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EUROPEAN PATENT APPLICATION

⑳ Application number: 85200687.3

⑤① Int. Cl.⁴: **D 01 F 9/14**

㉔ Date of filing: 29.04.85

③① Priority: 30.04.84 US 605064

④③ Date of publication of application:
04.12.85 Bulletin 85/49

⑧④ Designated Contracting States:
DE FR GB IT NL

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⑤④ **Carbon fibers and methods for producing the same.**

⑤⑦ Carbon yarn is produced by spinning continuous pitch yarn, treating the pitch yarn with an oxidizing composition, collecting the pitch yarn into a bulk form, and subjecting the treated pitch yarn to a heat treatment in a substantially non-reactive atmosphere to produce carbon yarn.

CARBON FIBERS AND METHODS FOR PRODUCING THE SAMEField of the Invention

5 The invention relates to a method for the
manufacture of carbon fibers which avoids critical
steps previously considered essential manufacturing
steps for the production of carbon fibers. More
particularly, the invention is directed to a process
which eliminates the independent step of
10 infusibilizing a mesophase pitch fiber prior to a
carbonizing step for producing carbon fibers. The
invention also relates to novel carbon fibers and
composite materials which include the carbon fibers.

Background of the Invention

15 Mesophase based carbon fibers are well
known in the art since the issuance of U.S. Patent
NO. 4,005,183. Numerous patents have issued
relating the manufacture of mesophase pitch suitable
20 for producing carbon fibers. Such patents include
U.S. Patent No. 4,026,788, U.S. Patent No.
3,976,729, and U.S. Patent NO. 4,303,631.

 It has been found in the art that mesophase
pitch suitable for spinning pitch fibers contains at
25 least 40% by weight mesophase so that the mesophase
is the continuous phase, and the mesophase pitch
upon quiescent heating forms domains at least 200
microns in size.

30 The spinning of mesophase pitch into
continuous pitch fibers for the manufacturing of
carbon fibers is usually carried out with a spinning
apparatus which spins hundreds of fibers
simultaneously, usually from 1500 to 2000 pitch

fibers simultaneously. The average diameter of the pitch fibers is about 13 microns. The pitch fibers, say 2000, are treated together in subsequent steps. A bundle of continuous fibers are commonly referred to as "yarn" in the art. The carbon fibers are usually produced, packaged for shipping, and used in composites as yarns. Such yarns are sometimes referred to as "carbon yarns".

As used herein, the term "yarn" is a plurality of continuous fibers spun and processed together and the terms "pitch yarn", "infusibilized yarn", "carbon yarn" and "graphite yarn" are used to refer to the yarn at various stages of the manufacturing process.

Generally, the method for producing carbon fibers from mesophase pitch includes the steps of spinning the mesophase pitch into a plurality of pitch fibers (pitch yarn), infusibilizing the pitch fibers (infusibilized pitch yarn), and thereafter subjecting the infusibilized pitch fibers to a carbonizing step in a substantially non-reactive atmosphere for producing the carbon fibers (carbon yarn).

It is known from the prior art that the step of infusibilizing the pitch fibers is essential for the manufacture of carbon fibers because it enables the carbonizing step to be carried out relatively rapidly. The carbonizing step usually requires the yarn to be raised to a temperature of at least about 1000°C. It is desirable to be able to raise the temperature of the yarn from about room temperature to the final temperature, for example 1000°C, in a short time without causing deformation

of the fibers, fusion between fibers, or a deterioration of the mechanical properties of the carbon yarn.

5 In the prior art, the infusibilizing step is particularly important for producing mesophase pitch based carbon fibers. Mesophase pitch derived carbon fibers are characterized by superior mechanical properties such as tensile strength and Young's modulus because the aromatic molecules of
10 the mesophase pitch tend to orient parallel to the pitch fiber during the spinning of the mesophase pitch fibers. Raising the temperature of mesophase pitch fibers which have not been infusibilized to the softening point of the pitch fibers can result
15 in the disorientation of the aromatic molecules and thereby substantially destroy the possibility of obtaining carbon fibers with superior mechanical properties.

20 The prior art has stressed the necessity of infusibilizing mesophase pitch yarn prior to the carbonizing step in order to avoid an extraordinary long period of time to raise the temperature of the yarn up from room temperature to the carbonizing temperature without deteriorating the qualities of
25 the carbon yarn to be produced.

It is also essential, according to the prior art, to infusibilize non-mesophase pitch fibers to avoid having the fibers soften and thereby result in fusion between fibers in a yarn.

30 The step of infusibilizing pitch yarn is also referred to in the art as a "thermosetting step". The infusibilizing step is an exothermic

reaction and the heat generated by the reaction can soften or deform fibers. The heat can cause fibers in a yarn to adhere or stick to each other and this reduces the tensile strength of the resulting carbon yarn as well as the properties of a composite made with the carbon yarn. This problem has been considered in U.S. Patent No. 4,275,051 and U.S. Patent No. 4,276,278.

