United States Patent [19]

Schulz

[11] **3,919,376**

[45] **Nov. 11, 1975**

[54] **PROCESS FOR PRODUCING HIGH MESOPHASE CONTENT PITCH FIBERS**

[75] Inventor: **David A. Schulz,** Fairview Park, Ohio

[73] Assignee: **Union Carbide Corporation,** New York, N.Y.

[22] Filed: **Dec. 26, 1972**

[21] Appl. No.: **318,482**

[52] **U.S. Cl.** **264/102;** 264/29; 264/DIG. 19; 423/447

[51] **Int. Cl.** **B24c 25/00**

[58] **Field of Search** . 423/447; 264/29, 87, DIG. 19, 264/102; 204/164, 192; 106/273 R

[56] **References Cited**

UNITED STATES PATENTS

3,040,005	6/1962	Bernhardt et al.	264/176 F
3,355,377	11/1967	King	106/273 R
3,552,922	1/1971	Ishikawa et al.	264/29
3,558,276	1/1971	Otani	264/29
3,595,946	7/1971	Joo et al.	264/29
3,629,379	12/1971	Otani	264/29
3,634,220	1/1972	Goan	204/164
3,718,493	2/1973	Joo et al.	106/273 R
3,767,741	10/1973	Toyoguchi et al.	264/29
3,787,541	1/1974	Grindstaff et al.	264/29

Primary Examiner—Jay H. Woo
Attorney, Agent, or Firm—J. S. Piscitello

[57] **ABSTRACT**

An improved process for producing carbon fibers from pitch which has been transformed, in part, to a liquid crystal or so-called "mesophase" state. According to the process, the mesophase content of fibers spun from such pitch is increased before the fibers are thermoset and carbonized by vacuum distillation of the non-mesophase content of the fibers.

36 Claims, No Drawings

PROCESS FOR PRODUCING HIGH MESOPHASE CONTENT PITCH FIBERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved process for producing carbon fibers from pitch which has been transformed, in part, to a liquid crystal or so-called "mesophase" state. More particularly, this invention relates to an improved process for producing carbon fibers from pitch of this type wherein the mesophase content of fibers spun from such pitch is increased before the fibers are thermoset and carbonized by vacuum distillation of the non-mesophase content of the fibers.

2. Description of the Prior Art

As a result of the rapidly expanding growth of the aircraft, space and missile industries in recent years, a need was created for materials exhibiting a unique and extraordinary combination of physical properties. Thus, materials characterized by high strength and stiffness, and at the same time of light weight, were required for use in such applications as the fabrication of aircraft structures, re-entry vehicles, and space vehicles, as well as in the preparation of marine deep-submergence pressure vessels and like structures. Existing technology was incapable of supplying such materials and the search to satisfy this need centered about the fabrication of composite articles.

One of the most promising materials suggested for use in composite form was high strength, high modulus carbon textiles, which were introduced into the market place at the very time this rapid growth in the aircraft, space and missile industries was occurring. Such textiles have been incorporated in both plastic and metal matrices to produce composites having extraordinary high-strength- and high-modulus-to-weight ratios and other exceptional properties. However, the high cost of producing the high strength, high modulus carbon textiles employed in such composites has been a major deterrent to their widespread use, in spite of the remarkable properties exhibited by such composites.

One recently proposed method of providing high modulus, high strength carbon fibers at low cost is described in copending application Ser. No. 239,490, entitled "High Modulus, High Strength Carbon Fibers Produced From Mesophase Pitch." Such method comprises first spinning a carbonaceous fiber from a carbonaceous pitch which has been transformed, in part, to a liquid crystal or so-called "mesophase" state, then thermosetting the fiber so-produced by heating the fiber in an oxygen-containing atmosphere for a time sufficient to render it totally infusible, and finally carbonizing the thermoset fiber by heating in an inert atmosphere to a temperature sufficiently elevated to remove hydrogen and other volatiles and produce a substantially all-carbon fiber. The carbon fibers produced in this manner have a highly oriented structure characterized by the presence of carbon crystallites preferentially aligned parallel to the fiber axis, and are graphitizable materials which when heated to graphitizing temperatures develop the three-dimensional order characteristic of polycrystalline graphite and graphitic-like properties associated therewith, such as high density and low electrical resistivity.

