07), Full text (Family: none)	1-9
A	JP 2006-69142 A (Teijin Techno Products Ltd.), 16 March, 2006 (16.03.06), Full text (Family: none)	1-9

☒ 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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"O"	document referring to an oral disclosure, use, exhibition or other means
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"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 05 February, 2009 (05.02.09)	Date of mailing of the international search report 17 February, 2009 (17.02.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/071677

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,A	JP 2008-303521 A (Teijin Techno Products Ltd.), 18 December, 2008 (18.12.08), Full text (Family: none)	1-9
P,A	JP 2008-7902 A (Teijin Fibers Ltd.), 17 January, 2008 (17.01.08), Full text (Family: none)	1-9
E,A	JP 2009-24295 A (Tomoegawa Paper Co., Ltd.), 05 February, 2009 (05.02.09), Full text (Family: none)	1-9

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2007239114 A **[0003]**
- JP 2007197859 A **[0003]**
- JP 2005154927 A **[0003]**

Non-patent literature cited in the description

- Plastic Data Book. Kogyo Chosakai Publishing Inc, 01 December 1999, 186 **[0014]**
- Plastic Data Book. Kogyo Chosakai Publishing Inc, 01 December 1999, 7-11 **[0043]**