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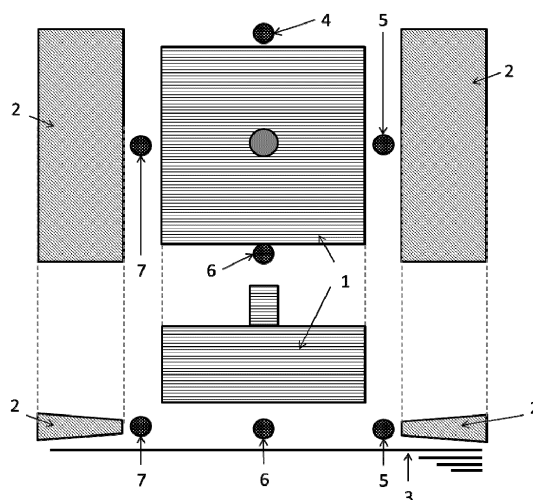
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(54) FIBER PRODUCTION METHOD AND CARBON FIBER PRODUCTION METHOD

(57) A method of producing a fiber, the method including discharge, from a spinneret 1, a spinning dope solution containing a fiber-forming polymer dissolved in a solvent, once allowing the solution to run in air, and then guiding the solution into the liquid of a coagulation bath 4 to allow coagulation, wherein a gas-phase portion formed in a vertically downward direction from a discharge surface of the spinneret 1 to the liquid surface of the coagulation bath 4 has an air flow rate per unit time (A_f) which satisfies, in relation to the amount of the solvent in the spinning dope solution per unit time (A_s) in the gas-phase-portion volume (V_h), the relational expression $0.0008 \text{ m}^3 \leq A_f/(A_s/V_h) \leq 0.0015 \text{ m}^3$, and the hourly average of the absolute humidity at each of four points in an outer periphery of the spinneret in the gas-phase portion is not more than 20 g/m^3 .

A method of producing a fiber, which, in dry-jet wet spinning, suppresses occurrence of dew condensation in the spinneret, and reduces deterioration of the appearance caused by winding on rollers in the subsequent process or by fuzzing or yarn break in the stretching process, to enable significant improvement of the productivity and the appearance as a whole, is provided.

[Figure 1]



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of producing a fiber, which method enables production of a fiber by the dry-jet wet spinning method without causing dew condensation or generation of water droplets on the spinneret surface, and with remarkable stability of running of fibers.

BACKGROUND ART

10 **[0002]** For production of a fiber by spinning of a fiber-forming polymer which hardly melts, such as a polyacrylonitrile, the wet spinning method or the dry-jet wet spinning method is employed. The dry-jet wet spinning method is a method in which a spinning dope solution containing a fiber-forming polymer dissolved in a solvent is discharged from a spinneret, and then once allowed to run in air, immediately followed by being guided into a coagulation bath liquid to allow coagulation.
 15 Unlike the wet spinning method, this method has less draft restriction in a gas, where the bath-liquid resistance is absent. Therefore, high-speed or high-draft spinning is possible, and the method is used for production of fibers for clothing and industrial uses. Further, since the dry-jet wet spinning method enables higher densification of fibers, the method has recently been utilized for production of precursor fibers for high strength/high modulus carbon fibers, and the productivity in the dry-jet wet spinning method has been enhanced by performing high-speed spinning or increasing the holes in the spinneret.
 20

[0003] In the dry-jet wet spinning method, since a spinning dope solution is discharged from a spinneret arranged outside a coagulation bath, a gas-phase portion is present between the spinneret surface and the coagulation bath. Therefore, when high-speed spinning is carried out, or when the number of holes in one spinneret is increased, that is, when the so-called hole multiplication is carried out, vapor of the solvent contained in the spinning dope solution increases
 25 in the gas-phase portion, and the vapor accumulates in the gas-phase portion, often leading to occurrence of dew condensation on the spinneret surface. The droplets generated by the dew condensation cause clogging of the discharge hole of the spinneret, fiber adhesion, uneven fineness, and single-fiber break, and further, spinneret immersion due to contact of the droplets with the coagulation liquid surface, leading to winding on rollers in the subsequent process and fuzzing or yarn break in the stretching process. Thus, the operability and the appearance are significantly deteriorated.
 30 Such problems become more serious especially when high-speed spinning is carried out, or when the number of holes in the spinneret is increased, in order to increase the productivity.

PRIOR ART DOCUMENTS

35 [Patent Documents]

[0004] For the purpose of reducing such problems, a method for preventing dew condensation in dry-jet wet spinning, wherein a gas is allowed to flow, from one direction, in the gas-phase portion of the spinneret surface and the coagulation bath, has been proposed (Patent Document 1).