Since carbonaceous fibers drawn from pitches having a high mesophase content can be thermoset in less time than carbonaceous fibers drawn from pitches having a lower mesophase content, it is desirable to employ pitches of high mesophase content in such process. However, because the spinning of mesophase-containing pitches becomes increasingly difficult as the mesophase content of the pitch increases, and must be done at higher and higher temperatures, the fibers are usually prepared from pitches having a mesophase content of only from about 40 percent by weight to about 70 percent by weight.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been discovered that pitch fibers having a high mesophaase content can be prepared from pitch fibers of lower mesophase content which have been spun from pitches of the type described in aforementioned copending application Ser. No. 239, 490, i.e., carbonaceous pitches which have been transformed, in part, to a liquid crystal or so-called "mesophase" state, by subjecting the fibers to low-pressure heat treatment so as to volatilize at least a portion of the non-mesophase content of the fiber; and that the so-treated fibers can be converted by further heat treatment into carbon fibers having a high young's modulus of elasticity and high tensile strength. The invention takes advantage of the differences in molecular weight and volatility between the molecules of the mesophase portion of the fiber and the molecules of the non-mesophase portion to effect removal of the non-mesophase portion and produce a fibrous residue of higher mesophase content. The non-mesophase molecules are of lower molecular weight than the higher molecular weight mesophase molecules and are preferentially volatilized from the fiber during the initial heat treatment to produce a fiber of higher mesophase content. This non-mesophase material can be substantially completely removed by the distillation or only partially, depending upon the relative amounts of mesophase and non-mesophase material present in the fibers, the diameter of the fibers, the heat treatment temperature, the pressure employed during the heat treatment, and the duration of the heat treatment. Surprisingly, it has been found from weight loss data on the fibers, together with solubility and polarized ligh microscopy studies, that the increase in mesophase content of the heat-treated fibers is not due solely to volatilization of the non-mesophase material, but results, in part, from conversion of this non-mesophase to mesophase.

The fibers produced in this manner have a high degree of preferred orientation of their molecules parallel to the fiber axis and can be converted by heat treatment into carbon fibers having a high Young's modulus of elasticity and high tensile strength. The carbon fibers so-produced have a highly oriented structure characterized by the presence of carbon crystallites preferentially aligned parallel to the fiber axis, and when heated to graphitizing temperatures develop the three-dimensional order characteristic of polycrystalline graphite and graphitic-like properties associated therewith, such as high density and low electrical resistance. At all stages of their development from the as-drawn condition to the graphitized state, the fibers are characterized by the presence of large oriented graphitizable domains preferentially aligned parallel to the fiber axis, with the fibers after vacuum distillation, however, containing a lesser amount of non-mesophase material than before such distillation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

When natural or synthetic pitches having an aromatic base are heated at a temperature of about 350°C.–450°C., either at constant temperature or with gradually increasing temperature, small insoluble liquid spheres begin to appear in the pitch and gradually increase in size as heating is continued. When examined by electron diffraction and polarized light techniques, these spheres are shown to consist of layers of oriented molecules aligned in the same direction. As these spheres continue to grow in size as heating is continued, they come in contact with one another and gradually coalesce with each other to produce larger masses of continuous aligned layers. Eventually, substantially the entire pitch coalesces and takes on the superficial appearance of a mosaic structure where, however, the transition from one oriented region to another occurs smoothly and continuously through gradual curving lamellar regions rather than through sharp boundaries between uniform areas of oriented lamellae.

The highly oriented, optically anisotropic, insoluble material produced by treating pitches in this manner has been given the term "mesophase," and pitches containing such material are known as "mesophase pitches". Such pitches, when heated above their softening points, are mixtures of two immiscible liquids, one the optically anisotropic, oriented mesophase portion in either spherulite or coalesced form, and the other the isotropic nonmesophase portion. The term "mesophase" is derived from the Greek "mesos" or "intermediate" and indicates the pseudo-crystalline nature of this highly-oriented, optically anisotropic material.

Carbonaceous pitches having a mesophase content of from about 40 percent by weight to about 70 percent by weight can easily be spun into fibers which can subsequently be converted by heat treatment into carbon fibers having a high Young's modulus of elasticity and high tensile strength. Although fibers can also be spun from pitches having a mesophase content in excess of about 70 percent by weight, e.g., up to about 90 percent by weight, these pitches are exceedingly difficult to work with because of their high softening temperatures, and fibers can only be spun from such pitches at elevated temperatures where the pitches readily undergo polymerization and/or coking.

