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[54] **METHOD OF PRODUCING CARBON FIBERS**

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[57] **ABSTRACT**

Nonflammable fibers are produced by subjecting a composite fiber comprising a pitch and a synthetic organic polymer bonded uniformly along the longitudinal direction of the fiber to an oxidation treatment to render it infusible and then to a set treatment in air or gaseous nitrogen at a temperature of 200° to 500° C. for at least 2 hours. The nonflammable fiber is converted to carbon fiber by heating to a temperature higher than 800° C. in gaseous nitrogen. Suitable pitches include petroleum asphalt, coal tar pitch, and pitch obtained by baking polyvinyl chloride. Suitable synthetic organic polymers include polyamides, polyesters, polyolefins, polyvinyl chloride, polyvinylidene chloride, polyurethane, epoxy resins, and phenol resins.

20 Claims, No Drawings

METHOD OF PRODUCING CARBON FIBERS

The present invention relates to an improved method of producing carbon fibers.

Recently, carbon fibers have been drawn attention as fibrous materials having various excellent properties, for example, fire resistance, heat resistance, corrosion resistance, electric conductivity and insulating property.

Carbon fibers have the same or higher fire resistance, corrosion resistance, insulating properties and the like as glass fibers and are substantially the same in strength as glass fibers. Furthermore, some carbon fibers have electric conductivity which has never been possessed by glass fibers and further carbon fibers are particularly superior in heat resistance under nonoxidizing atmosphere to glass fibers and are low in specific gravity. However, carbon fibers have particularly low elongation and are broken even by applying a very slight elongation and it has been impossible to obtain carbon fibers having a satisfactory length by conventional production processes. Heretofore, carbon fibers have been produced by spinning inexpensive pitches and carbonizing the resulting fibers.

The starting fibers obtained from pitches have a much higher carbon content than fibers of cellulose, polyacrylonitrile and lignin and therefore the yield in the carbonization step is considerably higher and lost materials are few and consequently the carbonization step can be easily carried out in a short time. On the other hand, the handling in the spinning or after the spinning is considerably difficult as compared with starting fibers such as polyacrylonitrile and the like.

The inventors have made investigations for solving these problems in conventional production of carbon properties. Another object is to provide carbon fibers having excellent physical properties commercially easily in present invention.

The object of the present invention is to provide carbon fibers having excellent physical properties commercially easily in a high yield.

The present invention consists in a method of producing carbon fibers which comprises spinning concurrently a pitch and a synthetic organic polymer melted separately through a common nozzle to obtain a composite fiber in which both the components are bonded uniformly along the longitudinal direction of the unitary filament, subjecting the resulting composite fiber to an oxidation treatment in air or gaseous nitrogen at a temperature of 200° to 500° C. for at least 2 hours and then to a carbonization treatment at least once in gaseous nitrogen at a temperature higher than 800° C.

The term "carbon fibers" used in the present invention means ones composed of carbon and the fibers include nonflammable fibers, in which carbon does not show a crystal structure but shows an organic amorphous structure, carbon fibers, in which carbon is microcrystalline and graphite fibers, in which carbon shows a distinct crystal structure.

In the above described nonflammable fibers, the carbon constituting the fibers has an amorphous structure, so that said fibers have a heat resistant temperature of about 250° to 300° C. and show an electrical insulating property. The carbon fibers composed of microcrystalline carbon have a higher heat resistance than the nonflammable fibers and an electric conductivity. The graphite fibers are superior in heat resistance and electric conductivity to the above-described nonflammable fibers and carbon fibers.

Pitches to be used in the present invention include petroleum asphalt, coal tar pitch, petroleum slag and pitch obtained by baking polyvinyl chloride, all of which can be melt spun. These pitches can provide carbon fibers by melt spinning them along and subjecting the resulting filament to an oxidation treatment and then to a baking treatment. Petroleum asphalt and coal tar pitch are most preferably in view of the carbon content ratio.

