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PROCESS FOR THE CARBONIZATION OF A STABILIZED
ACRYLIC FIBROUS MATERIAL
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3,677,705

FIG. 1



FIG. 2



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3,677,705

PROCESS FOR THE CARBONIZATION OF A STABILIZED ACRYLIC FIBROUS MATERIAL
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24 Claims

ABSTRACT OF THE DISCLOSURE

A process is provided for the rapid conversion of a continuous length of an inherently hygroscopic stabilized acrylonitrile homopolymer or copolymer to a carbonized form exhibiting improved physical properties. The stabilized starting material is supplied in an essentially anhydrous form immediately prior to its passage through a heating zone containing an inert atmosphere in which its temperature is relatively rapidly elevated to produce a carbonized fibrous material. The resulting continuous length of carbonized fibrous material may be subsequently converted to a continuous length of fibrous graphitic carbon possessing superior properties.

BACKGROUND OF THE INVENTION

The present invention represents an improvement over the carbonization or carbonization and graphitization process disclosed in U.S. Ser. No. 777,275, filed Nov. 20, 1968, of Charles M. Clarke, entitled "Process for the Continuous Carbonization of a Stabilized Acrylic Fibrous Material," which is assigned to the same assignee as the present invention.

In the past, procedures have been proposed for converting a stabilized acrylic fibrous precursor to a carbonized form in which elements in the stabilized material other than carbon, e.g. nitrogen, hydrogen, and oxygen are expelled. The term "carbonized fibrous material" as used herein is defined to be a product consisting of at least about 90 percent carbon by weight, and preferably at least about 95 percent carbon by weight.

The carbonization procedures of the prior art have been conducted on both batch and continuous bases, and have tended to require excessive heating times. See, for instance, U.S. Pat. No. 3,285,696 to Tsunoda which discloses the heating of a blackened preoxidized acrylic fiber on a batch basis at a temperature between 700° C. and 1200° C. for not less than one hour in an inert atmosphere to form a carbonized fiber U.S. Pat. No. 3,313,597 to Cranch et al. discloses the carbonization of a polyacrylonitrile thread by heating to a temperature between about 700° C. and 1100° C. at a rate of temperature increase which must be below about 100° C. per hour. British Pat. No. 1,093,084 discloses a heating schedule for graphitizing a polyacrylonitrile fibrous material comprising slowly heating from 100° C. to 300° C. at a rate of increase of 10° to 55° C. per hour, and from 900° C. to around 3000° F. at a rate of up to 3000° C. per hour. British Pat. No. 1,110,791 discloses a batch carbonization procedure in which a bundle of preoxidized polyacrylonitrile fibers is heated from 200° C. to 1000° C. in 24 hours. Belgian Pat. No. 690,072 discloses heating a preoxidized acrylic fibrous precursor from 400° C. to 720° C. or 1000° C. at a rate of 0.5° C. per minute to form a carbonized product. Belgian Pat. No. 700,655 discloses the continuous carbonization of an acrylonitrile copolymer in which the temperature is elevated from 300° C.

to 1000° C. in 45 minutes, and from 1000° C. to 1485° C. in 25 minutes.

It is an object of the invention to provide an improved process for the carbonization of a stabilized acrylic fibrous material.

It is another object of the invention to provide a continuous process for the carbonization of a continuous length of a stabilized acrylic fibrous material which may be conducted on a rapid and economical basis to form a fibrous product exhibiting improved physical properties.

It is a further object of the invention to provide an efficient process for converting a continuous length of a stabilized acrylic fibrous material to a graphitized product of high tenacity and high modulus.

These and other objects, as well as the scope, nature and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF INVENTION

It has been found in a process for the continuous carbonization of an inherently hygroscopic stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprising continuously passing a continuous length of the stabilized acrylic fibrous material having a temperature within the range of about 20 to about 500° C. through a heating zone provided with an inert atmosphere in which the fibrous material is raised within a period of about 3 seconds to about 10 minutes to a temperature within the range of about 900 to about 1600° C. to form a continuous length of carbonized fibrous material, that an improved product is achieved if the continuous length of stabilized acrylic fibrous material is supplied to the heating zone in an essentially anhydrous form. A graphitized fibrous material may optionally be formed by subsequently passing the carbonized fibrous material through a heating zone provided with an inert atmosphere in which the carbonized fibrous material is heated at a temperature within the range of about 2400 to about 3100° C. until substantial graphitic carbon is formed. In a preferred embodiment of the invention the stabilized acrylic fibrous material while in an essentially anhydrous form is continuously passed through a heating zone provided with a temperature gradient in which both carbonization and graphitization are relatively rapidly achieved.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph made with the aid of a scanning electron microscope of a graphite fiber produced in accordance with the present invention wherein the stabilized acrylic precursor was introduced into the carbonization zone in an essentially anhydrous form.

