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PROCESS FOR THE PREPARATION OF CARBON FIBERS

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ABSTRACT OF THE DISCLOSURE

Carbonaceous and carbon fibers of an improved quality are produced from each of cellulosic, polyvinyl alcoholic and acrylic fibers at a high yield by subjecting it to heat treatment in an acidic atmosphere containing a gaseous hydrogen chloride, which has been found to be effective for the manufacture of carbon fibers.

This invention relates to carbon fibers, and more particularly, to a process for the preparation of carbon fibers by an improved step including a novel chemical treatment.

With a recent development of industrial application of carbon fiber due to miscellaneous advantages inherent in it, many and varied methods for the manufacture thereof have been proposed in the past.

The group of starting fibrous materials for which the process of the present invention is applied includes the polymeric fibers containing oxygen or nitrogen atoms in their molecules and being thermally stable at 200° C. in an inert atmosphere. The most exemplary polymeric fibers coming under this group are cellulosic, polyvinyl alcoholic, acrylic, polyimide and polyamide fibers. The details of a process for the manufacture of a carbon fiber from each of cellulosic, polyvinyl alcoholic and acrylic fibers as a starting material will be described hereinafter.

In reference to the method for making carbon fiber from the above fibrous material, it is known that there is a two-step process which comprises subjecting the fiber to a heat treatment in an atmosphere containing oxygen, such as, air at a relatively low temperature between 100° and 500° C. in a first step, and subsequently, to a next heat treatment in an inert atmosphere, such as, nitrogen at a relatively high temperature above 500° C. in a second step. In order to increase the yield of carbon fiber as well as improve its quality, it is also known that in the first step of the above process the fibrous material is treated with a compound selected from the group of zinc chloride, iron chloride, aluminum chloride, magnesium chloride and calcium chloride prior to the heat treatment.

I, inventor of the present invention have discovered based on my experimental researches on the preparation of carbon fibers that the carbon fiber produced by a novel process of this invention which comprises subjecting the fibrous material to a heat treatment in an atmosphere containing acid vapor, in particular, non-oxidizing acid, in the low temperature step of the known method.

Furthermore, I, inventor, have also discovered that when the fibrous material is subjected to a predetermined tension while treated in the atmosphere containing acid vapor, such as, hydrochloric acid, the resulting fibrous carbon product has a higher tensile strength as well as a higher modulus than that of the one of prior art.

The known process of making carbon fiber from the fibrous material consists of the two steps described above.

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In accordance with a preferred embodiment of the invention, however, it has been found that the manufacture of carbon fiber is feasible by subjecting a fibrous material to a single treatment step in an acidic atmosphere, in particular containing hydrochloric acid, at a temperature in the range of 80° C. to 1500° C., and further, at a high yield together with a good quality.

As described hereinbefore, a fibrous material adapted for the process of this invention including the novel chemical treatment includes a cellulosic fiber such as, for example, cotton and other natural cellulose, rayon, regenerated cellulose, such as, cellulose nitrate, polyvinyl alcoholic fiber, polymeric fiber containing vinyl alcohol in polymer form, and acrylic fiber, containing acrylonitrile in polymer form.

This invention relates to the method of making a carbonaceous or carbon fiber from the above fibrous material and it is to be understood that in the invention "carbon fiber" includes a blackened fiber by heat treatment and a graphitized fiber as well. It is also understood that "fiber" includes short and long ones, yarn, string, felt, woven cloth and other various forms.

It is already known that a fibrous carbon product is obtained by subjecting a fiber material to heat treatment only in an inert atmosphere at a predetermined temperature for a predetermined period of time. However, it is also known in this case that the yield of carbonization of fiber is considerably low while the strength of a resulting fibrous carbon product is exceedingly low. For example, it has been found that when a cotton material, containing 90% cellulose, is subjected to heat treatment in an inert atmosphere at a temperature of 300°–400° C., the loss of weight of fiber occurs in the order of about 75% by weight, and furthermore, the yield of carbonization of fiber when heated up to 600° C. barely amounts to about 12%. One of known processes for the increase of carbonization yield of fibrous material consists in treating a cellulosic fibrous material with metallic chloride, such as, aluminum chloride described hereinabove, and subsequently firing it in an inert atmosphere.

In accordance with a preferred embodiment of the invention, one of the above fibrous materials is subjected to heat treatment in an atmosphere containing gaseous hydrochloric acid at a temperature of 100°–3000° C., whereby the fiber material is carbonized in a more efficient manner than in the conventional process for making carbon fiber. It is to be noted that the gaseous or vaporous hydrochloric acid has been found to be an effective agent for eliminating oxygen and nitrogen together with hydrogen, in the form of water and ammonium, from the fiber in the carbonization process. It is a widely accepted conception that hydrochloric acid and the like have no such function. On the contrary, however, it has been found that the gaseous hydrochloric acid and the like exhibit a good catalytic function for carbonization in the manufacture of carbon fiber from the fibrous materials.

Accordingly, it is an essential object of the invention to provide a process for the manufacture of a good quality carbon fiber at a high yield from a fibrous material by the application of the acidic atmosphere containing hydrochloric acid and the like to the fibrous material in a heat treatment step.

It is a further object of the invention to provide a process of making a carbon fiber having various degrees in properties.

It is another object of the invention to provide a process of making a good carbon fiber at a high yield by a novel method including a novel chemical treatment step.

It is an additional object to provide a process of mak-

ing a carbon fiber having high tensile strength and especially high modulus by applying a predetermined tension to the fibrous material while being heat treated at a relatively low temperature in an acidic atmosphere containing non-oxidizing acid vapor.

Other objects and advantages of the invention will be apparent from the description of many preferred embodiments.

The following description in accordance with the present invention will be divided into three sections: (1) cellulosic fiber, (2) polyvinyl alcoholic fiber, and (3) acrylic fiber.

(1) CELLULOSIC FIBER

The cellulosic fiber adapted for the process of this invention includes a vegetable fiber of natural origin, such as, cotton, hemp, flax, ramie, and Manila hemp, and an artificial fiber, such as, rayon, regenerated cellulose, cellulose nitrate, cupraammonium rayon, cellulose acetate, saponified cellulose, and a cellulose which contains lignin, etc.

