

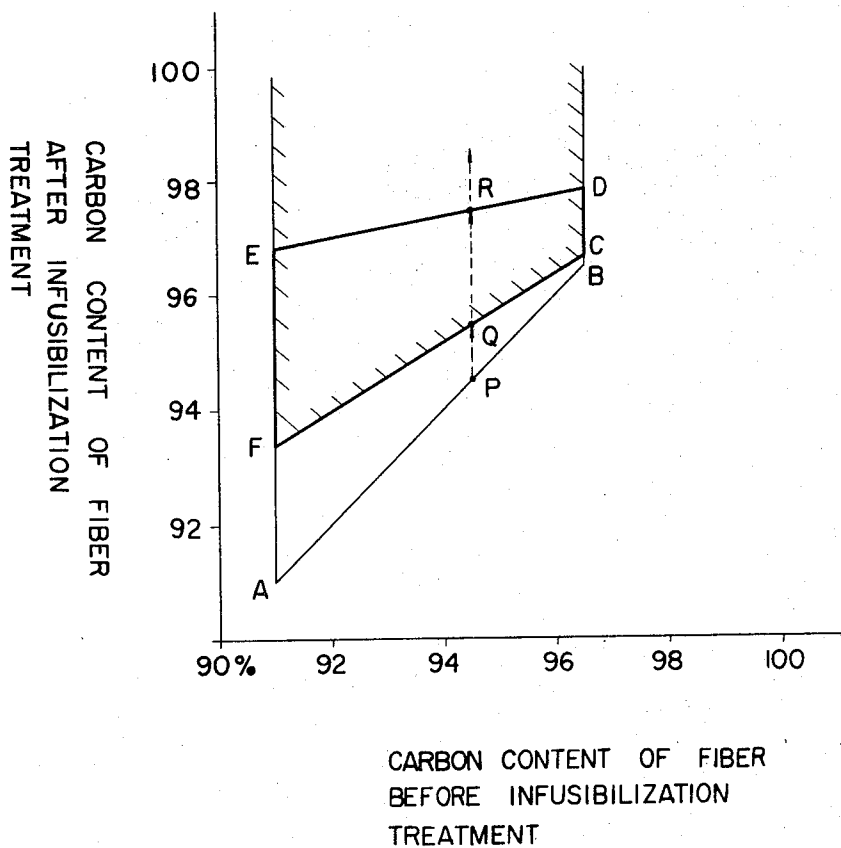
Dec. 21, 1971

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3,629,379

PRODUCTION OF CARBON FILAMENTS FROM LOW-PRICED PITCHES

Filed Nov. 6, 1969



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PRODUCTION OF CARBON FILAMENTS FROM LOW-PRICED PITCHES

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Continuation-in-part of application Ser. No. 695,356, Jan. 3, 1968, which is a continuation-in-part of application Ser. No. 521,408, Jan. 18, 1966, both now abandoned. This application Nov. 6, 1969, Ser. No. 874,653

The portion of the term of the patent subsequent to July 9, 1985, has been disclaimed

Int. Cl. C01b 31/07; D06m 11/12, 11/04

U.S. Cl. 264—29

20 Claims

ABSTRACT OF THE DISCLOSURE

A low-priced pitch containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent by weight and a mean molecular weight of at least 400 is readily melt-spun into a filament, which is then rendered infusible and thereafter carbonized, whereupon a carbon filament of good properties is obtained. This carbon filament can be further graphitized to produce a graphite filament. Pitches which do not meet the aforementioned requirements can be treated in various ways to make them melt-spinnable. The infusibilization treatment includes heating in air, oxygen, or ozone or the use of a hardening agent either admixed with the pitch prior to spinning or applied as a coating to the filaments at the time of spinning.

REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of my copending patent application, Ser. No. 695,356, filed Jan. 3, 1968, entitled "Production of Carbon Filaments From Low-Priced Pitches," which is in turn a continuation-in-part application of application Ser. No. 521,408, filed Jan. 18, 1966, both applications of which are now abandoned.

BACKGROUND OF INVENTION

This invention relates to the production of carbon filaments and more particularly to methods for producing carbon filaments from pitches that are low-priced, industrial starting materials having substantially high carbon contents.

More specifically, the invention concerns a new method for producing from inexpensive pitches carbon filaments of highly desirable properties such as high mechanical strength, modulus, thermal durability, oxidation-resistance, and so forth.

The term "pitches" herein used includes petroleum pitches, coal tar pitches, natural asphalts, pitches obtained as by-product in the naphtha cracking industry, pitches of high carbon content obtained from petroleum asphalt, and other substances having properties of pitches produced as by-products in various industrial production processes.

Among the methods known heretofore for producing carbon filaments, there are methods of carbonizing filaments of organic substances such as rayon filaments and polyacrylonitrile filaments with their original forms being preserved. These methods, however, have been accompanied by difficulties such as high prices of the starting materials and difficulty of producing filaments with sufficient mechanical strength.