In order to obtain highly oriented carbonaceous fibers capable of being heat treated to produce fibers having the three-dimensional order characteristic of polycrystalline graphite from carbonaceous pitches having a mesophase content of from about 40 percent by weight to about 90 percent by weight, however, it is not only necessary that such amount of mesophase be present, but also that it be present in the form of large, homogeneous, coalesced regions. Pitches which polymerize very rapidly develop small or stringy mesophase regions rather than large coalesced regions and are unsuitable. Likewise, pitches which do not form homogeneous coalesced regions of mesophase are unsuitable. The latter phenomenon is caused by the presence of non-mesophase insolubles (which are either present in the original pitch or which develop on heating) which are enveloped by the coalescing mesophase and serve to interrupt the homogeneity and uniformity of the coalesced domains.

Another requirement is that the pitch be nonthixotropic under the conditions employed in the spinning of the pitch into fibers i.e., it must exhibit a Newtonian or plastic flow behavior so that the viscosity coefficient is independent of the shear rate of the pitch during the spinning process. When such pitches are heated to a temperature where they exhibit a viscosity of from about 10 poises to about 200 poises, uniform fibers may be readily spun therefrom. Thixotropic pitches, on the other hand, which do not exhibit Newtonian or plastic flow behavior when attempts are made to spin fibers therefrom, but rather undergo changes in apparent viscosity, do not permit uniform fibers to be spun therefrom which can be converted by further heat treatment into fibers capable of developing the threedimensional order characteristic of polycrystalline graphite.

Carbonaceous pitches having a mesophase content of from about 40 percent by weight to about 90 percent by weight can be produced in accordance with known techniques, as disclosed in aforementioned copending application Ser. No. 239, 490, by heating a carbonaceous pitch in an inert atmosphere at a temperature above about 350°C. for a time sufficient to produce the desired quantity of mesophase. By an inert atmosphere is meant an atmosphere which does not react with the pitch under the heating conditions employed, such as nitrogen, argon, zenon, helium and the like. The heating period required to produce the desired mesophase content varies with the particular pitch and temperature employed, with longer heating periods required at lower temperatures than at higher temperatures. At 350°C., the minimum temperature generally required to produce mesophase, at least one week of heating is usually necessary to produce a mesophase content of about 40 percent. At temperatures of from about 400°C. to 450°C., conversion to mesophase proceeds more rapidly, and a 50 percent mesophase content can usually be produced at such temperatures within about 1–40 hours. Such temperatures are preferred for this reason. Temperatures above about 500°C. are undesirable, and heating at this temperature should not be employed for more than about 5 minutes to avoid conversion of the pitch to coke.

The degree to which the pitch has been converted to mesophase can readily be determined by polarized light microscopy and solubility examinations. Except for certain non-mesophase insolubles present in the original pitch or which, in some instances, develop on heating, the non-mesophase portion of the pitch is readily soluble in organic solvents such as quinoline and pyridine, while the mesophase portion is insoluble. [1] In the case of pitches which do not develop non-mesophase insolubles when heated, the insoluble content of the heat treated pitch over and above the insoluble content of the pitch before it has been heat treated is due to conversion of the pitch to mesophase.[2] In the case of pitches which do develop non-mesophase insolubles when heated, the insoluble content of the heat treated pitch over and above the insoluble content of the pitch before it has been heat treated is not solely due to the conversion of the pitch to mesophase, but also represents non-mesophase insolubles which are produced along with the mesophase during the heat treatment. Pitches which contain such non-mesophase insolubles (either present in the original pitch or developed by heating) in amounts sufficient to prevent the development of homogeneous coalesced mesophase regions are unsutiable for use in the present invention, as noted above. Generally, ptiches which contain in excess of about 2 percent by weight of such materials are unsuitable. The presence or absence of such homogeneous coalesced mesophase regions, as well as the

presence or absence of non-mesophase insolubles, can be visually observed by polarized light microscopy examination of the pitch (see, e.g., Brooks, J. D., and Taylor, G. H., "The Formation of Some Graphitizing Carbons," Chemistry and Physics of Carbon, Vol. 4, Marcel Dekker, Inc., New York, 1968, pp. 243–268; and Dubois, J., Agache, C., and White, J. L., "The Carbonaceous Mesophase Formed in the Pyrolysis of Graphitizable Organic Materials," Metallography 3, 337–369, 1970). The amounts of each of these materials may also be visually estimated in this manner. [1] The per cent of quinoline insolubles (Q.I.) of a given pitch is determined by quinoline extraction at 75°C. The percent of pyridine insolubles (P.I.) is determined by Soxhlet extraction in boiling pyridine. (115°C.,). [2] The insoluble content of the untreated pitch is generally less than 1 percent (except for certain coal tar pitches) and consists largely of coke and carbon black found in the original pitch.