Thermoplastic synthetic organic polymers to be used in the present invention are all known synthetic organic polymers having a thermoplasticity, for example, polyamide, polyester, polyester ether, polyolefin, polyvinyl chloride, polyvinylidene chloride, polyurethane, polyacryl and copolymers, modified polymers and blends thereof. Polyolefins, such as, polyethylene, polypropylene, etc., are particularly preferable.

Thermosetting synthetic organic polymers include, for example, epoxy resins, phenol resins, etc., and it is preferable not to contain any heat-setting agent.

Conjugate spinning of these pitches and thermoplastic or thermosetting polymers can be carried out according to conventional conjugate spinning processes and any particular attention is not necessary in the spinneret and the conjugate spinning of both the components and for example, the melt conjugate spinning of petroleum asphalt and polyamide can be carried out at a temperature of 200° to 300° C. by means of a spinneret provided with orifices having a diameter of 0.1 to 0.4 mm.

The structure bonding the above-described both components may be either a side-by-side relation or a sheath-core relation and can be selected by considering easiness in treatment and handling of the spun fibers.

In order to obtain a high yield when the starting fibers are carbonized to obtain carbon fibers, the starting fibers having a high carbon content ratio are preferably in view of the yield and other points. Accordingly, the starting fibers having a high ratio of pitch are preferable, but considering easiness of various steps, such as, spinning, taking-up, unwinding and the like or spinning rate, the conjugate ratio of pitch and the thermoplastic or thermosetting synthetic organic polymer is preferred to 1/1–10/1, more preferably 2/1–6/1, most preferably 3/1–5/1.

In the case of a conjugate ratio of pitch and the synthetic organic polymer being less than 1:1, the spinnability and the succeeding handlings are easy but the carbon content ratio is lower and consequently, the carbonization cannot be easily carried out and further the yield of carbon fibers lowers.

When the conjugate ratio is more than 10:1, the setting and the carbonization of the resulting fibers become easy and the yield of carbon fibers increases, but yarn breakage occurs frequently in the spinning and the conjugate spinning is difficult. In order to decrease such yarn breakage, the takeup velocity must be lowered to about 500–700 m./min., which is a usual takeup velocity in spinning of a monofilament composed of only pitch, but in such a low rate it is difficult to obtain uniform composite fibers.

If a draft to be applied to usual synthetic organic polymers is conducted in the spinning of pitches, a stress is concentrated just below the nozzle and therefore the fibers are broken. However, when the synthetic organic polymer and pitch are conjugate spun as in the present invention, the synthetic organic polymer endures the stress and the melt spinning can be carried out stably and the takeup velocity increases to 1,000 to 2,000 m./min. Furthermore, the spinning draft can be increased, so that carbon fibers having a fine denier can be produced.

As mentioned above, the conjugate spinning of pitches and the synthetic organic polymers is very important even in any bonding structure of both the components. For example, in view of penetration of an oxidizing agent in the oxidation treatment, it is preferable to conjugate spin the above-described polymer and pitch in a side-by-side relation or in a sheath-core relation, in which the synthetic organic polymer is arranged as the core component and the pitch is arranged as the sheath component.

However, when both the components are conjugate spun in a side-by-side relation, it is desirable to select such a bonding structure that both the components are not separated in the treatment. According to the present invention it is preferable to arrange both the components in a sheath-core relation, in which the above-described pitch forms the core and the synthetic organic polymer forms the sheath. In this case, since the core pitch is surrounded by the synthetic organic polymer in the composite fiber, it is possible to handle such a composite fiber in the same manner as in a conventional composite fiber, but considering penetration of an oxidizing agent

in the oxidation treatment, the sheath is preferred to be thin and it is desirable that the thickness of the sheath of the synthetic organic polymer in the cross section of the composite fiber is less than one-fifth of the diameter. When the pitch and the synthetic organic polymer are conjugate spun in a sheath-core relation, the number of core may be more than 2.

