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54 **Pitch-based carbon fibres superior in compressive physical properties and process for producing same.**

57 A process for producing a pitch-based carbon fiber comprises hydrogenating a carbonaceous pitch in the presence of a hydrogenation catalyst to add to the pitch two moles or more hydrogen per pitch molecule; heat-treating the hydrogenated pitch at atmospheric pressure or under reduced pressure to obtain an optically anisotropic pitch; collecting from said optically anisotropic pitch a component which is insoluble in an organic solvent having a solubility parameter at 25° C of 7.4 to 9.0 and soluble in an organic solvent having a solubility parameter at 25° C of 9.2 to 11.0 to obtain a spinning pitch having an optically anisotropic phase content of 5% to 40% by volume; spinning said spinning pitch; and thereafter making the resulting pitch fiber infusible and then carbonizing the thus-infusibilized pitch fiber.

Description

Pitch-Based Carbon Fibers Superior in Compressive Physical Properties and Process for Producing Same

Background of the Invention

The present invention relates to pitch-based carbon fibers superior in compressive physical properties and a process for producing same.

Heretofore, studies have been made about the method of producing carbon fibers having high strength and high modulus, using pitch as a starting material. However, composites (hereinafter referred to simply as "CFRP") containing pitch-based carbon fibers as constituent fibers are markedly inferior in compressive physical properties, particularly compressive strength, as compared with CFRP'S containing polyacrylonitrile (PAN)-based carbon fibers as constituent fibers. With respect to compressive strength, it has heretofore been considered impossible to obtain a CFRP of pitch-based carbon fibers equal or superior to a PAN-based CFRP.

For improving compressive physical properties of CFRP, it is necessary to improve compressive physical properties of carbonfibers themselves.

Having made extensive studies for obtaining pitch-based carbon fibers superior in compressive physical properties, the present inventors found that carbon fibers (see Japanese Patent Laid-Open No. 155491/1986) obtained using a pitch for carbon fiber having an optically anisotropic phase content of 5-40 vol.% was not only high in strength and modulus but also superior in compressive physical properties to conventional pitch-based carbon fibers. The said pitch is obtained by subjecting an optically anisotropic pitch to an extraction treatment with an organic solvent having a solubility parameter of 7.4 to 9.0, then collecting insoluble matter, subjecting the insoluble matter to an extraction treatment with an organic solvent having a solubility parameter of 9.2 to 11.0, and collecting soluble matter.

Summary of the Invention

Having made further studies, the present inventors found that a remarkable improvement in compressive physical properties could be attained by producing the aforesaid pitch for carbon fiber under extremely limited conditions.

It is therefore the object of the present invention to provide pitch-based carbon fibers remarkably superior in compressive physical properties and a process for producing such carbon fibers.

Although it has heretofore been considered difficult to obtain a pitch-based carbon fiber equal in compressive strength to conventional PAN-based carbon fibers, it is surprisingly made possible according to the present invention to obtain a pitch-based carbon fiber which in a high modulus region exhibits a compressive strength far higher than that of such conventional PAN-based carbon fibers. Such high compressive strength has so far been unattainable even by the PAN-based carbon fibers.

The present invention resides in a process for

producing a pitch-based carbon fiber, comprising hydrogenating a carbonaceous pitch in the presence of a hydrogenation catalyst to add to the pitch two moles or more hydrogen per pitch molecule; heat-treating the thus-hydrogenated pitch at atmospheric pressure or under reduced pressure to obtain an optically anisotropic pitch; collecting from the optically anisotropic pitch a component which is insoluble in an organic solvent having a solubility parameter at 25°C of 7.4 to 9.0 and soluble in an organic solvent having a solubility parameter at 25°C of 9.2 to 11.0 to obtain a spinning pitch having an optically anisotropic phase content of 5 to 40 vol.%; spinning the spinning pitch; and thereafter making the resulting pitch fiber infusible and carbonizing the thus-infusibilized pitch fiber.