40 **[0005]** Further, also for multi-hole spinnerets with more than 2,000 holes, a method for preventing accumulation of the solvent vapor, wherein the gas in the gas-phase portion formed between the discharge surface of the spinneret and the coagulation bath is sucked alternately from two directions sandwiching the discharge surface, has been studied (Patent Document 2).

45 **[0006]** Further, a method for controlling the temperature and the humidity in the vicinity of the spinneret to suppress dew condensation on the spinneret surface, wherein the inside of the coagulation chamber is surrounded, and wherein air with a controlled temperature and humidity is circulated therein, has also been studied (Patent Document 3).

[Patent Document 1] JP 5-044104 A

[Patent Document 2] JP 2007-239170 A

50 [Patent Document 3] JP 2010-236139 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

55 **[0007]** When the number of holes used in the spinneret is as small as, for example, about 300, the technique proposed in Patent Document 1 may be able to effectively suppress dew condensation in some cases. However, under conditions where the number of holes is not less than 2,000, where the hole density is increased, or where the gas-phase portion

in dry-jet wet spinning has a height of less than 20 mm in the vertically downward direction from the discharge surface of the spinneret to the coagulation bath liquid surface, that is, under conditions where the solvent vapor easily accumulates in the gas-phase portion, deflection of the air flow occurs even by application of the technique proposed in Patent Document 1, causing accumulation of the vapor in some cases. This has been problematic since the dew condensation

[0008] Regarding Patent Document 2, there are problems in that, when the hole density is high, insufficiency of suction in the gas-phase portion causes aggregation of the solvent vapor, and that the aggregation proceeds on surfaces not subjected to the exhaustion, causing dew condensation.

[0009] Regarding Patent Document 3, although the controlled air is introduced into the discharge hole in the spinneret outer layer portion, the controlled air does not reach the inside of the spinneret, so that the dew condensation-suppressing effect has been insufficient. Further, since the control of the temperature and the humidity is carried out by entirely surrounding the inside of the coagulation chamber, the method requires larger-scale equipment and a higher equipment cost, so that practical application of the method has been substantially difficult.

[0010] An object of the present invention is to provide a method of producing a fiber, which method suppresses occurrence of dew condensation on the spinneret, and reduces deterioration of the appearance caused by winding on rollers in the subsequent process or by fuzzing or yarn break in the stretching process, to enable significant improvement of the productivity and the appearance as a whole even under conditions where, for example, not less than 2,000 holes are present and the hole density is high, or where the gas-phase portion formed in the vertically downward direction from the discharge surface of the spinneret to the coagulation bath liquid surface in dry-jet wet spinning has a height of less than 20 mm.

MEANS FOR SOLVING THE PROBLEMS

[0011] For solving the above problems, the method of producing a fiber of the present invention has the following constitution. That is,

a method of producing a fiber, the method comprising discharge, from a spinneret, a spinning dope solution containing a fiber-forming polymer dissolved in a solvent, once allowing the solution to run in air, and then guiding the solution into a coagulation bath liquid to allow coagulation, wherein a gas-phase portion formed in a vertically downward direction from an discharge surface of the spinneret to a coagulation bath liquid surface has an air flow rate per unit time (A_f) which satisfies, in relation to the amount of the solvent in the spinning dope solution per unit time (A_s) in the gas-phase-portion volume (V_h), the relational expression $0.0008 \text{ m}^3 \leq A_f/(A_s/V_h) \leq 0.0015 \text{ m}^3$, and the hourly average of the absolute humidity at each of four points in an outer periphery of the spinneret in the gas-phase portion is not more than 20 g/m^3 .

[0012] The method of producing a carbon fiber of the present invention also has the following constitution. That is, a method of producing a carbon fiber, comprising producing a fiber by the above method of producing a fiber, performing oxidation treatment in an oxidizing gas at 200 to 300°C , and then heating the fiber in an inert gas at not less than $1,000^\circ\text{C}$.

[0013] In the method of producing a fiber of the present invention, the relative standard deviation of the wind velocities at four points in the outer periphery of the spinneret in the gas-phase portion is preferably not more than 40%.

[0014] In the method of producing a fiber of the present invention, the number of holes in the spinneret is preferably not less than 2,000 and not more than 50,000.

[0015] In the method of producing a fiber of the present invention, the fiber-forming polymer is preferably an acrylonitrile copolymer.

EFFECT OF THE INVENTION

[0016] According to the present invention, occurrence of dew condensation on a spinneret can be suppressed, and deterioration of the appearance caused by winding on rollers in the subsequent process or by fuzzing or yarn break in the stretching process can be reduced, thereby enabling significant improvement of the productivity and the appearance as a whole even under conditions of dry-jet wet spinning where, for example, not less than 2,000 holes are present and the hole density is high, or where the distance between the spinneret and the coagulation bath liquid is less than 20 mm. The present invention is especially suitable for production of acrylonitrile precursor fibers for carbon fibers.