The manufacturing of carbon fibers as reflected in the patent literature has been reviewed in the book entitled, "Carbon and Graphite Fibers, Manufacture and Application," published by Noyes Data Corporation, Park Ridge, New Jersey, 1980, edited by Marshall Sittig. This book sets forth the historical development of carbon fibers as derived from different precursor materials and the techniques patented for their manufacture. In addition, the book describes succinctly the various fiber treatment processes, matrices which are employed with carbon yarn in order to make composites, other reinforced materials which can be included in combination with carbon fibers to make effective composites, and the utilization of the carbon fibers in the manufacture of textile structures.

The International Committee for Characterization and Terminology of Carbon has published "First Publication of 30 Tentative Definitions" in Carbon, Vol. 20, pp. 445-449, 1982, to clarify the definition of many terms used in the art. The International Committee has defined "carbon fiber" as "filaments consisting of

Non-Graphite Carbon obtained by Carbonization either of organic synthetic or natural fibres (PAN or others) or of fibres drawn from organic precursors such as resins or pitches, and by subsequent heat treatment of the carbonized fibres (up to temperatures of about 3000°K)". The International Committee has also defined "Non-Graphitic Carbon" as "all varieties of substances consisting mainly of the element Carbon with two-dimensional long range order of the carbon atoms in planar hexagonal networks, but without any measurable crystallographic order in the third direction (c-direction) apart from more or less parallel stacking". The term "graphitic fiber" has been used in the art to describe carbon fibers which have been heat treated to between 2500 and 3000°K. The International Committee has pointed out that such fibers in most cases remain non-graphitic carbon so that the common term "graphitic fiber" is incorrect. The International Committee has pointed out, however, that "the term graphitic carbon is justified if Three Dimensional Crystalline Long Range Order can be detected in the material by diffraction methods, independent of the volume fraction and the homogeneity of distribution of such crystalline domains".

According to the prior art, the infusibilizing step is carried out in an oxidizing environment preferably at an elevated temperature in order to increase the rate at which the fibers become infusibilized. U.S. Patent No. 4,389,387 discloses the problems of infusibilizing pitch

fibers rapidly and effectively. The patent discloses that it is preferable to combine tens of thousands of pitch fibers into a tow of 10 to 30 mm in diameter in advance of the treatment for infusibilizing. The pitch fibers are loaded onto a net-belt conveyor and passed through a gaseous mixture of air and a gaseous oxidant such as oxygen, ozone, sulfur dioxide, nitrogen dioxide, etc. with the gaseous oxidant being 0.1 to 10% by volume of the gas mixture. The temperature for the infusibilizing step in the patent is lower than the softening point of the pitch fibers by at least 5°C to 50°C. The time for infusibilizing is disclosed in the patent as from 1 to 4 hours. The patent states that problems of infusibilizing pitch fibers are overcome by moving the gaseous mixture through the packed pitch fibers. Nevertheless, the patent cautions against too large a packing height of pitch fibers to avoid insufficient removal of the generated heat.

South African Patent Application No. 71/7853, filed November 4, 1971, entitled "Improvements In Or Relating To The Manufacture Of Carbon Fibers", discloses processes for infusibilizing a fiber after it has been spun and prior to a carbonizing step. The infusibilizing step in the patent is referred to as "stabilizing". That is, "stabilizing" and infusibilizing are the same and are used interchangeably in the patent. The precursor materials disclosed in the patent include solutions or extracts of coal, as well as pitches, pitch-like material and tar particularly if they are derived from coal.

The South African patent discloses "that spun or extruded fibre, filament or film consisting of the organic material may be stabilized by heat treatment by reacting it with either an aqueous solution of bromine or an aqueous solution of nitric acid containing at least 25%, and preferably at least 40% by weight of HNO_3 for at least sufficient time to stabilize the spun or extruded fibre, filament or film to heat treatment". The patent further discloses that the stabilized fiber can be further stabilized for a heat treatment by oxidation employing an oxidizing gas, preferably containing molecular oxygen at an elevated temperature.

The South African patent discloses that nitric acid reacts with coal and similar materials decomposing the coal and that the reaction of the nitric acid with the coal is a surface effect, the nitric acid in certain circumstances reacting with the coal violently, or even explosively.

According to the South African patent:

"If the nitric acid is allowed to react for an excessive period of time with the spun or extruded fibre, filament or film of the organic material, the nitric acid may react with the spun or extruded fibre, filament or film of the organic material in such a manner as to cause it to decompose. In the case where the organic material is a solution or extract of coal as hereinbefore referred to, it is believed the nitric acid may react with the solution or extract of coal, cleaving the large molecules of the solution or extract of coal, thereby causing the solution or extract of coal to have smaller molecules. This might have the effect of diminishing the strength of a spun or extruded fibre,

5 filament or film of the solution or extract
of coal or of the carbon fibre, filament or
film produced therefrom. Accordingly, the
spun or extruded fibre, filament or film,
whether of the solution or extract of coal
or of other organic material, should not be
allowed to react with the aqueous solution
of either bromine or nitric acid for such a
10 length of time as will seriously
detrimentally affect the properties of the
stabilized fibre, filament or film or the
carbon fibre, filament or film produced
therefrom."

15 The South African patent provides a single
example for the use of aqueous nitric acid. Example
1 discloses that a single filament having a diameter
of 30 microns was cut into lengths and immersed in a
solution comprising 50% by weight nitric acid at
20 ambient temperature, about 20°C. The number of cut
lengths was not stated in the Patent. The fiber
lengths were then washed with water to remove the
nitric acid and suspended in a vertical oven which
was heated in nitrogen to temperature about 260°C at
25 a heating rate of 300°C per hour and thereafter, the
nitrogen atmosphere was replaced by oxygen for five
minutes. Subsequently, the fibers were heated in
nitrogen at the rate of 80°C per hour to a
temperature of 1000°C and this temperature was held
30 for one hour.

The remaining two examples of the South
African patent disclose the use of bromine in water
instead of aqueous nitric acid. For each of these
examples, the rate of temperature increase for the
35 carbonizing step was 50°C per hour to a final
temperature of 1000°C.

The South African patent discloses that it is imperative that the nitric acid be washed from a fiber in order to avoid a deterioration of the fiber from the nitric acid. The commercial utilization of the disclosure of the South African patent would require a washing step subsequent to a nitric acid treatment and that subsequent to the nitric acid treatment, a heat treatment in oxygen similar to the aforementioned example 1 is necessary.

Significantly, each of the examples in the South African patents set forth a carbonizing treatment in which the temperature was increased to 1000°C at a rate of 50°C or 80°C per hour for separate cut lengths of the fiber suspended in a furnace. In contrast, a typically commercial carbonizing step for producing carbon fibers is for a yarn having typically at least 1000 filaments heated to a temperature of about 1000°C in a furnace through which yarn passes. The yarn is subjected to a change from room temperature to the carbonizing temperature and again to room temperature. The time the yarn is subjected to the carbonizing temperature is in the order of about one second or less.

Japanese Patent No. 564,648, based upon Patent Publication No. 2510/69, published February 3, 1969, discloses a process of producing carbon fibers from dry distilled petroleum sludge having a sulfuric acid content below 30%. Spun fibers are given a surface treatment by being exposed to chlorine gas stream at a temperature between room temperature and 60°C or dipped in a hydrogen peroxide, or hydrochloric acid, or nitric acid

solution. Subsequently, the fibers are heated to 200°C or more in an oxidizing atmosphere to complete the infusibilizing step. The final step is a heat treatment for carbonizing the treated fibers to produce carbon fibers.

The Japanese patent discloses that the surface treatment is necessary because the direct heating in an oxidizing atmosphere of the spun petroleum sludge fibers results in the fibers becoming soft and deformed.

U.S. Patent No. 3,595,946 discloses oxidizing treatments for filaments of pitch either continuously as the filaments are emerging from the spinning machine or for batches of filaments wound into packages. The hot filaments from the spinning machine are passed through an oxidizing atmosphere such as air, ozone, nitric oxide, etc. The patent discloses that the filament from the spinning machine can be cooled to a temperature below its fusion point and then passed through a liquid oxidizing bath such as nitric acid, sulfuric acid, chromic acid, permanganate solutions and the like. The patent discloses that the oxidizing treatments can be applied to batches of filament wound into packages. The patent cautions that "the support of the filament package must be of such nature and/or construction that it yields or collapses as the wound filament contracts during the oxidation process." The patent further cautions:

"The oxidation of filament wound to packages must follow a fairly critical heating regime if the superimposed and adjacent loops of filament are not to fuse together. This regime will naturally vary

with the pitch, its previous oxidation history and the type and quality of additive present, if any. The best heating rates and soaking temperatures for a given material are naturally difficult to determine since the fusion temperature of the pitch changes as the oxidation proceed. Nevertheless, it has been established that a heat treated pitch of the type preferred, as described earlier, will yield filaments that are successfully oxidized by raising the temperature to 100°C in less than 15 minutes, a non-critical step; holding the filament at 100° for about 20 hours; raising the temperatures from 100 to 195°C, at a preferred rate of about 5°C/hour; holding the filament at the later temperature for a period within the range of about 60 to about 120 hours, the upper part of that range being preferred. It should be noted that with certain materials temperature increase rates of up to 10°C/hour may be tolerated. In any event, the temperature at any time during the oxidation treatment should preferably be not higher than 10°C below the softening point of the pitch at the given time. This batch type oxidation is best carried out in a circulating oven through which passes a constant flow of air oxygen containing gas, both fresh and recycled, pre-heated at the desired temperature."

Such a heating schedule is extremely long in time even after tests have been carried out to optimize the process to avoid fusion between filaments.

In view of the prior art, it appears that it is essential to carry out a separate infusibilizing step prior to a carbonizing step and that considerable care must be taken for infusibilizing pitch yarn to avoid sticking or fusing of fibers. Many attempts have been made in the art to simplify and expedite the infusibilizing

step. The art, however, does not disclose any process for infusibilizing yarn other than as a separate step.