Aromatic base carbonaceous pitches having a carbon content of from about 92 percent by weight to about 96 percent by weight and a hydrogen content of from about 4 percent by weight to about 8 percent by weight are generally suitable for producing mesophase pitches which can be employed to produce fibers capable of being heat treated to produce fibers having the three-dimensional order characteristic of polycrystalline graphite. Elements other than carbon and hydrogen, such as oxygen, sulfur and nitrogen, are undesirable and should not be present in excess of about 4 percent by weight. The presence of more than such amount of extraneous elements may disrupt the formation of carbon crystallites during subsequent heat treatment and prevent the development of a graphitic-like structure within the fibers produced from these materials. In addition, the presence of extraneous elements reduces the carbon content of the pitch and hence the ultimate yield of carbon fiber. When such extraneous elements are present in amounts of from about 0.5 percent by weight to about 4 percent by weight, the pitches generally have a carbon content of from about 92–95 percent by weight, the balance being hydrogen.

Petroleum pitch, coal tar pitch and acenaphthylene pitch, which are well-graphitizing pitches, are preferred starting materials for producing the mesophase pitches which are employed to produce the fibers of the instant invention. Petroleum pitch, of course, is the residuum carbonaceous material obtained from the distillation of crude oils or the catalytic cracking of petroleum distillates. Coal tar pitch is similarly obtained by the distillation of coal. Both of these materials are commercially available natural pitches in which mesophase can easily be produced, and are preferred for this reason. Acenaphthylene pitch, on the other hand, is a synthetic pitch which is preferred because of its ability to produce excellent fibers. Acenaphthylene pitch can be produced by the pyrolysis of polymers of acenaphthylene as described by Edstrom et al. in U.S. Pat. 3,574,653.

Some pitches, such as fluoranthene pitch, polymerize very rapidly when heated and fail to develop large coalesced regions of mesophase, and are, therefore, not suitable precursor materials. Likewise, pitches having a high non-mesophase insoluble content in organic solvents such as quinoline or pyridine, or those which develop a high non-mesophase insoluble content when heated, should not be employed as starting materials, as explained above, because these pitches are incapable of developing the homogeneous regions of coalesced mesophase which are necesary to produce highly oriented carbonaceous fibers capable of developing the three-dimensional order characteristic of polycrystalline graphite. For this reason, pitches having a quinoline-insoluble or pyridine-insoluble content of more than about 2 percent by weight (determined as described above) should not be employed, or should be filtered to remove this material before being heated to produce mesophase. Preferably, such pitches are filtered when they contain more than about 1 percent by weight of such insoluble material. Most petroleum pitches and synthetic pitches have a low insoluble content and can be used directly without such filtration. Most coal tar pitches, on the other hand, have a high insoluble content and require filtration before they can be employed.

As the pitch is heated at a temperature between 350°C. and 500°C. to produce mesophase, the pitch will, of course, pyrolyze to a certain extent and the composition of the pitch will be altered, depending upon the temperature, the heating time, and the composition and structure of the starting material. Generally, however, after heating a carbonaceous pitch for a time sufficient to produce a mesophase content of from about 40 percent by weight to about 90 percent by weight, the resulting pitch will contain a carbon content of from about 94–96 percent by weight and a hydrogen content of from about 4–6 percent by weight. When such pitches contain elements other than carbon and hydrogen in amounts of from about 0.5 percent by weight to about 4 percent by weight, the mesophase pitch will generally have a carbon content of from about 92–95 percent by weight, the balance being hydrogen.

After the desired mesophase pitch has been prepared, it is spun into fibers by conventional techniques, e.g., by melt spinning, centrifugal spinning, blow spinning, or in any other known manner. As noted above, in order to obtain highly oriented carbonaceous fibers capable of developing the three-dimensional order characteristic of polycrystalline graphite the pitch must contain large homogeneous regions of coalesced mesophase and be nonthixotropic under the conditions employed in the spinning.

The temperature at which the pitch is spun depends, of course, upon the temperature at which the pitch exhibits a suitable viscosity. Since the softening temperature of the pitch, and its viscosity at a given temperature, increases as the mesophase content of the pitch increases, the mesophase content should not be permitted to rise to a point which raises the softening point of the pitch to excessive levels. For this reason, pitches having a mesophase content of more than about 70 percent are usually not employed. Pitches containing a mesophase content of about 40 percent by weight usually have a viscosity of about 200 poises at about 250°C. and about 10 poises at about 300°C., while pitches containing a mesophase content of about 70 percent by weight exhibit similar viscosities at about 390°C. and 440°C., respectively. Within this viscosity range, fibers may be conveniently spun from such pitches at a rate of from about 20 feet per minute to about 100 feet per minute and even up to about 3000 feet per minute. Preferably, the pitch employed has a mesophase content of from about 50 percent by weight to about 65 percent by weight and exhibits a viscosity of from about 30 poises to about 60 poises at temperatures of from about 340°C. to about 380°C. At such vis-

cosity and temperature, uniform fibers having diameters of from about 10 microns to about 20 microns can be easily spun. As previously mentioned, however, in order to obtain the desired fibers, it is important that the pitch be nonthixotropic and exhibit Newtonian or plastic flow behavior so that the viscosity coefficient is independent of the shear rate of the pitch during the spinning of the fibers.