The carbon fiber produced by the above process of the present invention has such compressive characteristics as have been unattainable by conventional pitch-based carbon fibers. More particularly, the pitch-based carbon fiber of the present invention has a novel structure, has La and Lc values both not larger than 1,000Å as measured by X-ray diffraction, has a texture content not less than 50 vol.% of the entire carbon fiber, the said texture being not larger than 1,000Å in terms of the width of fibrils when observed in the axial direction of the fiber using a transmission type electron microscope, has a density in the range of 1.95 to 2.12 g/cm³, and satisfies the relation of $3.82 \leq d_{002} + 0.212p \leq 3.87$ between an interlayer spacing d_{002} as measured by X-ray diffraction and a density ρ .

Detailed Description of the Invention

The carbonaceous pitch used in the present invention is not specially limited, but a petroleum pitch or a coal pitch is preferred.

The carbonaceous pitch is hydrogenated in the presence of a hydrogenation catalyst to add to the pitch 2 moles or more hydrogen per pitch molecule. As the hydrogenation catalyst there may be used one prepared by supporting on an inorganic solid carrier such as zeolite, silica, alumina or silica gel a Group VI-B metal in the Periodic Table such as chromium or molybdenum or a Group VIII metal in the same Table such as cobalt, nickel, palladium or platinum in the form of metal or oxide.

Conditions of the hydrogenation differ depending on the kind of the catalyst used, but usually involve a temperature in the range of 150° to 450°C, a pressure in the range of 30 to 250 kg/cm².G and a space velocity (LHSV) in the range of 0.15 to 3.0.

By the hydrogenation, the aromatic nucleus of an aromatic hydrocarbon of the pitch molecule is partially nuclear-hydrogenated to add thereto 2 moles or more, preferably 2 to 13 moles, more preferably 3 to 9 moles, of hydrogen per pitch molecule.

The pitch thus hydrogenated is then heat-treated at atmospheric pressure or under reduced pressure to obtain pitch having an optically anisotropic phase

content of 5-100 vol.%, preferably 5-60 vol.%, more preferably 5-40 vol.%. The heat treatment is performed at a temperature usually in the range of 340° to 500° C, preferably 370° to 450° C, for 1 minute to 30 hours. It is also preferable to carry out the heat treatment while introducing an inert gas such as nitrogen. In this case, the amount of such inert gas to be introduced is preferably in the range of 0.7 to 5.0 scfh/lb pitch.

Then, by collecting from the thus-obtained optically anisotropic pitch having an optically anisotropic pitch content of 5-100 vol.% a component which is insoluble in an organic solvent having a solubility parameter at 25° C of 7.4 to 9.0, preferably 7.6 to 8.4 and soluble in an organic solvent having a solubility parameter at 25° C of 9.2 to 11.0, preferably 10.0 to 10.8, there is obtained a spinning pitch having an optically anisotropic pitch content of 5-40 vol.%.

The order of such solvent extractions is not specially limited, but preferably the optically anisotropic pitch is subjected to an extraction treatment with an organic solvent having a solubility parameter of 7.4 to 9.0 and insoluble matter is collected, then the said insoluble matter is subjected to an extraction treatment with an organic solvent having a solubility parameter of 9.2 to 11.0 and soluble matter is collected.

The extraction treatments using such organic solvents are usually performed at an ordinary temperature or under heating (e.g. 15-230° C) and at atmospheric pressure or under the application of pressure. The pitch - organic solvent mixing ratio may be changed optionally according to temperature and pressure conditions, but usually 10 to 150 parts of an organic solvent is used for 1 part of pitch.

As the organic solvent having a solubility parameter of 7.4 to 9.0 there may be used not only an organic solvent which itself has a solubility parameter falling under the said range but also a mixture of two or more organic solvents which mixture has a solubility parameter in the range of 7.4 to 9.0. In this case, the solubility parameter of each of the two or more organic solvents may be outside the range of 7.4 to 9.0 provided the solubility parameter of the mixture is adjusted to a value in the range of 7.4 to 9.0. This also applies to organic solvents each having a solubility parameter of 9.2 to 11.0.

The following solvents are mentioned (the parenthesized values indicate solubility parameters) as examples of organic solvents each having a solubility parameter of 7.4 to 9.0: carbon tetrachloride (8.6), 1,1-dichloroethane (8.9), 1,2-dichloropropane (9.0), propyl chloride (8.4), methyl ethyl ether (7.6), furan (8.4), 1-chlorobutane (8.4), t-butyl chloride (7.5), diethyl ether (7.4), isobutylamine (8.5), cyclohexane (8.2), xylene (8.8), octane (7.6) and cumene (8.8).