5 Moreover, the prior art requires an oxidizing atmosphere to infusibilize pitch fibers even after the pitch fiber has been treated with an oxidizing liquid, such as nitric acid.

Summary of the Invention

10 The present invention involves a process for manufacturing mesophase based carbon yarn. The process comprises spinning mesophase pitch into a plurality of continuous fibers, combining the plurality of fibers to form a pitch yarn, contacting
15 the pitch yarn with an oxidizing liquid composition, collecting the pitch yarn into a bulk form and subjecting the pitch yarn in bulk form to a heat treatment in a substantially [inert] non-reactive atmosphere to produce carbon yarn in bulk form.

20 The process can be modified so that the pitch yarn is first collected into a bulk form and thereafter contacted with an oxidizing liquid composition.

25 The oxidizing liquid composition enables the infusibilizing of the pitch yarn in the process according to the invention and also serves as a "size" or "sizing" for the pitch yarn. The terms "size" and "sizing" are used interchangeably in the art. In this connection, "sizing" on the pitch yarn
30 tends to maintain the pitch fibers in the pitch yarn together and thereby minimize any separation of pitch fibers from the body of the pitch yarn. It is desirable to maintain the pitch fibers in the pitch

yarn close together for the handling of the pitch yarn in the manufacturing operations.

Discussion of the Invention

5 The invention substantially simplifies the manufacturing of mesophase based carbon yarn and also greatly reduces the cost of manufacturing. This can be better appreciated by comparing the invention with a conventional process of making
10 carbon yarn.

 Conventional manufacturing of mesophase based carbon yarn utilizes many operations and costly capital equipment. The following is a general description of a conventional manufacturing
15 operation. A spinning apparatus produces 2000 continuous mesophase pitch fibers which are individually drawn down by a drawdown ratio of about 50:1 so that the average fiber diameter is about 12 microns. A drawdown is necessary to obtain the
20 small diameter because spinning holes of about 12 microns in diameter would be expensive to produce and would clog easily.

 It is well known in the art that carbon fibers having small diameters have generally better
25 mechanical properties than relatively large diameter carbon fibers. Small diameter pitch fibers are used to obtain the small diameter carbon fibers.

 The 2000 pitch fibers are sized and gathered together to form a pitch yarn.

30 The infusibilizing step is carried out by laying the pitch yarn onto a conveyor belt in a uniform pattern and the conveyor belt moves the pitch yarn into an oven.

The pitch fiber is mechanically weak and must be manipulated with considerable care. Accordingly, the system for laying the pitch yarn onto the conveyor belt is complex and rate limited.

5 The spinning apparatus is physically located above the conveyor belt. The pitch yarn enters a movable apparatus which physically moves transverse to the conveyor belt in order to lay the pitch yarn uniformly. This movable apparatus is
10 referred to in the art as a "travelling godet" and is rate limited even for a careful design and can damage the pitch yarn because of the tendency of the pitch yarn to adhere to rolls within the apparatus. Such adhesion is due to surface tension arising from
15 the sizing used to maintain the pitch fibers together to form the pitch yarn.

 The travelling godet is followed by an apparatus called a "transvector" which draws the pitch yarn off of the last roll in the travelling
20 godet with suction and directs the pitch yarn downward towards the conveyor belt. The transvector is not rate limited, but the air pressure moving in the vicinity of the pitch yarn can damage the pitch fibers.

25 The transvector is followed by a "laydown tube" which deposits the pitch yarn in a predetermined pattern onto the conveyor belt. A poor pattern distribution or too high a pile of pitch yarn can produce very high local heating due
30 to the exothermic reaction during the infusibilizing step. The laydown tube is another potential problem because the pitch yarn wet with size occasionally

adheres to the side of the tube for a short time and this interferes with the laydown pattern on the conveyor belt.

5 The conveyor belt carries the pitch yarn into a large oven having an oxidizing atmosphere and which has a predetermined heat gradient for infusibilizing the pitch yarn with as little damage as is consistent with commercial operations. This heat treatment can take as long as several hours.
10 The cost of the oven as well as the energy costs are very high.

 Subsequently, the infusibilized yarn is pulled from the belt and is accumulated onto bobbins for easy handling and storage. This operation uses
15 what is called a "downstream drive" and can be troublesome because the infusibilized pitch yarn is not much stronger than the pitch yarn. The infusibilized pitch yarn must be collected at a rate consistent with the spinning rate.

20 The instant invention eliminates the need for the travelling godet, the transvector, the conveyor belt, the large oven and a downstream drive.

 In a preferred embodiment of the invention, a spinning apparatus produces a plurality of pitch
25 fibers, for example 2000, and these pitch fibers are drawn together and drawn down while being wound onto a bobbin after being sized with an oxidizing liquid composition. The combination of drawing down the pitch yarn while collecting the yarn onto a bobbin
30 greatly simplifies the operations and eliminates many expensive pieces of equipment. Thereafter, the bobbin loaded with sized pitch yarn is subjected to

a heat treatment in a substantially non-reactive atmosphere to produce carbon yarn. No heat treatment in an oxidizing atmosphere is needed for the pitch yarn according to the invention in contrast to the prior art which required a heat treatment in oxygen or air or the like before the heat treatment in a substantially non-reactive atmosphere.

The carbon yarn produced according to the invention provides a more efficient use of the precursor pitch than carbon yarn produced according to the prior art. The infusibilizing step of the prior art introduces considerable amounts of oxygen into the pitch yarn, as much as 18% or more by weight. During the carbonizing heat treatment, it is believed that some of the oxygen driven off carries along carbon atoms. As a result, the carbon yarn produced according to the prior art processes is less than 80% by weight of the pitch yarn. In contrast, the carbon yarn produced according to the invention is about 90% by weight of the pitch yarn. Thus, the invention provides a higher yield of product than the prior art besides simplifying the operations needed to produce carbon yarn.

The oxidizing liquid composition can serve many functions in addition to its use in the heat treatment. The composition can provide lubrication of the pitch yarn to minimize friction between the pitch yarn and portions of the equipment contacting the pitch yarn during the manufacturing operations. The composition can also provide adhesion between fibers so that the fibers remain together as a yarn.

In a preferred embodiment, the oxidizing liquid composition comprises an aqueous nitric acid. A concentration of the aqueous nitric acid of 10% to 50% by volume is preferable, but a concentration of 15% to 35% by volume is more preferable. It is preferable to use deionized water in the aqueous nitric acid to avoid introducing any undesirable ions onto and into the pitch fibers. Aqueous nitric acid is relatively inexpensive and has been found to be excellent in obtaining carbon yarn.

The concentration of the nitric acid depends on how long the nitric acid will be on the pitch yarn before the heat treatment is carried out. A concentration of about 25% by volume is suitable for commercial operations for which the time between the application of the nitric acid to the pitch yarn and the heat treatment varies from 1 to 5 days.

With regard to the oxidizing liquid composition, reference is had to the aforementioned U.S. patents No. 4,275,051 and No. 4,276,278, both entitled "Spin Size and Thermosetting Aid For Pitch Fibers". The former patent states that the invention "provides a method of treating a multifilament bundle of pitch fibers, such as yarn or tow, to prepare such multifilament bundle for further processing which comprises applying to the fibers thereof an aqueous finishing composition comprising a dispersion of graphite or carbon black in water in which is dissolved a first compound comprising a water-soluble oxidizing agent and a

separate second compound comprising a water-soluble surfactant". The other patent features a water-soluble surfactant which is also capable of functioning as an oxidizing agent. Both of these patents used the term "oxidizing agent" as a source of oxygen for the fiber in order to infusibilize the fiber. As used herein, "oxidizing liquid composition" includes a source of oxygen for infusibilizing the fiber. The disclosure of these patents is incorporated herein.

It is believed that the oxidizing liquid composition can comprise an aqueous acid or a water-soluble oxidizing agent such as a peroxygenated compound. Some water-soluble oxidizing agents compounds include sodium peroxide, potassium peroxide, ammonium peroxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium pyrosulfate, and sodium nitrate. Preferably, aqueous nitric acid is used in the composition.

The oxidizing liquid composition of the invention can also comprise carbon black particles or colloidal graphite and a surfactant.

The carbon black particles or colloidal graphite tend to separate the pitch fibers from each other and thereby minimize the occurrence of "sticking" or fusion between fibers during the heat treatment according to the invention.

One of the functions of the surfactant is to maintain a dispersion of the carbon black particles. Mechanical means in accordance with the prior art can be used to maintain a uniform

dispersion of the carbon black particles in the composition. The surfactant also improves the flow of the composition over the fibers. It is believed that the surfactant can be water-soluble and can be anionic or nonionic. Such surfactants are well known and typically include tetra-methyl sodium oleate, tetramethyl ammonium oleate, tetramethyl sodium laurate, tetramethyl ammonium laurate, sodium laurate and ammonium laurate.

The oxidizing liquid composition can be applied to the pitch fibers using prior art techniques for applying sizing. Preferably, the composition is applied by contacting the pitch yarn with a rotating wheel which passes through the solution and carries a portion of the solution on its surface to the pitch yarn. Such a wheel is often referred to in the art as a "kiss wheel" and rotates to minimize friction with the yarn as well as carrying new solution to the yarn. After the kiss wheel, the yarn can be accumulated for subsequent treatment.

The composition can be applied to the pitch yarn by passing the yarn through a bath of the composition. This has a drawback because high speeds can produce fiber damage due to drag in the bath.

Another way of applying the composition to the pitch yarn is to spray a mist of the composition onto the pitch fibers before the fibers are gathered to form the yarn in order to improve the distribution of the composition on the fibers.

A size of water can be used on the pitch fibers and the yarn wound onto a bobbin while a mist

of the composition is sprayed onto the yarn layers being produced on the bobbin.