In order to overcome these difficulties, I have previously invented a new method for producing carbon filaments which comprises baking an organic compound at a temperature of from 300 to 500° C. to produce a molten pyrolysis product, forming filaments from the molten pyrolysis product by melt-spinning, and then subjecting

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the filaments thus formed to a treatment to render them infusible (this treatment being hereinafter referred to as "infusibilization treatment") and to a carbonization treatment. This method has been granted a patent under U.S. Patent No. 3,392,216. By this method, it has become possible to produce carbon filaments of very high mechanical strength and high practical value from low-priced starting materials.

According to the abovementioned patented method, a molten pyrolysis product produced by heating in a temperature region immediately prior to carbonization of from 300 to 500° C. is melt-spun at the temperature in a region below the heating temperature, and the filaments so produced are subjected to a suitable treatment such as an oxidation treatment at a temperature within a range of from room temperature to a temperature at which the filaments do not actually fuse together, thereby rendering the filaments infusible, after which the filaments are subjected to carbonization treatment.

In the case of this patented method, the starting materials used must fulfill the following three conditions.

(1) The spinnability of the material must be high, and the material must be capable of being melt-spun.

(2) The material after spinning must be capable of being easily infusibilized.

(3) The material must be capable of being carbonized at high rate of carbonization.

SUMMARY OF INVENTION

It is therefore an object of the present invention to determine and clarify the conditions necessary for producing carbon filaments of excellent mechanical strength, thermal durability, and oxidation-resistance through the use of petroleum pitches, coal tar pitches, natural asphalts, and various other pitches which are the most low-priced starting materials among organic substances.

It is a further object of the present invention to provide a general method for producing pitches having high spinnability while having a high carbon content.

These objects have been achieved by the present invention which is the result of research on suitable treatment of pitches to transform them into materials which can be easily melt-spun and thereafter easily treated for rendering them infusible.

DETAILED DESCRIPTION OF INVENTION

Of the pitches for carbon products, the most general and advantageous ones from the economical point of view are petroleum pitches, coal tar pitches, natural asphalts, and some others. Many of these starting materials already have good spinnability but, in general, have low molecular weights, high H/C atomic ratios, and low contents of aromatic and other unsaturated components. Consequently, infusibilization treatment of these materials after melt-spinning is difficult, i.e., it is difficult to satisfy the above set forth second condition.

Furthermore, depending on the locality, from which the raw material pitch was obtained, and the reaction conditions as well as treatment conditions at the time of manufacturing such raw material, the properties of the material becomes different, so that there is possibility such that the raw material containing large amount of aromatic and other unsaturated components, but less H/C atomic ratio is obtained. In many of these cases, the spinnability of the material in molten state is poor and does not satisfy the above-stated first condition.

As a result of a detailed study on pretreatment of pitches, I have obtained the following findings.

When a pitch is pretreated under appropriate conditions to transform it into a melt-spinnable substance of a carbon content of from 91 to 96.5 percent, preferably from 92 to 96 percent, and a mean molecular weight of from

400 to 2,000 preferably 600 or higher, the resulting substance not only has good spinnability but also can be readily subjected to infusibilization treatment after spinning.

Thus, such a substance satisfies the aforesaid three conditions and becomes a very advantageous starting material for the production of carbon filaments.

The definitive conditions for a pitch for spinning to be used in the process of the invention as described in the preceding paragraphs are, in general, a content of 40 percent, preferably 25 percent or less, of matter insoluble in chloroform, a carbon content of from 91 through 96.5 percent, and a mean molecular weight of soluble constituents of from 400 to 2,000 as measured by the Rast method. Pitches having a content of insoluble constituents exceeding 40 percent are readily rendered infusible after spinning but have lowered spinnabilities.

In the case of a pitch having a high content of insoluble substances in the beginning, the insoluble substances tend to increase during heat-treatment for preparing the pitch for use in spinning. Accordingly, when a pitch containing a large quantity of insoluble substances from the beginning is used as a starting material, the spinnability is greatly lowered, and the strength of the ultimate carbon filament is also low. Furthermore, in the case of a pitch in which the mean molecular weight of the soluble substances is low, it is difficult to prevent local melting and fusing and mutual adhering of filaments during the infusibilization and carbonisation treatments.

The raw materials and method for preparing pitches for spinning meeting the above described conditions are not particularly limited. A most common example of a raw material pitch of high carbon content is coal tar pitch. In the case of coal pitch, the chloroform-insoluble matter therewithin is first extracted and removed, and then the soluble constituents are dry-distilled for several hours at as low a temperature as possible, for example, at a temperature not exceeding 250 degrees C. Thereafter, substances of low molecular weight are removed by a method such as distillation under reduced pressure at a temperature in the neighborhood of 300 degrees C. Since the chloroform-insoluble matter fuses with difficulty in most cases, it may be separated by heating and melting the starting material pitch.

The essential requirement is that the content of the substances of low fusibility and low solubility, which cause difficulty in the subsequent spinning process step, be adjusted to a value which does not exceed the aforementioned limit even after the heat-treatment step (e.g., dry-distillation or distillation under reduced pressure) prior to melt-spinning.