As examples of organic solvents each having a solubility parameter of 9.2 to 11.0 there are mentioned carbon disulfide (10.0), chloroform (9.3), dichloromethane (9.7), 1,1,2-trichloroethane (9.6), acetone (10.0), methyl ethyl ketone (9.3), pyridine (10.6), dichlorobenzene (10.0), chlorobenzene (9.5), benzene (9.2), naphthalene (10.6) and nitrobenzene (10.2).

Where two or more organic solvents are mixed into a mixture having a predetermined solubility parameter, there may be adopted any combination of organic solvents.

In this way there is obtained a spinning pitch to be used in the invention which pitch has an optically anisotropic phase content in the range of 5-40 vol.%, preferably 5-35 vol.% more preferably 10-30 vol.%.

Since the spinning pitch used in the invention is obtained by the extraction treatments using such solvents, it is presumed to contain substantially no insoluble solids which would cause a problem at the time of spinning. But it is also preferable to use a step for removing insoluble solids in advance. This step may be provided at any stage prior to spinning; preferably it may be carried out after the hydrogenation treatment, whereby insoluble solids and residual catalyst can be removed effectively.

As the method for removing insoluble solids, etc. there may be adopted a known method, e.g. centrifugal separation, filtration, or adsorption.

The spinning pitch is melt-spun into a pitch fiber by a known method such as, for example, an extrusion method or a centrifugal spinning method. The melt-spinning may be done under known conditions, but in order to obtain the object carbon fiber of the invention superior in compressive physical properties it is desirable to adopt a melt viscosity in the range of 500 to 9,000 poise, preferably 1,500 to 7,000 poise, and a take-up tension not lower than 25 mg/pc.

The resulting pitch fiber is then rendered infusible in an oxidative gas atmosphere using one or more of such oxidative gases as oxygen, ozone, air, nitrogen oxides, halogen and sulfurous acid gas. This infusibilization treatment is carried out under a temperature condition under which the melt-spun pitch fiber to be treated is not softened and deformed. For example, a temperature in the range of 20° to 360° C, preferably 20° to 300° C, is adopted. The treating time is usually 5 minutes to 10 hours.

The pitch fiber thus rendered infusible is then carbonized in an inert gas atmosphere to obtain the pitch-based carbon fiber of the present invention. The carbonization treatment is conducted usually at a temperature of 600° C to 3,500° C. The time required for this treatment is usually 0.5 minute to 10 hours.

The pitch-based carbon fiber of the present invention thus obtained is remarkably superior in compressive physical properties, especially compressive strength, and has a novel structure. More specifically, when the pitch-based carbon fiber of the invention is cut into an ultra-thin piece axially using a microtome and its interior structure is observed through an electron microscope, it is seen that the proportion of a fine texture not larger than 1,000Å in terms of the width of fibril is not less than 50 vol.%. The fibril is a constituent of an elongated fine texture and its size can be measured by observing an ultra-thin piece (thickness: 800-1,200Å) parallel to the axis of the carbon fiber through an electron microscope.

Further, when the pitch-based carbon fiber of the

present invention is determined for La and Lc values by X-ray diffraction, both values are found to be not larger than 1,000Å. The density thereof is in the range of 1.95 to 2.12 g/cm³ and the fiber satisfies the relation of $3.82 \leq d_{002} + 0.212p \leq 3.87$ between an interlayer spacing d_{002} as measured by X-ray diffraction and a density p . Conventional pitch-based carbon fibers do not satisfy this relation.

(Effects of the Invention)

As will be apparent from the following working examples, the pitch-based carbon fiber of the present invention is not only superior in tensile strength and tensile modulus but also has an extremely high compressive strength. When observed in its sectional structure parallel to the axis thereof, the fiber is found to have a fine structure comprising fibrils not larger than 1,000Å in width. These fibrils are arranged regularly in the fiber axis direction and a large number of entanglements are present between fibrils. Thus, the carbon fiber of the invention has a very strong structure.

(Examples)

The following examples are given to illustrate the present invention more concretely, but the invention is not limited thereto.