BRIEF DESCRIPTION OF THE DRAWING

[0017] Fig. 1 shows schematic top and front views of a spinning region in a case where an air supply nozzle or an exhaust nozzle is arranged in the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0018] The present invention is described below in more detail.

[0019] The method of the present invention can be used for production of acrylonitrile fibers for clothing, acrylonitrile fibers for production of carbon fibers, aromatic polyamide fibers, and the like. The method shows the most remarkable effect in cases of production of acrylonitrile fibers for production of carbon fibers.

[0020] In the present invention, a spinning dope solution containing a fiber-forming polymer dissolved in a solvent is used. Examples of the fiber-forming polymer that may be used include acrylonitrile copolymers and aromatic polyamides. As a polymerization method for obtaining the polymer, solution polymerization, emulsion/suspension polymerization, bulk polymerization, or the like is used. Either a batch method or a continuous method may be used.

[0021] In cases of an acrylonitrile copolymer, examples of the solvent in which the polymer is dissolved include dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc), aqueous zinc chloride solutions (ZnCl_2 aq), and aqueous sodium thiocyanate solutions (NaSCN aq). From the viewpoint of productivity, DMSO, DMF, or DMAc is preferred in dry-jet wet spinning since these allow rapid coagulation of the polymer. DMSO is especially preferred since it allows especially rapid coagulation.

[0022] The spinning dope solution is discharged from a discharge surface of a spinneret arranged above a coagulation bath through a gas-phase portion, and then the solution is allowed to coagulate in a coagulation bath, to form a fiber.

[0023] Regarding the temperature of the spinning dope solution and the temperature of the coagulation bath, their conditions are preferably set such that the difference that emerges between the atmospheric temperature and the dew point (atmospheric temperature - dew point) of the gas-phase portion formed in the vertically downward direction from the discharge surface of the spinneret to the coagulation bath liquid surface is as large as possible.

[0024] Regarding the temperature of the spinning dope solution, a low temperature is preferred from the viewpoint of reducing the amount of evaporation of the solvent as long as the temperature is not less than the freezing point of the solvent used for the spinning dope solution. The temperature is preferably not less than the freezing point and not more than the freezing point +20°C, further, not less than the freezing point +5°C, and not more than the freezing point +15°C. In cases where the temperature of the spinning dope solution is within this preferred range, the spinning dope solution maintains an appropriate viscosity, so that a favorable spinnability and an excellent operability can be achieved. As the coagulation bath, an aqueous solution of the same solvent as the solvent used for the spinning dope solution is usually used. Since dew condensation tends to occur especially in organic solvent systems, the effect of the present invention remarkably appears especially in cases where an aqueous solution of DMSO, DMF, or DMAc is used as the coagulation bath. The upper limit of the temperature of the coagulation bath is preferably not more than 20°C, more preferably not more than 10°C, still more preferably not more than 7°C. In cases where the upper limit of the temperature of the coagulation bath is within this preferred range, occurrence of dew condensation can be effectively suppressed. The lower limit of the temperature of the coagulation bath is preferably not less than 0°C, more preferably not less than 1°C. In cases where the lower limit of the temperature of the coagulation bath is within this preferred range, a favorable spinnability and an excellent operability can be achieved.

[0025] The number of holes in the spinneret is preferably 2,000 to 50,000, more preferably 4,000 to 20,000. In cases where the number of holes is within this preferred range, a good productivity can be achieved. Moreover, the mass of the spinneret does not increase excessively, and workability can be easily secured, and the increase in the equipment cost can be suppressed. The spinneret area occupied by each hole (spinneret area ÷ number of holes) is preferably 5 mm² to 10 mm². In cases where the spinneret area occupied by each hole is within this preferred range, a good productivity can be achieved. Moreover, even when a sufficient space is not secured in the gas-phase portion between the spinneret and the coagulation bath in dry-jet wet spinning, occurrence of dew condensation can be effectively suppressed.

[0026] In the present invention, it is important that a gas-phase portion formed between a discharge surface of the spinneret and a coagulation bath liquid surface has an air flow rate per unit time (A_f) which satisfies, in relation to the amount of the solvent in the spinning dope solution per unit time (A_s) in the gas-phase-portion volume (V_h), the relational expression $0.0008 \text{ m}^3 \leq A_f/(A_s/V_h) \leq 0.0015 \text{ m}^3$, and the hourly average of the absolute humidity at each of four points (measurement points A to D) in an outer periphery of the spinneret in the gas-phase portion is not more than 20 g/m³.

