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- Process for producing a carbon fiber from pitch material.
- A process for producing a carbon fiber from pitch material, which comprises melt spinning pitch material in a gaseous atmosphere to form precursory pitch fibers and bundling the precursory pitch fibers, followed by infusible treatment and carbonization and optionally by graphitization, characterized in that an aqueous emulsion of a silicone oil is applied as an oiling agent to the precursory pitch fibers prior to or during the bundling operation.

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PROCESS FOR PRODUCING A CARBON FIBER FROM PITCH MATERIAL

The present invention relates to a process for producing a carbon fiber from pitch material such as a coal-originated pitch, a petroleum pitch or a baked polymer pitch. More particularly, it relates to a process for producing such a pitch-type carbon fiber of high quality which is composed of carbon fiber monofilaments bound together without direct adhesion or fusion to one another, and which is easy to handle.

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Pitch-type carbon fibers are produced usually by melt-spinning the pitch material to form precursory pitch fibers and subjecting the precursory pitch fibers to infusible treatment and carbonization treatment. Such pitch-type carbon fibers have an advantage that they can be produced in good yield and at low costs as compared with carbon fibers made of e.g. polyacrylonitriles. On the other hand, they have a disadvantage that the precursory pitch fibers are extremely brittle and difficult to handle for the infusible treatment or carbonization treatment. The precursory pitch fibers are likely to undergo fluffing, twine round guide rollers or

break during such treatments. Further, there are additional difficulties such that adhesion or fusion is likely to take place among the precursory pitch fibers during the infusible treatment and the carbonization treatment, and the resulting carbon fiber surface is susceptible to damages.

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These problems are substantially different from the problems involved in the case of the polyacrylonitriletype carbon fiber which differs from the pitch-type 10 carbon fiber in the starting materials as well as in the manner of the production. Namely, in the case of the polyacrylonitrile-type carbon fiber, a molten polyacrylonitrile is subjected to wet spinning in which it is extruded through spinning nozzles into a spinning 15 bath composed essentially of a mixture of dimethylformamide with water or a mixture of dimethylsulfoxide with water and thereby forms solidified In such a wet spinning method, the formed fibers are wetted with the solution of the spinning bath and 20 bundles into a tow in the spinning bath. The tow withdrawn from the spinning bath is subjected to flame resistant treatment in an oxidizing atmosphere at a temperature of from 200 to 300°C and then to carbonization treatment in an inert atmosphere at a temperature of from 300 to 1400°C. For such treatments, 25 it is considered effective to apply a lubricant such as polyethylene glycol or polypropylene glycol to the surface of the tow. However, when such a lubricant is

used as an oiling agent for the step of bundling precursory pitch fibers, there will be difficulties such that the precursory pitch fibers are thereby partly dissolved, or the fibers tend to adhere or fuse to one another, whereby the tow tends to be stiff or rigid.

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As a method for overcoming the difficulties in the bundling of the precursory pitch fibers, the present inventors have previously proposed to use a silicone oil as the oiling agent for bundling.

According to this method, the bundling can smoothly be conducted. However, depending upon the operation, the silicone oil may be applied excessively. While not adversely affecting the bundling operation, such excessive application of silicone oil is likely to lead to difficulties such that the tow of precursory pitch fibers tends to be stiff after the infusible treatment or the carbonization treatment, and in an extreme case, the pitch fibers tend to fuse one another to form a tow which is hardly unbound or separated into individual fibers.

Under these circumstances, the present inventors have conducted further researches to overcome these difficulties. As a result, they have found it effective to use an aqueous emulsion of a silicone oil as the oiling agent. The present invention has been accomplished based on this discovery.

Namely, the present invention provides a process for producing a carbon fiber from pitch material, which comprises melt spinning pitch material in a gaseous

atmosphere to form precursory pitch fibers and bundling the precursory pitch fibers, followed by infusible treatment and carbonization and optionally by graphitization, characterized in that an aqueous emulsion of a silicone oil is applied as an oiling agent to the precursory pitch fibers prior to or during the bundling operation.

Now, the present invention will be described in detail with reference to the preferred embodiments.

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As the pitch material to be used in the present invention, there may be mentioned a coal-originated pitch such as coal tar pitch or liquefied coal; a petroleum pitch such as a distillation residue obtained by the distillation of crude oil under atmospheric or reduced pressure or a heat-treated product thereof, or a heat-treated product tar obtained by the pyrolysis of naphtha; and a baked polymer pitch obtained by the carbonization of a synthetic or natural resin.

The melt spinning of the pitch material is conducted by extruding it into a gaseous atmosphere through spinning nozzles in the same manner as in the case of the dry melt spinning of ordinary synthetic fibers. It is preferred to employ a method wherein the pitch material is melted by an extruder or the like and extruded into a gaseous atmosphere from spinning nozzles directed downwardly, whereupon the extruded fibers are cooled and solidified. It is usual to employ spinning nozzles with discharge outlets having a diameter of from 0.1 to

0.5 mm. The temperature of the spinning nozzles is determined depending upon the type of the pitch material to provide a melt viscosity most suitable for spinning, and it is usually selected within a range of from 250 to 350°C. It is effective for the stabilization of spinning to provide temperature-keeping cylinders below the spinning nozzles.

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In the present invention, an aqueous emulsion of a silicone oil is applied as an oiling agent to the precursory pitch fibers obtained by the spinning, prior to or during the bundling operation. As a specific example of such a silicone oil, dimethylpolysiloxane is usually employed. It is also possible to employ modified dimethylpolysiloxane derivatives obtained by introducing various groups to dimethylpolysiloxane. Specifically, there may be mentioned, for example, methylphenylpolysiloxane or hydrodienepolysiloxane. Further, there may be employed other derivatives obtained by modifying dimethylpolysiloxane with one or more groups selected from the group consisting of an epoxy group, an alkyl group such as ethyl or propyl, an amino group, a carboxyl group, an alcohol, a phenyl group or a polyether. These silicone oils may be used alone or in combination as a mixture of at least two different kinds.

The aqueous emulsion of a silicone oil may be prepared by mixing the silicone oil with water by means of a common mixing device such as a high speed mixer, a colloid mill or a homogenizer so that the silicone oil

constitutes from 0.1 to 35% by weight in the mixture. For the preparation of the emulsion, if the concentration of the silicone oil is too high to maintain the emulsified condition, from 0.25 to 2% by weight of an emulsifier may be added. As such an emulsifier, there may be employed conventional emulsifiers. For instance, there may be mentioned a nonionic emulsifier such as a sorbitan fatty acid ester e.g. sorbitan palmitic acid ester, sorbitan stearic acid ester, polyoxyethylene sorbitan fatty acid ester or polyoxyethylene sorbitan caproic acid ester, polyoxyethylene lauric acid ester, acetylated monoglyceride, acetylated glyceryl monostearate or a polyoxyethylene lanolin derivative; an anionic emulsifier such as an alkyl sulfate, sodium laurylsulfate, sodium cetylsulfate, a dialkyl sulfosuccinate or sodium di-2-ethylhexyl sulfosuccinate; or a cationic emulsifier such as alkyl pyridinium chloride. Further, a small amount of fine solid particles may be added to the aqueous emulsion of a silicone oil.

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As the fine solid particles, there may be employed, for instance, fine carbonaceous particles, fine inorganic oxide particles, fine inorganic salt particles or a mixture thereof. Specifically, there may be mentioned fine particles of graphite, carbon black, silica, calcium carbonate, titanium oxide, talc, clay, barium sulfate, potassium titanate or molybdenum disulfide.

The oiling agent may be applied to the precursory pitch fibers by various methods such as a spraying method, a roller coating method or a dipping method.

The amount of the deposition of the oiling agent onto the fibers is usually from 1 to 15% by weight, preferably from 2 to 10% by weight. If the amount of the deposition is less than 1% by weight, it is difficult to maintain the bundled state of the spun fibers adequately, whereby it becomes difficult to handle the bundled fibers, and the fibers are likely to be damaged. On the other hand, if the amount exceeds 15% by weight, depending upon the concentration of the oiling agent, the evaporation at the time of the infusible treatment will be inadequate, and the agent will remain on the filaments and thus hinders the infusible reaction, and a low molecular weight gas generated from the fibers during the infusible treatment will not sufficiently be dissipated, whereby the strength of the carbon fiber will be reduced.

The precursory pitch fibers having the aqueous solution of a silicone oil applied thereon and bundled, are subjected to infusible treatment and carbonization treatment in accordance with known methods. For instance, the infusible treatment may be conducted by heating the tow of fibers at a temperature of from 150 to 360°C for from 5 minutes to 10 hours in an oxidizing atmosphere such as oxygen, ozone, air, a nitrogen oxide, halogen or sulfur dioxide. The carbonization treatment may be conducted by heating the tow of fibers at a temperature

of from 1000 to 2500°C for from 0.5 minute to 10 hours in an inert gas atmosphere such as nitrogen or argon.