I have found that the addition of a suitable quantity (10 percent or less) during this process of sulphur, an organic compound containing sulphur such as tetramethylthiuram disulphide, mercaptobenzothiazole and its derivatives, or an organic-inorganic peroxide such as dicumyl peroxide, ditertiary butyl peroxide, barium peroxide, and potassium peroxide has the effect of promoting the increase of the mean molecular weight of the soluble substances. I have found further that the addition of chlorides and sulphides of various metals such as aluminum, iron, magnesium, and zinc, while causing a slight lowering of the spinnability of the pitch in some cases, is also an effective measure in the process of the invention. Alternatively, the pretreatment may, in some cases, comprise mere heating of the pitch for a long period of time at a temperature of 400° C. or lower, without the addition of any additive, to attain equivalent results.

The abovementioned additives are not only effective for the transformation of the starting materials but also play a role of promoting the infusibilization effect of the carbon fibers after spinning in cooperation with the effect rendered by an oxidizing gas from outside at the time of infusibilization treatment. Accordingly, these additives can also be regarded as hardening agent.

The additives are added by an appropriate method according to the properties of individual additive material. Organic peroxide and sulfur containing substances, etc., for example, which are soluble in molten pitch had better be used by being uniformly dissolved in the pitch. Also, in the case of inorganic sulfide, chloride, and the like which are insoluble with pitch, or the grain size of which, when it is too large, causes mal-effect at the time of spinning such as breakage of filament, irregularity in denier of the filament, etc., it is necessary to add such additives in as fine particles as possible. The maximum allowable grain size of such additives is preferably less than $\frac{1}{10}$ of the diameter of the carbon filament. In either case of using the organic peroxide additive soluble with the pitch or the inorganic additives insoluble with the pitch, they should be dispersed as uniformly as possible in the pitch. In order to realize such uniform dispersion, the pitch material itself is pulverized or melted beforehand, to which the additive in liquid or pulverized form is added and vigorously agitated, whereby the additive can be sufficiently dissolved or uniformly dispersed in the pitch.

In another way, when the additive is to be coated on the filament at the time of spinning, it is dissolved in water or any other appropriate solvent to prepare a 1-20% solution thereof, and the carbon filament is caused to pass through the additive solution or is wetted by spraying to uniformly coat the additive on the surface of the filament.

In this pretreatment, the raw material is not necessarily one kind of pitch but may be a mixture of different kinds of pitches, and aromatic, aliphatic, and other low molecular weight, organic compounds may be admixed therewith.

As mentioned hereinbefore, among the substances referred to as "pitches," there are included some with substantial differences in characteristics. In some cases, therefore, there is no necessity for a special treatment provided that the chemical composition and mean molecular weight of the pitch are within the ranges herein specified.

That is, the essential requirement for a pitch is that it can be transformed by any suitable treatment into hydrocarbon substance having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000 and having a high content of an aromatic compound and other unsaturated components. The treatment conditions applicable for this essential requirement are not limited to the aforementioned examples. In the limited range of carbon content of from 91 to 96.5%, the lower limit of 91% is the minimum possible carbon content at which spinnability of the pitch material is still easy and, at the same time, it is determined with a view to restricting the quantity of aliphatic chain components to be volatilized as gas such as methane, ethane, etc. from the interior of the carbon filament mainly at the initial stage of carbonization, while the upper limit of 96.5% has been experimentally found out to be the maximum point of the carbon content, at which spinnability of the pitch material still exists. The reason for setting the lower limit of the carbon content at 91% is that the aliphatic chain components which are converted to gases at the initial stage of the carbonization treatment may be small in respect of its weight, but it is considerably large from the point of volume of the gas, which is liable to damage the carbon fibre of delicate nature and causes deterioration of its quality. Such aliphatic chain components is restricted by the standard of the carbon content.

The limitation of the average molecular weight of more than 400 has been selected as its primary object to remove the low melting point substance which is harmful to infusibility of the carbon fiber. The secondary object of this limitation is to prevent the carbon fiber from being damaged, or deteriorated, due to gasification of low molecular weight substance. On the contrary, when the mean molecular weight becomes considerably large, not only the content of infusibilizing components increase, but also when the molten state is maintained for a long period at

the time of spinning, the quantity of the infusibilizing components further increases, with the consequence that it becomes difficult to continuously spin the smooth and fine fiber without breakage and, in some cases, the spinning of fiber becomes difficult on account of the spinning nozzle being clogged. In view of such consideration, the upper limit of the mean molecular weight has been determined at 2,000.

The term "carbon content" herein used refers to that determined by a method generally practiced as an organic elementary analysis method and, in the case where elements other than carbon and hydrogen are contained, is expressed as the value obtained by excluding said other elements and taking the total of the contents of the carbon and hydrogen as 100 percent.

The abovementioned "mean molecular weight" in this application refers to the value measured by the Rast method, wherein camphor is used as a solvent. Since each of these material pitches is not a single substance but is a mixture of a large number of compounds or respectively different molecular weights and kinds of molecules, the term "mean molecular weight" is especially used herein.

