

[54] **PROCESS FOR PRODUCING CARBON FIBERS**
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[56] **References Cited**
UNITED STATES PATENTS
 3,285,696 11/1966 Tsunoda 423/447

3,412,062	11/1968	Johnson et al.....	423/447 X
3,532,466	10/1970	Johnson et al.....	423/447
3,539,295	11/1970	Ram.....	423/447
3,552,923	1/1971	Carpenter et al.....	423/447
3,705,236	12/1972	Ishikawa et al.....	423/447

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[57] ABSTRACT

A process for producing carbon fibers which comprises (a) preoxidizing an acrylonitrile fiber at a temperature below 400°C., (b) applying ultrasonic waves having a frequency of not more than 200 KHz to the preoxidized fiber in a liquid medium and (c) thereafter carbonizing or graphitizing the treated fiber at a temperature above 800°C. The thus obtained carbon or graphite fibers have a high strength and high modulus of elasticity.

15 Claims, No Drawings

PROCESS FOR PRODUCING CARBON FIBERS

This invention relates to an improved process for producing carbon fibers (including graphite fibers) from an acrylonitrile fiber and more particularly to a process for producing carbon fibers high in strength and modulus of elasticity within a short time by firing an acrylonitrile fiber characterized by the step of treating a preoxidized acrylonitrile fiber, after the preoxidation, in a liquid medium with ultrasonic waves of a specific frequency.

It is already known that carbon fibers, excellent as reinforcing materials, keating elements and heat-resistant materials, are obtained by heating and preoxidizing an acrylonitrile fiber at 200° to 400°C. in an oxidizing atmosphere and then heating it at a high temperature (usually above 800°C.) in a non-oxidizing atmosphere.

However, the so-called preoxidation step, i.e. the step of forming a polynaphtyridine structure in an acrylonitrile fiber by heating it first in an oxidizing atmosphere is a very important step in influencing the physical properties of the final carbon fiber. A heating operation for a long time has been considered to be required for such step and has been the cause of the low productivity of carbon fibers.

In case a high temperature preoxidizing condition or quick temperature elevating operation is adopted to increase the productivity of carbon fibers, there occurs such radical reactions as intermolecular cross-linking and intramolecular cyclization at a temperature near the exothermic transition point of the fiber, and accordingly a local heat accumulation will be caused and non-uniform reaction occurs which results in the production of pitchy or tarry substances. This deleteriously affects the physical properties of the carbon fibers in that the filaments adhere to each other and the mechanical strength of the fibers is impaired.

As a result of making researches to obtain carbon fibers of a high quality in which the above mentioned drawbacks are overcome and to obtain such carbon fibers within a short time of firing, we have found that, when a preoxidized acrylonitrile fiber obtained by a preoxidation treatment is subjected to ultrasonic waves of a specific frequency in a liquid medium, the impurities such as the pitchy and tarry substances deposited on the surface of the preoxidized fiber can be removed and that, when the thus obtained preoxidized fiber is carbonized or graphitized, there is obtained a carbon fiber of a very high quality.

Therefore, an object of the present invention is to provide a carbon fiber of a high strength and high modulus of elasticity within a short time of firing.

Another object of the present invention is to obtain a carbon fiber which has been uniformly fired by removing impurities deposited on the surface of a preoxidized fiber and which is high in flexibility and bondability with resins.

Other objects of the present invention will become apparent from the following description.

The above mentioned objects of the present invention can be attained by (a) introducing a preoxidized acrylonitrile fiber obtained by preoxidation at a temperature below 400°C. into a liquid medium, and then (b) treating the fiber with ultrasonic waves at a frequency below 200 KHz and thereafter (c) carbonizing or graphitizing the same.

According to this invention, such impurities as pitchy and tarry substances deposited on the surface of a preoxidized fiber will be able to be effectively removed, and therefore a high temperature preoxidizing condition or quick temperature elevating operation can be adopted so that the firing time can be reduced. Further, a non-uniform reaction caused by the presence of impurities is prevented in the case of the carbonization or graphitization and uniform firing becomes possible. As a result, a carbon fiber remarkably improved in strength and modulus of elasticity and having uniform and excellent physical properties is obtained. Further, as there is no impurity on the surface of the obtained carbon fiber, the fiber will be high in bondability with resins and in flexibility.