The carbonaceous fibers produced in this manner are highly oriented graphitizable materials having a high degree of preferred orientation of their molecules parallel to the fiber axis. By "graphitizable" is meant that these fibers are capable of being converted thermally (usually by heating to a temperature in excess of about 2500°C., e.g., from about 2500°C. to about 3000°C.) to a structure having the three-dimensional order characteristic of polycrystalline graphite.

The fibers produced in this manner, of course, have the same chemical composition as the pitch from which they were drawn, and like such pitch contain from about 40 percent by weight to about 90 percent by weight mesophase. When examined under magnification by polarized light and scanning electron microscopy techniques, large fibrillar-shaped domains of mesophase interspersed with large elongated non-mesophase regions can be seen distributed throughout the fiber, giving the fibers the appearance of a "mini-composite". These fibrillar mesophase domains are highly oriented and preferentially aligned parallel to the fiber axis. Characteristically, these domains have diameters in excess of 5,000 A, generally from about 10,000 A to about 40,000 A, and because of their large size are easily observed when examined by conventional polarized light microscopy techniques at a magnification of 1000. (The maximum resolving power of a standard polarized light microscope having a magnification factor of 1000 is only a few tenths of a micron [1 micron = 10,000 A] and anisotropic domains having dimensions of 1000 A or less cannot be detected by this technique.)

After the fibers have been spun, as hereinbefore described, they are heated under reduced pressure so as to volatilize at least a portion of the non-mesophase portion of the fiber. As previously stated, the invention takes advantage of the differences in molecular weight and volatility between the molecules of the mesophase portion of the fiber and the molecules of the non-mesophase portion to effect removal of the non-mesophase portion and produce a fibrous residue of high mesophase content. As has been noted, the non-mesophase molecules are of lower molecular weight than the higher molecular weight mesophase molecules and are preferentially volatilized from the fiber during the heat treatment to produce a fiber of higher mesophase content. This non-mesophase material can be substantially completely removed by the distillation or only partially, depending upon the relative amounts of mesophase and non-mesophase present in the fibers, the diameter of the fibers, the heat treatment temperature, the pressure employed during the heat treatment, and the duration of the heat treatment. The extent of which non-mesophase has been volatilized can readily be determined by the loss in weight which the fibers undergo during the heat treatment.

Removal of the non-mesophase portion of the fibers is effected by heating the fibers under a pressure of less than about 100 microns Hg, preferably less than 30 microns Hg, at a temperature and for a time sufficient to volatilize as much of the non-mesophase material from the fibers as desired. The temperature employed must be sufficiently high to effect the desired degree of volatilization but must not, of course, exceed the temperature at which the fibers will soften or distort, or the temperature at which sintering of fibers in contact with each other occurs. Higher temperatures permit more complete volatilization of the non-mesophase material in a given time than do lower temperatures. By employing sufficiently high temperatures for an appropriate time, it is possible to substantially completely remove the entire non-mesophase content of the fibers.

A minimum temperature of at least 250°C. is generally necessary to volatilize non-mesophase material from the fibers. Temperatures in excess of 400°C. may cause melting of the fibers and should be avoided. Preferably, temperatures of from about 300°C. to about 390°C. are employed.

The time required to effect removal of the non-mesophase portion of the fibers will, of course, vary with such factors as the relative amounts of mesophase and non-mesophase material present in the fibers, the diameter of the fibers, the heat treatment temperature, and the pressure employed during the heat treatment. Relatively thick fibers and/or fibers having a relatively high non-mesophase content require longer heating times to effect the removal than do thinner fibers or fibers having a lower non-mesophase content. Likewise, the use of higher temperatures and/or lower pressures permit a given amount of non-mesophase material to be removed in shorter periods of time than is possible at lower temperatures and/or higher pressures. Removal of at least 5 percent by weight of the non-mesophase content of the fibers can usually be effected by heating at an appropriate temperature within from about 5 minutes to about 30 minutes. Removal of from about 10 percent by weight to about 40 percent by weight of the non-mesophase content usually requires more protracted heating times, e.g., from about 0.5 hour to about 100 hours or more.

The fibers produced in this manner, like their precursors, are characterized by the presence of large oriented graphitizable domains preferentially aligned parallel to the fiber axis, with the fibers after vacuum distillation, however, containing a lesser amount of non-mesophase material than before such distillation. By further heat treatment, these fibers can be converted into carbon fibers having a high Young's modulus of elasticity and high tensile strength.

While heat-treated fibers containing in excess of about 85 percent by weight mesophase are, at times, sufficiently infusible to permit them to be carbonized without any prior thermosetting treatment, fibers containing less than about 85 percent by weight mesophase require some thermosetting before they can be carbonized. (Evidently, the fibers containing more than 85 percent by weight mesophase are sufficiently reinforced by their fibrillar structure to allow them to be carbonized directly without any prior thermosetting treatment.) In any event, because of the higher ratio of mesophase to non-mesophase of the heat treated fibers compared to their precursors, they can be thermoset, at any given temperature, in shorter periods of time than said precursors.

Thermosetting of the fibers is readily effected by heating the fibers in an oxygen-containing atmosphere for a time sufficient to render them totally infusible. The oxygen-containing atmosphere employed may be

pure oxygen or an oxygen-rich atmosphere. Most conveniently, air is employed as the oxidizing atmosphere.

The time required to effect thermosetting of the fibers will, of course, vary with such factors as the particular oxidizing atmosphere, the temperature employed, the diameter of the fibers, the particular pitch from which the fibers are prepared, and the mesophase content of the fibers. Generally, however, thermosetting of the fibers can be effected in relatively short periods of time, usually in from about 4 minutes to about 50 minutes.

The temperature employed to effect thermosetting of the fibers must, of course, not exceed the temperature at which the fibers will soften or distort. The maximum temperature which can be employed will thus depend upon the particular pitch from which the fibers were spun, and the mesophase content of the fibers. The higher the mesophase content of the fiber, the higher will be its softening temperature, and the higher the temperature which can be employed to effect thermosetting. At higher temperatures, of course, fibers of a given diameter can be thermoset in less time than is possible at lower temperatures. Fibers having a lower mesophase content, on the other hand, require relatively longer heat treatment at somewhat lower temperatures to render them infusible.

A minimum temperature of at least 250°C. is generally necessary to effectively thermoset the heat-treated fibers produced in accordance with the invention. Temperatures in excess of 400°C. may cause melting and/or excessive burn-off of the fibers and should be avoided. Preferably, temperatures of from about 325°C. to about 390°C. are employed. At such temperatures, thermosetting can generally be effected within from about 4 minutes to about 50 minutes. Since it is undesirable to oxidize the fibers more than necessary to render them totally infusible, the fibers are generally not heated for longer than about 50 minutes, or at temperatures in excess of 400°C.

After the fibers have been thermoset, the infusible fibers are carbonized by heating in an inert atmosphere, such as that described above, to a temperature sufficiently elevated to remove hydrogen and other volatiles and produce a substantially all-carbon fiber. Fibers having a carbon content greater than about 98 percent by weight can generally be produced by heating to a temperature in excess of about 1000°C., and at temperatures in excess of about 1500°C., the fibers are completely carbonized.

Usually, carbonization is effected at a temperature of from about 1000°C. to about 2000°C., preferably from about 1500°C. to about 1900°C. Generally, residence times of from about 0.5 minute to about 25 minutes, preferably from about 1 minute to about 5 minutes, are employed. While more extended heating times can be employed with good results, such residence times are uneconomical and, as a practical matter, there is no advantage in employing such long periods.

In order to ensure that the rate of weight loss of the fibers does not become so excessive as to disrupt the fiber structure, it is preferred to heat the fibers for a brief period at a temperature of from about 700°C. to about 900°C. before they are heated to their final carbonization temperature. Residence times at these temperatures of from about 30 seconds to about 5 minutes are usually sufficient. Preferably, the fibers are heated at a temperature of about 700°C. for about one-half minute and then at a temperature of about 900°C. for like time. In any event, the heating rate must be controlled so that the volatilization does not proceed at an excessive rate.

In a preferred method of heat treatment, continuous filaments of the fibers are passed through a series of heating zones which are held at successively higher temperatures. Several arrangements of apparatus can be utilized in providing the series of heating zones. Thus, one furnace can be used with the fibers being passed through the furnace several times and with the temperature being increased each time. Alternatively, the fibers may be given a single pass through several furnaces, with each successive furnace being maintained at a higher temperature than that of the previous furnace. Also, a single furnace with several heating zones maintained at successively higher temperatures in the direction of travel of the fibers, can be used.

The carbon fibers produced in this manner have a highly oriented structure characterized by the presence of carbon crystallites preferentially aligned parallel to the fiber axis, and are graphitizable materials which when heated to graphitizing temperatures develop the three-dimensional order characteristic of polycrystalline graphite and graphite-like properties associated therewith, such as high density and low electrical resistivity.

If desired, the carbonized fibers may be further heated in an inert atmosphere, as described hereinbefore, to a still higher temperature in a range of from about 2500°C. to about 3300°C., preferably from about 2800°C. to about 3000°C., to produce fibers having not only a high degree of preferred orientation of their carbon crystallites parallel to the fiber axis, but also by a structure characteristic of polycrystalline graphite. A residence time of about 1 minute is satisfactory, although both shorter and longer times may be employed, e.g., from about 10 seconds to about 5 minutes, or longer. Residence times longer than 5 minutes are uneconomical and unnecessary, but may be employed if desired.

The fibers produced by heating at a temperature above about 2500°C., preferably above about 2800°C., are characterized as having the three-dimensional order of polycrystalline graphite. This three-dimensional order is established by the X-ray diffraction pattern of the fibers, specifically by the presence of the (112) cross-lattice line and the resolution of the (10) band into two distinct lines, (100) and (101). The short arcs which constitute the (00*l*) bands of the pattern show the carbon crystallites of the fibers to be preferentially aligned parallel to the fiber axis. Microdensitometer scanning of the (002) band of the exposed X-ray film indicate this preferred orientation to be no more than about 10°, usually from about 5° to about 10° (expressed as the full width as half maximum of the azimuthal intensity distribution). Apparent layer size (L_a) and apparent stack height (L_c) of the crystallites are in excess of 1000 A and are thus too large to be measured by X-ray techniques. The interlayer spacing (d) of the crystallites, calculated from the distance between the corresponding (00*l*) diffraction arcs, is no more than 3.37 A, usually from 3.36 A to 3.37 A.

EXAMPLE 1

A commercial petroleum pitch was employed to produce a pitch having a mesophase content of about 59 percent by weight. The precursor pitch had a density of 1.24 grams/cc., a softening temperature of 120°C. and

contained about 1 percent by weight pyridine insolubles (P. I. was determined by Soxhlet extraction in boiling pyridine.). Chemical analysis showed a carbon content of about 93%, a hydrogen content of about 6%, a sulfur content of about 1% and 0.15% ash.

The mesophase pitch was produced by heating the precursor petroleum pitch at a temperature of about 400°C. for about 20 hours under a nitrogen atmosphere. After heating, the pitch contained 59.8 percent by weight pyridine insolubles, indicating that the pitch had a mesophase content of close to 59 percent.

A portion of this pitch was transferred to an extrusion cylinder and spun into fiber by applying pressure to the pitch with an argur while the molten pitch was extruded through a pin-hole orifice (diameter 0.015 inch) at the bottom of the extruder at a rate of between 200 to 400 feet/minute. The filament passed through a nitrogen atmosphere as it left the extruder orifice and was then taken up by a reel. A considerable quantity of fiber 35 microns in diameter was produced in this manner at a temperature of 380°C.

A portion of the as-drawn fiber was heated at a temperature of 315°C. for 64 hours under a pressure of 20 microns Hg. The fiber showed a loss in weight of 11.5 percent as a result of the heat treatment.

Surprisingly, the fiber contained 90 percent by weight pyridine insolubles after heat treatment, indicating that the fiber had a mesophase content of about 90 percent. Based on the mesophase content of the as-drawn fiber and the loss in weight during the heat treatment, the mesophase content of the fiber should have been only 68 percent. This indicated that a portion of the non-mesophase present in the as-drawn fiber had been converted to mesophase during the heat treatment. Polarized light microscopy studies of the fiber also indicated a substantial increase in mesophase content as a result of the heat treatment.

The heat treated fiber essentially fully retained the integrity of the as-drawn fiber and showed no serious disruptions in the fiber surface.