I have found that a molten pyrolysis substance satisfying the above specified conditions has good spinnability, and infusibilization treatment thereof subsequent to spinning can be readily carried out. Accordingly, these substances can be used as starting materials for producing carbon filaments of high mechanical strength by further carbonization.

For the spinning, an ordinary melt-spinning process is used at a spinning temperature generally of 350° C. or lower, the viscosity of the molten substance suitable for spinning being considered in the selection of this spinning temperature. The ordinary melt spinning process to be employed in this invention is such one that is usually used in the spinning of thermoplastic materials like thermoplastic resins, glass, etc. There are various types of melt spinning process such as extrusion type, centrifugal type, pressure-extrusion type, spraying type, jet type, etc. Though any of these types of the melt spinning processes can be arbitrarily selected, the extrusion type is advantageous when the melt-viscosity of the pitch is high, and the other three types are particularly useful when the melt viscosity thereof is low. Further, when it is desired to obtain long, continuous filament, the extrusion type spinning process is preferable, and, when a particularly fine filament and wool are to be obtained, the centrifugal type spinning process is advantageous.

The filaments thus spun are then placed in contact for several minutes or longer with air or an oxidizing gas at a temperature below the spinning temperature or are subjected to another chemical and physical treatment thereby to render them infusible. For example, one method for obtaining excellent results comprises treating the filaments with air containing ozone or with oxygen at a suitable temperature of from room temperature to 100° C. for a suitable time of 7 hours or less and successively thereafter subjecting the filaments to an oxidizing treatment in air at a raised temperature up to 300° C. with the rate of temperature rise being approximately 1° C./min.

The chemical change produced by the ozone treatment is not clear in all cases, but it can be inferred from the increase to some extent in the weight and observation of the infrared absorption spectrum of the filaments that the change is due to $>C=O$, $C-O-C$ coupling. From the fact that absorption can be observed, it is apparent that addition of oxygen is easily accomplished at a low temperature, and a three-dimensional bridging in surface layer is formed and, at the same time, effectively promotes the formation of cross-links due to the immediately following oxidation in air.

The mechanism of the infusibilization due to ozone and oxygen may be interpreted to be as described above. Therefore, provided that the formation of cross-links is effectively accomplished at a temperature which will not

cause the filaments to fuse and adhere to each other, the suitable method is not necessarily limited to treatment with ozone and oxygen. I have found that, for example, it is also possible to accomplish infusibilization by using a hardening agent such as the aforementioned peroxides or metal chlorides which are previously admixed with the pitch or applied as coating to the filaments at the time of spinning.

In order that fine filament of pitch maintains its shape perfectly being sustained under heat-treatment in a non-oxidizing atmosphere in the course of the subsequent carbonization treatment, and becomes the carbonized or graphitized carbon filaments having excellent mechanical strength without causing fusion bonding among the filaments, the process step of infusibilization treatment is extremely important, which must be sufficiently given. It has however been found out that excess must be avoided in carrying out this treatment, because when the filaments are subjected to excessive oxidizing treatment, they are more perfectly infusibilized, but they become on the other hand brittle and breakable and moreover the surface of the filament loses its smoothness and a great many of small pores are produced overall portions of the filament, on account of which the mechanical strength of the end product is considerably deteriorated.

The method of producing carbon fibers from pitch material is already known by U.S. Patent No. 3,392,216. However, there has not been known at all as to the standard of inspection to ascertain the effective carrying out of the infusibilization as well as to limitation to such standard. The following two reasons are contemplated therefor.

(1) This kind of raw material pitches are not only of extremely complicated structure and composition and difficult to be analyzed with high accuracy, but also these structure and composition become much more complicated after the infusibilization treatment.

(2) After the infusibilization treatment, the carbon fibres are generally insoluble and infusible, so that every limited number of means for determining the structure and composition of the carbon fibers can be used, such as elementary analysis, infrared ray analysis, and so forth.

In spite of such circumstances, the present inventor discovered a very succinct standard of inspection as a result of detailed experiments.

That is, as shown in the graphical representation of the drawing, the carbon content of the pitch fibers prior to the infusibilization treatment (this carbon content is same as that of the raw material pitch) is taken on the abscissa, and the carbon content of the fiber after the infusibilization treatment is taken on the ordinate. The area surrounded by C-D-E-F provides the satisfactory infusibilization of the carbon fiber, which enable the subsequent carbonization treatment to be carried out efficiently and the end product of excellent quality to result.

In the drawing, the straight line AB indicates the carbon content of the pitch fiber immediately after the spinning. The carbon content at the point P on the straight line AB signifies that the carbon content of the fiber gradually increases by isolation of hydrogen with the progress in the oxidizing treatment. When the heat-treatment further proceeds and the carbon content reaches the point Q on the straight line FC, the carbon fiber attains the required infusibilization. The area between the point Q on the straight line FC and the point R on the straight line ED provides sufficient infusibilization, which meets the purpose of the present invention. The area beyond the point R causes remarkable consumption of the carbon fiber due to the oxidation, which brings about unfavorable effects to the end product.