Particularly, when an acrylonitrile fiber on which is deposited a carbon powder of an average particle diameter of not more than 20 microns (which particles contain not less than 40 percent by weight of particles having diameters of not more than 8 microns) is used as the fiber to be fired, pitchy and tarry substances seeping out of the fiber at the time of the preoxidation will be effectively adsorbed by said carbon powder. Thus, when the ultrasonic wave treatment according to the present invention is applied to the so preoxidized fiber to remove the carbon powder containing the adsorbed pitchy and tarry substances from said preoxidized fiber and when the fiber is carbonized or graphitized, a carbon fiber having better properties can be produced.

For the carbon powder to be deposited on the acrylonitrile fiber, it is necessary to use a carbon powder of an average particle diameter of not more than 20 microns in which particles of diameters of not more than 8 microns are not less than 40 percent by weight, based on the weight of all the particles, or preferably of an average particle diameter of not more than 10 microns in which the particles contain not less than 80 percent, based upon the weight of the particles, of particles having diameters of not more than 6 microns. In the cases where a carbon powder is used which have particle diameters etc., exceeding the above numerical values, it is difficult to uniformly deposit the carbon powder on the fiber. Further, the amount of deposition of carbon powder on an acrylonitrile fiber is generally 0.01 to 20 percent or preferably 0.1 to 5 percent, based on the weight of the fiber.

As a method of depositing a carbon powder on an acrylonitrile fiber, the fiber is treated with a dispersion prepared by uniformly dispersing carbon powder of the above mentioned particle diameter and granularity distribution with a surface active agent of an HLB value (hydrophile lipophile balance) in a range of 7 to 17. More concretely, the above mentioned carbon powder dispersion is sprayed onto well opened fibers or the fibers are dipped in said dispersion. As a dispersing medium to disperse carbon powder, water is generally preferably used. The above mentioned surface active agent is used generally in an amount of 0.001 to 5 percent, based on the weight of the fiber. When no surface active agent is used, or a surface active agent outside the above mentioned HLB value range is used, it will be difficult to uniformly deposit the fine carbon powder on the fiber and therefore it will be difficult to produce a carbon fiber having excellent properties. Provided that the HLB value is in a range of 7 to 17, any surface active agent, i.e. anionic surface active agents, cationic surface active agents, nonionic surface active agents

and amphoteric surface active agents may be used. However, generally polyoxyethylene alkylethers, polyoxyethylene alkylarylethers, aliphatic carboxylic acid polyethylene glycol esters and polyoxyethylene sorbitan monofatty acid esters are preferable.

The acrylonitrile fiber to be used in the present invention is a fiber produced from a polyacrylonitrile or an acrylonitrile copolymer containing at least 80 mole percent or preferably not less than 90 mole percent acrylonitrile. As components to be copolymerized with acrylonitrile, there can be enumerated such well known ethylenically unsaturated compounds as allyl alcohol, methallyl alcohol, oxypropionic acrylonitrile, acrylic acid, methacrylic acid, crotonic acid, methacrylonitrile, α -methylene glutaronitrile, isopropenyl acetate, acrylamide, dimethylaminoethyl methacrylate, vinyl pyridine, vinyl pyrrolidone, methyl acrylate, methyl methacrylate, vinyl acetate, allyl chloride, sodium methallylsulfonate and potassium p-styrenesulfonate.

Acrylonitrile fibers or acrylonitrile fibers on which carbon powder has been uniformly deposited are heated by generally well known methods, for example, at a temperature of 180° to 400°C. in an oxidizing atmosphere so as to produce a preoxidized fiber in which a polynaphtyridine structure is formed. Then the preoxidized fiber is subjected to ultrasonic wave treatment according to the present invention. However, the ultrasonic wave treatment according to the present invention may be applied to any known preoxidized fiber having the above mentioned structure and produced by any other method.

Thus, the preoxidized fiber is introduced into a liquid medium and is treated with ultrasonic waves of a frequency of not more than 200 KHz (kilohertz) according to the process of the present invention. The liquid medium to be used here may be any liquid which does not adversely affect the properties of the finally obtained carbon fiber. However, water is generally preferably used. Further, the effective frequency of the ultrasonic waves to be applied is particularly 10 to 100 KHz. In case it exceeds 200 KHz, the impurities deposited on the surface of the preoxidized fiber will cohere to each other. In such a case, it is difficult to remove these impurities from the surface of the fiber and thus the physical properties of the objective carbon fiber will be impaired.

Further, when the ultrasonic waves are applied while the preoxidized fiber is being shaken in the liquid medium without being fixed in place to prevent the deleterious effects of the standing waves, a uniform effect can be attained. The time for the ultrasonic wave treatment varies, depending on the particular frequency and ultrasonic wave output apparatus, but is generally not more than 60 seconds.

The preoxidized fiber thus treated with ultrasonic waves is carbonized or graphitized at a temperature above 800°C. in a non-oxidizing atmosphere in an ordinary manner to produce the objective carbon fiber. The carbonizing temperature is generally a temperature below 2000°C. In order to further graphitize the obtained carbon fiber, a temperature of 2000° to 3500°C. is generally adopted.

Nitrogen, hydrogen, helium or argon is preferably used for the atmosphere for conducting the carbonization or graphitization. It may be used under a reduced pressure or increased pressure. Further, in the case of producing a carbon fiber of a higher strength and modulus of elasticity, it is preferable to heat the fiber under tension as is known in the art. It is effective to apply a tension to the fiber particularly when it is preoxidized and carbonized or graphitized.

Thus, according to the present invention, the substances deposited on the surface of the preoxidized fiber will be favorably removed, the fiber can be fired within a short time, and a uniform carbon fiber high in strength and modulus of elasticity will be produced and therefore the industrial productivity of carbon fibers can be increased.

The invention will be further explained by means of the following examples wherein the percentages and parts are by weight unless otherwise specified.

EXAMPLE 1

Acrylonitrile fiber (960 filaments/monofilament denier of 15 deniers) produced from a copolymer consisting of 98 mole percent acrylonitrile and 2 mole percent methacrylic acid were introduced into an electric furnace and continuously heated from 200°C. to 280°C. for 40 minutes in air so as to be preoxidized. Then the preoxidized fibers were dipped in water and then treated with ultrasonic waves of various wave lengths of a frequency of 10 to 400 KHz for 10 seconds, while being quietly moved in the water bath by using a wide band ultrasonic wave generating apparatus USV-300 V (manufactured by Ultrasonic Wave Industrial Company, Ltd.). Then, the preoxidized fibers treated with these ultrasonic waves were carbonized by continuously elevating the temperature up to 1200°C. for 100 minutes in a nitrogen atmosphere to form carbon fibers.

The strength and Young's modulus of each of the thus obtained various carbon fibers were measured and the results are shown in Table 1.

As evident from the results shown in Table 1, a carbon fiber of a high strength and high modulus of elasticity is obtained from a preoxidized fiber treated with ultrasonic waves at a frequency of not more than 200 KHz.

Table 1

Frequency (KHz)	Strength (kg./mm. ²)	Carbon fibers	
		Young's modulus (tons/mm. ²)	
10	243	21	
15	269	21	
20	281	24	
28	280	24	
50	271	22	
100	250	20	
200	198	17	
400	167	12	
Not treated with ultrasonic waves	163	12	

EXAMPLE 2

Acrylonitrile fibers (1000 filaments/monofilament denier of 1.4 deniers) produced from a copolymer consisting of 96 mole percent acrylonitrile and 4 mole percent methyl acrylate were subjected to a static electricity so that the monofilaments are well separated from each other and then an active carbon-containing aqueous dispersion consisting of 3 parts of an active carbon (produced by Yamahisa Carbon Industrial Co.) of an

average diameter of 5 microns, 100 parts of water and 0.2 part of a surface active agent polyoxyethylene (10 moles) nonylphenylether of an HLB value of 13.6 was sprayed onto the fibers by a weight equal to that of the fiber. The fibers on which the fine active carbon was deposited were dried and continuously heated from 200°C. to 300°C. for 30 minutes in air so as to be preoxidized. Then the preoxidized fibers were introduced into water, and irradiated with ultrasonic waves of a frequency of 20 KHz for 10 seconds while being quietly moved in the water bath. Then the fibers were carbonized by continuously elevating the temperature up to 1300°C. for 90 minutes in a nitrogen atmosphere to form carbon fibers.

The physical properties of the thus obtained carbon fibers together with those of carbon fibers obtained in the same manner but without being treated with ultrasonic waves are shown in Table 2. As evident from the results in Table 2, if a fiber is treated with an active carbon and then with ultrasonic waves, the physical properties are improved.

Table 2

Carbon fibers	Treated with active carbon	Treated with ultrasonic waves	Carbon fiber properties	
			Strength (kg/mm. ²)	Young's modulus (tons/mm. ²)
(a)	Yes	Yes	325	25
(b)	Yes	No	258	25

EXAMPLE 3

The acrylonitrile fibers used in Example 2 were sprayed with an active carbon in the same manner as in Example 2 and then continuously heated from 200°C. to 300°C. for 15 minutes in air so as to be preoxidized. Then the preoxidized fibers were treated with ultrasonic waves of a frequency of 20 KHz for 20 seconds in a trichlorethane solution and then continuously heated up to 1200°C. for 90 minutes in a nitrogen atmosphere so as to be carbonized. The obtained carbon fibers had a strength of 267 kg./mm.² and Young's modulus of 23 tons/mm.².

On the other hand, when the same preoxidized fibers were not treated with ultrasonic waves and were carbonized under the same conditions as in the above, the strength was 89 kg./mm.² and the Young's modulus was 10 tons/mm.² and adhesion of the fibers to each other was recognized.

EXAMPLE 4

A composite material of 55 percent of one of the two kinds of carbon fibers obtained in Example 2 and 45 percent of a polyester resin was prepared. In case the carbon fiber (a) treated with ultrasonic waves by the process of the present invention was used for the carbon fiber, the bending strength of the composite material was 18.5 kg./mm.² but, in the case wherein the carbon fiber (b) not treated with ultrasonic waves was used, it was only 7 kg./mm.².

EXAMPLE 5

Acrylonitrile fibers (960 filaments/monofilament denier fineness of 1.5 deniers) produced from a copolymer consisting of 96 mole percent acrylonitrile and 4 mole percent methyl acrylate were subjected to a static

electricity to well separate the monofilaments from each other and were then sprayed with an aqueous dispersion containing an active carbon (produced by Yamahisa Carbon Industrial Co.), having any of various particle diameters, by a weight equal to that of the fiber so that the active carbon is deposited on the fiber. The said aqueous dispersion was prepared by adding 3 parts of the active carbon and 0.2 part of a surface active agent polyoxyethylene (10 moles) nonylphenylether, of an HLB value of 13.6, to 100 parts of water.

The thus obtained acrylonitrile fibers on which active carbon of any of various particle diameters was deposited were dried and then preoxidized by continuously elevating the temperature from 180°C. to 280°C. for 35 minutes in air. As a result, in the case of using the active carbon of the particle diameter according to the present invention deposited thereupon, no adhesion between the monofilaments was recognized but, in the case of using active carbon of a larger particle diameter, adhesion between the filaments was recognized. Then the preoxidized fibers were introduced into water and treated with ultrasonic waves of a frequency of 20 KHz for 10 seconds while being quietly moved in the water bath and then continuously heated from 300°C. to 1500°C. for 2 hours in a nitrogen atmosphere so as to be secondarily fired to obtain carbon fibers. The strength and modulus of elasticity of each of the thus obtained various carbon fibers were measured and the results are shown in Table 3.

Table 3

	5	10	20	25	30
Average particle diameter of active carbon (microns)					
Amount of active carbon of a particle diameter of not more than 8 microns (%)	99	48	41	22	5
Adhesion of filaments	Not	Not	Not	Some-what adhered	Adhered
Strength (kg./mm. ²)	260	238	210	120	98
Modulus of elasticity (tons/mm. ²)	20.8	19.2	15.8	12.3	11.6

As apparent from the results in Table 3, it is recognized that, when an acrylonitrile fiber on which the active carbon of the particle diameter according to the present invention is deposited is used as a material fiber to be fired, a carbon fiber is obtained in which the filaments do not adhere to each other and also the strength and modulus of elasticity of the fibers are improved.

EXAMPLE 6

Any of two or more kinds of active carbon of different average particle diameters was deposited on the surface of the acrylonitrile fiber used in Example 5 in the same manner as in Example 5 and a carbon fiber was produced under the same as in Example 5. The results are shown in Table 4.

It is recognized from the results in Table 4 that, even with a carbon powder of an average particle diameter of not more than 20 microns, in the case wherein carbon particles contain a large amount of larger particle diameters, the filaments will adhere to each other and the strength and modulus of elasticity of the obtained carbon fiber will be reduced.

Table 4

Average particle diameter of active carbon (microns)	7	13	18
Amount of active carbon of a particle diameter of not more than 8 microns (%)	78	43	37
Adhesion of filaments	Not	Not	Somewhat adhered
Strength (kg./mm. ²)	255	213	164
Modulus of elasticity (tons/mm. ²)	21.0	17.6	13.3

EXAMPLE 7

An acryl filament tow (1000 filaments/monofilament denier fineness of 1.5 deniers) produced from a copolymer consisting of 98 mole percent acrylonitrile and 2 mole percent methacrylic acid was subjected to a static electricity so that the filaments are well separated from each other and then a carbon suspension consisting of 3 parts of an artificial graphite (produced by Oriental Production Co.) of a particle diameter of 2 microns, 100 parts of water and 0.2 part of any of various surface active agents shown in Table 5 was deposited on the fiber in an amount of 30 percent based on the weight of the fiber. Then the fiber on which the artificial graphite was deposited was dried and was then preoxidized and treated with ultrasonic waves under the same conditions as in Example 5. As a result, carbon fibers having such properties as are shown in Table 5 were obtained.

As evident from the results in Table 5, it will be understood that a surface active agent having an HLB value in a range of 7 to 17 contributes to the prevention of the adhesion of the filaments to each other and also to the improvement of the strength and modulus of elasticity of the obtained carbon fiber.

Table 5

HLB value	Surface active agents	Adhesion of filaments	Strength (kg./mm. ²)	Modulus of elasticity (tons/mm. ²)
4	Sorbitane dilaurate	Adhered	95	12.1
7	Stearyl ether	Little adhered	201	18.3
12	Ethylene oxide additive of oleyl alcohol	Not	260	20.3
17	Ethylene oxide additive of stearyl alcohol	Not	250	19.2
19	Ethylene oxide additive of stearyl alcohol	Somewhat adhered	152	16.2

We claim:

1. A process for producing carbon fibers which comprises (a) preoxidizing an acrylonitrile fiber at a temperature of 180° to 400°C. in an oxidizing atmosphere, (b) applying ultrasonic waves having a frequency of not more than 200 KHz to the preoxidized fiber in a liquid medium and (c) thereafter carbonizing the preoxidized

fiber in a non-oxidizing atmosphere at a temperature above 800°C.

2. The process for producing carbon fibers as in claim 1 wherein said ultrasonic waves have a frequency of 10 to 100 KHz.

3. The process for producing carbon fibers as in claim 1 wherein said liquid medium is water.

4. The process for producing carbon fibers as in claim 1 wherein said acrylonitrile fiber is a fiber made from an acrylonitrile homopolymer or an acrylonitrile copolymer containing at least 80 mole percent acrylonitrile and an ethylenically unsaturated compound.

5. The process for producing carbon fibers as in claim 4 wherein said acrylonitrile fiber is a fiber made from an acrylonitrile copolymer containing at least 90 mole percent acrylonitrile.

6. The process for producing carbon fibers as in claim 1 wherein said oxidizing atmosphere is air.

7. The process for producing carbon fibers as in claim 1 wherein said non-oxidizing atmosphere is nitrogen gas.

8. The process for producing carbon fibers as in claims 1, wherein said ultrasonic waves are applied while the preoxidized fiber is being shaken in the liquid medium.

9. The process for producing carbon fibers as in claim 1 wherein said preoxidized fiber, to which the ultrasonic waves have been applied, is carbonized in a nonoxidizing atmosphere at a temperature of 800 to 2000°C. and is thereafter graphitized in a non-oxidizing atmosphere at a temperature of 2000 to 3500°C.

10. A process for producing carbon fibers according to claim 1, wherein there is uniformly deposited on said acrylonitrile fiber, carbon powder having an average particle diameter of not more than 20 microns and wherein at least 40% by weight of the particles have diameters of not more than 8 microns.

11. The process for producing carbon fibers according to claim 1, wherein there is uniformly deposited on said acrylonitrile fiber, carbon powder having an average particle diameter of not more than 10 microns, and wherein at least 80 percent by weight of the particles have diameters of not more than 6 microns.

12. The process for producing carbon fibers according to claim 10 wherein said carbon powder is deposited on the acrylonitrile fiber in an amount of 0.01 to 20 percent, based on the weight of the fiber.

13. The process for producing carbon fibers according to claim 12 wherein said carbon powder is deposited on the acrylonitrile fiber in an amount of 0.1 to 5 percent, based on the weight of the fiber.

14. The process for producing carbon fibers according to claim 10 wherein said acrylonitrile fiber is treated with a liquid dispersion prepared by uniformly dispersing the carbon powder in a liquid with a surface active agent of an HLB value in the range of 7 to 17.

15. The process for producing carbon fibers according to claim 14 wherein said liquid dispersion is obtained by using water as the liquid.

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