Example 1

Heavy oil (properties are as shown in Table 1) which had been obtained by catalytic cracking of a vacuum-distilled light oil from Arabic crude oil at 495°C using a silica-alumina catalyst was heat-treated for 3 hours at a pressure of 15 kg/cm².G and a temperature of 430°C and then distilled at 250°C/1 mmHg to afford a starting pitch having a softening point of 85°C and a benzene insolubles content of 25%.

The starting pitch was treated in a fixed bed of a nickel-molybdenum supported catalyst at 340°C, a hydrogen pressure of 150 kg/cm². G and an LHSV of 0.25, then the residual catalyst and insoluble solids were filtered under pressure using a 0.5 μm filter to obtain a hydrogenated pitch having a softening point of 35°C, a benzene insolubles content of 0.8 wt.%, and 9 moles of hydrogen added thereto per pitch molecule.

30 g of the hydrogenated pitch was stirred while introducing nitrogen at a rate of 1,200 ml/min, and heat-treated at 400°C for 3 hours to afford an optically anisotropic pitch having a softening point of 197°C and a mesophase content of 40 vol.%.

The optically anisotropic pitch thus obtained was pulverized and then subjected to an extraction treatment at 60°C using a mixed solvent (solubility parameter: 7.9) of hexane (50 vol.%) and benzene (50 vol.%) at a rate of 100 ml for 3 grams of the pitch. Thereafter, insolubles in the mixed hexane-benzene solvent were collected.

Then, the said insolubles were subjected to an extraction treatment at 80°C using a mixed solvent (solubility parameter: 9.5) of benzene (85 vol.%) and quinoline (15 vol.%) at a rate of 100 ml for 3 grams of the insolubles, and soluble matter in the mixed benzene-quinoline solvent was obtained.

Then, the solvent was removed from the said soluble matter, leaving pitch for carbon fiber having a softening point of 193°C and a mesophase content of 20 vol.%.

The pitch for carbon fiber thus produced was spun at a melt viscosity of 6,500 poise and a take-up tension of 35 mg/pc. using a spinning apparatus having a nozzle diameter of 0.2 mm and an L/D ratio of 1 to obtain pitch fiber 12μm in diameter.

The pitch fiber thus obtained was heated up to 300°C at a rate of 2°C/min in oxygen containing 2 vol.% of NO₂ and held at this temperature for 2 minutes, then heated up to 650°C at a rate of 10°C/min in nitrogen and held at this temperature for 30 minutes, and then heated up to 2,500°C at a rate of 100°C/min in nitrogen to afford carbon fiber.

The carbon fiber thus obtained was found to have crystallite sizes of Lc '190Å, La '195Å, an interlayer spacing of 3.384Å, a density of 2.08 g/cm³, a tensile strength of 410 kg/mm², a Young's modulus of 62 ton/mm² and a compressive strength of 95 kg/mm².

An internal structure of this carbon fiber is as shown in Fig. 1, which is a transmission type electron micrograph of an ultra-thin piece of the fiber parallel to the fiber axis. As is apparent from Fig. 1, fibrils ranging in width from 200 to 500Å and not smaller than 1,000Å in length are arranged in the direction parallel to the fiber axis and the fiber has a texture content not less than 70 vol.% in which texture a large number of entanglements are present between the fibrils.

Table 1

Specific Gravity (15°C/4°C)	0.965
<u>Distillation Properties</u>	
Initial boiling point	320°C
50%	340°C
100%	353°C
300%	385°C
500%	415°C
700%	445°C
900%	512°C

Example 2

A commercially available petroleum pitch (A-240) was hydrogenated in the same way as in Example 1 to afford a hydrogenated pitch having a softening point of 74°C, a benzene insolubles content of 0.3 wt.% and 5 moles of hydrogen added thereto per pitch molecule.

30 g of the hydrogenated pitch was stirred while nitrogen was introduced at a rate of 1,200 ml/min, and heat-treated at 400°C for 7 hours to obtain an optically anisotropic pitch having a softening point of 245°C and a mesophase content of 50 vol.%.