As mentioned in the foregoing, infusibilization of the carbon fiber by the oxidizing treatment is due to production of three-dimensional cross-linking structure. Although the process and results are both extremely complicated, it has been successfully found out that the neces-

sary control for the sufficient infusibilization can be done by paying attention to the ratio of carbon and hydrogen contained in the pitch material. In other words, it has been found out that the degree of infusibilization can be determined simply by decrease in hydrogen content, i.e., H/C atomic ratio, or increase in the carbon content. Moreover, the measurement for the H/C atomic ratio can be sufficiently done by the elementary analysis alone. Thus, by the above-described procedure on the basis of the graphical representation, the infusibilization treatment can be performed easily and accurately.

Thus, it has become possible from such finding that, whatever raw material pitches that can be obtained through the transformation are used for spinning the carbon fibers, if they contain at least carbon and hydrogen, possess the mean molecular weight of 400-2,000, and the carbon content of 91 to 96.5%, and meets the relationship indicated in the graphical representation in the drawing after the oxidation treatment, it can be considered that the infusibilization treatment is effectively completed and the subsequent step of the carbonization treatment can be carried out. The carbon fiber (or graphite fiber) finally obtained in this way possesses superior quality to any of the known carbon fibers.

The infusibilized filaments obtained in the above described manner are thereafter subjected to thorough carbonization in a state wherein they are prevented from contacting an oxidizing gas such as air. I have found that during this treatment a temperature rise rate of approximately 10° C. per minute or lower is preferable. I have found further that, when the carbonization temperature reaches a value of from 600 to 700° C., or higher, the resulting carbon filament attains mechanical strength of practical value and, when necessary, can be transformed into graphite filaments by heat-treatment at a temperature of 2,000° C. or higher.

Particular notice should be given here to a case, wherein a pitch having a high carbon content of 95% and above is used as a starting material. With such material pitch, not only the excellent physical properties of the carbon filaments can be fully maintained, but also the following additional improvements in the production process can be obtained, whereby economy in the process can be greatly increased.

(1) The process step ("infusibilization treatment") wherein the pitch filament obtained by spinning a pitch as the starting material is rendered infusible by oxidation has been remarkably facilitated. For example, the ozone treatment set forth in the foregoing has become unnecessary, oxidation with air being sufficient, and, moreover, it has become possible to increase further the rate of temperature rise during this process step.

(2) The heating conditions in the process step of carbonizing (carbonization treatment), in an inert gas, the filament which has been subjected to the infusibilization treatment have become less critical. For example, no adverse effects are observable when a temperature rise rate of the order of 10 degrees C./minute or higher is used. Accordingly, an economical saving can be made in the time required for carbonization, the quantities of environmental gas and heat supply, and other items of cost.

(3) Furthermore, the yield in this carbonization process has been further increased, becoming from 70 to 85 percent by weight, and it has become possible to hold the shrinkage coefficient in the filament direction to within a small value of approximately 10 percent.

The mechanical strength of a carbon filament produced by the new process of this invention is 5 metric tons/cm.² or higher in the case of a filament baked at 1,000 degrees C., which filament therefore has ample utility for practical use. Moreover, because of the simplification of the process together with the possibility of using pitches of low price as starting materials, the process of the invention becomes highly economical, whereby carbon fila-

ments of excellent properties can be produced at low cost.

The carbon filaments or graphite filaments produced by the above described process according to the present invention can be advantageously used as heat insulation material, as carbon electrode material, and for other shaped articles of carbon or graphite, as reinforcement material for shaped articles of heat-resistant resin, for electrically conductive and heating mats, as heat-resistant packing, as a filler for electrically conductive paints, and as material for heating elements, resistances, etc., for various electronic industries. In addition, these filaments can be effectively used as materials such as filter elements in chemical industries.

PREFERRED EMBODIMENTS

In order to indicate still more fully the nature of the invention, the following examples of typical procedure are set forth, it being understood that these examples are presented as illustrative only, and that they are not intended to limit the scope of the invention.

Example 1

500 grams of petroleum pitch (83.40 percent C, 9.42 percent H, 0.65 percent N, and 4.15 percent S, manufactured by Daikyo Sekiyu Company, Japan) was dry-distilled for one hour in nitrogen gas at a temperature of 380° C., and the residue was thereafter heated for 3 hours in a vacuum of 10⁻⁴ mm. Hg at a temperature of 300° C. thereby to distill out low molecular weight components and, at the same time, to accomplish heat treatment.

The resulting residue contained 86.55 percent of carbon and 8.35 percent of hydrogen, and, according to the afore-described representation, the carbon content was 91.2 percent. According to the Rast method, this residue had a mean molecular weight of 650 and was a black, lustrous solid at room temperature, melting at a temperature of 120° C. and above.

This substance was melted and heated to 240° C. and spun by extrusion through a nozzle of 0.3 mm. diameter with application of nitrogen gas under a pressure of atmospheric pressure plus 20 mm. Hg and take-up at a speed of 300 metres per minute.