The spun fibers obtained by conjugate spinning of the pitch and the synthetic organic polymer according to the present invention are much more flexible than the fibers obtained by melt spinning pitch along and are considerably improved in a resistance against elongation stress and further the spun fibers are very easily taken-up.

According to the present invention, the spun fibers are firstly subjected to an oxidation treatment. For the oxidation, inorganic or organic substances, such as oxygen, air, ozone, hydrogen peroxide, hypochlorites, bichromates, permanganates, benzoyl peroxide, cumen peroxide, and the like are used.

This oxidation treatment makes the pitch and the synthetic organic polymer constituting the composite fiber infusible and insoluble to heat and solvent.

The oxidation treatment is carried out in a gaseous phase or an aqueous phase by using the above-described oxidizing agent. The gaseous oxidation is carried out by using oxygen, air, ozone, and hydrogen peroxide and the aqueous oxidation is carried out by using hydrogen peroxide, hypochlorites, bichromates, permanganates, benzoyl peroxide, cumen peroxide, etc.

When the pitch forms the surface of the fiber, it is preferable to effect the oxidation in a gaseous phase by means of ozone and the like and in the case of oxidation by ozone, the oxidation is carried out at a temperature of 20° to 200° C. for 10 minutes to 5 hours.

When the oxidation treatment is effected in an aqueous phase there is a fear of stickiness of the fibers and it is preferable to use an aqueous solution of hydrogen peroxide containing at least one of manganese, iron, cobalt and nickel salts of organic or inorganic acids or an aqueous solution of sodium, potassium, calcium and barium salts of permanganic acid in order to prevent the stickiness.

When an aqueous solution of hydrogen peroxide is used, the above-described manganese, iron, cobalt and nickel salts of organic or inorganic acids are added in order to prevent the above-described stickiness. As the acids constituting the above-described metal salts mention may be made of inorganic acids, such as, hydrochloric acid, sulfuric acid and phosphoric acid or organic acids, such as acetic acid, and oxalic acid.

The concentration of hydrogen peroxide in the aqueous solution is selected properly within the range of 1 to 30 percent by weight and the content of the above-described metal salts in the aqueous solution is 0.05 mg. to 5 g. as the anhydrous salts per 1 l. of aqueous solution of hydrogen peroxide, preferably, 0.2 mg. to 1 g.

When the concentration of the metal salts in the aqueous solution of hydrogen peroxide is less than the lower limit, the decomposition rate of hydrogen peroxide is too slow and therefore, it is difficult to oxidize the spun fibers sufficiently and to make the fibers infusible and insoluble. On the other hand, when the concentration is higher than the upper limit, the decomposition rate of hydrogen peroxide is too rapid and hydrogen peroxide is decomposed in a short time, and therefore, it is difficult to generate nascent oxygen continuously.

The spun fibers are treated in the above-described aqueous solution of hydrogen peroxide at 0° to 90° C., preferably, 10° to 80° C. for 1 min. to 2 hours. The pH value of the aqueous solution of hydrogen peroxide may be 1 to 13.

In this case the oxidation treatment of the spun fibers is carried out in the above-described aqueous solution of hydrogen peroxide and the treating process is not limited, if the spun fibers are contacted with an aqueous solution of hydrogen peroxide containing the metal salt and oxidized and converted into infusible and insoluble fibers.

For example, the spun fibers may be passed through the aqueous solution of hydrogen peroxide or the spun fibers may be formed into a skein and then dipped in the aqueous solution or the spun fibers may be would around a perforated bobbin and then dipped in the aqueous solution.

In order to contact the spun fibers with the treating solution effectively, 0.01 to 3 percent by weight of a surfactant may be dissolved in the treating solution. In this case the surfactant may be anionic, cationic, nonionic or amphoteric type, such as anionnonionic surfactant.

In this case hydrogen peroxide is rapidly decomposed in the oxidation treatment of the spun fibers, by the catalytic function of the metal salt and by heating to discharge nascent oxygen and the nascent oxygen acts effectively the spun fibers and oxidizes them and the spun fibers are converted into infusible and insoluble fibers.

When the spun fibers are oxidized in an aqueous phase by an aqueous solution of hydrogen peroxide containing metal salts, such an oxidation treatment in an aqueous phase may be repeated several times, if necessary and further after the oxidation treatment in an aqueous phase an additional oxidation treatment may be performed in a gaseous phase. The oxidation treatment in a gaseous phase is performed under air or an oxidizing atmosphere at a temperature lower than 260° C. by depositing hydrogen peroxide or other oxidizing agent on the fibers in a solution state or other proper manner or without depositing it.

When the oxidation treatment is carried out by means of an aqueous solution of a permanganate, potassium salt is particularly preferable. In this case, the treatment for making the spun fibers infusible and insoluble may be effected in an aqueous solution of a permanganate or after the spun fibers are deposited with an aqueous solution of a permanganate, an oxidation in a gaseous phase may be effected in air.

The concentration of the permanganate in the aqueous solution is preferred to be at least 0.6 percent by weight. As far as the concentration of salt is more than 0.6 percent by weight, a saturated concentration may be used but if the concentration is less than 0.6 percent by weight, the spun fibers cannot be sufficiently oxidized and it is impossible to make the spun fibers infusible and insoluble sufficiently. Furthermore, the concentration of permanganate in the aqueous solution can be properly selected in relation to the treating conditions, particularly, treating temperature. pH value of the aqueous solution of the above salt is not particularly limited. The oxidation treatment with such a solution may be effected in the same manner as described in the aqueous solution of hydrogen peroxide.

When the spun fibers are made infusible and insoluble by an oxidation in a gaseous phase after effecting the oxidation in an aqueous phase it is preferable that the spun fibers have been previously deposited with the above-described aqueous solution of the salt uniformly.

In order to deposit the above-described aqueous solution of the salt on the fibers, the fibers are dipped in the aqueous solution of the salt or are sprayed with the aqueous solution of the salt.

An amount of an aqueous solution of permanganate deposited on the surface of the fibers before the oxidation in a gaseous phase is at least 0.1 part by weight in pure salt component per 100 parts by weight of the fibers. When the amount of pure salt component deposited is less than the lower limit, it is impossible to make sufficiently the spun fiber infusible and insoluble and such an amount is not preferable. As in the case of aqueous solution of hydrogen peroxide, the above-described aqueous solution may be added with a surfactant. The oxidation treatment may be carried out either in an aqueous phase or in a gaseous phase or a plurality of oxidation treatments may be effected.

The temperature in the above oxidation treatment in an aqueous phase is 0° to 90° C., preferably, 10° to 80° C. and in the case of the oxidation in a gaseous phase the temperature of hot air is preferred to be lower than 260° C. Furthermore, the treating time is about 1 minute to 3 hours in any case of an

aqueous phase and a gaseous phase and is selected by considering the concentration of salt in the aqueous solution, treating temperature and the other operating conditions.

After the oxidation treatment in a gaseous phase and in an aqueous phase, the spun fibers are treated in air or gaseous nitrogen at 200° to 500° C. for at least 2 hours and they are set. The fibers after this treatment are nonflammable fibers. The heat-resistant and flame-resistant temperatures of these fibers are at most 250° to 300° C. and the fibers are electric insulator. Accordingly, when the heat-resistant temperature is within the above-described range or the fibers are used for an electric insulator, the nonflammable fibers can be used as such. The set treatment is generally carried out in air at 200° to 350° C. for 2 to 4 hours.