The optically anisotropic pitch thus obtained was pulverized, then subjected to an extraction treatment in the same way as in Example 1 and insolubles in the mixed hexane-benzene solvent were collected. The insolubles were then subjected to an

extraction treatment at 80°C using chlorobenzene (solubility parameter: 9.5) at a rate of 100 ml for 3 grams of the insolubles and soluble matter in the chlorobenzene was obtained, followed by removal of the solvent, leaving pitch for carbon fiber having a softening point of 205°C and a mesophase content of 10 vol.%.
 The pitch for carbon fiber thus obtained was spun at a melt viscosity of 5,600 poise and a take-up tension of 28 mg/pc. using the spinning apparatus used in Example 1, to afford pitch fiber 10.8 µm in diameter. The pitch fiber was heat-treated in the same manner as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained was found to have Lc and La values of 120Å and 150Å, respectively, an interlayer spacing of 3.405Å, a density of 2.04 g/cm³, a tensile strength of 355 kg/mm², a Young's modulus of 45 ton/mm and a compressive strength of 83 kg/mm².

An internal structure of this carbon fiber is as shown in Fig. 2. As is apparent from this figure, fibrils ranging in width from 100 to 400Å and not smaller than 1,000Å in length are arranged in the direction parallel to the fiber axis and the fiber has a texture content not less than 80 vol.% in which texture a large number of entanglements are present between the fibrils.

Example 3

30 g of the hydrogenated pitch obtained in Example 1 was stirred while nitrogen was introduced at a rate of 1,200 ml/min, and heat-treated at 400°C for 2.5 hours to afford an optically anisotropic pitch having a softening point of 193°C and a mesophase content of 20 vol.%.

The optically anisotropic pitch thus obtained was pulverized, then subjected to an extraction treatment at 60°C using a mixed solvent (solubility parameter: 8.0) of hexane (60 vol.%) and benzene (40 vol.%) at a rate of 100 ml for 3 grams of the pitch, and insolubles in the mixed hexane-benzene solvent were collected.

Then, the said insolubles were subjected to an extraction treatment at 80°C using a mixed solvent (solubility parameter: 9.1) of benzene (95 vol.%) and quinoline (5 vol.%) at a rate of 100 ml for 3 grams of the insolubles to obtain soluble matter in the mixed benzene-quinoline solvent.

The solvent was removed from the soluble matter thus obtained, leaving pitch for carbon fiber having a softening point of 188°C and a mesophase content of 10 vol.%.

The pitch for carbon fiber thus produced was melt-spun at a melt viscosity of 6,300 poise and a take-up tension of 40 mg/pc. using the spinning apparatus used in Example 1, followed by infusibilization and carbonization treatments in the same manner as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained was found to have Lc and La values of 210Å and 200Å, respectively, an interlayer spacing of 3.385Å, a density of 2.08 g/cm³, a tensile strength of 370 kg/mm², a Young's modulus of 58 ton/mm² and a compressive strength of 105 kg/mm².

An internal structure of this carbon fiber is as

shown in Fig. 3. As is apparent from this figure, fibrils ranging in width from 100 to 400Å and not smaller than 1,000Å in length are arranged in the direction parallel to the fiber axis, and the fiber has a texture content not less than 80 vol.% in which texture a large number of entanglements are present between the fibrils.

Comparative Example 1

Using the optically anisotropic pitch having a mesophase content of 40 vol.% used in Example 1, there was performed melt-spinning in the same way as in Example 1. As a result, there occurred fiber breakage frequently and it was impossible to effect spinning continuously.

Comparative Example 2

The starting pitch used in Example 1 was hydrogenated to afford a hydrogenated pitch having a softening point of 73°C, a benzene insolubles content of 14 wt.% and 0.5 mole of hydrogen added thereto per pitch molecule.

30 g of the hydrogenated pitch was stirred while nitrogen was introduced at a rate of 1,200 ml/min, and heat-treated at 400°C for 2 hours to afford an optically anisotropic pitch having a softening point of 223°C and a mesophase content of 45 vol.%.

The optically anisotropic pitch thus obtained was pulverized and then subjected to an extraction treatment in the same way as in Example 1 to obtain pitch for carbon fiber having a softening point of 208°C and a mesophase content of 30 vol.%.