5 As an alternate, the composition can be applied to the pitch yarn after the yarn has been accumulated. For example, the pitch fiber can be wound onto a bobbin and the bobbin with the yarn can be subjected to the composition. This can be carried out simply by placing the bobbin in a bath of the composition. For this case, a relatively
10 loose winding of the yarn will allow the flow of the composition through the windings more readily and thereby improve the treatment. A bobbin having a plurality of holes has the advantages of allowing the composition to be forced, under pressure, out
15 from the core to the outer layer using an appropriate arrangement so that the fibers near the bobbin are not inadvertently omitted from the treatment. For this treatment it would be desirable to use some sizing on the pitch yarn prior to
20 winding the yarn onto the bobbin. It is convenient to use water for this sizing.

A suitable bobbin has been described in U.S. Patent No. 4,351,816. The bobbin can be shaped like a cylinder or a cylinder with end faces. The
25 bobbin will be subjected to elevated temperature in order to carbonize the yarn on the bobbin. Accordingly, the bobbin should be made from a material appropriate for the practice of the invention. Preferably, the bobbin comprises a
30 cylindrical body made of stainless steel, or a refractory alloy, or ceramic, or boron nitride, or more preferably a graphite material. That is, the

bobbin is made from a material which is thermally and mechanically stable at the temperatures which will be used to carbonize the pitch yarn on the bobbin.

5 The aforementioned patent No. 4,351,816 discloses a method for producing a mesophase based carbon yarn in which thermoset yarn was wound onto a bobbin as described above and subjected to a heat treatment in a substantially non-reactive atmosphere
10 to produce carbon yarn.

 The pitch yarn which has been contacted with the oxidizing liquid composition reacts and incorporates oxygen thereby. Tests were carried out to determine the range of oxygen pickup in pitch
15 yarn over a period of 0.1 hour to 70 hours. The yarn had 2000 pitch fibers which had an average diameter of 13.5 microns. Nitric acid with a concentration of 25% by volume was used. After the yarn was contacted with the nitric acid, a
20 predetermined time was allowed to elapse at room temperature and thereafter, the yarn was washed with water for this test and dried at 125°C for 16 hours prior to the test for oxygen content. Surprisingly, the range of oxygen pickup was 1.5 % to 4.8% by
25 weight for 0.1 hour to 70 hours with most of the oxygen pickup taking place during the first 24 hours. The test points substantially define the following relationship:
$$\text{oxygen pickup in \% by wt.} = 1.2355 \log (\text{time in hrs.}) + 2.5278$$

30 Thus, the variations in the pitch yarn after contact with the nitric acid in this concentration is not expected to have any significant effect on the

commercial operations. That is, treated pitch yarn can be stored prior to being carbonized. This is advantageous in commercial manufacturing.

5 The heat treatment of the treated pitch yarn can be carried out in batches in a closed volume furnace or as a continuous process using for example a conveyor belt furnace or a so-called "walking beam furnace" in which bobbins can be moved into and out of the furnace continuously.

10 The furnace should be capable of providing sufficient heat to pyrolyze the yarn and allow a substantially non-reactive atmosphere to be maintained so that the yarn is not consumed. The non-reactive atmosphere in the furnace can be
15 nitrogen, argon, helium or the like. For temperatures greater than about 2500°C, argon and helium are preferable.

 Preferably, the heat treatment is carried out in a completely non-reactive atmosphere
20 established by purging the furnace thoroughly. It is believed that a small amount of oxygen would not be harmful, particularly if the temperature was not raised too rapidly. It can be appreciated that yarn wet from being treated with oxidizing liquid
25 composition will produce an atmosphere of steam which should be purged before elevated temperatures are reached at which steam is no longer substantially non-reactive. The use of boron or similar graphitizing components could be used in the
30 furnace atmosphere and are considered non-reactive as used herein.

In carrying out the invention, the furnace was purged of air prior to raising the temperature of the yarn. The purging step can be carried out by subjecting the interior of the furnace to a vacuum and then allowing the interior to fill with nitrogen.

The heat treatment according to the invention has three broad ranges which are important in deciding a heating schedule for rate of temperature increase. The rate of temperature increase up to about 400°C should take into account that the pitch fibers do not become completely infusibilized until they reach about 400°C. Too rapid increase in temperature up to 400°C can result in fiber deformation due to softening, fusion between fibers, and/or disorientation of mesophase molecules.

The temperature increase above 400°C can be at a higher rate, but must take into account that most of the gas loss for the pyrolyzing or carbonizing process occurs as the fibers are heated between about 400°C and about 800°C. Too rapid an increase can result in damage due to evolving gases.

The increase in temperature above 800°C can be as great as desired. Typically, the final temperature is from 1300°C to 2700°C depending on the intended use of the carbon yarn.

Generally, the heat treatment according to the invention is carried out in a substantially non-reactive atmosphere and the temperature can be raised from room temperature at a rate of about 100°C per hour until 800°C. Thereafter, the temperature can be increased as fast as desired to a predetermined final temperature.

The rate of increase in temperature up to 400°C depends, in part, on the sizing used, contact time between the pitch yarn and the oxidizing liquid composition, the softening point of the pitch, the diameter of the fibers, and the composition of the pitch.

Preferably, the heat schedule for the furnace is 25°C per hour from room temperature to about 400°C then 50°C per hour until about 800°. Thereafter, the temperature can be raised as fast as desired to a predetermined final temperature.

Preferably, the pitch yarn is accumulated onto a refractory bobbin. This has the advantage that after the heat treatment the yarn is in a package suitable for storage and shipment to a location for commercial use, as is the practice.

The yarn can be wound onto the bobbin with a cross winding or essentially parallel winding. The tension can be monitored and controlled in accordance with prior art technology. This is particularly important for the situation in which the drawdown is carried out simultaneously with the winding onto the bobbin.

EXAMPLES

Several examples were carried out to demonstrate the invention and to measure properties of carbon yarn produced by the invention.

The pitch fibers for the examples were produced according to conventional melt spinning processes. The mesophase pitch is heated in an extruder above the melting point of the mesophase pitch to obtain a molten state. The extruder pushes

the molten pitch through a filter to a metering pump in the spin block. The molten pitch passes through a filterpack before reaching the spinnerette cavities. Each spinnerette contains 1,000 or 2,000 holes of 0.3mm diameter and 0.6mm capillary length. As the pitch fibers emerge from the spinnerette plate they are drawn down to about 13 microns and are immediately quenched with nitrogen so that the pitch hardens. Below the quench chamber, a lubricant or size is applied to the filaments. The pitch yarn is wound on a bobbin by a takeup and draw winder at a winding speed of about 200 to 1000 meters per minute.

Example 1

A mesophase pitch having a mesophase content of about 78% by weight and a Mettler softening point of about 324.6°C was spun into 2000 filaments according to the conventional spinning process. The pitch fibers were drawdown so that the average diameter was about 13 microns and all the fibers were drawn together to form a pitch yarn. Nitric acid having a concentration of 20% by volume was applied to the rapidly moving pitch yarn using 2 rotating kiss wheels. The acid treated pitch yarn was wound onto a motor driven rotating graphite bobbin which supplied the force necessary to draw down the fibers and sustain the movement of the pitch yarn. The graphite bobbin had a layer of graphite felt on the surface to receive the yarn. The bobbin was 28 centimeters long and had an outside diameter of about 9 centimeters. The yarn was wound in a cross pattern with a tension of about 85 grams. Each loaded bobbin had a diameter about

14 centimeters and contained approximately 2.5 kilograms (dry weight) of yarn. The composition of the yarn based on a sample which had been dried is as follows:

5 carbon 81.5%
 hydrogen 3.3%
 sulfur 0.8%
 nitrogen 2.8%
 oxygen 11.6%

10 The yarn on the bobbin was given a heat treatment in a nitrogen atmosphere in a furnace. The furnace was purged with nitrogen for four hours before the temperature was increased. The temperature of the furnace was increased from room
15 temperature at the rate of 100°C per hour until a temperature of 1300°C was reached and that temperature was maintained for 2 hours. Thereafter, the furnace was allowed to cool back to room
20 temperature. An analysis of the carbon yarn produced by the heat treatment showed that the carbon fibers compared to the original dried pitch fibers were about 90.5% by weight of the original dried pitch. In addition, the composition of the carbon yarn was determined to be:

25 carbon 98.0%
 hydrogen 0.1%
 sulfur 0.8%
 nitrogen 0.5%
 oxygen 0.5%

30 The mechanical properties of the yarn were measured and the average carbon fiber had a tensile strength of 1.54 GPa and a Young's modulus of about 152 GPa.

It can be seen that the carbon fibers obtained possessed a very high carbon content and such carbon fibers are useful in production of composites made with carbon yarn.

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Example 2

The carbon yarn produced in Example 1 as a result of shrinkage during the heat treatment had imprints of wind pattern. In order to remove these imprints and improve the carbon yarn, the carbon yarn from Example 1 was subjected to a threadline carbonizing furnace having a temperature of 2400°C. The carbon yarn was unwound and extended between rollers along a linear path through a nitrogen purge seal into a carbonizing furnace and out through a nitrogen purge seal. The furnace was heated by electrical resistance. Threadline carbonizing is well known in the prior art. For example, see U.S. Patent No. 4,301,136. The carbon yarn was subsequently sized, dried, and wound onto a second spool for storage. Mechanical properties of the resulting carbon fibers were an average fiber tensile strength of 2.03 GPa and an average fiber Young's modulus of 434 GPa. The fibers had an excellent appearance similar to carbon fibers produced by expensive conventional processes.

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Example 3

A mesophase pitch having a mesophase content of 80% by weight and a Mettler softening point of about 325°C was used to produce 1000 pitch fibers in the conventional spinning apparatus as used in Example 1 with the modification of a

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different spinnerette to produce 1000 pitch fibers. The pitch fibers were coated with an oxidizing liquid solution using a rotating graphite kiss wheel. The solution consisted of 25% by volume nitric acid, 75% by volume deionized water and carbon black in the amount of 20 grams per liter. The rate of rotation of the kiss wheel was adjusted so that the pitch fibers picked up an amount of the solution equivalent to about half the weight of the pitch fibers.

The pitch fibers were pulled from the spinning apparatus by directing them onto a rotating mandrel (winder) so that the rotation of the mandrel resulted in the fibers being drawdown to approximately an average diameter of 13 microns. The mandrel was a graphite bobbin 28 centimeters long, 9 centimeters in diameter, and having a 0.6 centimeters wall thickness. A 0.6 centimeter layer of carbon felt was wrapped around the core of the bobbin. The pitch yarn was wrapped in a crosswind pattern with the yarn having a linear speed of approximately 250 meters per minute. Each bobbin contained from 0.5 to 1.0 kilograms of pitch yarn.

The bobbins containing the moist pitch yarn were placed in sealed plastic containers for 24 hours at a temperature of about 30°C and thereafter removed from the plastic bags and loaded onto a graphite rack. The rack with the bobbins was then placed into an electric induction furnace. The furnace was purged for 4 hours with nitrogen in order to be certain that a substantially non-reactive atmosphere would be present for the

carbonization. The nitrogen was supplied continuously to the furnace throughout the heat treatment in order to maintain the non-reactive atmosphere. The temperature was raised 25°C per hour until 400°C, thereafter the temperature was raised 50°C per hour until 800°C, and finally the temperature was raised to 1300°C in about 1 hour. The final temperature was maintained for 2 hours and the furnace was allowed to cool back to room temperature.

The carbon yarn produced by this example was very flexible and easily removed from the bobbin. This indicates that fusion between portions of the yarn did not occur. An analysis of the carbon yarn using scanning photomicrographs showed that less than approximately 5% of the carbon fibers exhibited some adhesion to adjacent fibers. Carbon yarn produced by prior art processes typically exhibit a level of 10% or more.

The carbon yarn of this example showed the imprint of the crosswinding. As in Example 2, a conventional threadline furnace was used with the furnace having a temperature of 2400°C, the line speed was about 12 meters per minute, and a line tension of approximately 300 grams. The fibers were straightened out and the mechanical properties showed an average fiber tensile strength of 2.34 GPa and an average fiber Young's modulus of 407 GPa.

Example 4

The mesophase pitch used in Example 3 as well as the process steps were repeated except that the oxidizing liquid solution also contained 0.001% of a surfactant sold by DuPont as FC-170C.

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The carbon yarn resulting from the heat treatment in the furnace was excellent and had very little sticking between fibers. A subsequent threadline heat treatment at 2400°C resulted in carbon yarn having an average fiber tensile strength of 2.55 GPa and an average Young's modulus of 345 GPa.

CLAIMS

1. A process for manufacturing carbon yarn, comprising steps of:

5 spinning pitch into a plurality of continuous fibers;

combining the plurality of continuous fibers to form a pitch yarn;

10 treating the pitch yarn with an oxidizing liquid composition;

collecting the pitch yarn into a bulk form; and

15 subjecting the treated pitch yarn in bulk form to a heat treatment in a substantially non-reactive atmosphere to produce carbon yarn in bulk form.

2. The process of claim 1, wherein the pitch is mesophase pitch.

20 3. The process of claim 1, wherein said oxidizing liquid composition comprises aqueous nitric acid having a concentration of from about 10% to about 50% by volume.

25 4. The process of claim 2, wherein the aqueous nitric acid has a concentration of from about 15% to about 35% by volume.

30 5. The process of claim 1, wherein the oxidizing liquid composition comprises a dispersion of graphite or carbon black.

6. The process of claim 5, further comprising an aqueous surfactant.

7. The process of claim 1, wherein the oxidizing liquid composition comprises a water soluble oxidizing agent and a water soluble surfactant.

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8. The process of claim 1, wherein the pitch fiber is treated with the oxidizing liquid using a kiss wheel.

9. The process of claim 1, wherein the
10 continuous fibers are drawn down due to tension exerted by the step of collecting the pitch yarn into a bulk form.

10. The process of claim 1, wherein the
15 bulk form is pitch yarn on a bobbin.

11. The process of claim 1, wherein the pitch yarn is contacted with said oxidizing liquid composition subsequent to the pitch yarn being
20 collected into a bulk form.

12. The process of claim 1, wherein the heat treatment is carried out by raising the temperature of the fiber from room temperature to a
25 predetermined final temperature at a rate which avoids exceeding the softening point of the fiber during the heat treatment.

13. The process of claim 12, wherein the
30 temperature is raised at the rate of 100°C per hour.

14. The process of claim 12, wherein the temperature is raised from room temperature to about 400°C at the rate of about 25°C per hour and then
35 raised to 800°C at the rate of about 50°C per hour.

15. The process of claim 1, wherein a non-reactive gas is supplied to maintain a substantially non-reactive gas during the heat treatment.

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16. The process of claim 15, wherein the non-reactive gas is nitrogen, argon, helium or combination of two or more thereof.