The nonflammable fibers obtained by the above-described treatment are carbonized at least once under nitrogen atmosphere at a high temperature higher than 800° C. In the set treatment, a heat treatment in the presence of air is rather preferable in order to promote the reaction, while since the carbonization treatment is a reaction at a high temperature, the treatment must be effected in an inert gas, such as nitrogen. When the temperature for carbonization treatment is 800° to 1,800° C., carbon fibers having microcrystalline carbon structure can be obtained. When the temperature for carbonization treatment is raised to 2,000° to 3,500° C., carbon fibers having graphite structure, namely, graphite fibers can be obtained. The carbonization treatment may be two step treatments, in which the nonflammable fibers are heat treated at a temperature of 800° to 1,800° C. and then further treated at a temperature of 2,000° to 3,500° C. or one step treatment in which the nonflammable fibers are treated at a temperature of 800° to 1,800° C. or a temperature of 2,000° to 3,500° C.

The time of carbonization varies depending upon pitches and synthetic organic polymers to be used, conditions for the conjugate spinning and temperature of carbonization and the like but generally is 10 minutes to 10 hours.

According to the present invention, the set treatment or the carbonization treatment of the oxidized fibers can be selected in a proper stage depending upon the properties of the aimed carbon fibers.

According to the present invention, the spun fibers can be easily, uniformly and rapidly oxidized and be converted into infusible and insoluble fibers and the oxidized fibers have no stickiness and are flexible and can be very easily handled while maintaining the shape of the spun fibers. Accordingly, the fibers are not deformed by the succeeding carbonization treatment as in the conventional case, the shape of the spun fibers is maintained and carbon fibers having a sufficient flexibility can be easily obtained. The thus obtained spun fibers are superior in flexibility and in a resistance against an elongation stress to the spun fibers obtained by the conventional method for producing carbon fibers and further yarn breakage does not occur in the spinning and the taking-up is easy and such fibers can be produced commercially easily. Carbon fibers having improved properties and satisfactory length can be obtained. Consequently, according to the present invention the carbon fibers can be produced commercially advantageously.

The following examples are given in illustration of this invention and are not intended as limitations thereof. The percent used in the examples means by weight, unless otherwise mentioned.

EXAMPLE 1

Nylon-6 chips having an intrinsic viscosity of 1.2 measured in m-cresol at 30° C. was used as a core component. Petroleum asphalt containing 85.8 percent of carbon, which had been obtained by subjecting blown asphalt (made by Maruzen Sekiyu K.K.) having a softening point of 150° C. to dry distillation under nitrogen atmosphere, was used as a sheath component. These spinning materials were conjugate spun in a conjugate ratio (by weight) of core/sheath of one-fourth at a melter temperature of 280° C. through nozzles having a diameter of 0.2 mm. and for producing sheath-core composite fibers into air at room temperature. The spun fibers were taken up on a bobbin spaced 6 m. just under the nozzles at a takeup velocity of 500 m./min.

When the resulting composite fibers were unwound from the bobbin, the fibers were not broken nor deformed at all. Moreover, adhesion between the starting asphalt and nylon-6 was favorable.

The spun fibers were dipped into 36.5 percent aqueous solution of hydrogen peroxide at 25° C. for 24 hours in the form of a skein to oxidize the surface. The resulting fibers were suspended in a tube, heated up to 280° C. at a rate of 5° C./min. in the presence of air and maintained at this temperature for 2 hours, whereby the fibers were heat set. Following to this heat set, the fiber were heated up to 1,000° C. at the same rate under nitrogen atmosphere, maintained at this temperature for 30 minutes to effect a carbonization treatment, and then cooled to room temperature to obtain carbon fibers. The resulting carbon fibers had a strength of 8 t./cm.^{2} and an elongation of 1.8 percent.

COMPARATIVE EXAMPLE

The petroleum asphalt obtained by dry distillation under the same condition as described in Example 1 alone was heated and melted at 280° C. in a melter and spun through nozzles having a diameter of 0.2 mm. into air at room temperature. The spun fibers were taken up on a bobbin spaced 1 m. from the nozzles at a takeup velocity of 200 m./min.

When the spun fibers were taken up under the same condition as described in Example 1, that is, the space was 6 m. and the takeup velocity was 500 m./min., the fibers were broken and were not able to be taken up, and the workability was considerably inferior to that in the method of the present invention shown in Example 1.

Furthermore, the fibers taken up under the above-mentioned condition had a very low strength, and moreover the fibers were deformed during unwinding from the bobbin, oxidation and heat set. Therefore, it was impossible to produce long filamentary carbon fibers.

EXAMPLE 2

Epikote 1009 (trademark of an epoxy resin made by Shell international Chemicals Corp.) was used as a core component. Coal tar pitch containing 86.2 percent of carbon was used as a sheath component. These spinning materials were melted and conjugate spun in a conjugate ratio (by weight) of core/sheath of 1/6 at a temperature of 220° C. through the same nozzles having a diameter of 0.2 mm. and for producing a sheath-core composite fibers as used in Example 1, and the spun fibers were taken up at a takeup rate of 400 m./min.

The resulting composite fibers were not broken nor deformed at all during various treatments.

The composite fibers were subjected to an oxidation treatment at 70° C. for 1.5 hours in air containing 8–11 g./m.^{3} of ozone to make the fibers insoluble and infusible. Then, the fibers were heat set in the presence of air and subjected to a carbonization treatment under nitrogen atmosphere in the same manner as described in Example 1 to obtain carbon fibers. The resulting carbon fibers had a strength of 9 t./cm.^{2} and an elongation of 1.5 percent.

EXAMPLE 3

A spinneret for producing side-by-side composite fibers, in which one component is entered into the other component in the form of a neck so that both components do not separate, was used. Petroleum asphalt used in Example 1 was used as one component. Yukaron YM-60 (trademark of a high pressure process polyethylene resin made by Mitsubishi Yuka K.K.) was used as the other component. These spinning materials were melted and conjugate spun in a conjugate ratio of petroleum asphalt/polyethylene of 2/1 at 260° C., and the spun fibers were taken up under the same condition as described in Example 1.

The resulting composite fibers were able to be subjected to various treatment under the same condition as described in Example 1, while keeping filamentary configuration without breakage and deformation. Carbon fibers having a strength of 11 t./cm.^{2} and an elongation of 2.0 percent were obtained.

EXAMPLE 4

The petroleum asphalt used in Example 1 was used as a core component, and Noblen MA-3A (trademark of a polypropylene resin made by Mitsubishi Yuka K.K.) was used as a sheath component. These spinning materials were melted and conjugate spun in various conjugate ratio at a melter temperature of 290° C. through nozzles having a diameter of 0.2 mm. and for producing sheath-core composite fibers into air at room temperature in the same manner as described in Example 1. The spun fibers were contacted with 5 percent solution of benzoyl peroxide in benzene between the nozzles and a bobbin, whereby the benzoyl peroxide was applied to the fiber surface, and then the fibers were taken up on the bobbin. The resulting fibers were oxidized at 80° C. for 4 hours in air having the same ozone concentration as described in Example 2 to make the fibers insoluble and infusible, and then the fibers were heat set in the presence of air and further subjected to a carbonization treatment at 1,000° C. under nitrogen atmosphere in the same manner as described in Example 1 to obtain carbon fibers. The obtained result is shown in the following Table 1.

TABLE 1

Sample No.	Conjugate ratio of core/sheath	Spinnability	Property of fibers after carbonization treatment at 1,000° C.	Strength of carbon fibers (t/cm.^{2})
1	0.5/1	Excellent	Brittle and readily break.	
2	1/1	do	Stick between a part of fibers.	5
3	2/1	do	Slightly rigid	7
4	3/1	do	Very flexible	10
5	5/1	do	do	11
6	6/1	Good	do	11
7	11/1	Fibers break very often and spinning is impossible.	Carbonization is possible.	

EXAMPLE 5

Thermally cracked polyvinyl chloride pitch having a softening point of 170° C. was used as a core component, and a novolack resin having an average molecular weight of 1,200 was used as a sheath component. The pitch was melted at a melter temperature of 220° C. and the novolack resin was melted at a melter temperature of 170° C. and both the components were conjugate spun in a conjugate ratio of core/sheath of 5/1 through nozzles having a diameter of 0.3 mm. and for producing sheath-core composite fibers at a nozzle temperature of 220° C. into air at room temperature, and the spun fibers were taken up on a bobbin at a takeup velocity of 1,000 m./min.

The resulting raw fibers were dipped in 20 percent aqueous solution of hexamethylenetetramine at 25° C. for 2 hours, and then the fibers were oxidized at 80° C. for 2 hours in the ozone-containing air used in Example 1 to make the fibers insoluble and infusible. The fibers were further heat set in the presence of air in the same manner as described in Example 1 to obtain nonflammable fibers (8).

Then, the nonflammable fibers (8) were divided into two parts. One part was heated up to 1,000° C. at a rate of 3° C./min. under dried nitrogen atmosphere, maintained at this temperature for 1 hour and cooled to room temperature under the above described nitrogen atmosphere to obtain carbon fibers (9). Another part was heated up to 2,500° C. at a rate of 3° C./min. under the same dried nitrogen atmosphere as described above, maintained at this temperature for 30 minutes and cooled to room temperature under the above described nitrogen atmosphere to obtain graphite fibers (10).

The properties of the resulting fibers are shown in the following Table 2.

TABLE 2

Fiber	Specific gravity	Strength (t./cm.^{2})	Elasticity 10^2t./cm.^{2})
Non-flammable fibers (8)	1.2	4.3	0.2
Carbon fibers	1.5	10	0.7
Graphite fibers (10)	1.8	16.5	3.1

EXAMPLE 6

Petroleum asphalt having a softening point of 240° C., which had been obtained by subjecting petroleum blown asphalt to dry distillation at 280° C. for 4 hours under a reduced pressure of 2 mm.Hg. in the absence of air, was used as a core component. Polyethylene terephthalate having a relative viscosity of 0.62 measured in o-chlorophenol at 30° C. was used as a sheath component. These spinning materials were conjugate spun in a conjugate ratio of core/sheath of 4/1 at a melter temperature of 300° C. through nozzles having a diameter of 0.25 mm. and for producing sheath-core composite fibers into air at room temperature in the same manner as described in Example 1. The spun fibers were contacted with 2 percent aqueous solution of cobalt chloride between the nozzles and a bobbin, whereby the cobalt chloride was applied to the fiber surface, and then the fibers were taken up on the bobbin. The thus obtained fibers were dipped in 36 percent aqueous solution of hydrogen peroxide at 250° C. for 24 hours in the form of a skein to oxidize the surface. Then, the fibers were heat set in the presence of air under the same condition as described in Example 1, and further carbonized and baked at 1,000° C. under nitrogen atmosphere to obtain aimed carbon fibers. The resulting carbon fibers had a strength of 10 t./cm.^{2}.

EXAMPLE 7

The sheath-core composite fibers obtained in Example 1 were dipped and oxidized in an aqueous solution, which contained 10 percent by weight of potassium permanganate and a small amount of an anionic surfactant consisting of sodium alkylbenzenesulfonate and was kept at a temperature of 60° C. and at a pH of about 7, for 10 hours in the form of a skein.

The thus treated fibers were charged directly in an electric furnace under nitrogen atmosphere without washing and drying, heated up to 1,000° C. at a rate of 5° C./min., maintained at this temperature for 30 minutes to effect a carbonization treatment, and cooled to room temperature to obtain carbon fibers. The resulting carbon fibers had electric conductivity and had a strength of 8.2 t./cm.^{2} and an elongation of 1.5 percent.

What is claimed is:

1. A method of producing nonflammable fibers, which comprises spinning concurrently a pitch and a synthetic organic polymer melted separately through a common nozzle to obtain a composite fiber, in which both the components are bonded uniformly along the longitudinal direction of the unitary filament, subjecting the resulting composite fiber to an oxidation treatment to render it infusible and thereafter to a set treatment in air of gaseous nitrogen at a temperature of 200° to 500° C. for at least 2 hours.

2. A method of producing carbon fibers which comprises spinning concurrently a pitch and a synthetic organic polymer melted separately through a common nozzle to obtain a composite fiber, in which both the components are bonded uniformly along the longitudinal direction of the unitary filament, subjecting the resulting composite fiber to an oxidation treatment to render it infusible and thereafter to a set treatment in air or gaseous nitrogen at a temperature of 200° to 500° C. for at least 2 hours, and then to a carbonization treatment at least once in gaseous nitrogen at a temperature higher than 800° C.

3. The method as claimed in claim 2, wherein said composite fiber has a conjugate ratio (by weight) of the pitch to the synthetic organic polymer of 1/1 to 10/1.

4. The method as claimed in claim 2, wherein said composite fiber has a conjugate ratio of the pitch to the synthetic organic polymer of 2/1 to 6/1.

5. The method as claimed in claim 2, wherein said composite fiber has a conjugate ratio of the pitch to the synthetic organic polymer of 3/1 to 5/1.

6. The method as claimed in claim 2, wherein said pitch and said synthetic organic polymer are bonded in a side-by-side relation in the composite fiber.

7. The method as claimed in claim 2, wherein said pitch and said synthetic organic polymer are bonded in a sheath-core relation in the composite fiber.

8. The method as claimed in claim 7, wherein said pitch forms the core in the composite fiber.

9. The method as claimed in claim 2, wherein said synthetic organic polymer is a thermoplastic polymer selected from the group consisting of polyethylenes, polypropylenes, polyamides, and polyesters.

10. The method as claimed in claim 2, wherein said synthetic organic polymer is a thermosetting polymer selected from the group consisting of epoxy resins and phenol resins.

11. The method as claimed in claim 2, wherein said pitch is a substance selected from the group consisting of petroleum asphalt, coal tar, and pitch obtained by baking polyvinyl chloride.

12. The method as claimed in claim 2, wherein said oxidation treatment is effected in a gas selected from the group consisting of oxygen, air, ozone and hydrogen peroxide.

13. The method as claimed in claim 2, wherein said oxidation treatment is effected by means of at least one of permanganates selected from the group consisting of sodium permanganate, potassium permanganate, calcium permanganate and barium permanganate.

14. The method as claimed in claim 2, wherein said oxidation treatment is effected by means of an aqueous solution of hydrogen peroxide containing at least one of salts of metals selected from the group consisting of manganese, iron, cobalt and nickel with an acid selected from the group consisting of inorganic and organic acids.

15. The method as claimed in claim 14, wherein said inorganic acid is an acid selected from the group consisting of hydrochloric acid, sulfuric acid and phosphoric acid.

16. The method as claimed in claim 14, wherein said organic acid is an acid selected from the group consisting of acetic acid and oxalic acid.

17. the method as claimed in claim 2, wherein said set treatment is effected at a temperature of 200° to 350° C. for 2 to 4 hours.

18. The method as claimed in claim 2, wherein said carbonization treatment is effected at a temperature of 800° to 1,800° C.

19. The method as claimed in claim 2, wherein said carbonization treatment is effected in two heat treatment steps, the temperature of the first heat treatment being 800° to 1,800° C. and the temperature of the second heat treatment being 2,000° to 3,500° C.

20. The method as claimed in claim 2, wherein said carbonization treatment is effected in one step at a temperature of 2,000° to 3,500° C.

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