The pitch for carbon fiber thus produced was melt-spun at a melt viscosity of 1,800 poise and a take-up tension of 25 mg/pc. using the spinning apparatus used in Example 1, followed by infusibilization and carbonization treatments in the same manner as in Example 1 to afford carbon fiber. The carbon fiber was found to have a tensile strength of 270 kg/mm², a Young's modulus of 48 ton/mm² and a compressive strength of 63 kg/mm².

According to an internal structure of this carbon fiber, fibrils ranging in width from 300 to 800Å and not smaller than 1,000Å in length are arranged in the direction parallel to the fiber axis, and the fiber has a texture content of 45 vol.% in which texture there are present entanglements between the fibrils.

Comparative Example 3

The optically anisotropic pitch having a mesophase content of 50 vol.% used in Example 2 was pulverized, then subjected to an extraction treatment at 60°C using a mixed solvent (solubility parameter: 7.9) of hexane (50 vol.%) and benzene (50 vol.%) at a rate of 100 ml for 3 grams of the pitch, and insolubles in the mixed hexane-benzene solvent were collected.

Then, said insolubles were subjected to an extraction treatment at 80°C using a mixed solvent (solubility parameter: 10.5) of xylene (45 vol.%) and quinoline (55 vol.%) at a rate of 100 ml for 3 grams of the insolubles to obtain soluble matter in the mixed benzene-quinoline solvent.

The solvent was removed from the said soluble matter, leaving pitch for carbon fiber having a

softening point of 226°C and a mesophase content of 50 vol.%.
 The pitch for carbon fiber thus produced was melt-spun at a melt viscosity of 2,400 poise and a take-up tension of 25 mg/pc. using the spinning apparatus used in Example 1, followed by infusibilization and carbonization treatments in the same way as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained was found to have a tensile strength of 290 kg/mm², a Young's modulus of 52 ton/mm² and a compressive strength of 54 kg/mm².

Comparative Example 4

30 g of the commercial petroleum pitch used in Example 2 was stirred while nitrogen gas was introduced at a rate of 1,200 ml/min, and heat-treated at 400°C for 13 hours to afford an optically anisotropic pitch having a softening point of 305°C and a mesophase content of 100 vol.%.
 The optically anisotropic pitch was melt-spun at a melt viscosity of 2,300 poise and a take-up tension of 30 mg/pc. using the spinning apparatus used in Example 1, followed by infusibilization and carbonization treatments in the same way as in Example 1 to obtain carbon fiber.

The carbon fiber thus obtained was found to have a tensile strength of 255 kg /mm², a Young's modulus of 43 ton /mm² and a compressive strength of 57 kg /mm².

An internal structure of this carbon fiber is as shown in Fig. 4. As is apparent from this figure, fibrils not smaller than 1,000Å in width are present in a proportion not less than 60 vol.% in the direction parallel to the fiber axis.

Comparative Example 5

A commercially available PAN-based carbon fiber (Torayca M-40) was found to have Lc and La values of 55Å and 48Å, respectively, an interlayer spacing of 3.441Å, a density of 1.88 g/cm³, a tensile strength of 265 kg/mm², a Young's modulus of 40 ton/mm² and a compressive strength of 67 kg/mm².

According to an internal structure of this carbon fiber, fibrils not larger than 100Å in width and not larger than 500Å in length were arranged in the direction parallel to the fiber axis.

Brief Description of the Drawings

Figs. 1 to 5 are transmission type electron micro-photographs showing crystal structures of carbon fibers. In all of them, the vertical direction corresponds to the fiber axis direction and all are the same in size.

Claims

1. A pitch-based carbon fiber having La and Lc values each not larger than 1,000Å as measured by X-ray diffraction, having a texture content not less than 50% by volume of the entire carbon fiber, said texture being not larger than 1,000Å in terms of the width of fibrils when

observed in the axial direction of the fiber using a transmission type electron microscope, also having a density in the range of 1.95 to 2.12 g/cm³, and satisfying the relation of $3.82 \leq d_{002} + 0.212p \leq 3.87$ between an interlayer spacing d_{002} as measured by X-ray diffraction and a density p .