When cellulosic fibers such as, for example, cotton and rayon are heated in an acidic atmosphere, they begin to decompose, mainly owing to the progress of dehydration reaction, at a temperature near 100° C. The carbonization reaction of them proceeds remarkably in the temperature range between 150° and 250° C., and fairly rapidly in the temperature range between 250° and 600° C. At the temperature of 600° C. the degree of carbonization of them was 90%.

In carrying out the carbonization treatment procedure of the present invention for cellulosic fibers, they are heated in an acidic atmosphere at a temperature between 100° and 250° C. and they also can be heated at a temperature between 250° and 600° C. in the acidic atmosphere. The fibers heated in the acidic atmosphere at a temperature between 100° C. and 600° C. can be heated at a higher temperature than those temperatures in an inert atmosphere to reach to a higher degree of carbonization. However, to obtain satisfactory results of the carbon fibers, the heat treatment of cellulosic fibers in the acidic atmosphere is preferable at the temperature of 250° C. To obtain much more satisfactory results of the carbon fibers, it is recommended that the heat treatment in the acidic atmosphere should be carried out at a temperature between 150° and 250° C. Furthermore, raising the temperature of the fiber continuously from a temperature near 150° C. to a temperature near 600° C. in the acidic atmosphere is much more preferable to obtain the carbon fibers having good qualities. A period of time for which the fibers are heated at a temperature in the range from 150° to 250° C. in the acidic atmosphere is preferred to be between 30 minutes and 10 hours. If it is sufficient to blacken the cellulosic fibers in the acidic atmosphere, a period of time shorter than 30 minutes also may be employed.

To obtain the carbon fibers having various degrees of properties, the fibers heated at a temperature below 600° C. can be heated in an inert atmosphere at a higher temperature below 3000° C. or the temperature at which carbon fiber sublimates substantially. At a temperature below 1500° C. the fibers also are preferred to be heated in the acidic atmosphere because of the efficacy of acid vapor for eliminating impurities in the fibers.

(2) POLYVINYL ALCOHOLIC FIBER

The process of this invention as applied to cellulosic fiber can be also applied to "polyvinyl alcoholic fiber," which includes a high polymeric fibrous material containing vinyl alcohol in polymer form. The polyvinyl alcohol modified with a partial formalization, a partial acetalization, a partial ketalization, a partial amino-acetalization, or a partial esterification can be also used. The fiber material containing vinyl alcohol high polymer or

a copolymer therewith, or a mixed high polymer can be employed. As a mixed high polymer, it includes cellulose or lignin. A vinyl alcoholic polymer with cross-linking can be used as a starting material. It includes polyvinyl alcoholic fiber material cross-linked with an unsaturated aldehyde. Each of the polyvinyl alcoholic fibrous material is desirable to contain at least 70% of vinyl alcohol by weight of monomer in polymer form. If below 70%, it can be used, too. A fiber material adapted for a starting material is preferred to be drawn to at least twice their original as-spun length. It is preferable to use the fiber prepared by a dry spinning as the starting fiber.

When polyvinyl alcoholic fibers are heated in an acidic atmosphere, for example, hydrochloric acid vapor, the dehydration reaction begins to proceed at a temperature near 120° C., and proceeds rapidly in the range between 150° to 250° C., and slowly in the range between 250° to 450° C. In the heat treatment in an inert atmosphere polyvinyl alcoholic fiber melts at a temperature near 230° C., but it increases remarkably its thermal stability by being heated in an acidic atmosphere at a temperature between 120° C. and 230° C. The polyvinyl alcoholic fibers with the treatment of dehydration become much more stable thermally by being oxidized with an oxidizing atmosphere such as, for example, air and chlorine gas.

In order to dehydrate polyvinyl alcoholic fibers, it is possible to employ aluminium chloride vapor at a temperature above its sublimation point, near 180° C. However, acid vapors such as hydrochloric acid is preferable because of a high efficacy in dehydration and convenience in handling.

In carrying out the dehydration treatment procedure of the present invention for polyvinyl alcoholic fibers, it is recommended that the heat treatment of the fibers should be made to start at a temperature between 150° C. and 200° C.

The fiber heated in an acidic atmosphere at a temperature between 150° C. and 200° C. also is desirable to be heated in an acidic atmosphere at a temperature between 250° C. and 450° C., to obtain the good results of the carbon fiber after the peroxidation treatment and then the carbonization treatment.

The dehydrated polyvinyl alcoholic fibers obtained in accordance with the dehydration treatment procedure of the present invention are fairly stable thermally, but its thermal stability is not high enough to be satisfied. To reach sufficiently high thermal stability of the dehydrated fibers, in accordance with the preoxidation treatment of the present invention, the fibers are heated in an oxidizing atmosphere containing air, halogen and the like.

The temperature at which the dehydrated polyvinyl alcoholic fibers are preoxidized in an oxidizing atmosphere containing chlorine gas is between 200° C. and 700° C. With air the fibers are heated at a temperature between 170° C. and 500° C. However, in the preoxidation treatment with air it is preferable to heat the dehydrated fibers at a temperature between 200° C. and 350° C. Furthermore, it is recommended to start heating in air at a temperature between 170° C. and 200° C. to accomplish the preoxidation treatment. In the heat treatment in halogen gases it is preferable to start heating at a temperature between 200° C. and 400° C. To accomplish the preoxidation treatment, it is preferable to heat the fibers for a period of time between 30 minutes to 20 hours. However, a period of time shorter or longer than those also may be employed on the dehydrated fibers. The fibers preoxidized with an atmosphere containing chlorine or bromine are not always necessary to be heated in an acidic atmosphere. However, the fibers preoxidized with an atmosphere containing oxygen are preferable to be heated in an acidic atmosphere at a temperature below 600° C. or 1500° C. However, the carbon fibers having good qualities desired for industrial needs can be obtained by heating the dehydrated and then preoxidized polyvinyl alcoholic fibers in an inert atmosphere.