[0027] Examples of methods therefor include a method in which a dehumidified air blower is arranged at a position distant from the spinneret, and the air is blown into the gas-phase portion at a certain air flow rate, and a method in which an air supply nozzle or an air exhaust nozzle is arranged in the outer periphery of the spinneret, and the air is supplied and exhausted at the same time or the direction of the air supply/exhaust is changed over time.

[0028] In the present invention, $A_f/(A_s/V_h)$ is 0.0008 m³ to 0.0015 m³, preferably 0.0009 m³ to 0.0014 m³, more preferably 0.0010 m³ to 0.0013 m³. In cases where $A_f/(A_s/V_h)$ exceeds 0.0015 m³, the coagulation bath liquid surface fluctuates, leading to instability of the spinning performance, so that the effect may be insufficient. Further, the hourly average of the absolute humidity at each of the four points in the outer periphery of the spinneret is preferably not more than 20 g/m³, more preferably not more than 15 g/m³, still more preferably not more than 10 g/m³.

[0029] From the viewpoint of performing scavenging without variation of the wind velocity among the four points in the

outer periphery of the spinneret, the relative standard deviation of the wind velocities at the four points in the outer periphery of the spinneret is preferably not more than 40%, more preferably not more than 20%, still more preferably not more than 10%. In cases where the relative standard deviation of the wind velocities at the four points in the outer periphery of the spinneret is within this preferred range, occurrence of dew condensation on the discharge surface of the spinneret can be suppressed irrespective of the shape of the spinneret, that is, irrespective of whether it is circular, rectangular, or the like.

[0030] In the present invention, the air flow rate per unit time (Af) is calculated from, among the wind velocities measured at the four measurement points in the outer periphery of the spinneret, the wind velocity at one point positioned in the upstream side of the air flow, and the cross-sectional area as determined by seeing the spinneret from the upstream side of the air flow. The gas-phase-portion volume (Vh) is calculated from the discharge area calculated from the outermost discharge holes of the spinneret, and the height of the gas-phase portion formed in the vertically downward direction from the discharge surface to the coagulation bath liquid surface. The amount of the solvent in the discharged dope solution (As) is the amount of the solvent contained in the dope solution discharged from the spinneret per unit time.

[0031] Furthermore, in the present invention, as shown in Fig. 1, the wind velocities and the absolute humidities at the four points in the outer periphery of the spinneret are measured at positions arranged such that the outer periphery of the spinneret is equally divided into four portions, and such that each position is at the middle point of the height from the liquid surface to the spinneret surface, and 30 mm distant from the outermost discharge holes of the spinneret, irrespective of the shape of the spinneret. Here, in the present invention, regarding the four points in the outer periphery of the spinneret, in cases where the spinneret has a circular shape, arbitrary four points on the circumference may be selected such that the outer circumference is equally divided into four portions. In cases where the spinneret has a rectangular shape, the four midpoints of the segments constituting the outer periphery may be selected. The wind velocity, the temperature, and the relative humidity can be measured using Climomaster MODEL 6501 (Kanomax Japan Inc.). The absolute humidity (AH) [g/m³] is calculated from the temperature (T) [°C] and the relative humidity (RH) [%] measured with the Climomaster, using the following calculation equation. (e: saturated vapor pressure [hPa])

$$e = 6.11 \times 10^{(7.5T/(T + 237.3))}$$

$$AH = 217 \times e/(T + 273.15) \times RH/100$$

[0032] Here, the hourly average of the absolute humidity at four points in the outer periphery of the spinneret is obtained by measuring the wind velocity, the temperature, and the relative humidity as described above 12 times at 5-minute intervals, calculating the absolute humidities using the above calculation equation, and then calculating their average for each measurement point.

[0033] Further, in cases where an air supply or exhaust nozzle is used for supplying or exhausting a gas, the direction of the nozzle is preferably set such that the nozzle outlet is arranged in the spinneret direction, and in parallel to the coagulation bath liquid surface as shown in Fig. 1. More specifically, the nozzle is arranged such that it is inclined at an angle of preferably 60° to 120°, more preferably 80° to 100° from the vertically downward direction (defined as 0°) toward the spinneret direction, and still more preferably at an angle of 90°. Fig. 1 shows a case where each nozzle is arranged at an angle of 90°. In cases where the nozzle is arranged such that it is inclined at an angle (nozzle angle) of 90°, vapor generated from the solvent can be efficiently scavenged, and adhesion of dewdrops on the spinneret surface can be highly effectively suppressed. In cases where the nozzle is inclined at an angle within this preferred range, in cases of the air supply nozzle, the air flow is less likely to hit the spinneret surface and cause a turbulent flow, so that the accumulation does not happen and occurrence of dew condensation can be effectively prevented; in cases of the air exhaust nozzle, although the vapor generated from the solvent is easily sucked while it is in contact with the spinneret surface, the growth of droplets can be effectively prevented. Either the air supply nozzle or the exhaust nozzle is less likely to cause fluctuation of the coagulation bath liquid surface. Thus, phenomena which affect negatively the appearance and the process stability, including spinneret immersion due to contact of the liquid surface with the spinneret, adhesion between single fibers and the like, can be effectively prevented.