Further, the graphitization may be conducted by heating the tow of fibers at a temperature of from 2500 to 3500° C for from 1 second to 1 hour.

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If necessary, a load or tension may be applied to the tow of fibers to some extent during the infusible treatment, the carbonization treatment or the graphitization treatment for the purpose of preventing shrinkage or deformation.

Further, for the infusible treatment, it is desirable to preliminarily adjust the deposition of water on the precursory pitch fibers to a level of at most 0.1% by weight either by providing a drier immediately before the infusible treatment furnace, or by drying, at the initial stage of the infusible treatment, the precursory pitch fibers at from 50 to 100° C for 5 minutes to 2 hours.

From the foregoing description, it should be understood that according to the present invention, the handling of brittle fibers can be made easy and it is possible to prevent the adhesion or fusion of the fibers to one another or to prevent the damages to the fiber surface, by a simple operation of applying an aqueous emulsion of a silicone oil to the precursory pitch fibers. Thus, a pitch-type carbon fiber having good quality is obtainable in the form of a continuous fiber in an industrially advantageous manner and condition. Further, the heat-treatments can thereby be conducted

under uniform and sufficient tension, whereby a pitch-type carbon fiber having superior properties is obtainable at low costs.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by these specific Examples.

EXAMPLES 1 to 4

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Coal tar-originated pitch material (meso-phase pitch 10 having an optical anisotropy of 100%) was melt-spun into a gaseous atmosphere at a spinneret temperature of 330°C. Then, an oiling agent as identified in Table 1 was applied by spraying to the precursory pitch fibers having a diameter of 10 μm thereby obtained, and the fibers were 15 bundled together. The bundled fiber (i.e. tow) was dried in air at 80°C for 30 minutes. Then, it was heated from 150°C to 350°C over a period of 2 hours 40 minutes and held at that temperature for 30 minutes to conduct infusible treatment. Then, the fiber was subjected to 20 carbonization treatment by heating it in argon from room temperature to 1,400°C over a period of 2 hours 20 minutes, and then maintaining it at that temperature for one hour, whereby a carbon fiber was obtained. The state of the bundling of fibers, the state of the fibers after 25 the infusible treatment and the adhesion or fusion of monofilaments during the process of the production of the carbon fiber, were observed, and the tensile strength of the carbon fiber was measured. The results are shown in Table 1.

COMPARATIVE EXAMPLES 1 to 5

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The operation was conducted in the same manner as in Example 1 except that no oiling agent was used or the amount or the type of the oiling agent was varied. The results are shown in Table 1.

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Notes						Substantially breakage of monofilaments and fluffing	Dimethylsilicone was used alone	So brittle that fibers were not suitable for sub-sequent processing	=	н
Carbon fibers	Tensile strength (kg/mm²)	294	270	282	272	262	202	1	t	1
19	Adhesion or fusion of monofilaments	No	No	No	No	No	Slight	ſ	1	I
Fibers aft treatment	State	Very flexible	=	ı	н	E	Slightly flexible	Brittle	¥	#
Bundling properties (Efficiency in the handling of fibers)		0	0	0	0	×	0	X - \(\tau \)	0	0
Oiling agent	Deposited amount (% by weight)	5	5	5	ç	1	ഹ	2	5	9
	Emulsion concentration (% by weight)	3.3	9.6	1.7	3.3	t	100	4	4	10
	Type	Dimethylsilicone	п	Amino-modified silicone	п	None	Dimethylsilicone	Polyether	11	Aliphatic monoester
		1	2	3	4		7	ဗ	4	ಬ
	EXYMBLE					COMPARATIVE EXAMPLE				

 \bigcirc : Excellent \bigcirc : Good \triangle : Inferior X: No good

CLAIMS:

- 1. A process for producing a carbon fiber from pitch material, which comprises melt spinning pitch material in a gaseous atmosphere to form precursory pitch fibers and bundling the precursory pitch fibers, followed by infusible treatment and carbonization and optionally by graphitization, characterized in that an aqueous emulsion of a silicone oil is applied as an oiling agent to the precursory pitch fibers prior to or during the bundling operation.
 - 2. The process according to Claim 1, wherein the concentration of the silicone oil in the oiling agent is from 0.1 to 35% by weight.
- 3. The process according to Claim 1, wherein the oiling agent is applied in an amount of from 1 to 15% by weight relative to the fibers.