FIG. 2 is a photograph made with the aid of a scanning electron microscope of a graphite fiber wherein the stabilized acrylic precursor was introduced into the carbonization zone while in intimate association with a substantial quantity of moisture adhering thereto.

DETAILED DESCRIPTION OF THE INVENTION

The disclosure of U.S. No. 777,275, filed Nov. 20, 1968, of Charles M. Clarke is herein incorporated by reference. The present process represents an improvement over the process disclosed therein.

The continuous length of acrylic fibrous material which is carbonized or carbonized and graphitized in accordance with the present invention is preliminarily stabilized to a

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heat-resistant form, and supplied in an essentially anhydrous form to the heating zone in which a continuous length of carbonized product is produced. The term "stabilized acrylic fibrous material" as used herein is defined as an acrylic fibrous material which is non-burning when subjected to an ordinary match flame and capable of undergoing carbonization while retaining its original fibrous configuration essentially intact. The stabilization reaction may be conducted by heating the acrylic fibrous material at relatively moderate temperatures. Such a stabilization procedure is commonly conducted in a presence of oxygen and results in the formation of a preoxidized product which exhibits thermal stability not exhibited by the unmodified acrylic material. U.S. Ser. Nos. 749,957, filed Aug. 5, 1968 of Dagobert E. Stuetz; 749,959, filed Aug. 5, 1968 of Michael J. Ram (now U.S. Pat. No. 3,539,295); 750,018, filed Aug. 5, 1968 of Michael J. Ram and Richard N. Rulison (now abandoned); and 760,658, filed Sept. 18, 1968 of John P. Riggs disclose suitable stabilization procedures. Each of the above-identified applications is assigned to the same assignee as the instant invention and is herein incorporated by reference. Other stabilization procedures capable of imparting thermal stability to the acrylic material may be selected. For instance, stabilization procedures catalyzed by Lewis acids such as disclosed in U.S. Ser. No. 777,901 (now U.S. Pat. No. 3,592,595) and No. 777,902, filed Nov. 21, 1968 of Klaus H. Gump and Dagobert E. Stuetz may be utilized.

The stabilized acrylic fibrous material is derived from a polymeric material formed primarily of recurring acrylonitrile units. For instance, the acrylic fibrous material should generally contain at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith, such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like. In a particularly preferred embodiment of the invention the stabilized acrylic fibrous material is derived from an acrylonitrile homopolymer. Preferred acrylonitrile copolymers contain at least about 95 mol percent of acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith. Particularly preferred copolymers contain no more than about 1 mol percent of one or more monovinyl comonomers copolymerized with acrylonitrile.

The continuous length of stabilized acrylic fibrous material which is carbonized or carbonized and graphitized in accordance with the present invention may be in any one of a variety of configurations. For instance, single continuous filaments, yarns, or tapes may be utilized. In a preferred embodiment of the invention, the stabilized acrylic fibrous material is in the form of a continuous filament yarn. Such a yarn may be formed prior to stabilization by conventional techniques which are well known to those skilled in the art. For instance, dry spinning or wet spinning techniques may be employed. The yarn may optionally be provided with a twist which improves its handling characteristics. For example, a twist of about 0.1 to 3 t.p.i., and preferably about 0.1 to 1.0 t.p.i., may be utilized.

The acrylic fibrous material which serves as the starting material may be highly oriented prior to stabilization. For instance, the starting material may be highly oriented by hot drawing to a relatively high single filament tensile strength of at least about 4 grams per denier (e.g. 4 to 9 grams per denier) prior to stabilization.

The stabilized acrylic fibrous materials commonly used as starting materials in the production of carbonized products have been found to be hygroscopic in nature. When exposed to the atmospheric for even short periods of time (e.g. a few minutes), substantial quantities of water become absorbed by the same. The hygroscopic properties of the stabilized materials are generally not exhibited by the acrylic fibrous materials prior to their

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stabilization. For instance, when the unstabilized fibrous acrylic starting materials are placed in air having a temperature of 70° F., and a relative humidity of 65 percent, moisture gain of only about 0.5 percent by weight has been observed. However, following stabilization a moisture gain of about 11 to 15 percent by weight based upon the weight of the dry yarn has been observed under identical conditions.

The exact nature of the absorption phenomena between the stabilized acrylic fibrous materials and water is considered complex and incapable of simple explanation. It is believed, however, that hydrogen bonding may exist between oxygen present in the stabilized acrylic fibrous materials and the water molecules. For instance, it has been observed that the maximum quantity of water picked up by a given sample of stabilized acrylic fibrous material, is generally directly proportional to the bound oxygen content of the same as determined by the Unterzaucher analysis. After 3 hours a stabilized acrylic yarn having a bound oxygen content of 12.2 percent by weight was found to have picked up about 11 percent water by weight, while a stabilized acrylic yarn having a bound oxygen content of 14.8 percent by weight was found to have picked up about 15 percent water by weight under the same conditions. It is also possible that some degree of chemisorption may occur between the stabilized acrylic fibrous materials and water.

It has been found that if the stabilized acrylic fibrous material which is introduced into the heating zone utilized to produce carbonization is in an essentially anhydrous form, then a carbonized or carbonized and graphitized product of improved physical properties is achieved. The presence of an appreciable quantity of absorbed water in intimate association with the stabilized acrylic fibrous material is believed to result in a rapid, destructive volatilization of the water in the heating zone which is capable of generating voids and strength reducing flaws. In accordance with the present invention this possibility for void or flaw generation is effectively obviated.

From the time of the formation of the stabilized acrylic fibrous material to the time of its introduction into the heating zone utilized to produce a carbonized product, it may be maintained under substantially anhydrous conditions so that its essentially anhydrous form is preserved. For instance, the continuous length of stabilized material may be stored exclusively under substantially anhydrous conditions or passed directly from the stabilization zone to the heating zone utilized to produce carbonization through a hermetically sealed tube from which water vapor is excluded. Heretofore it has been a common practice to expose the stabilized acrylic fibrous material to ambient conditions whereby moisture is picked up prior to its introduction into the heating zone (i.e. carbonization zone). For instance, the stabilized material has commonly been stored under ambient conditions and/or conveyed to the carbonization zone while in contact with moisture containing air.

Should the continuous length of stabilized acrylic fibrous material be exposed to atmospheric conditions, then it is essential that absorbed water be removed from the same prior to carrying out the carbonization step of the present process. The absorbed water may be removed by the controlled drying of the material prior to supplying the same to the heating zone in which a carbonized product is formed. Suitable drying may be conducted by heating the material under relatively mild conditions until an essentially anhydrous form of the same is produced. The drying may be carried out by subjecting the stabilized fibrous material to a relatively constant drying temperature, or to a drying temperature profile (i.e. gradient) in which the temperature is gradually or incrementally raised. The drying conditions selected are such that the physical properties of the fibrous material are not ad-

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versely influenced; i.e. the volatilization of water is not so rapid as to harm the same.

The drying of the hygroscopic stabilized acrylic fibrous material may be conveniently conducted on either a batch or a continuous basis. For instance, continuous lengths of the fibrous material may be placed in a circulating air oven for several hours (e.g. at least about two hours) while wound upon a bobbin or support. The temperature of the fibrous material under such circumstances is preferably below that at which additional pre-oxidation will occur to an appreciable degree. Preferred batch drying temperatures are about 80 to 150° C., and about 105 to 115° C. in a particularly preferred embodiment of the invention. If one chooses to conduct the drying under reduced pressure conditions, e.g. 25 inches of mercury, correspondingly lower temperatures may be conveniently selected as will be apparent to those skilled in the art.

When utilizing a continuous in line drying procedure, the hygroscopic stabilized acrylic fibrous material may be passed through a drying zone positioned immediately in front of the heating zone in which carbonization occurs. For instance, a plurality of muffle furnaces placed end to end and provided with a circulating air atmosphere at progressively increasing temperatures as the fibrous material approaches the carbonization zone may be selected. The temperature profile (i.e. gradient) within the drying furnace may conveniently range from about 150 to 400° C., and preferably from about 200 to 350° C. Alternatively, the hygroscopic stabilized fibrous materials may be passed through a drying oven positioned immediately in front of the heating zone (i.e. carbonization zone) which is provided at a relatively constant drying temperature, preferably below about 300° C., e.g. about 150 to 275° C. Continuous in line drying times are preferably about 2 to 10 minutes depending upon the temperature, pressure, configuration of the continuous length of fibrous material, and the quantity of moisture adhering to the same.

If the drying zone is positioned at a location removed from the heating zone in which carbonization occurs, then the dried material is conveyed to carbonization zone under conditions whereby its essentially anhydrous form is preserved. A hermetically sealed tube from which water vapor is excluded may be selected for this purpose. If desired, the dried stabilized material may be stored under anhydrous conditions prior to transfer to the carbonization zone.

The continuous length of hygroscopic fibrous material while in an essentially anhydrous form is rapidly carbonized by increasing its temperature from within the range of about 20 to about 500° C. to a temperature within the range of about 900 to 1600° C. (preferably to a temperature within the range of about 1400 to about 1600° C.), within a period of about 3 seconds to about 10 minutes, and preferably within a period of about 3 seconds to about 5 minutes. The process is conducted by passing the continuous length of stabilized acrylic fibrous material through a heating zone capable of producing the requisite heating which is provided with an inert atmosphere. Suitable inert atmospheres in which the carbonization reaction may be conducted include nitrogen, argon, helium, etc. During the carbonization reaction elements present in the continuous length of stabilized acrylic fibrous material other than carbon, e.g. nitrogen, hydrogen, and oxygen, are expelled to a substantial degree.

A carbonized fibrous product which retains essentially the same configuration as the starting material is produced. If the stabilized acrylic fibrous material is raised from a temperature within the range of about 20 to about 500° C. to a temperature within the range of about 900 to about 1600° C. in less than about 3 seconds, then the physical properties of the resulting product are adversely affected. If the period of temperature elevation is more

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than about 30 seconds, then any further improvement in physical properties resulting from the slower rate of temperature increase generally tends to be slight. Periods of temperature increase greater than about 10 minutes are generally to be avoided because of economic considerations.

In a preferred embodiment of the process suitable mean heating rates for elevating the stabilized acrylic fibrous material to a temperature of about 1400 to about 1600° C. range from about 2° C. per second to about 300° C. per second. In a particularly preferred embodiment of the invention, the continuous length of acrylic fibrous material is heated to a temperature of about 1400 to about 1600° C. in about 20 to about 60 seconds. Particularly preferred mean heating rates for heating to a temperature of about 1400 to about 1600° C. accordingly range from about 23° C. per second to about 45° C. per second. The heating rates employed need not be constant, but may be varied within the period of temperature elevation. Particularly satisfactory results have been achieved when the rate is progressively increased. The continuous length of stabilized acrylic fibrous material undergoing treatment may be maintained at a temperature within the range of about 900 to about 1600° C. for about 3 seconds to about 5 minutes to produce a carbonized fibrous product which is ready for use, or exposed to a more highly elevated temperature in the same or a different heating zone to form a carbonized and graphitized product as discussed in detail hereafter. In a further embodiment of the invention the continuous length of stabilized fibrous material is heated to a temperature within the range of about 1400 to 1600° C. where it is maintained for about 3 seconds to about 60 seconds to produce a carbonized fibrous material. The carbonized fibrous material optionally may next be continuously passed through an inert atmosphere where it is heated at a temperature of about 2400° to 3100° C. until substantial graphitic carbon is formed.

In a preferred embodiment of the process a carbonized and graphitized product is formed by passing a continuous length of the fibrous material in an essentially anhydrous form through a heating zone provided with an inert atmosphere and a temperature gradient in which the fibrous material is initially raised within a period of about 3 seconds to about 10 minutes from a temperature in the range of about 20 to 500° C. to a temperature within the range of about 900 to 1600° C. to form a continuous length of carbonized fibrous material, and in which the carbonized fibrous material is subsequently raised to a temperature within the range of about 2400 to about 3100° C. where it is maintained until substantial graphitization occurs. The presence of graphitic carbon may be detected by the characteristic X-ray diffraction pattern of graphite. Suitable inert atmospheres include nitrogen, argon, helium, etc. A graphitized product of superior modulus may generally be formed in about 10 seconds to about 1 minute while heating at about 2400 to about 3100° C. Longer graphitization heating times may be used if desired. The modulus of the graphitized product tends to increase with the maximum temperature achieved during graphitization. The temperature of the continuous length of fibrous material is preferably progressively increased from a temperature within the range of about 900 to about 1600° C. (preferably about 1400 to about 1600° C.) to the graphitization temperature within a period of about 2 seconds to about 30 seconds.

The equipment utilized to produce the requisite heating to carry out the process of the invention may be varied widely. It is essential that the apparatus selected be capable of producing the required temperatures while excluding the presence of an oxidizing atmosphere. For instance, suitable apparatus include induction furnaces, tube furnaces in which a hollow graphite susceptor is heated by direct resistance heating, direct resistance heating ap-

paratus in which electric current is passed directly through the fibrous material, apparatus capable of producing reducing flames, electric arc furnaces, lasers, thermal image equipment such as solar furnaces, apparatus capable of producing low temperature plasma flames, and the like. The continuous length of fibrous material undergoing treatment is passed through one or more heating apparatus and subjected to the requisite temperatures. A temperature profile (i.e. a gradient) may be provided within a given heating apparatus, or the material may be successively passed through a series of apparatus maintained at progressively increasing temperatures.

In a preferred embodiment the stabilized acrylic fibrous material while in an essentially anhydrous form is heated by use of an induction furnace. In such a procedure, the continuous length stabilized material is passed through a hollow graphite tube or susceptor which is situated within the windings of an induction coil. By varying the length of the graphite susceptor, the length of the induction coil, and the rate at which the material is passed through the susceptor, many apparatus arrangements capable of carrying out the present process may be selected. For large scale production, it is of course preferred that relatively long susceptors be used so that the continuous length of material may be more rapidly passed through the same while being heated. Care must be taken to provide a susceptor of sufficient length to insure that the rate of temperature increase is not so rapid that a product of adequate tenacity is unachievable. When producing a carbonized and graphitized product, adequate provision must be made for reaching the highly elevated temperatures if a product of maximum modulus is desired. Also, when a carbonized and graphitized product is produced in accordance with the present invention, it is preferred that moderate tension be applied to the continuous length of material undergoing treatment.

The following examples are given as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

EXAMPLE I

A continuous length of 800 fil. water washed dry spun acrylonitrile homopolymer continuous filament yarn having a total denier of 1040 was selected as the starting material. The yarn was highly oriented and drawn to a single filament tenacity of about 8.2 grams per denier. The yarn was continuously stabilized in accordance with the teachings of U.S. Ser. Nos. 749,957 and 749,959, filed Aug. 5, 1968, of Dagobert E. Stuetz and Michael J. Ram, respectively, which are assigned to the same assignee as the present invention and are herein incorporated by reference. During the stabilization reaction (i.e. preoxidation) the yarn was continuously passed in the direction of its length through a muffle furnace provided with an air atmosphere at 285° C. for a residence time of 42 minutes, and then passed through a skewed roll oven provided with an air atmosphere at 335° C. for a residence time of 5 minutes. During the stabilization procedure the yarn was allowed to shrink approximately 4 percent in length. The resulting stabilized yarn was black in appearance, contained a bound oxygen content of 9 percent by weight as determined by the Unterzaucher analysis, and was non-burning when subjected to an ordinary match flame.

The stabilized yarn was exposed to ambient conditions (i.e. 25° C. and about 60 percent relative humidity) for 48 hours, and upon testing was found to be highly hygroscopic in nature and to have picked up approximately about 11.3 percent moisture by weight based upon the weight of the yarn when free of moisture.

The hygroscopic stabilized yarn was dried on a batch basis to an essentially anhydrous form by heating at 110° C. while wound upon a support and present in a forced air drying oven for a residence time of 140 hours.

The dried stabilized yarn immediately thereafter was passed in the direction of its length through a heating zone (i.e. carbonization zone) where it was converted to a carbonized form containing 93 percent carbon by weight and exhibiting an essentially amorphous X-ray diffraction pattern. Exposure of the dried yarn to a moisture containing atmosphere prior to its introduction into the carbonization zone was avoided by passage under an infra red lamp. The yarn was accordingly in an essentially anhydrous form and at a temperature of about 80° C. when introduced into the heating zone. The apparatus utilized to produce carbonization comprised a stainless steel tube having a length of 48 inches, an inner diameter of 0.42 inch, and an outer diameter of 0.50 inch. A pair of electrodes were connected to the stainless steel tube at each end and were connected to an AC power source of 10 volts and 5 amps. A temperature gradient existed within the stainless steel tube having a maximum temperature of 1250° C. situated from about 12 to 36 inches from the entrance end. An inert atmosphere of argon was provided within the stainless steel tube. Air was substantially excluded from the tube by purging with argon.

The dried yarn was continuously passed through the heating zone at a rate of 0.5 meter per minute (i.e. at about 20 inches per minute). A tension of 100 grams was exerted upon the dried stabilized yarn as it passed through the heating zone. The yarn was raised from a temperature of 80° C. to a temperature of 1250° C. in approximately 36 seconds.

The carbonized yarn was next passed through a Lepel 450 kc. induction furnace utilizing a 20 kw. power source. The induction furnace comprised a 10 turn water cooled copper coil having an inner diameter of $\frac{3}{4}$ inch and a length of 2 inches, and a hollow graphite tube suspended within the coil having a length of 8½ inches, an outer diameter of $\frac{1}{2}$ inch and an inner diameter of $\frac{1}{8}$ inch through which the carbonized yarn was continuously passed. The copper coil which encompassed a portion of the hollow graphite tube was positioned at a location essentially equidistant from the respective ends of the graphite tube. An inert atmosphere of nitrogen was maintained within the induction furnace. Air was substantially excluded from the induction furnace by purging with nitrogen. The carbonized yarn was passed through the induction furnace at a rate of about 1.5 inches per minute. The carbonized yarn was raised to a maximum temperature of approximately 2900° C. while present within the induction furnace at which temperature it was maintained for approximately 40 seconds. A tension of 100 grams was exerted upon the carbonized yarn as it passed through the induction furnace. While present within the induction furnace the carbonized yarn was converted to a substantially graphitic form as evidenced by the characteristic X-ray diffraction pattern of graphite. The resulting graphitized yarn exhibited a single filament tenacity 11.3 grams per denier, and a single filament initial modulus of 2800 grams per denier.

In a comparative run Example I was repeated with the exception that the hygroscopic stabilized yarn was not dried prior to introduction into the carbonization zone. Following graphitization the yarn exhibited a single filament tenacity of 9.7 grams per denier and a single filament initial modulus of 3200 grams per denier. The comparison illustrates that a fiber of higher tenacity resulted when the process of the invention was practiced.

EXAMPLE II

Example I is repeated with the exception that the dried stabilized yarn is passed through the heating zone at the increased rate of 2.0 meters per minute (i.e. at about 80 inches per minute). The yarn was raised from a temperature of 80° C. to a temperature of 1250° C. in approximately 9 seconds. A photograph of a representative fiber from the graphitized yarn made with the aid of a scanning electron microscope at a magnification of 4400 is provided as FIG. 1. The resulting graphitized yarn ex-

hibited a single filament tenacity of 12.0 grams per denier and an initial modulus of 3100 grams per denier.

In a comparative run Example II was repeated with the exception that the hygroscopic stabilized yarn was not dried prior to introduction into the heating zone. Following graphitization the yarn exhibited a single filament tenacity of 6.8 grams per denier and an initial modulus of 2900. This comparison illustrates that a more accelerated heat-up rate during carbonization may be utilized when employing the process of the present invention while continuing to produce a more uniform fiber of improved tenacity. A photograph of a representative fiber from the graphitized yarn made with the aid of a scanning electron microscope at a magnification of 4400 is provided as FIG. 2. Numerous voids and continuity breaches are visible in FIG. 2 which are absent in fibers formed in accordance with the present invention (e.g. FIG. 1).

EXAMPLE III

A continuous length of preoxidized acrylonitrile homopolymer yarn substantially similar to that utilized in Example I was selected as the starting material. The yarn following preoxidation was exposed to ambient conditions and picked up approximately 11 to 12 percent water by weight.

The yarn was dried in an in line continuous manner immediately prior to its introduction into an induction furnace (i.e. heating zone) provided with an inert atmosphere and a temperature gradient wherein both carbonization and substantial graphitization occurred.

The preoxidized yarn containing substantial moisture adhering thereto was continuously unwound from a bobbin and introduced into a 48 inch muffle furnace provided with a circulating air atmosphere at 200° C. through which it was continuously passed in the direction of its length. The yarn was passed through the muffle furnace at a rate about 1 meter per minute (i.e. about 40 inches per minute). The preoxidized yarn was in an essentially anhydrous form as it left the muffle furnace.

Without exposure to ambient conditions the dried yarn was continuously introduced into the induction furnace. The dried yarn was continuously passed in the direction of its length through the induction furnace at a rate of about 1 meter per minute (i.e. about 40 inches per minute). A tension of about 0.41 gram per denier was exerted on the dried yarn as it passed through the induction furnace. The induction furnace comprised an Inductotherm model Integral 50 unit provided with a 50 kw. power source, a 12 turn water cooled copper coil having a length of 19 inches, a hollow graphite tube suspended within the coil having a length of 52 inches, an outer diameter of 3 inches, and an inner diameter of 0.75 inch. The copper coil which encompassed a portion of the hollow graphite tube was positioned at a location essentially equidistant from the respective ends of the graphite tube. An inert atmosphere of nitrogen was maintained within the induction furnace. Air was substantially excluded from the induction furnace by purging with nitrogen. The yarn was raised to a maximum temperature of 2850° C. while present within the induction furnace at which temperature it was maintained for approximately 12 seconds.

While present within the induction furnace, the preoxidized yarn was initially carbonized and subsequently converted to a substantially graphitic form as evidenced by the characteristic X-ray diffraction pattern of graphite. The resulting graphitized yarn exhibited a single filament tenacity of 13.0 grams per denier, and a single filament initial modulus of 3015 grams per denier.

In a comparative run Example III was repeated with the exception that the preoxidized yarn was not passed through a muffle furnace prior to its introduction into the induction furnace, and was accordingly undried when introduced into the induction furnace. The resulting graphitized yarn exhibited a single filament tenacity of 9.62 grams per denier, and a single filament initial modulus of 2900 grams per denier.

EXAMPLE IV

A continuous length of 1600 fil. unwashed dry spun acrylonitrile homopolymer continuous filament yarn having a total denier of 2,880 was selected. The yarn was highly oriented and had been drawn at a draw ratio of 5:1. The yarn was subjected to a heating treatment by passage for 6.5 minutes through a muffle furnace provided with air at 200° C. during which time the yarn shrank 10.5 percent in length.

The yarn was preoxidized on a continuous basis in the absence of shrinkage by passage for 160 minutes through a multi-wrap skewed roll oven provided with circulating air at 270° C. The stabilized yarn was black in appearance, non-burning when subjected to an ordinary match flame, and had a bound oxygen content of 9.7 percent by weight as determined by the Unterzaucher analysis.

The preoxidized yarn was exposed to ambient conditions (i.e. 25° C. and about 60 percent relative humidity) during which time the yarn picked up approximately 11.5 percent moisture by weight.

The preoxidized yarn was dried in an in line continuous manner immediately prior to its introduction into an induction furnace provided with an inert atmosphere and a temperature gradient wherein both carbonization and substantial graphitization occurred. The drying, carbonization, and graphitization were conducted as in Example III with the exception that the temperature in the drying zone was incrementally raised as the yarn approached the induction furnace and a yarn speed of 0.5 meter per minute (i.e. about 20 inches per minute) was utilized throughout.

The drying zone consisted of four 12 inch muffle furnaces placed in an end to end relationship and provided with circulating air at 200° C., 250° C., 300° C., and 340° C., respectively. During passage through the induction furnace a tension of 200 grams was maintained upon the dried yarn. The resulting graphitized yarn exhibited a denier per filament of 0.56, a single filament tenacity of 15.5 grams per denier, and a single filament initial modulus of 3130 grams per denier.

In a comparative run Example IV was repeated with the exception that the preoxidized yarn was not passed through the muffle furnaces prior to introduction into the induction furnace, and was accordingly undried. The resulting graphitized yarn exhibited a denier per filament of 0.89, a single filament tenacity of 14.2 grams per denier, and a single filament initial modulus of 2560 grams per denier.

The fibrous products of the present invention may be incorporated in a binder or matrix and serve as a reinforcing medium. Such resulting composite materials may accordingly serve as light-weight load bearing structural elements in high performance structures which find particular utility in the aerospace industry.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. In a continuous process for the carbonization of a hygroscopic stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprising continuously passing a continuous length of said stabilized acrylic fibrous material through a heating zone provided with an inert atmosphere in which said fibrous material is raised from a temperature within the range of about 20 to about 500° C. within a period of about 3 seconds to about 10 minutes to

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a temperature within the range of about 900 to about 1600° C. to form a continuous length of carbonized fibrous material, the improvement of supplying said continuous length of stabilized acrylic fibrous material to said heating zone in an anhydrous form.

2. A process according to claim 1 in which said continuous length of hygroscopic stabilized acrylic fibrous material is maintained under anhydrous conditions from the time of the formation of the same to the time said stabilized acrylic fibrous material is supplied to said heating zone.

3. A process according to claim 1 in which said hygroscopic stabilized acrylic fibrous material having a substantial quantity of water adhering thereto is dried on a batch basis at a temperature of about 80 to 150° C. until an anhydrous form of the same is produced prior to supplying said acrylic fibrous material to said heating zone.

4. A process according to claim 1 in which said hygroscopic stabilized acrylic fibrous material having a substantial quantity of water adhering thereto is dried by continuously passing the same through a drying zone at a temperature of about 150 to 400° C. until an anhydrous form of the same is produced prior to supplying said fibrous material to said heating zone.

5. A process according to claim 1 in which said hygroscopic stabilized acrylic fibrous material is derived from an acrylonitrile homopolymer.

6. A process according to claim 1 in which said hygroscopic stabilized acrylic fibrous material is derived from an acrylonitrile copolymer which contains at least about 95 mol percent of acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith.

7. A process according to claim 1 in which said continuous length of hygroscopic stabilized acrylic fibrous material is a yarn.

8. A process according to claim 1 in which said continuous length of hygroscopic fibrous material is raised within a period of about 3 seconds to about 5 minutes to a temperature within the range of about 900 to about 1600° C.

9. A process according to claim 1 in which said hygroscopic fibrous material is raised within a period of about 3 seconds to about 5 minutes to a temperature within the range of about 1400 to about 1600° C.

10. A process according to claim 1 in which said hygroscopic fibrous material is raised within a period of about 20 seconds to about 60 seconds to a temperature within the range of about 1400 to about 1600° C.

11. A process according to claim 10 in which said fibrous material is maintained at a temperature within the range of about 1400 to about 1600° C. for about 3 seconds to about 60 seconds.

12. A process according to claim 1 wherein said carbonized fibrous material is subsequently continuously passed through an inert atmosphere where it is heated at a temperature of about 2400 to 3100° C. until substantial graphitic carbon is formed.

13. In a continuous process for the graphitization of a hygroscopic stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprising continuously passing a continuous length of said fibrous material through a heating zone provided with an inert atmosphere and a temperature gradient in which said fibrous material is initially raised from a temperature within the range of about 20 to about 500° C. within a period of about 3 seconds to about 10 minutes to a temperature within the range of

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about 900 to about 1600° C. to form a continuous length of carbonized fibrous material, and in which said carbonized fibrous material is subsequently raised to a temperature within the range of about 2400 to about 3100° C. to form a continuous length of graphitized fibrous material, the improvement of supplying said continuous length of stabilized acrylic fibrous material to said heating zone in an anhydrous form.

14. A process according to claim 13 in which said continuous length of hygroscopic stabilized acrylic fibrous material is maintained under anhydrous conditions from the time of the formation of the same to the time said stabilized acrylic fibrous material is supplied to said heating zone.

15. A process according to claim 13 in which said hygroscopic stabilized acrylic fibrous material having a substantial quantity of water adhering thereto is dried on a batch basis at a temperature of about 80 to about 150° C. until an anhydrous form of the same is produced prior to supplying said acrylic fibrous material to said heating zone.

16. A process according to claim 13 in which said hygroscopic stabilized acrylic fibrous material having a substantial quantity of water adhering thereto is dried by continuously passing the same through a drying zone at a temperature of about 150 to 400° C. prior to supplying said fibrous material to said heating zone.

17. A process according to claim 13 in which said hygroscopic stabilized acrylic fibrous material is derived from an acrylonitrile homopolymer.

18. A process according to claim 13 in which said hygroscopic stabilized acrylic fibrous material is derived from an acrylonitrile copolymer which contains at least about 95 mol percent of acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith.

19. A process according to claim 13 in which said continuous length of hygroscopic stabilized acrylic fibrous material is a yarn.

20. A process according to claim 13 in which said temperature gradient within said heating zone initially raises said fibrous material within a period of about 3 seconds to about 5 minutes to a temperature within the range of about 900 to about 1600° C.

21. A process according to claim 13 in which said temperature gradient within said heating zone initially raises said fibrous material within a period of about 3 seconds to about 5 minutes to a temperature within the range of about 1400 to about 1600° C.

22. A process according to claim 13 in which said temperature gradient within said heating zone initially raises said fibrous material within a period of about 20 to about 60 seconds to a temperature within the range of about 1400 to about 1600° C.

23. A process according to claim 20 in which said temperature gradient within said heating zone subsequently raises said carbonized fibrous material from a temperature within the range of about 900 to 1600° C. within a period of about 2 to about 30 seconds to a temperature within the range of about 2400 to about 3100° C. where it is maintained for about 10 seconds to about 1 minute.

24. In a continuous process for the graphitization of a hygroscopic stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith comprising continuously passing a continuous length of said fibrous material through a heating zone provided with an inert atmosphere and a temperature gradient in which said fibrous material is initially raised from a temperature within the range of about 20 to about 500°

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C. within a period of about 20 to about 60 seconds to a temperature within the range of about 1400 to about 1600° C. where it is maintained for about 3 seconds to about 60 seconds to form a continuous length of carbonized fibrous material, and in which said carbonized fibrous material is subsequently raised from a temperature within the range of about 1400 to about 1600° C. within a period of about 2 to about 30 seconds to a temperature within the range of about 2400 to about 3100° C. where it is maintained for about 10 seconds to about 1 minute, the improvement of supplying said continuous length of stabilized acrylic fibrous material to said heating zone in an anhydrous form.

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