2. A process for producing a pitch-based carbon fiber, comprising hydrogenating a carbonaceous pitch in the presence of a hydrogenation catalyst to add to the pitch two moles or more hydrogen per pitch molecule; then, heat-treating the hydrogenated pitch at atmospheric pressure or under reduced pressure to obtain an optically anisotropic pitch; collecting from said optically anisotropic pitch a component which is insoluble in an organic solvent having a solubility parameter at 25°C of 7.4 to 9.0 and soluble in an organic solvent having a solubility parameter at 25° C of 9.2 to 11.0 to obtain a spinning pitch having an optically anisotropic phase content of 5% to 40% by volume; then, spinning said spinning pitch; and thereafter making the resulting pitch fiber infusible and then carbonizing the thus-infusibilized pitch fiber.

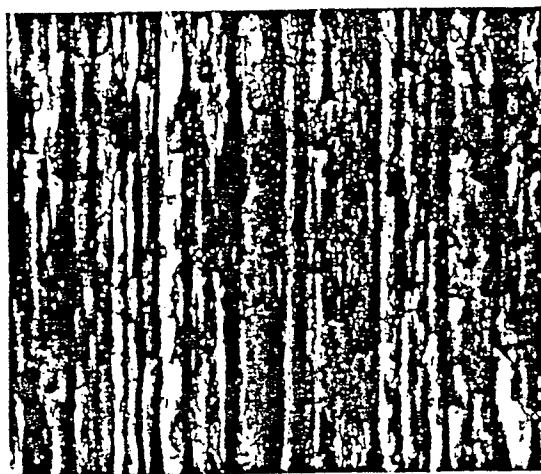


Fig. 1 $\overline{1000\text{\AA}}$



Fig. 4

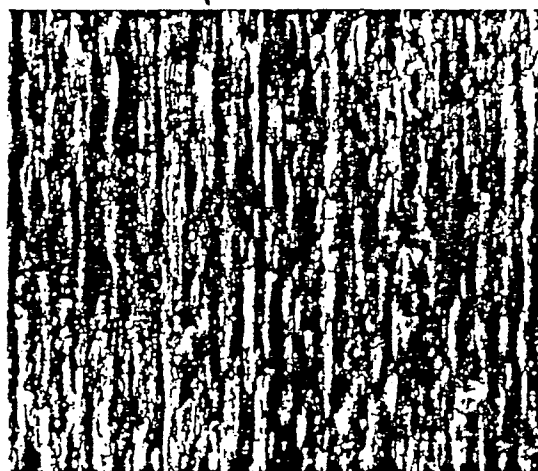


Fig. 2

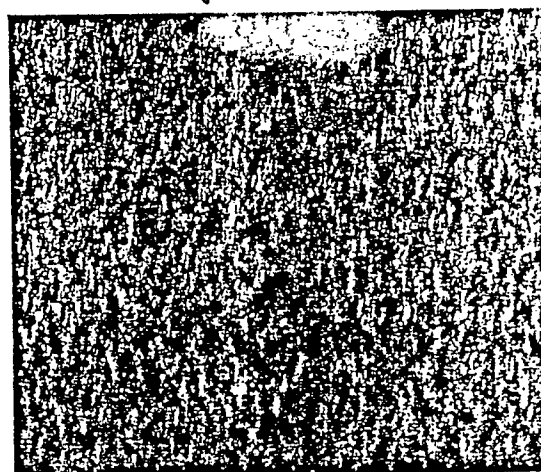


Fig. 5

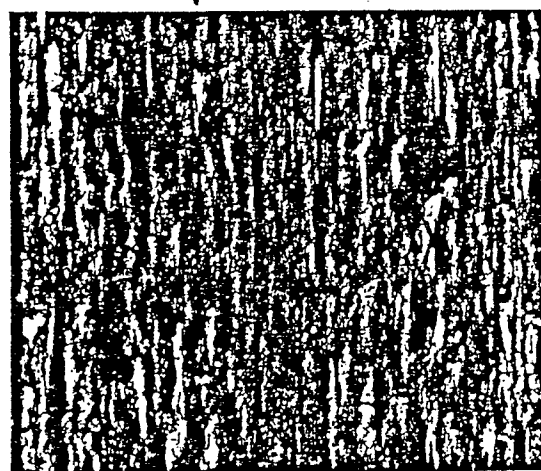


Fig. 3