(3) ACRYLIC FIBER

The process of this invention as applied to cellulosic and polyvinyl alcoholic fibers can be also applied to "acrylic fiber," which includes a fibrous material containing acrylonitrile in polymer form, and besides, a fiber consisting of graft polymer, other copolymers or mixed polymers. Each of the acrylic fibrous materials is desirable to contain at least 70% of acrylonitrile by weight of monomer in polymer form. If below 70%, it can be used, too. A fiber material adapted for a starting material is preferred to be drawn to at least twice their original as spun length.

In the carbonization treatment procedure of acrylic fibers, in the present invention, the fibers are heated in an acidic atmosphere at a temperature between 150° C. and 1500° C. However, when acrylic fibers are heated in an acidic atmosphere, the carbonization reaction proceeds remarkably at a temperature between 200° C. and 450° C., and at a lower rate at a higher temperature than 450° C. However, the rate at which the carbonization reaction proceeds at a temperature between 450° C. and 800° C. is faster than that between 800° C. and 1500° C. Accordingly, it is recommended that to reach good qualities of the heat treated fibers the carbonization treatment procedure of acrylic fibers is made to comprise a process of heating them in an acidic atmosphere at a temperature between 200° C. and 450° C. In accordance with the heat treatment procedure of the present invention, the fibers heated at a temperature between 200° C. and 450° C. can be heated in an inert atmosphere to obtain the carbon fibers having properties desired for industrial needs. However, it is preferable to start heating in an acidic atmosphere at a temperature between 250° C. and 350° C., and to further heat in an acidic atmosphere at a temperature above 450° C., to obtain the carbon fibers having good qualities.

A period of time for which the fibers are heated at a temperature below 450° C. in an acidic atmosphere is to be between 20 minutes and 20 hours. However, a period of time shorter or longer than those also may be employed in the acidic atmosphere treatment.

From the preoxidized acrylic fibers, also the carbon fibers being superior in properties to that obtained by heating in an inert atmosphere can be produced with a higher yield than that by the known method by heating them, in accordance with the carbonization treatment procedure of the present invention, in an acidic atmosphere.

The preoxidation treatment is accomplished by heating the acrylic fibers in air at a temperature between 180° C. and 350° C. for a period of time from 30 minutes to 20 hours, or by heating the acrylic fibers in an atmosphere containing halogen gas, chlorine or bromine, at a temperature between 150° C. and 350° C. for a period of time between 10 minutes and 5 hours.

The rate of carbonization reaction of the preoxidized acrylic fibers is most rapid in the range between 250° C. and 450° C., and next in order of the rate comes the range between 450° C. and 800° C. Accordingly, the carbonization treatment procedure of the preoxidized acrylic fibers in the present invention is similar to that of the acrylic fibers without preoxidation treatment.

In the present invention, the fibers such as, for example, threads and fabrics of acrylic fiber and polyvinyl alcoholic fiber upon which silica fine powder solids are discontinuously deposited in accordance with the known method may also be used as one of the starting materials with or without the preoxidation treatment. On these powder solids coated fibers the heat treatment procedure in an acidic atmosphere described hereinbefore can be employed. The powder solids deposited on the fiber is preferable to be removed from the fibers after the heat treatment below 450° C.

In the course of reaching this invention, it has been

found that imposing stress on the fibers during the heat treatments at a temperature below 450° C. and at a temperature between 2500° C. and 3000° C. or above is effective for the increase of tensile strength and modulus of carbon fibers to be produced.

On each fiber of cellulosic, polyvinyl alcoholic and acrylic fibers, when it is heated, the linear shrinkage occurs substantially below 800° C. as one of the results of the progress of decomposition or carbonization of the fibers. To reach a higher tensile strength of the carbon fibers, in the carbonization treatment procedure of the present invention, a temperature between 150° C. and 450° C. is preferable as the temperature at which a stress is imposed on the fibers so as to make the linear shrinkage lower. However, in the treatment at a temperature below 450° C., when the stress imposed on the fibers is excessively high or low, the stress has no efficacy in increasing the tensile strength of the carbon fiber products. When the stress is excessively high, the fibers are broken or become lower in its tensile strength.

The rate to which the fibers shrink lengthwise during the heat treatment depends on various factors such as the kinds of polymeric material of which the fibers are formed, the thickness of filament of the fibers, the kinds of atmospheric gases and the ways of raising temperature of the fibers. Therefore, it is difficult to give detailed explanation of the relation between the rate of the linear shrinkage and these various conditions. However, the linear shrinkage during the heat treatment below 450° C. of the cellulosic, polyvinyl alcoholic and acrylic fibers without imposed stress were between 14 and 30%, 25 and 55%, and 15 and 40%, respectively.

It was found that the 1000° C. carbon fibers having higher tensile strength by 10-30%, 10-50% and 10-50% than that of the 1000° C. fibers without the treatment of imposing stress can be produced from the cellulosic, polyvinyl alcoholic and acrylic fibers, respectively, by imposing stress on them during the heat treatment at a temperature of below 450° C. so as to become the linear shrinkage of 6-24%, 19-53% and 3-24%, respectively. These values of the linear shrinkage corresponded to 40-80%, 75-97%, and 20-60% of the linear shrinkage during the heat treatment to 450° C. without imposing stress.

Thus, it has been found that when the fibers are imposed a stress at a temperature between 150° C. and 450° C. in such a manner that the linear shrinkage, at a temperature of heat treatment of 450° C., of the fibers with the treatment of imposing stress become 40-80%, 75-97%, and 20-60% of those of the cellulosic, polyvinyl alcoholic and acrylic fibers without the treatment of imposing stress, respectively, the carbon fibers having higher tensile strength can be obtained after the carbonization treatment of them. However, it is preferable that the ratios of the shrinkage of the fibers with the treatment of imposing stress against that of the fibers without the treatment of imposing stress are 50-60%, 80-90% and 25-40% for the cellulosic, polyvinyl alcoholic and acrylic fibers, respectively.

It has been found that in the heat treatment at a temperature above 2500° C. of the carbon fibers with the heat treatment in an acidic atmosphere, the carbon fibers having particularly high modulus can be produced by stretching them with imposing stress. This stretching treatment is efficacy in increasing the modulus of the carbon fibers produced from, in particular, the polyvinyl alcoholic and acrylic fibers, because they (carbon fibers) have such a structure that carbon crystallites are oriented remarkably. However, it is preferable that the temperature at which the fibers are stretched is above 2700° C. The rate of stretching the carbon fiber can exceed a value of 40% by length and may be lower than 5%. It is not desirable to stretch the fibers at a exceedingly high speed, because stretching by such a high speed causes the breakdown of the fibers during the heat treatment. The speed of

stretching the carbon fiber depends on the kinds of the origins of carbon fibers, thickness of them and the heat treatment temperature. However, at 2700° C. it can be slower 1–2% per minutes and at 3000° C. can be slower than 5–10% per minute. It is to increase the properties of the stretched carbon fibers that the stretching speed is slower than the values mentioned above.

The acid vapor for use in the present invention contains hydrochloric acid, bromic acid, formic acid, acetic acid or other acid, nitrous oxide gas, sulfur dioxide gas or other acid anhydride. As the acidic atmosphere for use in the present invention, an inert gas containing one of these compounds. In practice, however, hydrochloric acid vapor is most preferred. The term "hydrochloric acid vapor" here is used synonymously with "hydrogen chloride gas."

The concentration of acid vapor in the acidic atmosphere for use in the present invention is desirable to be above 10% by volume, but below 10% by volume can be used. The pressure of the acidic atmosphere can be selected to be a high pressure above the atmospheric one or reduced.

In reference to the inert atmosphere, nitrogen or argon is usually used, but in practice nitrogen is preferable to use.

At a relatively low temperature at which the carbonization proceeds substantially, a large amount of decomposing gases is evaporated from the fibrous material. These gases tend to deposit on the fibers to be carbonized as soot. To avoid this disadvantage it is preferable to flow always at a sufficiently high rate a fresh acidic atmosphere or inert one to remove decomposing gaseous products from the fibers.

In the heat treatment of the present invention, it is possible to heat the fiber at a constant rate of raising temperature, at a step-by-step temperature rise, or at a variable rate of raising temperature in a certain temperature range. However, it is preferable that at a temperature below 500° C. the fibers are heated at a rate of raising temperature below 500° C./hr.

The heat treatment of the present invention can be carried out by using any convenient type tunnel furnace or batch type furnace.

The following Examples 1–11 relate to cellulosic fibers, 12–21 to polyvinyl alcoholic fibers, and 22–35 to acrylic fibers. All the percentages of yield will be seen in the examples are expressed by weight, and all the percentages of concentration of atmosphere used in the examples by volume. The composition percentages of the copolymers from which the starting fiber material has been formed is expressed by weight of monomer.

Example 1

A loose batt of cotton having a random fiber orientation was heated in an atmosphere of hydrochloric acid vapor from 100° C. to 500° C. Rates of raising temperature in the ranges from 100° C. to 200° C., from 200° C. to 300° C., and from 300° C. to 500° C. were 100° C./hr., 500° C./hr. and 200° C./hr., respectively. A loose batt of highly flexible carbonaceous fiber was obtained, with a yield of 41% by weight, which corresponded to 270% of the yield of carbonaceous material obtained by heating another batt of the same cotton fiber that used above under the same condition of raising temperature that employed above only in an atmosphere of nitrogen.

Example 2

A bundle-like mass of viscose rayon filamentary fiber (6 denier per filament) was heated from 100° C. to 700° C. in a flow of acidic atmosphere containing 60% of hydrochloric acid and 40% of nitrogen by volume. Rates of raising temperature in the ranges from 100° C. to 500° C. and from 500° C. to 700° C. were 60° C./hr. and 120° C./hr., respectively. At 700° C. the fiber was held for one hour. A bundle-like mass of carbon fiber was obtained, with a yield of 37% by weight, which corresponded to 320% of the yield of carbon fibers obtained by heating another portion of the same fiber that used above solely

in nitrogen though under the same condition of raising temperature that employed above.

Example 3

A loose bundle-like mass of viscose rayon filamentary fiber (4 denier per filament) was heated from 120° C. to 240° C. at a rate of 180° C./hr. in a flow of hydrochloric acid vapor, and then in a stream of nitrogen from 240° C. to 530° C. at a rate of 260° C./hr. and at 530° C. for 20 minutes. The product was highly flexible, its yield being 38% by weight, which corresponded to 290% of the yield of the fiber obtained by heating another portion of the same rayon fiber that used above solely in a nitrogen stream under the same condition of raising temperature that employed above.

Example 4

A batt of cotton was heated from 130° C. to 420° C. at a rate of 240° C./hr. in a flow of atmosphere containing 30% of hydrochloric acid and 70% of nitrogen, and then in a flow of nitrogen from 420° C. to 1000° C. at rates of 350° C./hr. and 450° C./hr. in the ranges from 420° C. to 600° C. and from 600° C. to 1000° C., respectively. The fibrous mass was held at 1000° C. for 20 minutes. The yield was 33% by weight, which corresponded to 300% of the yield of the product obtained by heating another batt of the same cotton that used above under the same condition that employed above solely in a nitrogen gas stream.

Example 5

A bundle-like mass of yarns of rayon filamentary fiber (4 denier per filament) was heated from 100° C. to 340° C. at a rate of 120° C./hr. in a flow of hydrochloric acid vapor, and then was heated in a nitrogen gas flow from 340° C. to 900° C. at a rate of 240° C./hr. and at 900° C. for 20 minutes. The carbon fiber obtained exhibited an average tensile strength of 6.8×10^3 kg./cm.². Another bundle-like mass of the same starting fiber that employed above was heated under the same conditions that described above except being held under tension during the heat treatment from 240° C. to 340° C. The linear shrinkage of this 340° C. fiber was 76% of the shrinkage of the 340° C. fiber obtained without being held under tension. The 900° C. carbon fiber, with the treatment of imposing stress, exhibited a tensile strength of 8.7×10^3 kg./cm.² and a modulus of 2.9×10^5 kg./cm.².