[0034] The present invention is especially effective for production of an acrylonitrile fiber, especially an acrylonitrile fiber as a carbon fiber precursor, using an acrylonitrile copolymer.

[0035] The spinning dope solution used for the dry-jet wet spinning is a solution containing: an acrylonitrile copolymer containing acrylonitrile at not less than 90% by mass; and a vinyl monomer copolymerizable therewith; dissolved in the solution. In cases where the rate of copolymerization of the acrylonitrile used in the acrylonitrile copolymer is within this preferred range, carbon fibers obtained by carbonization of the acrylonitrile fibers obtained from the method of the present invention have high strength, and therefore carbon fibers having excellent mechanical properties are easily produced.

In cases where the concentration of the polymer in the spinning dope solution is within this preferred range, the content of the solvent is appropriate and the amount of the solvent vapor is not too large in the gas-phase portion between the spinneret and the coagulation bath liquid in dry-jet wet spinning, so that dew condensation is less likely to occur. Further, an increase in the viscosity and gelation during polymerization of the acrylonitrile copolymer can be suppressed, and in dry-jet wet spinning, the discharge hole of the spinneret is less likely to be clogged, so that fiber adhesion, uneven fineness, and single-fiber break can be effectively prevented. Moreover, winding on rollers in the subsequent process, and fuzzing or yarn break in the stretching process can be also effectively prevented. Thus, excellent operability is achieved and the deterioration of the appearance of products can be effectively prevented.

[0036] The present invention can be preferably applied to cases where each fiber having a filament number of usually within the range of 2,000 to 50,000, and a single fiber fineness of usually within the range of 0.5 dtex to 3 dtex, are obtained. The fibers after fiber formation in the coagulation bath may be stretched directly in a stretching bath, or stretching in a bath may be carried out after removal of the solvent by washing with water.

[0037] Usually, after the stretching in the bath, an oil agent is applied, and drying with a hot roller or the like is carried out. Further, when necessary, this is followed by stretching such as steam stretching, to obtain fibers.

[0038] The following is a description of a method of producing a carbon fiber from a fiber obtained by the method of producing a fiber wherein the fiber-forming polymer is an acrylonitrile copolymer.

[0039] An acrylonitrile fiber produced by the method of producing an acrylonitrile fiber is subjected to oxidation treatment in an oxidizing gas such as air at 200 to 300°C. From the viewpoint of obtaining a oxidized fiber, the processing temperature is preferably increased from a low temperature to a high temperature in a plurality of steps. Further, from the viewpoint of allowing sufficient exertion of the performance of the carbon fiber, the fiber is preferably stretched at a high stretch ratio as long as fuzzing does not occur. Subsequently, the resulting oxidized fiber is heated at not less than 1,000°C in an inert gas such as nitrogen, to produce a carbon fiber. Thereafter, by performing anodic oxidation in an aqueous electrolyte solution, addition of a functional group(s) to the carbon fiber surface becomes possible, so that adhesiveness to resins can be improved. Further, it is preferred to add a sizing agent such as an epoxy resin to obtain a carbon fiber having excellent abrasion resistance.

EXAMPLES

[0040] The present invention is described below more concretely by way of Examples. As shown in Fig. 1, the wind velocities and the absolute humidities at the four points in the outer periphery of the spinneret used in the present Examples were measured at positions arranged such that the outer periphery of the spinneret having a rectangular shape was equally divided into four portions, wherein each point was positioned at the middle point of the height from the liquid surface to the spinneret surface, and 30 mm distant from the outermost discharge holes of the spinneret. The wind velocity, the temperature, and the relative humidity were measured using Climomaster MODEL 6501 (Kanomax Japan Inc.). The absolute humidity (AH) [g/m³] was calculated from the temperature (T) [°C] and the relative humidity (RH) [%] measured with the Climomaster, using the following calculation equation (e: saturated vapor pressure [hPa]).

$$e = 6.11 \times 10^{(7.5T/(T + 237.3))}$$

$$AH = 217 \times e / (t + 273.15) \times RH / 100$$

Here, the hourly average of the absolute humidity at each of the four points in the outer periphery of the spinneret was obtained by measuring the wind velocity, the temperature, and the relative humidity as described above 12 times at 5-minute intervals, calculating the absolute humidities using the above calculation equation, and then calculating their average for each measurement point.

[0041] The air flow rate per unit time (Af) was calculated from, among the wind velocities measured at the four measurement points, the wind velocity at one point positioned in the upstream side of the air flow, and the cross-sectional area as determined by seeing the spinneret from the upstream side of the air flow. The gas-phase-portion volume (Vh) was calculated from the discharge area calculated from the outermost discharge holes of the spinneret, and the height of the gas-phase portion formed in the vertically downward direction from the discharge surface to the coagulation bath liquid surface. The amount of the solvent in the discharged dope solution (As) is the amount of the solvent contained in the dope solution discharged from the spinneret per unit time.

[0042] The degree of dew condensation on the spinneret surface, the appearance of the acrylonitrile fibers, and the process stability were judged as follows.

(Degree of Dew Condensation on Spinneret Surface)

[0043] The sizes and the number of dewdrops on the spinneret surface were measured after one week of continuous spinning, and scored according to the following standard.

[0044] Dewdrop diameter, less than 2 mm: 1 point/dewdrop

Dewdrop diameter, not less than 2 mm and less than 5 mm: 5 points/dewdrop

Dewdrop diameter, not less than 5 mm: 10 points/dewdrop

(Appearance of Acrylonitrile Fibers)

[0045] Before taking the acrylonitrile fibers, the fuzz number in the acrylonitrile fibers was counted for a length of 1000 m to evaluate the appearance on a scale of 1 to 5. The evaluation standard was as follows.

1: (Fuzz number/fiber · 1,000 m) $\leq$ 1

2: $1 < (\text{Fuzz number/fiber} \cdot 1,000 \text{ m}) \leq 2$

3: $2 < (\text{Fuzz number/fiber} \cdot 1,000 \text{ m}) \leq 5$

4: $5 < (\text{Fuzz number/fiber} \cdot 1,000 \text{ m}) < 60$

5: $60 \leq (\text{Fuzz number/fiber} \cdot 1,000 \text{ m})$.

(Process Stability of Acrylonitrile Fibers)

[0046] Evaluation was carried out on a scale of 1 to 5 and based on the yarn break frequency during production of 10 t of acrylonitrile fibers. The evaluation standard was as follows.

1: (Yarn break frequency /production of 10 t of acrylonitrile fibers) $\leq$ 1

2: $1 < (\text{Yarn break frequency} / \text{production of 10 t of acrylonitrile fibers}) \leq 2$

3: $2 < (\text{Yarn break frequency} / \text{production of 10 t of acrylonitrile fibers}) \leq 3$

4: $3 < (\text{Yarn break frequency} / \text{production of 10 t of acrylonitrile fibers}) < 5$

5: $5 \leq (\text{Yarn break frequency} / \text{production of 10 t of acrylonitrile fibers})$

<Examples 1 to 4>

[0047] A solution of an acrylonitrile copolymer composed of 99% by mass acrylonitrile and 1% by mass itaconic acid in DMSO was prepared by solution polymerization.

[0048] Using a spinneret whose total number of dope solution discharge holes is 6,000, the resulting acrylonitrile copolymer solution (spinning dope solution) was discharged once into air from the discharge surface of the spinneret to allow the solution to pass through the gas-phase portion, and then discharged into a coagulation bath liquid composed of 35% by mass DMSO/65% by mass water, to obtain a coagulated fiber.

[0049] Here, for the spinning, an air supply nozzle and an exhaust nozzle in each of which an aperture of 5 mm $\times$ 200 mm is formed were arranged on the front side of the spinneret such that the spinneret was sandwiched between these. Dehumidified air was blown from the air supply nozzle and sucked with the exhaust nozzle to scavenge the solvent vapor generated in the gas-phase portion between the discharge surface and the coagulation bath. The nozzle angle of the air supply/exhaust nozzles, $A_f/(A_s/V_h)$, and the relative standard deviation of the wind velocities at the four measurement points, were changed among the Examples as shown in Table 1. Table 1 also shows the degree of dew condensation on the discharge surface, the appearance of the acrylonitrile fibers, and the process stability in each Example.

[0050] The resulting coagulated fiber was then washed with water, and an oil agent was applied thereto while performing stretching in a bath stretching process, followed by performing drying and a stretching process. By this, acrylonitrile fibers of 6,000 single fibers could be stably produced.

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
A/(AsVh)	0.0011	0.0013	0.0012	0.0008	0.0012	0.0010	0.0014	0.0002	0.0510	0.0010	0.0011	0.0009
Nozzle Angle	90	70	110	90	90	90	90	-	90	90	90	90
Relative Standard Deviation of the Wind Velocities at the four measurement points	15	26	33	55	10	35	22	6	20	30	40	20
Hourly Average of the Absolute Humidity at measurement point	14.3	18.8	12.8	17.1	8.9	14.2	12.5	24.5	17.3	12.5	21.8	24.1
Hourly Average of the Absolute Humidity at measurement point	15.6	17.8	10.7	18.3	8.8	12.3	15.8	23.9	12.0	23.3	24.1	22.8
Hourly Average of the Absolute Humidity at measurement point	16.8	18.1	9.9	19.0	9.2	12.8	19.8	24.6	14.8	10.5	20.2	23.2
Hourly Average of the Absolute Humidity at measurement point	13.4	19.2	13.1	18.1	9.4	19.8	17.5	24.2	16.6	13.1	18.8	22.7
Spinneret Front Surface	1	1	2	5	0	2	1	70	1	3	52	79
Spinneret Back Surface	2	4	1	3	0	3	2	60	1	11	58	87
Spinneret Side Surface	2	2	3	2	0	6	3	21	3	44	18	101
Appearance of Acrylonitrile Fiber Bundle during	1	1	2	2	1	2	1	5	4	2	4	5

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(continued)

Yarn Break Frequency of Acrylonitrile Fiber Bundle during Manufacture	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Compara- tive Example 1	Compara- tive Example 2	Compara- tive Example 3	Compara- tive Example 4	Compara- tive Example 5
	-	1	2	1	2	1	2	3	5	4	5	5

<Example 5>

[0051] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that the degree of dehumidification was increased.

<Example 6>

[0052] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that a 9,000-hole spinneret was used.

<Example 7>

[0053] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that a 2,000-hole spinneret was used.

<Comparative Example 1>

[0054] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that the air supply/exhaust nozzles were not operated.

<Comparative Example 2>

[0055] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1.

<Comparative Example 3>

[0056] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that the degree of dehumidification was decreased.

<Comparative Example 4>

[0057] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that the degree of dehumidification was further decreased.

<Comparative Example 5>

[0058] An acrylonitrile precursor fiber was obtained in the same manner as in Examples 1 to 4 except that Af/(As/Vh) was changed as shown in Table 1, and that the supplied air was not dehumidified.

[0059] Table 1 also shows the degree of dew condensation on the discharge surface, the appearance of the acrylonitrile fibers, and the process stability in each of the Examples and the Comparative Examples.

[0060] As shown in Table 1, it can be seen that dew condensation on the discharge surface of the spinneret was suppressed, and the appearance and the process stability were improved by the present invention.

INDUSTRIAL APPLICABILITY

[0061] The present invention can be practically used not only for suppressing occurrence of dew condensation on the spinneret surface in production of precursor fibers for carbon fibers, but also as means for improving productivity by suppression of dew condensation in any dry-jet wet spinning.

DESCRIPTION OF SYMBOLS

[0062]

1. Spinneret
2. Air supply nozzle or exhaust nozzle
3. Coagulation bath
4. Wind velocity/air flow measurement point A

5. Wind velocity/air flow measurement point B
6. Wind velocity/air flow measurement point C
7. Wind velocity/air flow measurement point D

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Claims

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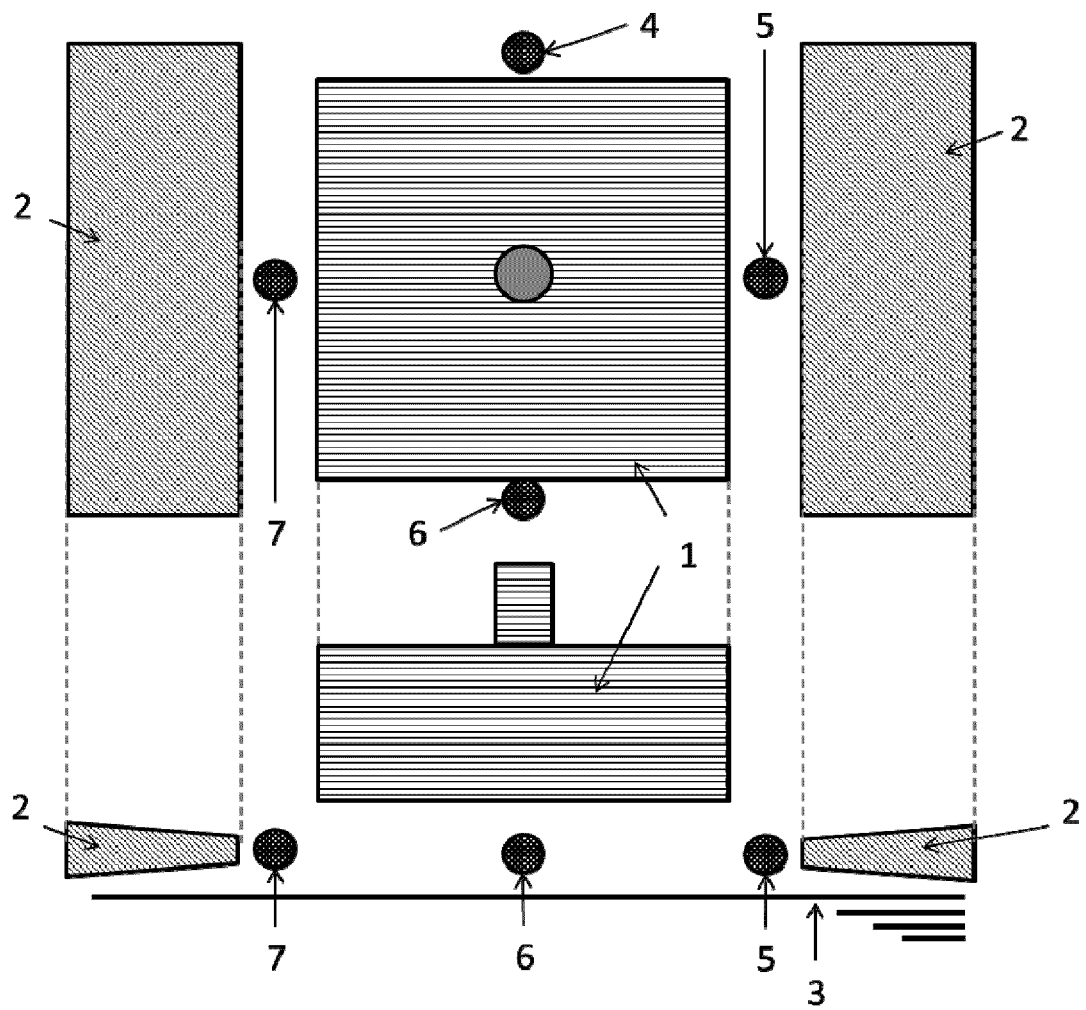
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1. A method of producing a fiber, the method comprising discharge, from a spinneret, a spinning dope solution containing a fiber-forming polymer dissolved in a solvent, once allowing the solution to run in air, and then guiding the solution into a coagulation bath liquid to allow coagulation, wherein a gas-phase portion formed in a vertically downward direction from a discharge surface of the spinneret to a coagulation bath liquid surface has an air flow rate per unit time (A_f) which satisfies, in relation to the amount of the solvent in the spinning dope solution per unit time (A_s) in the gas-phase-portion volume (V_h), the relational expression $0.0008 \text{ m}^3 \leq A_f/(A_s/V_h) \leq 0.0015 \text{ m}^3$, and the hourly average of the absolute humidity at each of four points in an outer periphery of the spinneret in the gas-phase portion is not more than 20 g/m^3 .
2. The method of producing a fiber according to claim 1, wherein the relative standard deviation of the wind velocities at four points in an outer periphery of the spinneret in the gas-phase portion is not more than 40%.
3. The method of producing a fiber according to claim 1 or 2, wherein the number of holes in the spinneret is not less than 2,000 and not more than 50,000.
4. The method of producing a fiber according to any one of claims 1 to 3, wherein the fiber-forming polymer is an acrylonitrile copolymer.
5. A method of producing a carbon fiber, comprising producing a fiber by the method of producing a fiber according to claim 4, performing oxidation treatment in an oxidizing gas at 200 to 300°C , and then heating the fiber in an inert gas at not less than $1,000^\circ\text{C}$.

[Figure 1]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/040807

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D01D5/06(2006.01)i, D01F6/18(2006.01)i, D01F9/22(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. D01D5/06, D01F6/18, D01F9/22

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.
X	JP 5-44104 A (UNITIKA LTD.) 23 February 1993, claim 1, paragraphs [0016]-[0019] (Family: none)	1-5
A	JP 8-510516 A (COURTAULDS FIBRES (HOLDINGS) LIMITED) 05 November 1996 & US 5639484 A & WO 1994/028218 A1 & EP 700463 A1 & CN 1124509 A	1-5
A	JP 2007-119973 A (TEIJIN TECHNO PRODUCTS LTD.) 17 May 2007 (Family: none)	1-5
A	WO 03/014436 A1 (TENECAL LIMITED) 20 February 2003 & EP 1415026 A1 & KR 10-0912305 B1 & TW 220907 B & CN 1541289 A & AT 373122 T & ES 2292808 T	1-5
P, X	WO 2018/180188 A1 (TORAY INDUSTRIES, INC.) 04 October 2018 (Family: none)	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search
03 December 2018 (03.12.2018)Date of mailing of the international search report
11 December 2018 (11.12.2018)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 5044104 A [0006]
- JP 2007239170 A [0006]
- JP 2010236139 A [0006]