Another portion of the as-drawn fiber was heated at a temperature of 360°C. for a total of 2.5 hours under a pressure of 20 microns Hg. After each half hour period, the fiber was removed from the oven, cooled, and weighed. The weight loss of the fiber during each half hour period is indicated below:

Time, minutes	Weight Loss, %
30 minutes	11.2
60 minutes	13.4
90 minutes	14.3
120 minutes	14.7
150 minutes	14.8

What is claimed is:

1. A process for producing a pitch fiber having a high mesophase content which comprises spinning a carbonaceous fiber from a nonthixotropic carbonaceous pitch containing from 40 percent by weight to 70 percent by weight mesophase, said mesophase being present in the form of large, homogeneous, coalesced regions, and heating the spun fiber under a pressure of less than 100 microns Hg at a temperature and for a time sufficient to volatilize at least a portion of the non-mesophase content of the fiber and produce a fiber of higher mesophase content.

2. A process as in claim **1** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

3. A process as in claim **1** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

4. A process as in claim **1** wherein the fiber is heated at a temperature and for a time sufficient to volatilize at least 5 percent by weight of the non-mesophase content of the fiber.

5. A process as in claim **4** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

6. A process as in claim **4** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

7. A process as in claim **1** wherein the fiber is heated at a temperature and for a time sufficient to volatilize from 10 percent by weight to 40 percent by weight of the non-mesophase content of the fiber.

8. A process as in claim **7** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

9. A process as in claim **7** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

10. A process as in claim **1** wherein the fiber is heated under a pressure of less than 30 microns Hg.

11. A process as in claim **10** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

12. A process as in claim **10** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

13. A process as in claim **10** wherein the fiber is heated at a temperature and for a time sufficient to volatilize at least 5 percent by weight of the non-mesophase content of the fiber.

14. A process as in claim **13** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

15. A process as in claim **13** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

16. A process as in claim **10** wherein the fiber is heated at a temperature and for a time sufficient to volatilize from 10 percent by weight to 40 percent by weight of the non-mesophase content of the fiber.

17. A process as in claim **16** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

18. A process as in claim **16** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

19. A process as in claim **1** wherein the pitch contains from 50 percent by weight to 65 percent by weight mesophase.

20. A process as in claim **19** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

21. A process as in claim **19** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

22. A process as in claim **19** wherein the fiber is heated at a temperature and for a time sufficinet to volatilize at least 5 percent by weight of the non-mesophase content of the fiber.

23. A process as in claim **22** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

24. A process as in claim **22** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

25. A process as in claim **19** wherein the fiber is heated at a temperature and for a time sufficient to volatilize from 10 percent by weight to 40 percent by weight of the non-mesophase content of the fiber.

26. A process as in claim **25** wherein the fiber is heated at a temperature of from 250°C. to 400°C.

27. A process as in claim **25** wherein the fiber is heated at a temperature of from 300°C. to 390°C.

28. A process as in claim **19** wherein the fiber is heated under a pressure of less than 30 microns Hg.

29. A process as in claim 28 wherein the fiber is heated at a temperature of from 250°C. to 400°C.

30. A process as in claim 28 wherein the fiber is heated at a temperature of from 300°C. to 390°C.

31. A process as in claim 28 wherein the fiber is heated at a temperature and for a time sufficient to volatilize at least 5 percent by weight of the non-mesophase content of the fiber.

32. A process as in claim 31 wherein the fiber is heated at a temperature of from 250°C. to 400°C.

33. A process as in claim 31 wherein the fiber is heated at a temperature of from 300°C. to 390°C.

34. A process as in claim 28 wherein the fiber is heated at a temperature and for a time sufficient to volatilize 10 10 percent by weight to 40 percent by weight of the non-mesophase content of the fiber.

35. A process as in claim 34 wherein the fiber is heated at a temperature of from 250°C. to 400°C.

36. A process as in claim 34 wherein the fiber is heated at a temperature of from 300°C. to 390°C.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,919,376 Dated November 11, 1975

Inventor(s) David A. Schulz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 15, "aase" should read -- ase --.

Column 2, line 25, "young's" should read -- Young's --.

Column 2, line 45, "ligh" should read -- light --.

Column 3, line 69, insert a comma (,) after "fibers".

Column 4, line 11, "threedi-" should read -- three-di- --.

Column 4, line 66, "unsutiable" should read -- unsuitable --.

Column 4, line 67, "ptiches" should read -- pitches --.

Column 5, line 15, "(115°C.,)" should read -- (115°C.)-

Column 7, line 61, "of" should read -- to --.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,919,376 Dated November 11, 1975

Inventor(s) David A. Schulz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 54, "to" (second occurrence) should be deleted.

Column 12, line 52, "sufficinet" should read -- sufficient --.

Column 14, line 5, "10 10" should read -- from 10 --.

Signed and Sealed this

Seventh Day of November 1978

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

DONALD W. BANNER
Commissioner of Patents and Trademarks