The resulting filament was treated for 2 hours in air containing 10.4 grams per cubic metre of ozone at a temperature of 40° C. and thereafter subjected to heating in air at a temperature rise rate of 10° C. per hour up to 260° C., which temperature was then maintained for one hour. Thereafter, the filament was carbonized by the ordinary process.

The resulting carbon filament was found to have a diameter of from 10 to 15 microns, a tenacity of 10 t./cm.², and an elongation of 2.5 percent.

For comparison, the starting material petroleum pitch, while exhibiting good spinnability at a spinning temperature of 140° C., melted when treated thereafter by exactly the same oxidizing treatment process as described above and did not become a carbon filament.

Example 2

A substance identical to the residue obtained after one hour of dry-distillation according to Example 1 was thereafter heat-treated for 3 hours in a vacuum at temperature of 300° C. To the resulting residue, 5 percent of dicumyl peroxide was added. The resulting substance was divided into five samples, four of which were heat-treated at 300° C. respectively for 30 minutes, 1 hour, 5 hours, and 10 hours.

The sample so heat-treated for 10 hours hardened at an intermediate point during the treatment and did not exhibit a molten state, but the samples of the other treatment times, in all cases, exhibited superior spinnability relative to that exhibited in the case of Example 1, and infusibilization treatment of the spun filaments resulting from these samples also was easily accomplished. The treated samples had carbon contents and molecular

weights as given in the following table, these values being represented in the terms defined hereinbefore.

Treatment time (hr.)	0	0.5	1	5
Carbon content (percent)	91.2	92.0	92.3	92.8
Mean molecular weight	650	680	700	750

These starting materials were used and, by the same procedure as set forth in Example 1, were subjected to melt spinning, infusibilization treatment, and carbonization treatment followed by heating at 1,000° C. The resulting filament had a diameter of about 10 microns, a tenacity of 12 t./cm.², and an elongation of 2.8 percent.

Example 3

A mixture prepared by adding one part of petroleum pitch to one part of coal tar pitch (87.5 percent C, 6.0 percent H, and 0.42 percent S) was used as a starting material and subjected to the same treatment procedure as set forth in Example 1, whereupon a pitch of a carbon content of 93.5 percent as hereinbefore defined was obtained.

This pitch was slightly inferior in spinnability to those of Example 2, but its spinnability was improved by adding thereto 5 percent of a low polymer of benzyl chloride.

This pitch was spun at 280° C. and then subjected successively to the same infusibilization treatment as set forth in Example 1 and a carbonization treatment at temperatures up to 1,000° C., whereby a carbon filament of a diameter of from 10 to 13 microns and a tenacity of 15 t./cm.² was obtained.

Example 4

Coal tar pitch containing 5 percent of chloroform-insoluble matter was heat-treated in nitrogen gas for 3 hours at a temperature of 150 degrees C. and then for 3 hours at 200 degrees C. and thereafter heated for 1 hour under reduced pressure at a temperature not reaching 300 degrees C. As a result, a pitch containing 14 percent of matter insoluble in chloroform and soluble matter of a mean molecular weight (by the Rast method) of 650 and having a total carbon content of 95.5 percent was obtained with a yield of 30 percent.

This pitch was melt spun at a temperature of from 320 to 330 degrees C., and the resulting filament was heated in air from room temperature to 250 degrees C. at a temperature rise rate of 1 degree C./minute and then carbonized by heating in nitrogen gas to 1,000 degrees C. at a rate of 5 degrees C./minute.

The carbonization yield in this process, that is, the yield of formed carbon filament with respect to the pitch prior to spinning was 75 percent. The filament strength was from 5 to 6 metric tons/cm.², and the shrinkage was 9 percent.

A coal tar pitch containing 24 percent of chloroform-insoluble matter was used as the starting material and subjected to the same heat-treatment steps as set forth above, whereupon a pitch containing 44 percent of chloroform-insoluble matter and having a total carbon content of 95.7 percent was obtained with a yield of 45 percent. The pitch thus obtained exhibited difficulty in spinning.

Example 5

Chloroform-soluble matter was extracted from a coal tar pitch, at a room temperature, and 5 percent of tetramethylthiuram disulphide was added thereto. The pitch was then subjected to the same heat-treatment steps as set forth in Example 4. As a result, a pitch of a mean molecular weight of 950 and a carbon content of 95.7 percent was obtained with a yield of the same order as that in Example 1.

The pitch thus obtained was melt-spun in the same manner as set forth in Example 1, and the resulting filament was heated in air to 250 degrees C. at a rate of 1.5 degrees C./minute and then further heated in helium gas to 1,000 degrees C. at a rate of 10 degrees C./minute. The carbon filament thus produced has a strength of

from 6 to 7 metric tons/cm.². The carbonization yield in this process was 80 percent.

Example 6

100 grams of a pitch obtained by flame cracking at approximately 2,000° C. of naphtha was subjected to extraction with chloroform at a room temperature, whereupon 90 grams of soluble matter was obtained. This matter was further subjected to extraction with n-hexane to remove substances of low molecular weight, whereupon a pitch of a mean molecular weight of 600 and a carbon content of 96.2 percent was obtained.

When the pitch thus obtained was melt-spun at a temperature of from 330 to 340 degrees C. and then subjected to the same treatment as set forth in Example 4, a carbon filament of a strength of from 5 to 6.5 metric tons/cm.² was obtained.

Example 7

Viscous solution of blackish brown color resulting as a distillation residue from production of benzyl-chloride by reaction of toluene and chlorine was dissolved by adding thereto 3% by weight of tetramethylthiuram disulfide, then it was heated for 6 hours at a temperature of from 220 to 270° C., thereafter it was distilled up to 300° C. under a reduced pressure of 10⁻⁴ mm. Hg to remove low temperature distillation components as well as decomposition products, whereby black pitch was obtained.

The pitch contains 94.8% carbon, and 18% of chloroform insoluble component. The mean molecular weight of this pitch containing the chloroform insoluble component is 1,840 and shows generally excellent spinnability.

This pitch was melt-spun by pressure-extrusion into fiber of 15 to 20 microns in diameter at a spinning temperature of 290 to 320° C. by means of a spinning apparatus provided with 30 nozzles of 0.5 mm. dia. each, while the pitch is being pressurized at 30 kg./cm.² by a gear pump.

The obtained pitch fiber was heated to 200° C. by raising the heating temperature from a room temperature at a rate of 5° C./min. Subsequently, it was heat-treated in the air for 30 min. at 200° C. to infusibilize the fiber. The carbon content of the infusibilized pitch fiber was 96.9%. The infusibilized pitch fiber was further subjected to the carbonization treatment at an elevating speed of 10° C./min. in a nitrogen gas atmosphere, and the carbon fiber having strength of 11 to 12 tons/cm.² was resulted.

Example 8

Crude petroleum oil of Syria origin heated to 500° C. was atomized in steam which had previously been heated to 2,000° C. to subject the crude oil to thermal decomposition, where a tar-like substance was obtained. This tar-like substance was dry-distilled at a temperature up to 280° C. under a reduced pressure of 10⁻⁴ mm. Hg to remove low boiling point component of less than 280° C., from which a pitch-like substance was obtained. This pitch contained 96.4% carbon and had the mean molecular weight of 1.050. The pitch was subjected to melt-spinning at 300 to 330° C. by using a rotating cylindrical spinning apparatus having a diameter of 100 mm. and a depth of 20 mm., and provided with 30 small holes of 0.3 mm. in dia. each, whereby pitch fiber of about 8 microns in diameter was obtained.

The pitch fiber was heat-treated up to a temperature of 350° C. at a rate of 1.5 to 2° C./min. During the temperature elevation, the pitch fiber was sampled at respective temperature points of 150° C., 200° C., 250° C., 300° C., and 350° C., and the samples were measured for their carbon content (C/C+H%). Thereafter, the respective fibers were subjected to carbonization in a nitrogen gas by raising the temperature to 1,000° C. at a rate of 5° C./min. The measured carbon content of the respective-samples subjected to the oxidizing treatment were, respectively, 96.55%, 96.65%, 97.15%, 97.82%, and 98.06%

of the carbon fibers thus produced. Of these, three carbon fibers treated at 200° C., 250° C., and 300° C. indicated favorable results and the strength measured was 12 to 15 tons/cm.². However, the carbon fiber treated at 150° C. was observed to have brought about fusion-bonding among the filaments to some extent, whereby the rate of yield of perfect filament was lowered and, at the same time, long filaments were difficult to obtain. Further, in the carbon fiber treated at 350° C., no fusion-bonding was observed at all, but the fibers were locking in luster and when observed under an electron microscope, a number of small pores were observed on the surface of the fiber, which indicates that the fiber is damaged by excessive oxidizing treatment. The strength thereof was not only as low as 1 to 3 tons/cm.², but the fibers were prone to break into small pieces during handling.

The abovementioned three carbon fibers of favorable quality were further treated for graphitization by heating them to 2,800° C. in a nitrogen gas, and the graphite fibers of 10-14 tons/cm.² strength were obtained.

What I claim is:

1. A method for producing carbon filaments which comprises the successive steps of: producing filaments by melt spinning a member selected from the group consisting of (a) a pitch containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000 and (b) a pitch transformed by treating a pitch having a mean molecular weight below 400 and/or carbon content below 91 percent into a composition containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000; contacting the filaments with air or an oxidizing gas at a temperature below the spinning temperature of the filaments for a length of time necessary to render them infusible; and subjecting the resulting filaments to a carbonization treatment by firing the filaments in an inert atmosphere at a temperature below 2,000° C.

2. A method according to claim 1, wherein the starting material is a pitch containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000.

3. A method according to claim 1, wherein the starting material is a pitch transformed by treating a pitch having a mean molecular weight of below about 400 and/or carbon content of below 91 percent into a composition containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000, and wherein up to 10% by weight of an auxiliary substance selected from the group consisting of sulphur, benzyl chloride, tetramethylthiuram disulfide, mercaptobenzothiazole, dicumyl peroxide, di-tert-butyl peroxide, potassium peroxide, chlorides of aluminum, iron, magnesium and zinc, barium peroxide and sulfides of aluminum, iron, magnesium and zinc is added to said composition at the melt-spinning step.