Example 6

A continuous yarn of rayon filamentary fiber was heated from 130° C. to 500° C. in a flow of acidic atmosphere containing 70% of hydrochloric acid and 30% of nitrogen by volume by being moved through a heating zone from 130° C. to 250° C. in 30 minutes and through a zone from 250° C. to 500° C. in 25 minutes. The 500° C. fiber was further heated in a flow of atmosphere having the same composition that in the case of heat treatment below 500° C. by being moved through a zone from 500° C. to 800° C. in 20 minutes and through a zone at 800° C. in 5 minutes. The product exhibited a tensile strength of 5.4×10^3 kg./cm.² and a yield of 36%, which corresponded to 300% of the yield in the case of heat treatment in an atmosphere containing only nitrogen. The heat treatment was carried out in a tunnel furnace.

Example 7

A continuous yarn of filamentary fiber of rayon was heated in an acidic atmosphere, containing 80% of hydrochloric acid and 20% of nitrogen, from 120° C. to 600° C. at a rate of 60° C./hr., and from 600° C. to 1200° C. at a rate of 200° C./hr. This 1200° C. yarn was heated from 1200° C. to 2700° C. at a rate of 600° C./hr., and at 2700° C. for 30 minutes. During the heat treatment at 2700° C. the yarn was stretched 18% by length by being held under tension. The unstretched 2700° C. fiber ex-

hibited a modulus of 3.1×10^5 , but the stretched 2700° C. fiber a modulus of 140% of this value.

Example 8

A portion of continuous carbon yarn obtained in Example 6 was heated in nitrogen gas by being moved through a zone from 800° C. to 2500° C. and through a zone at this latter temperature in 36 minutes. During the heat treatment at 2560° C. the yarn was imposed stress and stretched by 4% by length. The carbon fiber stretched exhibited a modulus higher by 40% than that of the unstretched 2560° C. fiber which was obtained by heating another portion of the 800° C. yarn in Example 6 under the same condition that in the case of the stretched fiber except imposing stress.

Example 9

A continuous yarn of rayon filamentary fiber was continuously heated in a flow of acidic atmosphere containing 40% of hydrochloric acid and 60% of nitrogen by being moved through a zone from 120° C. to 440° C. in 40 minutes. Furthermore, the 440° C. yarn was continuously heated in a flow of acidic atmosphere of the same condition that in the case below 440° C. by being moved through a zone from 440° C. to 700° C. in 20 minutes, through a zone from 700° C. to 1100° C. in 20 minutes, and through a zone at 1100° C. in 10 minutes. During the heat treatment from 120° C. to 440° C. the fiber yarn was imposed stress. The linear shrinkage of the yarn during heat treatment from 120° C. to 440° C. was 53% of the shrinkage of the 440° C. fiber obtained without imposing stress. The 1100° C. carbon fiber without the treatment of imposing stress exhibited a tensile strength of 7.1×10^3 kg./cm.² and a modulus of 3.2×10^5 kg./cm.². The 1100° C. carbon fiber with the treatment of imposing stress exhibited a tensile strength of 8.4×10^3 kg./cm.² and a modulus of 5.4×10^5 kg./cm.².

Example 10

The carbon yarn produced in Example 5 was heated in an atmosphere of nitrogen by being moved through a zone from 1500° C. to 300° C. and a zone at 3000° C. During the heat treatment for 8 minutes at 3000° C. the yarn was imposed stress and stretched by 31%. The unstretched 3000° C. carbon fiber yarn exhibited a modulus of 3.6×10^5 kg./cm.². The stretched 3000° C. fiber yarn exhibited a modulus higher by 170% than that of the unstretched 3000° C. fiber yarn.

Example 11

A portion of the carbon fiber obtained in Example 9 was heated in a flow of argon gas from 1100° C. to 2800° C. at a rate of 750° C./hr. and was held at this latter temperature for 30 minutes. During the heat treatment at 2800° C. the fiber was imposed stress and stretched by 20%. The 2800° C. fiber obtained by heating another portion of the same starting carbon fiber that used above under the same condition that employed above except without imposed stress exhibited a modulus of 3.2×10^5 kg./cm.². The stretched 2800° C. fiber exhibited a modulus higher by 82% than that of the unstretched 2800° C. fiber.

Example 12

A bundle-like mass of polyvinyl alcoholic filamentary material containing 85% of vinyl alcohol and 15% of vinyl acetate by weight of monomer in polymer form (6 denier per filament) was heated in a flow of hydrochloric acid gas by raising the temperature from 100° C. to 250° C. at a rate of 120° C./hr. and by being held at the latter temperature for 30 minutes. The fiber was cooled in a stream of nitrogen gas. The product was of blackish-brown color and semiconductive electrically, and exhibited a tensile strength and a flexibility desired for industrial needs. The yield was 66% by weight.

Example 13

A bundle-like mass of filamentary fiber of polyvinyl alcoholic material having a degree of saponification of 95% (4 denier per filament), prepared from polyvinyl acetate, was heated in a flow of acidic atmosphere containing 40% of hydrochloric acid and 60% of nitrogen from 130° C. to 250° C. at a rate of 60° C./hr. and from 250° C. to 350° C. at a rate of 200° C./hr. The blackish-brown colored fiber obtained exhibited a strength and flexibility desired for industrial needs. The yield was 61% by weight.

Example 14

A bundle-like mass of polyvinyl alcoholic filamentary fiber having a degree of saponification of 99% (7 denier per filament) was heated in an acidic atmosphere containing 20% of hydrochloric acid vapor and 80% of nitrogen gas by volume from 100° C. to 200° C. at a rate of 120° C. and from 200° C. to 340° C. at rate of 240° C./hr. The fiber having a strength and flexibility desired for industrial needs was obtained. The degree to which the dehydration reaction of the fiber had been in the fiber during the heat treatment was 96%.

Example 15

The dehydrated polyvinyl alcoholic fiber obtained in Example 14 was preoxidized by heating in air successively at a temperature of 170° C., 180° C., 190° C. and 200° C. for one hour at every temperature. The blackish-brown colored fiber having an electric semiconductivity was obtained. During this heat treatment the substantial weight loss did not occur. The product was thermally stable and exhibited a strength and flexibility desired for industrial needs.

Example 16

The fiber obtained in Example 13 was heated to 250° C. in a flow of nitrogen gas, and then was heated in a flow of chlorine from 250° C. to 500° C. at a rate of 60° C./hr. and from 500° C. to 600° C. at a rate of 120° C./hr. The 600° C. fiber was further heated in a stream of nitrogen from 600° C. to 1050° C. at a rate of 250° C./hr. and was held at this latter temperature for 30 minutes. The product exhibited a tensile strength of 8.9×10^3 kg./cm.² and a modulus of 7.8×10^5 kg./cm.².

Example 17

The same starting fiber as used in Example 14 and the fiber obtained in Example 15 were heated in a nitrogen gas flow from 200° C. to 700° C. at a rate of 120° C./hr., from 700° C. to 900° C. at a rate of 200° C./hr., and at 900° C. for 30 minutes. The product with the treatment of dehydration, in an acidic atmosphere, exhibited a tensile strength of 9.8×10^3 kg./cm.² and a modulus of 8.2×10^5 kg./cm.². The yield was 43%. The product without the heat treatment in acidic atmosphere exhibited a tensile strength of 3.6×10^3 kg./cm.² and a modulus of 3.2×10^5 kg./cm.², its yield being 31%. Other portions of the same dehydrated and preoxidized 200° C. fiber that obtained in Example 15 also are heated in a nitrogen gas flow from 200° C. to 430° C., with or without imposed stress, under the same condition of raising temperature that employed above. The linear shrinkage of the 430° C. fiber with the treatment of imposing stress was 74% of the shrinkage of the 430° C. fiber without the treatment of imposing stress. These 430° C. fibers were heated in a nitrogen gas flow to 900° C. under the same condition that employed above. The 900° C. fiber with the treatment of imposing stress exhibited a tensile strength of 14.8×10^3 kg./cm.² and a modulus of 11.8×10^5 kg./cm.².

Example 18

A continuous yarn of polyvinyl alcoholic filamentary fiber (6 denier per filament) was heated in a flow of atmosphere containing 80% of hydrochloric acid and 20% of nitrogen, in a tunnel furnace, by being moved continuously through a heating zone from 120° C. to 230° C.

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in 40 minutes and through a zone from 230° C. to 340° C. in 15 minutes. This fiber was heated in air by being moved through a zone from 170° C. to 250° C. in 30 minutes. The fiber product was thermally stable and flexible, and exhibited a tensile strength desired for industrial needs. Another portion of the same starting fiber that used above also was heated in a flow of acidic atmosphere having the same composition that employed above from 120° C. to 340° C. under the same condition that employed in the case mentioned above but under tension. The linear shrinkage of the fiber with the treatment of imposing stress during the heat treatment corresponded to 96% of that of the fiber without the treatment of imposing stress. This fiber also was preoxidized with air in the same way. Both of the preoxidized fibers were heated in an acidic atmosphere containing 40% of hydrochloric acid and 60% of nitrogen by being moved successively through a zone from 250° C. to 550° C. in 35 minutes, a zone from 550° C. to 1100° C. in 40 minutes and a zone at 1100° C. in 10 minutes. The 1100° C. fiber without the treatment of imposing stress exhibited a tensile strength of 10.5×10^3 kg./cm.² and modulus of 9.5×10^5 kg./cm.², and its yield was 42% by weight. The 1100° C. fiber with the treatment of imposing stress exhibited a tensile strength of 13.4×10^3 kg./cm.².

Example 19

The carbon fiber obtained in Example 18 was heated from 1200° C. to 2600° C. at a rate of 550° C./hr., and was held at this latter temperature for 35 minutes. During this heat treatment at 2600° C. the fiber was imposed stress and stretched by 8%. The unstretched 2600° C. fiber exhibited a modulus of 21.0×10^5 kg./cm.², but the stretched 2600° C. fiber a modulus higher by 9% than this value.

Example 20

The fiber obtained in Example 14 was heated in a flow of acidic atmosphere containing 10% of hydrochloric acid and 90% of nitrogen from 200° C. to 480° C. at a rate of 120° C./hr., and then was heated in a flow of nitrogen gas to 1200° C. at a rate of 300° C./hr. A portion of this fiber was heated in a flow of argon gas to 2800° C. at a rate of 500° C./hr., and was held at this temperature for 54 minutes. During the heat treatment at 2800° C. the fiber was held under tension and was stretched by 18%. Another portion of the 1200° C. fiber also was heated to 2800° C. under the same condition that above, but a stress was not imposed on this fiber. This 2800° C. fiber exhibited a modulus of 23×10^5 kg./cm.², but the stretched 2800° C. fiber a modulus higher by 24% than this modulus.

Example 20a

A portion of the carbon fiber obtained in Example 17 was heated in a flow of nitrogen gas from 1500° C. to 2900° C. at a rate of 560° C./hr. and at 2900° C. for 20 minutes. During the heat treatment at 2900° C. the fiber was held under tension and was stretched by 26%. Another portion of the carbon fiber obtained in Example 17 was heated to 2900° C. under the same condition that above, but a stress was not imposed on this fiber. This fiber exhibited a modulus of 24.1×10^5 kg./cm.², but the stretched 2900° C. fiber a modulus higher by 28% than this value.

Example 21

A bundle-like mass of the dehydrated polyvinyl alcoholic fiber obtained in Example 14 was heated in a flow of acidic atmosphere containing 6.0 of hydrochloric acid and 94% of nitrogen gas from 200° C. to 650° C. at a rate of 240° C./hr. and from 650° C. to 1300° C. at a rate of 350° C./hr. The fiber was held at 1300° C. for 30 minutes. The tensile strength of this fiber was 10.8×10^3 kg./cm.² and the yield of was 42%.

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Example 22

A bundle-like mass of yarns of polyacrylonitrile filamentary fiber (5 denier per filament and bright) was heated in a flow of hydrochloric acid vapor from 160° C. to 420° C. at a rate of 120° C./hr. and was held at this latter temperature for 10 minutes. The blackened fiber obtained was thermally stable, flexible and electrically semiconductive. The yield was 88%.

Example 23

Bundle-like masses of filamentary fiber of acrylic polymer material containing 85% of acrylonitrile and 15% of methylmethacrylate by weight of monomer in polymer form (1.5 denier per filament and bright) was heated in a flow of acidic atmosphere containing 40% of hydrochloric acid and 60% of nitrogen gas by volume or in a stream of atmosphere containing only nitrogen from 200° C. to 440° C. at a rate of 180° C./hr. This 440° C. fibers were further heated in a flow of nitrogen gas to 800° C. at a rate of 250° C./hr. The tensile strength and yield of the 800° C. fiber with the treatment in acidic atmosphere were 8.6×10^3 kg./cm.² and 70%, respectively. This yield corresponded to 152% of the yield of the 800° C. fiber without the heat treatment in acidic atmosphere. Another portion of the same starting fiber that used above also was heated under the same conditions that in the case of the fiber with the treatment in acidic atmosphere mentioned above, but this fiber was imposed stress, during the heat-treatment from 200° C. to 440° C. The linear shrinkage of the 440° C. fiber with the treatment of imposing stress was 38% of that of the 440° C. without the treatment of imposing stress. The 800° C. fiber with the treatment of imposing stress exhibited a tensile strength of 12.4×10^3 kg./cm.².

Example 24

A bundle-like mass of continuous filament of acrylic material containing 90% of acrylonitrile and 10% of vinyl chloride was heated in a flow of acidic atmosphere containing 20% of hydrochloric acid and 80% of nitrogen from 200° C. to 500° C. at a rate of 40° C./hr. and from 500° C. to 750° C. at a rate of 200° C./hr. The yield of the 750° C. fiber was 68%, which corresponded to 148% of the yield of the 750° C. fibrous mass obtained by heating another portion of the same starting fiber that used above solely in nitrogen under the same condition of raising temperature. This fiber exhibited a tensile strength desired for industrial needs.

Example 25

A plain weave fabric woven relatively loosely of warps and files of staple fiber threads of acrylic fibrous material containing 80% of acrylonitrile (3 denier per single staple fiber) was treated with an aqueous dispersion of silica fine particle powder to substantially fill the voids among staple fibers. After it had been dried in an oven, the fabric was heated in a flow of hydrochloric acid vapor from 250° C. to 350° C. at a rate of 60° C./hr. and from 350° C. to 480° C. at a rate of 10° C./hr. From this 480° C. fabric, silica powder solids were removed by washing successively the fabric with an aqueous solution of hydrofluoric acid and with water. The fabric obtained exhibited a high flexibility and thermal stability. The yield was 83%, which corresponded to 157% of the yield of fabrics (brittle) obtained by heating another portion of the same starting fabric that above solely in nitrogen.

Example 26

The flexible fabric obtained in Example 25 was heated in a flow of acidic atmosphere containing 10% of hydrochloric acid and 90% nitrogen from 480° C. to 800° C. at a rate of 160° C./hr. and from 800° C. to 1200° C. at a rate of 200° C./hr. The carbon fabric having a high flexibility was obtained.

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Example 27

A bundle-like mass of filamentary fiber of polyacrylonitrile (2 denier per filament) was preoxidized by being heated in air at 200° C. for 5 hours and from 200° C. to 300° C. at a rate of 100° C./hr. The blackened fiber was obtained. This fiber was further heated in a flow of hydrochloric acid from 200° C. to 500° C. at a rate of 460° C./hr. The yield of this 500° C. fiber was 85% by weight, which corresponded to 138% of the yield of the 500° C. fiber obtained by heating another portion of the same starting fiber that used above under the same condition of raising temperature that employed above in air and then in nitrogen.

Example 28

A bundle-like mass of filamentary fiber prepared from acrylic polymer material containing 95% of acrylonitrile, having a substantially parallel fiber orientation was heated in air at 200° C. for 5 hours, and from 200° C. to 300° C. at a rate of 100° C./hr. After that, the fiber was heated a stream of acidic atmosphere of 40% of hydrochloric acid and 60% of nitrogen from 300° C. to 900° C. at a rate of 320° C./hr., and then in nitrogen from 900° C. to 1200° C. at a rate of 420° C./hr. The yield was 63%. The tensile strength was 11.0×10^3 kg./cm.². These yield and tensile strength corresponded to 121% and 128% of the yield and tensile strength of the 120° C. fiber obtained by heating another portion of the same preoxidized fiber that used above only in nitrogen from 300° C. to 1200° C. under the same conditions of raising temperature that employed above, respectively.

Example 29

A polyacrylonitrile filamentary fiber mass was heated in a flow of acidic atmosphere containing 40% of chlorine gas and 60% of nitrogen at 200° C. for 30 minutes and then at 240° C. for 10 minutes. A blackened fiber was obtained. This fiber was heated in a flow of acidic gas containing 10% of hydrochloric acid and 90% of nitrogen from 250° C. to 460° C. at a rate of 5° C./hr., from 460° C. to 800° C. at a rate of 60° C./hr., and from 800° C. to 1300° C. at a rate of 180° C./hr. The tensile strength and the yield of the 1300° C. fiber were 9.1×10^3 kg./cm.² and 58%, respectively. These values corresponded to 128% and 124% of the tensile strength and the yield of the 1300° C. fiber obtained by heating only in nitrogen another portion of the same 240° C. fiber preoxidized with chlorine that obtained above, respectively.

Example 30

A continuous yarn of acrylonitrile filamentary fiber was preoxidized by being moved in air through a heating zone from 190° C. to 260° C. in 30 minutes with imposed stress or without imposed stress. After that, the preoxidized yarns were heated by being moved through a zone from 260° C. to 450° C. in a flow of hydrochloric acid vapor in 45 minutes, and then through a zone from 450° C. to 940° C. in a stream of nitrogen in 40 minutes. The linear shrinkage of the fiber with the treatment of imposing stress during the heat treatment to 450° C. was 26% of that of the 450° C. fiber without the treatment of imposing stress. The 940° C. fiber with the treatment of imposing stress exhibited a tensile strength of 12.8×10^3 kg./cm.², and the 940° C. fiber without the treatment of imposing stress a tensile strength of 11.6×10^3 kg./cm.². The yield was 67%, which corresponded to 124% of that of the 940° C. fiber obtained by heating only in nitrogen from 260° C. to 940° C.

Example 31

A portion of the continuous yarns of 940° C. carbon fiber prepared by heating another portion of the same starting fiber that used in Example 30 under the same condition that employed in Example 30 were heated by being moved in an argon flow through a zone from 1000°

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C. to 2500° C., and in 45 minutes through a zone at 2500° C. During the heat treatment at 2500° C., the fiber was imposed stress and was stretched by 28%. Another portion of the 940° C. carbon fiber yarn was heated to 2500° C. under the same condition than employed above, but without imposed stress at 2500° C. The stretched fiber exhibited a modulus 20.8×10^5 kg./cm.², which corresponded to 108% of that of the unstretched fiber.

Example 32

Continuous yarns of acrylic filaments were heated by being moved in air through a zone from 180° C. to 300° C. in 40 minutes with imposed stress or without imposed stress. The preoxidized fiber yarns were heated in a flow of acidic atmosphere containing 80% of hydrochloric acid and 20% of nitrogen through a heating zone from 300° C. to 560° C. in 90 minutes, through a heating zone from 560° C. to 1100° C. in 60 minutes and through a zone at 1100° C. in 16 minutes. The linear shrinkage of the 300° C. fiber with the treatment of imposing stress was 25% of that of the 300° C. fiber without the treatment of imposed stress. The yield and the tensile strength of the 1100° C. fiber with the treatment of imposing stress were 62% and 14.6×10^3 kg./cm.², respectively. The tensile strength of the 1100° C. fiber without the treatment of imposing stress was 11.3×10^3 kg./cm.².

Example 33

A portion of the carbon yarn with the treatment of imposing stress obtained in Example 31 was heated by being moved, in a nitrogen flow, through a zone from 1100° C. to 27° C., and in 55 minutes through a 2700° C. zone. During the heat treatment at 2700° C. the fiber was imposed stress and stretched by 18%. The stretched fiber exhibited a modulus higher by 24% than that, 21.9×10^5 kg./cm.², of the unstretched fiber.

Example 34

A continuous yarn of filamentary fiber of acrylic material containing 95% of acrylonitrile by weight of monomer in polymer form was heated by being moved through a zone from 190° C. to 450° C. in 40 minutes with imposed stress in an acidic atmosphere containing 50% of hydrochloric acid and 50% of nitrogen by volume. The 450° C. yarn was further heated by being moved successively through a zone from 450° C. to 800° C. in 30 minutes and through a zone from 800° C. to 1200° C. in 25 minutes. The linear shrinkage of the 450° C. fiber with the treatment of imposing stress during the heat treatment to 450° C. was 48% of the shrinkage of the 450° C. fiber without the treatment of imposing stress. The 800° C. fiber with the treatment of imposing stress exhibited a tensile strength of 12.8×10^3 kg./cm.² and a modulus of 13.8×10^5 kg./cm.².

Example 35

The carbon yarn obtained in Example 33 was heated in an argon stream, in a tunnel furnace, by raising the temperature from 1500° C. to 3000° C. at a rate of 400° C./hr. and then by holding at 3000° C. for 30 minutes. During the heat treatment at 3000° C., the fiber yarn was held under tension and was stretched by 26% by length. This carbon fiber exhibited a modulus higher by 34% than that, 23×10^5 kg./cm.², of the unstretched fiber.

I claim:

1. A process for the preparation of a carbonaceous fiber which comprises treating a fiber selected from the group consisting of polyvinyl alcoholic and acrylic fibers in an atmosphere containing from 10 to 100% hydrogen chloride, the remainder being inert gas, said atmosphere flowing over said fiber at a rate sufficient to remove gases resulting from decomposition of said fiber, at a temperature between 150° and 1500° C.

2. A process according to claim 1 where in the fiber is stretched at temperatures below 450° C. during the treatment with hydrogen chloride.

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3. A process wherein the product of claim 1 is heated in an inert atmosphere at temperatures up to 300° C.

4. A process according to claim 3 wherein the fiber is stretched at temperatures between 2500° C. and 3000° C.

5. A process according to claim 4 wherein the stretching is between 5 and 40%.

6. A process according to claim 1 wherein the fiber is polyvinyl alcoholic.

7. A process according to claim 6 wherein the polyvinyl alcoholic fiber is partially oxidized before the hydrogen chloride treatment.

8. A process according to claim 1 wherein the fiber is acrylic.

9. A process according to claim 1 wherein the acrylic fiber is partially oxidized before the hydrogen chloride treatment.

10. A process according to claim 8 wherein the acrylic fiber is polyacrylonitrile.

11. A process according to claim 6 wherein the poly-

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vinyl alcoholic fiber is treated with the hydrogen chloride atmosphere at temperatures between 150° and 450° C.

12. A process according to claim 8 wherein the acrylic fiber is treated with the hydrogen chloride atmosphere at temperatures between 250° C. and 450° C.

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EDWARD J. MEROS, Primary Examiner

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8—115.5, 116; 23—209.2

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,529,934 Dated September 22, 1970

Inventor(s) AKIO SHINDO

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

Column 15:

Claim 3, change "calim" to -- claim --;

line 2 - change "300°C" to -- 3000°C --.

SIGNED AND
SEALED
JAN 5 1971

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents