United States Patent [19]

Shindo et al.

[11] **3,886,263**

[45] **May 27, 1975**

[54] METHOD FOR MANUFACTURE OF HEAT-RESISTANT FIBERS

[75] Inventors: **Akio Shindo; Yoichiro Nakanishi; Yoshihiro Sawada,** all of Osaka, Japan

[73] Assignee: **Agency of Industrial Science & Technology,** Tokyo, Japan

[22] Filed: **Feb. 2, 1973**

[21] Appl. No.: **329,172**

[30] **Foreign Application Priority Data**

Feb. 3, 1972	Japan	47-12728
Mar. 23, 1972	Japan	47-29602

[52] **U.S. Cl.** **423/447;** 8/115.5; 264/29

[51] **Int. Cl.** **C01b 31/07**

[58] **Field of Search** 423/447; 8/115.5; 264/29

[56] **References Cited**

UNITED STATES PATENTS

3,441,378	4/1969	Didchenko	423/447
3,529,934	9/1970	Shindo	423/447
3,647,770	3/1972	Gump et al.	423/447 X
3,666,417	5/1972	Araki et al.	423/447
3,671,192	6/1972	Ezekiel	423/447

OTHER PUBLICATIONS

Shindo et al., "Applied Polymer Symposia", No. 9 (1969), pages 305–313.

Primary Examiner—Edward J. Meros
Attorney, Agent, or Firm—Kurt Kelman

[57] ABSTRACT

According to the method of this invention, heat-resistant fibers and flame-retardant fibers are produced from organic fibers by heating the said organic fibers to a temperature between 180°C and 350°C in an atmosphere containing oxygen gas in a concentration of at least 25%, in a high oxygen content atmosphere containing acid vapor, or in a high oxygen content atmosphere and then in an acid-vapor containing, high-oxygen content atmosphere. Furthermore, the heat-resistant fibers having higher heat-resistant property (carbon and graphite fibers) are produced by heating the said flame-retardant fibers to a temperature between 350°C and 3,000°C in a non-oxidizing atmosphere or in vacuum. In accordance with the method of this invention, the duration of the entire operation of heat treatment for producing the said heat resistant fibers can be shortened to a great extent while the said-heat treatment procedure enables the heat-resistant fibers produced to have quality favorably comparable with that of the heat-resistant fibers obtainable by the conventional method.

3 Claims, 6 Drawing Figures

FIG. 1

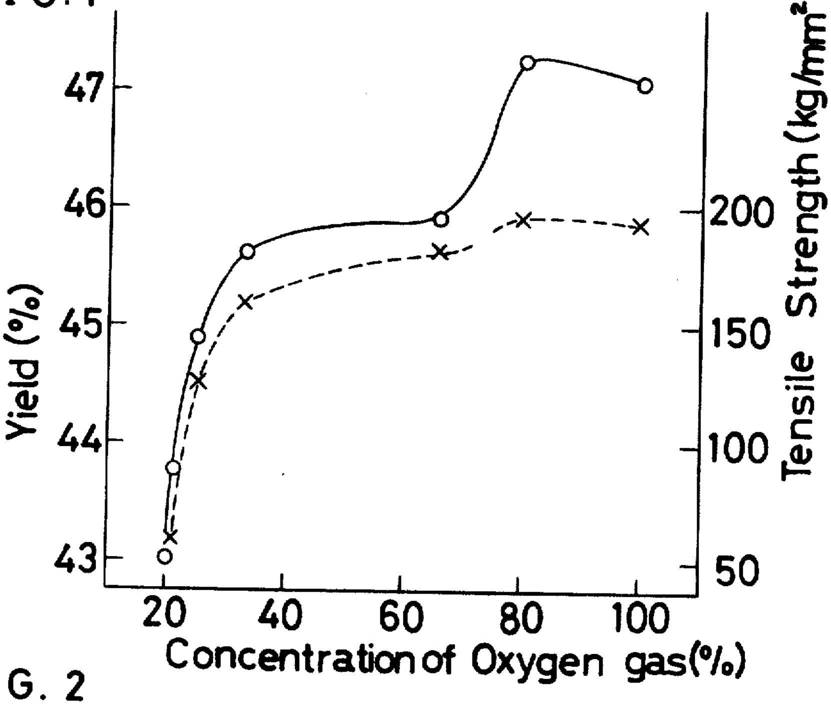

Yield (%)
47
46
45
44
43
Tensile Strength (kg/mm²)
200
150
100
50
20
40
60
80
100
Concentration of Oxygen gas(%)

FIG. 2

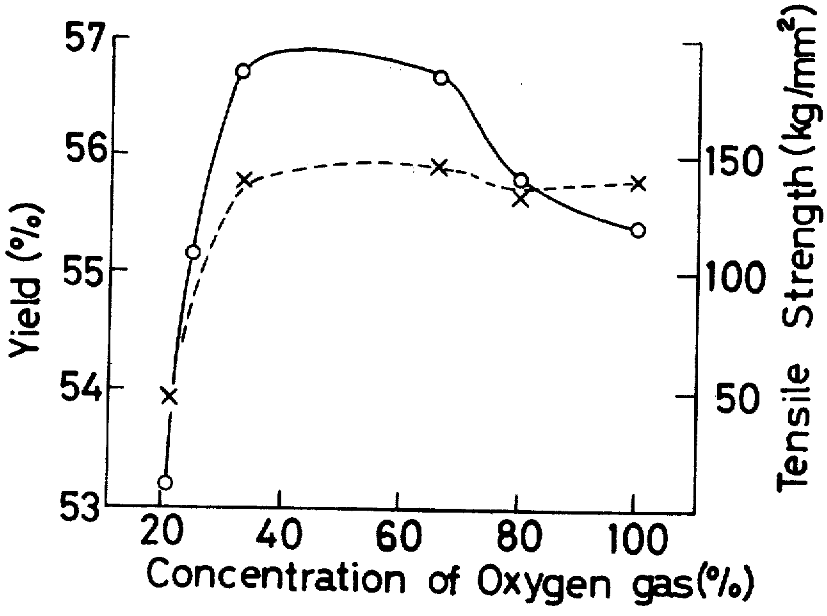

Yield (%)
57
56
55
54
53
Tensile Strength (kg/mm²)
150
100
50
20
40
60
80
100
Concentration of Oxygen gas(%)

FIG. 3

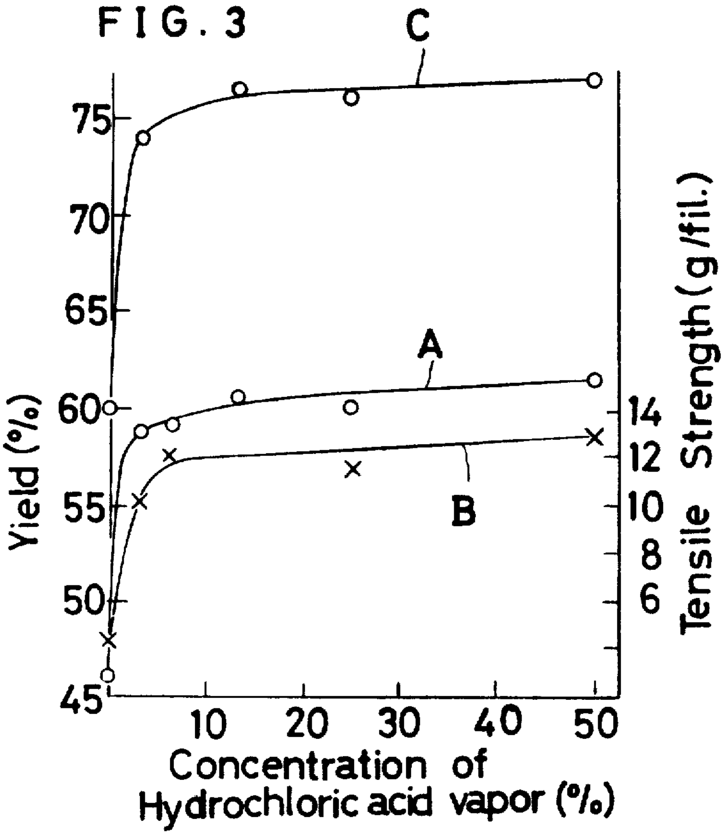

C
A
B
Yield (%)
75
70
65
60
55
50
45
Tensile Strength (g/fil.)
14
12
10
8
6
10
20
30
40
50
Concentration of
Hydrochloric acid vapor (%)

FIG. 4

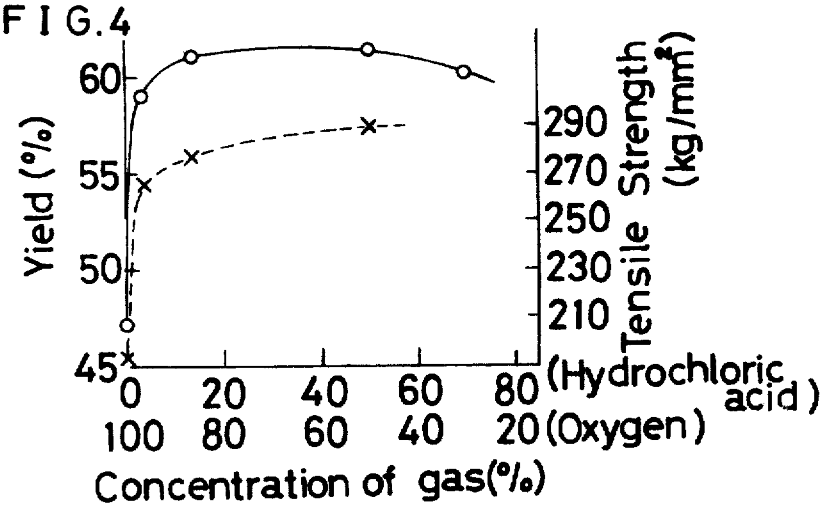

Yield (%)
60
55
50
45
Tensile Strength (kg/mm²)
290
270
250
230
210
0
20
40
60
80
(Hydrochloric acid)
100
80
60
40
20
(Oxygen)
Concentration of gas(%)

FIG. 5

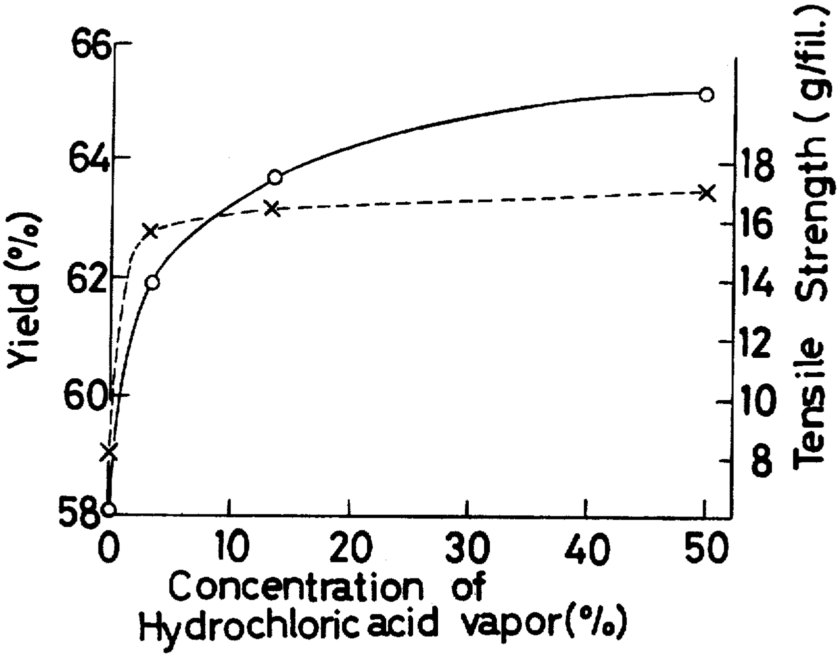
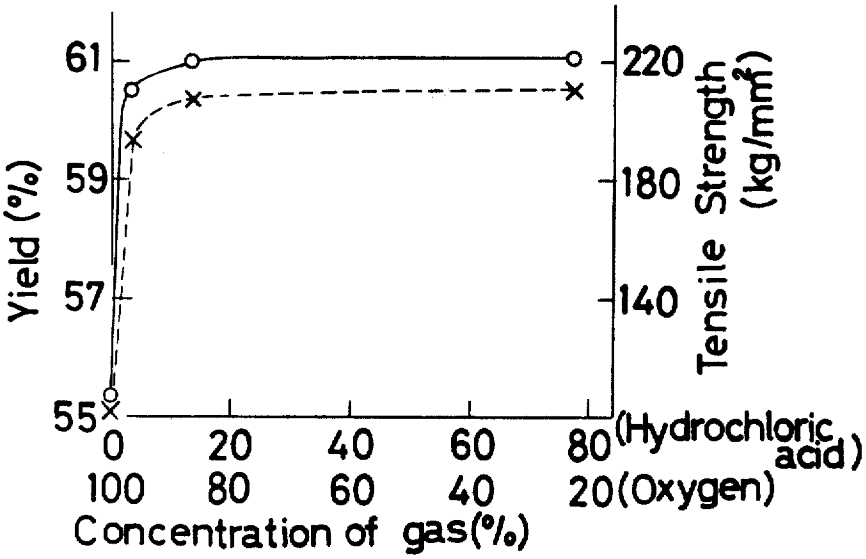

66
64
62
60
58
Yield (%)
18
16
14
12
10
8
Tensile Strength (g/fil.)
0
10
20
30
40
50
Concentration of
Hydrochloric acid vapor(%)

FIG. 6


61
59
57
55
Yield (%)
220
180
140
Tensile Strength (kg/mm²)
0
20
40
60
80 (Hydrochloric acid)
100
80
60
40
20 (Oxygen)
Concentration of gas(%)

METHOD FOR MANUFACTURE OF HEAT-RESISTANT FIBERS

BACKGROUND OF THE INVENTION

This invention relates to a method for the manufacture of heat-resistant fibers by the heat treatment of organic fibers.

The term "heat-resistant fiber" as used in the present specification refers not only to carbon fiber and graphite fiber but equally to any fiber which has undergone a preliminary oxidation treatment or flame-retardation treatment which may be given prior to the carbonization treatment heretofore employed for the production of carbon fiber. In the specification of this invention, the term "flame-retardation treatment" may refers to the process which precedes the carbonization treatment.

An oxygen-containing atmosphere was heretofore used for the flame-retardation treatment in the manufacture of heat-resistant fibers. In actuality, however, it has invariably been air. The carbon fiber or graphite fiber has conventionally been produced by first heating in air at 180°C – 350°C and then heating in an inert atmosphere at a temperature of 800°C or above. In this case, the heat treatment given in air is required to last a long period of 5 to 6 hours. Among the techniques known to the art is included a method for producing a carbon fiber by effecting the required carbonization in the acid containing atmosphere subsequent to the heat treatment in air. In this case, the use of the atmosphere containing acid vapor not in any way serve the purpose of shortening the time phase of the production.

Many uses are being developed at present for composite materials using heat-resistant fibers particularly carbon fiber and graphite fiber as their reinforcing materials. For further expansion of the demand for carbon fiber, however, it is necessary to take measures for lowering the production cost. From such point of view, the need for reducing the time phase of the production of carbon fiber has been emphasized. Also in the production of continuous filaments which are indispensable for manufacturing composite materials by the filament-winding technique, pressing need is felt for the reduction of the time phase of heat treatment.

It is a primary object of this invention to provide a method for markedly curtailing the process of flame-retarding heat treatment employed for producing a heat-resistant fiber from a corresponding organic fiber.

It is another object of this invention to provide a method for the manufacture of a heat-resistant fiber not inferior in terms of mechanical properties and yield to that obtainable by the conventional methods, the said method utilizing a heating atmosphere of a substance inexpensive, innoxious and easy of recovery thereby reducing the time phase of the flame-retarding heat treatment.

It is another object of this invention to provide a method for the manufacture of a heat-resistant fiber, carbon or graphite fiber, not inferior in mechanical properties and yield by the curtailed process of heat treatment.

SUMMARY OF THE INVENTION

To accomplish the objects mentioned above, the method of this invention performs the flame-retardation heat treatment in an atmosphere containing oxygen gas at a higher concentration than air or in an atmosphere containing acid vapor in conjunction with oxygen gas present in a high concentration or in a high oxygen-content atmosphere and then in an acid containing, high oxygen-content atmosphere. Consequently, the time requirement for the flame-retardation heat treatment given to the organic fiber can now be reduced to one-tenth or less.

Other objects of the present invention will become apparent from the description to be given in further detail hereinafter.

BRIEF EXPLANATION OF THE DRAWING

FIGS. 1 through 6 are graphs showing the relationship of yield, tensile strength and concentration of oxygen gas or acid vapor as observed with heat-resistant fibers manufactured in accordance with the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As already pointed out, the methods heretofore employed for the production of heat-resistant fibers by the heat treatment of organic fibers have a serious disadvantage that they inevitably involve a process of time-consuming flame-retardation heat treatment. With a view to overcoming this disadvantage, the inventors conducted investigation into various gases in search for atmospheres usable effectively for flame retardation in place of air. As a consequence, they have made the discovery that oxygen gas or a mixed gas containing oxygen gas and acid vapor can serve as highly effective atmosphere for the flame-retardation treatment of organic fibers. As a result of further investigation pursued on the basis of this knowledge, they have succeeded in developing a method for manufacturing, in a decisively shorter period of time, a heat-resistant fiber not inferior in quality to the heat-resistant fibers obtainable by the conventional methods utilizing the atmosphere of air. According to their method, the given organic fiber is treated in an atmosphere containing oxygen gas in a higher concentration than air or in an atmosphere containing acid vapor in conjection with oxygen gas contained in a high concentration, or the fiber is first treated in a high oxygen-content atmosphere and subsequently in an acid-containing high oxygen-content atmosphere.

Although an oxygen-containing atmosphere has to date been used for the heat-resistant treatment of organic fibers, the oxygen source has invariably been limited to air which has a mild oxidizing effect. In none of the conventional methods has oxygen gas been used directly as the oxygen source. This is partly because oxygen gas or a high oxygen-content gas has too high oxidizing capacity to permit easy setting of appropriate treating conditions for conferring a suitable degree of oxidation upon the fiber in the process of the flame-retardation treatment and partly because it is generally thought that the presence of oxygen gas rather entails heavy degradation of the mechanical properties or heat-resistant property of the fiber. The inventors actually tested oxygen gas or a high oxygen-content gas as an atmosphere for the flame-retardation treatment and studied various heating conditions. As a consequence, they have learned that highly effective flame-retardation treatment can be accomplished by holding organic fibers at a temperature in the range of 180°C – 350°C in an atmosphere containing oxygen gas in a higher concentration than air. They have confirmed that the effect of the flame-retardation treatment is improved conspicuously where the said atmosphere contains oxygen gas in a concentration higher than 25% and that more effective treatment is obtained where the oxygen gas content in the atmosphere exceeds 30%.

In the flame-retardation treatment heretofore performed in air there occurs bonding reactions of oxygen atoms to the constituent molecules of the fiber. In the stage of baking treatment to be given subsequent to the said flame-retardation treatment, the oxygen atoms thus combined to the fiber molecules are caused to combine with hydrogen atoms of the fiber molecules and are eliminated in the form of water (H_2O). Thus, the dehydrogenation reaction proceeds, with the result that the fiber will acquire further improved heat-resistance. One of the present inventors had been continuing a study for further curtailment of the flame-retardation treatment and finally conceived the idea of utilizing an acid-incorporating high oxygen-content atmosphere. On the further presumption that incorporation of the vapor of an acid in an oxygen-containing atmosphere would accelerate the dehydration reaction and consequently the dehydrogenation reaction in the fiber, he set out to study the conditions of flame-retardation treatment in air containing acid vapor. This study, however, failed to suggest any conspicuous reduction of the time requirement for the flame-retardation treatment. So, he substituted oxygen gas for air, mixed oxygen gas with an acid vapor and used this mixture as an atmosphere for the flame-retardation treatment. In this case, he observed quite conspicuous effects such as in the reduction of the time phase of treatment, in the enlargement of yield, and so on. Continued study made it clear that, for the improvement of strength and other properties of the heat-resistant fiber, it is more desirable to have the organic fiber heated in an atmosphere of oxygen gas or in a high oxygen-content atmosphere to effect partial oxidation of the fiber prior to subjecting the organic fiber to heat treatment in an acid-incorporating high oxygen-content atmosphere.

There has already been brought to public knowledge a method of manufacturing a heat-resistant fiber or carbon fiber by heating a given fiber in an oxidizing atmosphere such as air and thereafter heating the oxidized fiber in an acid-containing atmosphere. This method does not represent a process for utilizing the synergistic activites of oxygen and the acid in use. Thus, it hardly serves the purpose of reducing the time phase of the process of heat-resistant treatment as contemplated by the present invention. In manufacturing a heat-resistant fiber by the heat treatment of an organic fiber, the method of the present invention utilizes a high oxygen-content atmosphere or an acid-containing high oxygen-content atmosphere for the flame-retardation heat treatment as described above. Otherwise, in the method of the present invention the fiber is heated in a high oxygen-content atmosphere until the fiber is partially oxidized and, thereafter, the partially oxidized fiber is further heated in an acid-containing, high oxygen-content atmosphere until the fiber undergoes sufficient flame-retardation treatment. To satisfy further requirements, if any, for additional heat resistance or mechanical properties, the fiber may be carbonized by being heated to a higher temperature so as to afford a heat-resistant fiber, carbon fiber or graphite fiber, suited to the intended application.

The fibers to which the method of this invention is applicable include nitrogen-containing polymeric fibers, oxygen-containing polymeric fibers and organic fibers of hydrocarbon family. The nitrogen-containing polymeric fibers include acrylic (polyacrylonitrile) fiber, polyamide fiber, oxathiazole fiber, thiadiazole fiber, benzoxazole fiber, polyamide fibers containing aromatic rings, tetrabenzophenazine fiber, silk and wool. Examples of the oxygen-containing polymeric fibers are polyvinyl alcoholic fibers and vinyl alcohol-vinyl chloride copolymer fiber. Formalized fiber is also included in the polyvinyl alcohol fibers. Examples of the fibers of hydrocarbon family are those derived from pitches, dehydrated polyvinyl alcohol and poly-1,2-butadiene. Every exemplary fiber mentioned above refers to the fibers of polymer being composed of molecules containing the corresponding monomer as the main constituent in polymer form. The various kinds of fibers mentioned above, even when they are in an insufficiently oxidized state, may be used as the starting materials for the method of this invention. The aforesaid fibers to be used for the method of this invention can retain their fibrous shape when they are subjected to heat treatment in air at 200°- 250°C for four to ten hours and subsequently elevated in the atmosphere of argon up to 600°C at a uniform rate of temperature rise of 100°C per hour according to the conventional procedure.

For the purpose of this invention, the atmosphere used for the flame-retardation treatment is required to contain oxygen gas by at least 25%. This atmosphere is obtained by mixing the oxygen gas with an inert gas such as, for example, nitrogen or argon. An atmosphere consisting wholly of oxygen gas can also be used for the treatment. The acid to be incorporated in the vapor form in this atmosphere is a member selected from the group of Brönsted acids and Lewis acids such as hydrochloric acid (hydrogen chloride), hydrogen bromide and phosphorus pentachloride. For the convenience of handling, the acid thus selected is desired to be such that it retains its gaseous state at normal room temperature. For the practical purpose, hydrochloric acid offers the greatest ease of handling. The recommended acid content in the atmosphere is in the range of 0.5 – 50%.

The flame-retardation treatment in the case of this invention is carried out at temperatures in the range of 170°- 350°C. In the case of acrylic, polyamide, polyvinyl alcoholic, dehydrated polyvinyl alcoholic or poly-1, 2-butadiene fiber, the heat treatment in the aforesaid atmosphere is desired to be started at temperatures below 230°C. The heat-resistant fiber as the end product can acquire improvements in tensile strength and Young's modulus when the fiber is subjected to heat treatment under simultaneous application of tension. The tension to be applied generally should not exceed 1 *g/d*, although it differs from one fiber to another. Although the period of heating time is variable with the temperature of treatment, the composition of atmosphere and the kind of fiber, a period less than one hour proves sufficient. Satisfactory results can be obtained even with a period of heating time less than 30 minutes.

The heat-resistant fiber obtained by the flame-retardation treatment mentioned above are industrially utilizable. Thus, the fiber is highly suitable for the production of packing materials for mechanical seals which are expected to make effective use of the fiber's resistance to friction, heat and chemicals. A heat-resistant fiber (carbon or graphite fiber) excelling in flexibility, tensile strength and Young's modulus can be obtained in a high yield by heating the flame-retardant fiber in a non-oxidizing atmosphere or in vacuum. This fact clearly indicates that the flame-retardation treatment according to this invention is truly an excellent method for conferring heat-resisting property to the organic fiber. Accordingly, in accordance with the method of the present invention the flame-retardant fibers can be converted into still more heat-resistant fibers, namely carbon or graphite fiber, which is possessed of improved tensile strength and Young's modulus when the fiber is heated up to temperatures higher than 350°C, such as 500°C, 800°C, 1,500°C or 3,000°C, or up to a temperature intermediate between them in a non-oxidizing atmosphere or in vacuum. Some working examples of this invention will be cited hereinafter for the purpose of illustration. In the examples, all the gas concentrations are given in terms of % by volume and the yields in terms of % by weight.

EXAMPLE 1

Yarns composed of 2-Denier acrylic filaments were heated in a current of mixed gas consisting of oxygen and argon at 220°C for 30 minutes, with the oxygen gas concentration varied from one run to another. Blackened heat-resistant fibers were obtained in runs in which the oxygen gas concentrations in the gas streams were higher than about 25%. These fibers were found to possess commercially utilizable flexibility. The yields invariably exceeded 96%. These fibers were heated up to 1,000°C in a current of argon. The relationship of the yield and the tensile strength of the carbon fibers obtained vs. the concentration of the oxygen gas present in the atmosphere used for the flame-retardation treatment is shown in FIG. **1.**

Referring to FIG. **1,** the horizontal axis represents the concentration of the oxygen gas in the flame-retardation treatment atmosphere, the vertical axis on the lefthand side the yield of fiber and the vertical axis on the righthand side the tensile strength respectively. In this figure, each solid line depicts the relationship between the oxygen gas concentration and the yield, and each dotted line the relationship between the oxygen gas concentration and the tensile strength.

The said figure clearly indicates that the carbon fiber obtained from a yarn treated in an atmosphere containing oxygen gas in a concentration higher at all times than air showed conspicuously improved values of yield and tensile strength. It also indicates an outstanding improvement in yield for the carbon fiber resulting from the yarn which was treated in an atmosphere containing oxygen gas in a concentration higher than 80%.

EXAMPLE 2

A yarn composed of 1.5-Denier acrylic filaments was heat-treated in a current of 100% oxygen gas at 220°C for four minutes and subsequently elevated to 250°C in a period of eight minutes. Consequently, there was obtained a blackened flame-retardant fiber having flexibility. When this fiber was further heated up to 500°C and then to 1,200°C in a current of argon, it was converted into a flexible carbon fiber. This carbon fiber

was found to have a tensile strength of 210 kg/mm^2. A graphite fiber having a tensile strength of 180 kg/mm^2 was obtained by heating the carbon fiber up to 2,850°C in a current of argon.

EXAMPLE 3

Yarns composed of 2.5-Denier filaments of hydrocarbon material (dehydrated polyvinyl alcoholic, blackish brown) were heated at 180°C for 125 minutes, to 240°C in 15 minutes and at 240°C for 10 minutes in currents of high oxygen-content gases. Consequently, there were obtained fibers having flexibility. These fibers were further heated to 1,000°C in a current of argon. The relationship of the yield (solid line) and the tensile strength (dotted line) of the carbon fiber obtained vs. the concentration of the oxygen gas present in the flame-retardation treatment atmosphere is shown in FIG. **2.** The vertical axis and the horizontal axis of this figure have the same meanings as those in FIG. **1.**

The figure clearly indicates that the carbon fibers obtained from the yarns which had undergone the flame-retardation treatment in the currents of gases containing the oxygen gas at concentrations higher than air, particularly, above 25%, showed higher values of yield and tensile strength.

EXAMPLE 4

Three fiber samples of a yarn composed of 4.0-Denier filaments of polyvinyl alcohol were heated at 200°C for 6 minutes, heated to 240°C in 12 minutes and held at 240°C for 6 minutes, respectively in a current of argon containing oxygen gas in a concentration of 30%, or 80%, or in a current of air. Consequently, there were obtained blackish brown flame-retardant fibers having flexibility. When these fibers were further heated up to 1,000°C in a current of argon, there were obtained carbon fibers having 43, 52 and 18 kg/mm^2 of tensile strength respectively. The yields of these fibers on the basis of the starting yarn were 28, 30 and 21%, suggesting that both tensile strength and yield would be improved by flame-retardation treating in currents of gases containing oxygen gas at a higher concentration than air.

EXAMPLE 5

Several fiber samples of a yarn composed of 1.5-Denier acrylic filaments were heated at 220°C for 30 minutes in respective currents of mixed gases containing 50% of oxygen gas, and argon and hydrogen chloride gas at different proportions. Consequently, there were obtained blackened fibers having flexibility. A part of every blackened fiber was heated to 700°C, and another part to 1,000°C in a current of argon. The relationship of the yield based on the corresponding starting fiber, and the average tensile strength per filament for the carbon fibers obtained vs. the concentration of hydrochloric acid gas at the time of the flame-retardation treatment is shown in Table 1 and FIG. **3.**

In FIG. **3,** curves A, B and C show the variation of yield of the 1,000°C fiber with the concentration of hydrochloric acid vapor, the tensile strength for the 1,000°C fibers, and the yield of the 700°C fibers, respectively.

Table 1

Oxygen gas content (%)	Hydrochloric acid gas content (%)	Argon gas content (%)	Yield of the 700°C fiber (%)	Yield of the 1,000°C fiber (%)	Tensile strength of the 1,000°C fiber (g/fil.)
50	0	50.0	60.0	46.1	4.3
50	3.3	46.7	74.0	58.8	10.2
50	6.6	43.4	—	59.2	12.0
50	13.3	36.7	76.5	60.6	—
50	25.0	25.0	76.0	60.1	11.5
50	50.0	0	76.8	61.3	12.7

The figure and the table mentioned above clearly indicate that the use of the dehydrogenating atmosphere in the flame-retardation treatment brings about marked improvements in the yield of carbon fiber and in the tensile strength.

When the same yarn of acrylic filaments was subjected to heat treatment under the same temperature conditions in a current of air and then heated up to 1,000°C in a current of argon, the carbon fiber obtained was found to have quite a low degree of flexibility.

EXAMPLE 6

Several samples of yarn composed of 1.5-Denier acrylic filaments were heated at 220°C for 30 minutes in respective currents of mixed gases containing oxygen gas and hydrochloric acid gas at different proportions. Consequently, there were obtained blackened flame-retardant fibers having high flexibility. These dehydrogenated fibers were further heated up to 1,000°C in a current of argon to produce carbon fibers. The yield of the carbon fibers thus obtained is shown as a function of the concentration of hydrochloric acid gas or oxygen gas in the flame-retardation treatment atmosphere in Table 2 and FIG. **4**. The vertical axes and the horizontal axis in the figure have the same meanings as those in FIG. **1**. Separately, dehydrogenated fiber samples were heated up to 1,000°C under the same conditions as mentioned above, except a tension of 0.08 g/d was applied to the fibers in the heating process. The average tensile strength of the carbon fibers thus obtained is indicated in Table 2 and plotted as a dotted line in FIG. **4**. When oxygen gas coexisted with hydrochloric acid gas in the flame-retardation treatment atmosphere, the yield of the 1,000°C fiber obtained was increased by 30% and the tensile strength by 50%, respectively, as compared with the 1,000°C fiber from the flame-retardant fiber obtained in the current of acid-free gas.

Table 2

Hydrochloric acid gas content (%)	Oxygen gas content (%)	Yield of the 1,000°C fiber (%)	Tensile strength of the 1,000°C fiber (kg/mm²)
0	100	47.1	193
3.3	96.7	59.0	265
13.3	86.7	61.1	277
50.0	50.0	61.3	289
70.0	30.0	60.2	—

EXAMPLE 7

Several fiber samples of yarn composed of 2.0-Denier hydrocarbon filaments (dehydrated polyvinyl alcohol) were heated at 180°C for 5 minutes, heated from 180°C to 320°C in 20 minutes, and then held at 320°C for 5 minutes in respective currents of mixed gases containing 50% of oxygen gas and different proportions of hydrochloric acid gas and argon. Consequently, there were obtained blackened fibers having industrially utilizable flexibility. These fibers were heated in a current of argon up to 1,000°C over 1 hour ½. There were produced fibers having flexibility. The yield based on the starting yarn and the tensile strength for the 1,000°C fibers are shown as a function of the concentration of hydrochloric acid in the flame-retardation treatment atmosphere in Table 3 and FIG. **5**. In the figure, the solid line depicts the yield and the dotted line depicts the tensile strength.

Table 3

Hydrochloric acid gas content (%)	Yield of the 1,000°C fiber (%)	Tensile strength of the 1,000°C fiber (kg/mm²)
0	58.1	8.2
3.3	61.9	15.6
13.3	63.7	16.3
50.0	65.1	17.1

EXAMPLE 8

Several fiber samples of yarn composed of 2.0-Denier hydrocarbon filaments were heated at 180°C for 5 minutes, heated from 180°C to 325°C in a period of 20 minutes and held at 325°C for 5 minutes in respective currents of mixed gases containing oxygen gas and hydrochloric acid gas in different proportions. There were obtained blackened fibers having flexibility. These dehydrogenated fibers were further heated to 1,000°C in a current of argon. The yield, based on the starting yarn, for the 1,000°C fibers obtained are shown as a function of the concentrations of hydrochloric acid gas and oxygen gas in the flame-retardation treatment atmosphere in Table 4 and as a solid line in FIG. **6**. Other fiber samples of the same yarn of hydrocarbon filaments as mentioned above were heat-treated to 1,000°C under the same conditions as the case mentioned above, except that a tension 0.05 g/d was applied to the fibers in the stage of carbonization. The tensile strength exhibited by the carbon fibers obtained is also indicated in Table 4 and plotted as a dotted line in FIG. **6**. From the table and the figure, it is clearly seen that heat-resistant fibers can easily be obtained by heat treating the said organic fiber in the current of dehydrogenating gas.

Table 4

Hydrochloric acid gas content (%)	Oxygen gas content (%)	Yield of the 1,000°C fiber (%)	Tensile strength of the 1,000°C fiber (kg/mm²)
0	100	55.4	110
3.3	96.7	60.5	194
13.3	86.3	61.0	207
77.5	22.5	61.2	211

EXAMPLE 9

A tow of pitch filaments 21 – 34 μ in thickness (thermal decomposition product of polyvinyl chloride) was heated at 220°C for 7 minutes and then heated to 300°C in a period of 20 minutes in a current of mixed gas consisting of 85% of oxygen gas and 15% of phosphorus pentachloride. The fiber obtained consequently was heated to 1,400°C in a current of argon. A carbon fiber having an average tensile strength 104 kg/mm² and flexibility was obtained in a yield of 69%. Another sample of the same tow as mentioned above was subjected to heat treatment under the same conditions as mentioned above, except that the current of gas did not contain any hydrochloric acid gas. A carbon fiber having a tensile strength of 67 kg/mm² was obtained in a yield of 55%. When the pre-treatment was performed under the same temperature conditions in a current of 100% air, no carbon could be obtained.

EXAMPLE 10

An acrylic filament yarn having a total denier of 3,000 and a filament denier of 1.0 was heated separately for 20 minutes at 220°C in a current of air and a separate sample in a current of 100% oxygen gas using a continuous line, while the fiber yarn was held under tension. The same yarns as mentioned above were heated at 220°C for 10 minutes in a current of 100% oxygen gas and for the next 10 minutes in a current of mixed gas consisting of 93% of oxygen gas and 7% of hydrochloric acid gas, being kept in continuous transfer through a heating zone. The yarns treated in the current of air turned yellow, while those treated in the current of 100% oxygen gas and those treated in the current of oxygen gas-acid vapor mixture both turned blackish brown. These fibers were gradually heated up to 1,300°C by passing through an argon-atmosphere heating zone maintained at successively elevated temperatures. The 1,300°C fibers obtained from the fibers heat-treated in the atmosphere of 100% oxygen gas and in the atmosphere consisting of oxygen gas and acid vapor exhibited 186 and 230 kg/mm² of tensile strength, respectively. The fibers which had undergone the flame-retardation treatment in the current of air were broken in the course of this carbonization treatment.

EXAMPLE 11

A filamentary yarn, having a total denier of 4,000 and filament denier of 2.0, of hydrocarbon material (dehydrated polyvinyl alcohol) was heated from 180°C to 220°C and then held at 220°C for 30 minutes in a current of air (**1**) while a separate sample was processed in a current of 100% oxygen gas (**2**) using in a continuous line. Another part of the same yarn of hydrocarbon as mentioned above was subjected to heat treatment at 220°C for 15 minutes in an atmosphere of 100% oxygen gas and for the next 15 minutes in a dehydrogenating atmosphere consisting of 88% of oxygen gas and 12% of hydrochloric acid gas (**3**) by continuously passing through two atmosphere heating zones. In all cases, there were obtained fibers having flexibility. These fibers were gradually heated up to 1,200°C by passing through an argon-atmosphere heating zone maintained at successively elevated temperatures. The carbon fibers obtained from the flame-retardant fibers (**2**) and (**3**) exhibited 140 and 176 kg/mm ² of tensile strength, respectively. By contrast, the carbon fibers from the fiber which had been heated in air were broken in the course of carbonization treatment.

EXAMPLE 12

A fiber sample of the same tows of pitch filaments as used in Example 9 was heated from 200°C to 320°C in a period of 15 minutes and then held at 320°C for 15 minutes in a current of air while a separate sample was processed in a current of 100% oxygen gas. Another fiber sample of the same tows as stated above was separately heated from 200°C to 320°C in a period of 15 minutes and then held at the latter temperature for 5 minutes in a current of 100% oxygen gas and, thereafter, they were held at the same temperature for 10 minutes in a current of gas consisting of 20% of hydrogen bromide and 80% of oxygen gas. All these fibers were heated up to 1,400°C in an atmosphere of argon. The fiber which had been heated in the atmosphere of 100% oxygen gas and that which had been heated in the atmosphere consisting of oxygen gas and acid gas exhibited 72 and 130 kg/mm² of tensile strength, respectively. By contrast, the carbon fibers obtained from the tow heated in air were so weak as to make the measurement of tensile strength difficult.

We claim:

1. In a method for the manufacture of heat-resistant fibers by first heating in an atmosphere at 180°C to 350°C and then in a nonoxidizing atmosphere at a temperature up to 3,000°C an organic fiber selected from the group consisting of acrylic fiber, thermally decomposed polyvinyl chloride pitch fiber and dehydrated polyvinyl alcohol fiber, the improvement which comprises effecting said first heating in an atmosphere containing oxygen gas and an acid gas selected from the group consisting of hydrogen chloride, hydrogen bromide, and phosphorus pentachloride, the acid gas content being in the range of 0.5% to 50% by volume and the oxygen gas content being in the range of 25% to 99.5% by volume.

2. The method of claim **1** wherein during heat-treatment, the fiber is subjected to tension up to 1 gram per denier.

3. The method of claim **1** wherein the fiber is subjected to heat treatment in an oxygen-containing atmosphere to partly preoxidize the fiber prior to said first heating in oxygen gas and acid gas atmosphere.

* * * * *