4. A method according to claim 1, wherein the starting material is a pitch transformed by treating a pitch having a mean molecular weight below about 400 and/or carbon content below 91 percent into a composition containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000, and wherein up to about 10% by weight of an auxiliary substance selected from the group consisting of sulphur, benzyl chloride, tetramethylthiuram disulfide, mercaptobenzothiazole, dicumyl peroxide, di-tert-butyl peroxide, potassium peroxide, chlorides of aluminum, iron, magnesium, and zinc, barium peroxide and sulfides of aluminum, iron, magnesium, and zinc is added to said composition prior to, or at least at the melt-spinning, and wherein the filament resulting from the carbonization is further subjected to a graphitization treatment at a temperature of 2,000 c. or higher in an inert atmosphere.

5. A method according to claim 2, wherein the filament resulting from the carbonization is subjected to a further graphitization treatment, whereby the carbon filament is converted into a graphite filament.

6. A method according to claim 1, wherein the starting material is a pitch prepared by transforming a pitch containing hydrocarbons having a mean molecular weight below about 400 and/or carbon content below 91 percent into a composition containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000, and wherein up to about 10% by weight of an auxiliary substance selected from the group consisting of sulphur, organic compounds containing sulphur, organic peroxides, inorganic peroxides, and chlorides and metal sulphides is added to said composition at a time prior to, and at least at the melt-spinning step, and where the filament resulting from the carbonization is subjected to a further graphitization treatment at a temperature of 2,000° C. or higher in an inert atmosphere, whereby the carbon filament is converted into a graphite filament.

7. A method for producing carbon filaments which comprises the successive steps of: producing filaments by melt-spinning at a melt-spinning temperature a member selected from the group consisting of (a) a pitch containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000, (b) a pitch transformed by treating a pitch having a mean molecular weight of below 400 and/or carbon content of below 91 percent into a composition containing carbon and hydrogen and having a carbon content of from 91 to 96.5 percent and a mean molecular weight of from 400 to 2,000, and (c) a pitch heat-treated at a temperature outside of the temperature range of 300 to 500° C. and having a carbon content of from 91 to 96.5 percent and the mean molecular weight of from 400 to 2,000; contacting the filaments with an oxidizing gas at a temperature between room temperature and 350° C. to render them infusible; and subjecting the resulting filament to a carbonization treatment by firing the filaments in an inert gas atmosphere at a temperature below 2,000° C.

8. A method according to claim 7, wherein the filament is further subjected to graphitization treatment by heating the same in an inactive gas at a temperature of 2,000° C. and above.

9. A method according to claim 7, wherein the infusibilization treatment satisfies the conditions defined by the lines C-D-E-F shown in the accompanying drawings.

10. A method according to claim 7, wherein the material pitch contains from 93.5 to 96.5% carbon and possesses the mean molecular weight of from 400 to 2,000.

11. A method according to claim 7, wherein the oxidizing gas to be used for the infusibilization treatment is air.

12. A method according to claim 7, wherein the infusibilization treatment is carried out by heating the filament in the presence of an oxidizing gas, thereby to increase the carbon content of the filament to the region defined by the lines C-D-E-F shown in the accompanying drawings.

13. The method according to claim 1, in which the pitch in (b) is obtained by heat-treatment.

14. The method according to claim 7, in which the pitch in (b) is obtained by heat-treatment.

15. The method according to claim 1, in which the pitch in (b) is obtained by distillation.

16. The method according to claim 7, in which the pitch in (b) is obtained by distillation.

17. The method according to claim 1, in which the pitch in (b) is obtained by extraction.

18. The method according to claim 7, in which the pitch in (b) is obtained by extraction.

19. The method according to claim 1, in which the pitch in (b) is obtained by heating in the presence of an additive selected from the group consisting of sulphur, benzyl

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chloride, tetramethylthiuram disulfide, mercaptobenzothiazole, dicumyl peroxide, ditertiary butyl peroxide, potassium peroxide, chlorides of aluminum, iron, magnesium and zinc, barium peroxide and sulfides of aluminum, iron, magnesium and zinc.

20. The method according to claim 7, in which the pitch in (b) is obtained by heating in the presence of an additive selected from the group consisting of sulphur, benzyl chloride, tetramethylthiuram disulfide, mercaptobenzothiazole, dicumyl peroxide, ditertiary butyl peroxide, potassium peroxide, chlorides of aluminum, iron, magnesium and zinc, barium peroxide and sulfides of aluminum, iron, magnesium and zinc.

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U.S. Cl. X.R.

23—209.1; 264—Digest 19

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,629,379 Dated December 21, 1971

Inventor(s) Sugio Otani

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

Column 1, under the title, between lines 6 and 7, under the title, please insert:

-- Claims priority, application Japan, Serial No. 2928/1965, filed January 20, 1965. --.

Signed and sealed this 9th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents