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3,539,295

THERMAL STABILIZATION AND CARBONIZATION OF ACRYLIC FIBROUS MATERIALS

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30 Claims

ABSTRACT OF THE DISCLOSURE

An improved process is provided for the stabilization of a fibrous material composed of an acrylic polymer. The fibrous acrylic material is subjected to a multiple stage preoxidation treatment in an oxygen containing atmosphere which has been found to produce a product which when carbonized or carbonized and graphitized possesses a tensile strength superior to that obtained if a single stage preoxidation treatment were selected for a similar residence time or if a multiple stage preoxidation treatment were conducted not in accordance with the invention. The initial preoxidation stage is carried out at a temperature below the critical temperature at which the fibrous configuration of the starting material would be destroyed until the fibrous material contains at least about 5 percent oxygen by weight. Such treatment beneficially modifies the starting material and imparts the requisite stability to the fibrous material to enable the subsequent stage of the process to be endured without deleterious results. Carbonized or carbonized and graphitized fibrous materials may be formed upon heating the stabilized product in an inert atmosphere. For example, fibrous products consisting of graphitic carbon may be produced having a high tenacity of at least about 14 grams per denier.

BACKGROUND OF INVENTION

In the past procedures have been proposed for the conversion of fibers formed from acrylic polymers to a modified form possessing enhanced thermal stability. Such modification has generally been accomplished by heating the fibrous material in an oxygen-containing atmosphere at moderate temperatures for extended periods of time. The resulting product may be suitable for use as an intermediate in the formation of carbonized fibrous materials, or for direct utilization as a fire resistant fiber. U.S. Pat. Nos. 2,913,802 to Barnett and 3,285,696 to Tsunoda disclose processes for the conversion of fibers of acrylonitrile homopolymers or copolymers to a heat resistant form. Such prior art stabilization techniques have commonly been directed to batch operations employing acrylonitrile copolymers. Belgian Pat. No. 700,655 discloses a procedure whereby a continuous length of an acrylonitrile copolymer may be continuously subjected to a preoxidation treatment to produce essentially complete oxygen saturation while maintained in air at a temperature not exceeding 250° C., e.g., three hours or more at 220° C.

The stabilization of fibers of acrylonitrile homopolymers and copolymers in an oxygen-containing atmosphere involves (1) an oxidative cross-linking reaction of adjoining molecules as well as (2) a cyclization reaction of pendant nitrile groups to a condensed dihydropyridine structure. While the reaction mechanism is complex and not readily explainable, it is believed that these two reactions occur concurrently, or are to some extent competing reactions.

The cyclization reaction is exothermic in nature and must be controlled if the fibrous configuration of the acrylic polymer undergoing stabilization is to be preserved.

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As indicated, prior art techniques have commonly overcome this difficulty by heating the fiber at moderate temperatures generally extended over many hours. However, such techniques have not been commercially attractive because of their excessive time requires. Also, upon subsequent carbonization or carbonization and graphitization of the previously stabilized fiber the ultimate product has tended to be of limited utility because of its low strength characteristics.

It is an object of the invention to provide an improved process for the stabilization of fibrous materials formed from acrylic polymers resulting in a product which when carbonized or carbonized and graphitized possesses superior tensile strength.

It is an object of the invention to provide an improved process for the flame-proofing of fibrous materials formed from acrylic polymers.

It is another object of the invention to provide an improved stabilization process for fibrous materials formed from acrylic polymers which results in a product which is suitable for carbonization, or carbonization and graphitization.

It is another object of the invention to provide a carbonized or carbonized and graphitized fibrous material possessing superior strength which is derived from an acrylic polymer.

It is another object of the invention to provide a process for the stabilization of a fibrous material formed from an acrylic polymer which in at least some of its embodiments may be conducted on a highly expeditious continuous basis.

It is a further object of the invention to provide a stabilized lightweight fibrous material which is capable of end use applications in the aerospace industry.

It is a further object of the invention to provide a process for the efficient conversion of acrylic fibrous materials to a non-burning form which effectively overcomes the difficulty normally presented by the critical exotherm upon the subjection of such starting materials to heat.

It is a further object of the invention to provide a process for converting a fibrous acrylic material to a stabilized form possessing essentially the identical fibrous configuration as the starting material.

It is a further object of the invention to provide a stabilized fibrous material derived from an acrylic precursor consisting primarily of recurring acrylonitrile units which is capable upon graphitization of yielding a high strength fibrous product having a tenacity of at least about 14 grams per denier.

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 that an improved process for the stabilization of an acrylic fibrous material consisting primarily of recurring acrylonitrile units comprises heating the material in an oxygen containing atmosphere at a temperature from about 10° C. to 100° C. below its critical temperature until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, and subsequently subjecting the resulting fibrous material to an oxygen containing atmosphere at a temperature from about the critical temperature of the starting material up to about 50° C. in excess of the critical temperature of the starting material for at least about one minute to form a stabilized fibrous product capable of undergoing carbonization which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame. The stabilized product may be

optionally carbonized or carbonized and graphitized by heating in an inert atmosphere.

DESCRIPTION OF PREFERRED EMBODIMENTS

The acrylic fibrous materials which are stabilized in accordance with the present invention may be present in any one of a variety of configurations. For instance, the fibrous materials may be present in the form of continuous single filaments, staple fibers, tows, yarns, ropes, tapes, knits, braids, fabrics, or other fibrous assemblages. In a preferred embodiment of the invention the fibrous material is present in a continuous length, e.g., a single continuous filament, a yarn, or a tape. In a particularly preferred embodiment of the invention the acrylic fibrous material is in the form of a continuous filament yarn. Such a yarn may be formed 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 which serves as the starting material in the process may optionally be provided with a twist which improves its handling characteristics. For example, a twist of about 0.1 to 1 t.p.i., and preferably about 0.1 to 0.7 t.p.i. may be utilized. Yarns or other fibrous assemblages may generally be formed (1) prior to the stabilization treatment, (2) between the preoxidation stages of the process, or (3) immediately subsequent to the stabilization treatment.

The acrylic polymer utilized as the starting material is formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should generally contain not less than about 85 mol per cent of acrylonitrile with not more than about 15 mol percent of a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine and the like, or a plurality of such monomers.

When it is desired to conduct the process of the present invention on a continuous basis in which a continuous length of fibrous material is stabilized, it is recommended that the starting material be selected in accordance with the teachings of U.S. Ser. No. 749,957 of Dagobert E. Stuetz, filed Aug. 5, 1968 concurrently herewith, which is assigned to the same assignee as the instant invention, and is hereby incorporated by reference. More specifically, the copolymer should contain no more than about 5 mol percent of one or more monovinyl comonomers copolymerized with acrylonitrile. In a particularly preferred embodiment of the invention the acrylic polymer is either (1) an acrylonitrile homopolymer or (2) an acrylonitrile copolymer which contains no more than about 1 mol percent of one or more monovinyl comonomers copolymerized with acrylonitrile.

The acrylic fibrous material which serves as the starting material is preferably highly oriented. Such orientation is capable of enhancing the tensile properties of the resulting stabilized fibrous material, as well as of any carbon materials derived therefrom. For instance, the starting material may be highly oriented by hot drawing to a relatively high single filament tensile strength of at least about 5 grams per denier prior to stabilization. Fibrous starting materials which possess a single filament strength of about 7.5 to 8 grams per denier are particularly preferred for use in the process.

When a highly oriented continuous length of acrylic fibrous material having a single filament tensile strength of at least about 5 grams per denier is stabilized in accordance with the present invention on a continuous basis, it is preferred that the fibrous material be maintained throughout the heat treatment under conditions whereby appreciable shrinkage may occur in accordance with the teachings of U.S. Ser. No. 750,018 of Michael J. Ram and Richard N. Rulison, filed Aug. 5, 1968 concurrently herewith, which is assigned to the same assignee as the instant invention and is hereby incorporated by reference.

The cyclization reaction involving pendant nitrile groups which occurs upon exposure of the acrylic fibrous material to heat is generally highly exothermic and if uncontrolled results in the destruction of the fibrous configuration of the starting material. In some instances this exothermic reaction will occur with explosive violence and result in the fibrous material being consumed by flame. More commonly, however, the fibrous material will simply rupture, disintegrate and/or coalesce when the critical temperature is reached. As the quantity of comonomer present in an acrylonitrile copolymer is increased, a fibrous material consisting of the same tends to soften at a progressively lower temperature and the possible destruction of the original fibrous configuration through coalescence of adjoining fibers becomes a factor of increasing importance. Such softening is generally accompanied by a marked reduction in strength which may in severe instances lead to the destruction of the original fibrous configuration through breakage brought about by the inability of the fibrous material to support its own weight. Also, fibrous materials which are highly oriented tend to exhibit a higher critical temperature than the corresponding materials which lack such orientation. The "critical temperature" referred to herein is defined as the temperature at which the fibrous configuration of a given sample of acrylic fibrous starting material will be destroyed in the absence of prior stabilization.

In a preferred embodiment of the invention the starting material exhibits a critical temperature of at least about 300° C., e.g., about 300° C. to 330° C. In addition to visual observation, the detection of the critical temperature of a given acrylic material may be aided in some instances by the use of thermoanalytical methods, such as differential scanning calorimeter techniques, whereby the location and magnitude of the exothermic reaction can be measured quantitatively. Such methods are particularly useful when the acrylic material is an acrylonitrile homopolymer or a closely related acrylonitrile copolymer.

Once the cyclization reaction is begun in the absence of a provision for heat dissipation the critical temperature may be rapidly approached or even exceeded with the concomitant destruction of the product. It accordingly follows that if one chooses to stabilize a package of yarn in accordance with the present invention where heat dissipation is possibly impaired within the interior thereof, and where portions of the fibrous material are in contact, the initial heat applied to the same must be relatively moderate so that the exothermic heat of reaction generated within the package as the cyclization reaction progresses does not exceed the threshold temperature for any portion of the package.

For best results uniform heat treatment throughout all portions of the fibrous acrylic material during the stabilization treatment, and particularly during the initial stage thereof, is encouraged. Such uniform reaction conditions can best be accomplished by limiting the mass of fibrous material at any one location so that heat dissipation from within the interior of the material is not unduly impaired. For instance, the fibrous material undergoing treatment may be placed in a heated oxygen containing atmosphere, such as ordinary air, with generally free access to an appreciable portion of its surface area being provided. In a preferred embodiment of the invention a continuous length of the acrylic starting material, such as a yarn, is continuously passed through suitable heating zones while suspended in the same. Also, the fibrous material may be present as windings on a support during the stabilization treatment provided means are available for the effective dissipation of heat generated within the windings, such as circulating fans.

During the initial stage of the stabilization procedure of the present invention the fibrous acrylic material is heated at a temperature ranging from about 10° C. to 100° C. below its critical temperature until the preoxidation reaction has proceeded to a point where bound oxy-

gen is present in the same in a concentration of at least about 5 percent by weight. The weight percentage of bound oxygen present in the material may be determined by conventional techniques, such as the Unterzaucher analysis. At this point in the process the fibrous material generally exhibits a lustrous appearance, and the fibrous configuration of the starting material remains essentially intact. It has been surprisingly found that if the subsequent stage of the stabilization procedure is commenced much prior to the point when an oxygen content of at least about 5 percent by weight is achieved, then the process yields an ultimate product upon carbonization or upon carbonization and graphitization which exhibits less desirable strength properties even if sufficient stabilization is imparted during the initial stabilization stage so that the usual critical temperature can be subsequently endured. A bound oxygen content from about 5 to about 12 percent by weight is commonly achieved during the initial stage of the process. Higher oxygen contents tend to require extended residence times, and generally yield no commensurate advantage. The fibrous material at the completion of the initial stage of the present stabilization process may or may not be of a non-burning character when subjected to an ordinary match flame depending primarily upon its bound oxygen content. As the bound oxygen content increases, there is a lesser tendency for the material to burn if subjected to an ordinary match flame. If a bound oxygen content of at least about 7 percent by weight is achieved during the first stage of the process, the material is normally non-burning.

The time required to complete the initial stage of the stabilization reaction is inversely related, but not necessarily proportional to the temperature to which the fibrous material is subjected. Heating times during the initial stage of the process commonly range from about 30 minutes to about 3 hours. In a preferred embodiment of the invention the temperature employed is about 10° C. to about 40° C. below the critical temperature of the starting material. By carrying out the first stage of the preoxidation reaction at such relatively severe conditions just short of the critical temperature the present process offers time advantages and process efficiencies in addition to yielding a superior product. When the fibrous material is an acrylonitrile homopolymer, the first stage of the process is preferably carried out at a temperature of about 260° C. to about 290° C., and at a temperature of about 270° C. to 285° C. in a particularly preferred embodiment of the invention. Under such preoxidation conditions heating times of about 30 minutes to 2 hours are commonly utilized during the initial stage of the preoxidation treatment. The initial treatment below the critical temperature imparts sufficient stability to the fibrous acrylic material so that this threshold temperature normally exhibited by the starting material may be endured without the destruction of its original fibrous configuration.

The subsequent heating stage of the preoxidation treatment is conducted for at least about 1 minute in an oxygen containing atmosphere, such as ordinary air. The temperature is elevated over that utilized in the initial stage, and ranges from about the critical temperature of the starting material up to about 50° C. in excess of the critical temperature of the starting material. In a preferred embodiment of the invention a temperature ranging from about the critical temperature of the starting material up to about 30° C. in excess of the critical temperature of the starting material is used. Heating times for the subsequent stage of the stabilization process commonly range from about 1 minute to about 15 minutes. In a preferred embodiment of the invention in which an acrylonitrile homopolymer serves as the starting material the subsequent stage of the preoxidation treatment is conducted at a temperature of about 310° C. to about 350° C. In a particularly preferred embodiment of the invention in which an acrylonitrile homopolymer serves as the starting material the subsequent stage of the preoxidation treatment is conducted at a temperature of about 320° C. to about

340° C. for about 3 to 9 minutes. The stabilized product should be non-burning when subjected to an ordinary match flame and contain at least about 7 percent bound oxygen by weight at the termination of the subsequent preoxidation stage in order to be sufficiently stabilized for carbonization.

The preoxidation stages of the present invention yield a stabilized fibrous material which may be carbonized or carbonized and graphitized in an inert atmosphere to a product of unusually high tensile strength. Carbonization temperatures ranging from about 900° C. to 3000° C. may be employed for about 3 seconds to about 5 minutes. The carbonization step may generally follow immediately after the multiple stage preoxidation treatment previously described without the necessity to use an intermediate heating schedule. During the carbonization reaction elements present in the stabilized fibrous material other than carbon, e.g., nitrogen, hydrogen and oxygen, are expelled. The term "carbonized product" as used herein is defined to be a product consisting of at least about 90 percent atomic carbon by weight, and preferably at least about 95 percent atomic carbon by weight. Graphitic carbon may or may not be present in the same. Suitable inert atmospheres in which the carbonization step may be conducted include nitrogen, argon, helium, etc.

A carbonized product including substantial amounts of graphitic carbon results if the temperature is more severe, e.g., about 2000° C. to about 3000° C. Essentially complete graphitization of the carbonized product was generally be accomplished in about 5 seconds to about 2 minutes which may be detected by the characteristic X-ray diffraction pattern of graphite. In a particularly preferred embodiment of the invention a graphitized product is formed by heating the carbonized fibrous material at a temperature of about 2900° C. for at least about 5 seconds, e.g., about 5 to 60 seconds. By varying the temperature the properties of the resulting product may be varied. For instance, the modulus of the carbonized product tends to increase with increasing temperatures, while the tensile strength tends to remain constant for all temperatures above about 1400° C. provided the fiber is not damaged by handling or thermal shock.

The equipment utilized to produce the requisite temperatures to carry out the process of the invention may be varied widely as will be apparent to those skilled in the art. For instance, during the stabilization reaction the fibrous material may be placed in or continuously passed through a circulating air oven, or the tube of a muffle furnace while in contact with air. A single oven or furnace may be employed in which the temperature is varied to encompass each stage of the preoxidation treatment, or the material may be consecutively placed in a series of ovens with each maintained at the proper temperature. If desired, a single tube furnace may be provided with zones heated to the required temperatures and the fibrous material continuously passed through the same. In a continuous operation a continuous length of the fibrous material may be optionally passed through a given preoxidation zone for a plurality of passes until the desired residence time at each stage of the process is achieved.

The carbonization or carbonization and graphitization treatment may be conducted in any apparatus capable of producing the required temperatures while excluding the presence of an oxidizing atmosphere. For instance, suitable apparatus include an induction furnace, arc furnace, solar furnace, low temperature plasma flame, etc. When an induction furnace of the Lepel type is utilized, the stabilized fibrous material may be passed through a graphite tube or shroud which is situated within the windings of an induction coil. Also, the fibrous material may be passed through a hollow graphite resistance tube which is provided with suitable electrodes, or alternatively heated by direct resistance techniques.

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

With multiple stage preoxidation treatment of the invention.—A continuous length of an 80 fil dry spun acrylonitrile homopolymer continuous filament yarn having a total denier of 1150 was selected for use as the starting material. The yarn was highly oriented and drawn to a single filament tenacity of 7.5 to 8.0 grams per denier, and exhibited a critical temperature of approximately 310° C.

A Lindberg muffle furnace having a tube diameter of 1¼ inches and length of 52 inches was utilized to carry out the stabilization treatment in an air atmosphere. The yarn was continuously passed over rollers situated at each end of the furnace and suspended along the axial center of the tube furnace for a total residence time of 48 minutes at 285° C. During the first stage of preoxidation treatment a bound oxygen content of 7.2 percent by weight was achieved. The yarn was black and lustrous in appearance at the termination of the initial stage of the preoxidation treatment.

The temperature of the muffle furnace was raised to 330° C. and the yarn was again continuously introduced into the same for a total residence time of 2 minutes. The bound oxygen content at the termination of this subsequent stage of the preoxidation treatment was 9.5 percent by weight. The stabilized yarn was black and lustrous in appearance and was suitable for use in the formation of non-burning textile articles, or as an intermediate in the formation of carbonized materials. Throughout the stabilization procedure the bobbin winding tension exerted on the yarn was adjusted so that a shrinkage of 16 to 17 percent of its initial length took place.

The stabilized yarn was next continuously introduced and withdrawn from a Lepel 450° kc. induction furnace for a total residence time of 40 seconds in order to carbonize and graphitize the same where it was heated to a maximum temperature of approximately 2900° C. The induction furnace comprised a 1 turn water cooled copper coil having an inner diameter of ¾ inch and a length of 2 inches, a 20 kw. power source, and was equipped with hollow graphite tube suspended within the coil of the same having a length of 8½ inches, an outer diameter of ½ inch and an inner diameter of ⅛ inch through which the previously stabilized 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. The graphitized product was composed of essentially pure carbon and exhibited a single filament tenacity of 13.9 grams per denier.

With single stage preoxidation treatment.—Example I was repeated with the exception that the subsequent stage of the preoxidation treatment which was conducted for 2 minutes at 330° C. was omitted. Following graphitization the product was composed of essentially pure carbon, but exhibited a reduced single filament tenacity of 12.5 grams per denier.

Example II

With multiple stage preoxidation treatment of the invention.—A yarn sample identical to that employed in Example I was stabilized, carbonized and graphitized in accordance with the procedure of Example I subject to the exceptions indicated below.

The first stage of the preoxidation treatment was conducted at 285° C. for 73 minutes, and a bound oxygen content of 10.3 percent by weight was achieved. The second stage of the preoxidation treatment was conducted at 335° C. for 5 minutes and the total bound oxygen content was found to be 10.8 percent by weight of the stabilized product.

Following graphitization the product was composed of

essentially pure carbon, and exhibited a single filament tenacity of 16.2 grams per denier.

With single stage preoxidation treatment.—Example II was repeated with the exception that the subsequent stage of the preoxidation treatment which was conducted at 335° C. for 5 minutes was omitted. Following graphitization the product was composed of essentially pure carbon, but exhibited a reduced single filament tenacity of 13.1 grams per denier.

Example III

With multiple stage preoxidation treatment of the invention.—A yarn sample identical to that employed in Example I was stabilized, carbonized and graphitized in accordance with the procedure of Example I subject to the following modifications in the multiple stage preoxidation treatment.

The initial stage of the preoxidation treatment was conducted at 270° C. for 50 minutes, and a bound oxygen content of 5.2 percent by weight was achieved. The subsequent stage of the preoxidation treatment was conducted at 315° C. for 10.5 minutes, and the total bound oxygen content was found to be 8.0 percent by weight of the stabilized product.

Following graphitization the product was composed of essentially pure carbon, and exhibited a single filament tenacity of 14.3 grams per denier.

Example IV

With multiple stage preoxidation treatment of the invention.—A yarn sample identical to that employed in Example I was stabilized, carbonized and graphitized in accordance with the procedure of Example I subject to the modifications in the multiple stage preoxidation treatment indicated below.

The initial stage of the preoxidation treatment was conducted at 285° C. for 35 minutes, and a bound oxygen content of 5.3 percent by weight was achieved. The subsequent stage of the preoxidation treatment was conducted at 330° C. for 2 minutes, and the total bound oxygen content was found to be 7.1 percent by weight of the stabilized product.

Following graphitization the product was composed of essentially pure carbon, and exhibited a single filament tenacity of 15.1 grams per denier.

With imperfect multiple stage preoxidation treatment.—Example IV was repeated with the exception that an insufficient bound oxygen content was achieved during the initial stage of the preoxidation treatment, and the length of the subsequent stage of the preoxidation treatment was extended to obtain a comparable bound oxygen content at the termination of the stabilization procedure.

More specifically, the initial stage of the preoxidation treatment was conducted at 285° C. for 21 minutes, and a bound oxygen content of only 3.5 percent by weight was achieved. The subsequent stage of the preoxidation treatment was conducted at 315° C. for 10.5 minutes, and a total bound oxygen content of 7.1 percent by weight was present in the product.

Following graphitization the product was composed of essentially pure carbon, and exhibited a single filament tenacity of only 10.8 grams per denier. Even though the bound oxygen content was identical to that of Example IV at the termination of the imperfect multiple stage preoxidation treatment, the strength of the resulting carbonized and graphitized product was substantially lower.

Example V

With multiple stage preoxidation treatment of the invention.—A yarn sample identical to that employed in Example I was stabilized, carbonized and graphitized in accordance with the procedure of Example I subject to the following modifications in the multiple stage preoxidation treatment.

The initial stage of the preoxidation treatment was conducted at 285° C. for 45 minutes, and a bound oxygen

content of 7.2 percent by weight was achieved. The subsequent stage of the preoxidation treatment was conducted at 325° C. for 5 minutes, and the total bound oxygen content was found to be 9.2 percent by weight of the stabilized product.

Following graphitization the product was composed of essentially pure carbon, and exhibited a single filament tenacity of 14.7 grams per denier.

The stabilized fibrous material resulting from the pre-oxidation treatment of the present invention is suitable for use in applications where a fire resistant fibrous material is required. For instance, non-burning fabrics may be formed from the same. As previously indicated, the preoxidized fibrous materials are particularly suited for use as intermediates in the production of high strength, high modulus fibrous graphite products. Such fibrous graphite products may be incorporated in a binder or matrix and serve as a reinforcing medium. The graphite component may accordingly serve as a light weight load bearing component 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.

I claim:

1. An improved process for the stabilization of an acrylic fibrous material comprising heating a fibrous material consisting primarily of recurring acrylonitrile units in an oxygen containing atmosphere at a temperature from about 10° C. to 100° C. below its critical temperature until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, and subsequently subjecting the resulting fibrous material to an oxygen containing atmosphere at a temperature from about the critical temperature of the starting material up to about 50° C. in excess of the critical temperature of the starting material for at least about one minute to form a stabilized fibrous product capable of undergoing carbonization which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame.

2. A process according to claim 1 in which said acrylic fibrous material is an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith.

3. A process according to claim 1 in which said acrylic fibrous material is 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.

4. A process according to claim 1 in which said acrylic fibrous material is an acrylonitrile homopolymer.

5. A process according to claim 1 in which said acrylic fibrous material possesses a single filament tenacity of at least about 5 grams per denier prior to stabilization.

6. A process according to claim 1 in which the oxygen containing atmosphere is air.

7. A process according to claim 1 in which said acrylic fibrous material is a yarn.

8. A process for the stabilization of an acrylic fibrous material comprising heating a fibrous material consisting primarily of recurring acrylonitrile units in an oxygen containing atmosphere at a temperature from about 10° C. to 40° C. below its critical temperature until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, and subsequently subjecting the resulting fibrous material to an oxygen containing atmosphere at a temperature from about the critical temperature of the starting material up to about 30° C. in excess of the

critical temperature of the starting material for at least about one minute to form a stabilized fibrous product capable of undergoing carbonization which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame.

9. A process according to claim 8 in which said acrylic fibrous material is a yarn.

10. A process according to claim 8 in which said acrylic fibrous material is an acrylonitrile copolymer which contains at least about 99 mol percent of acrylonitrile units and up to about 1 mol percent of one or more monovinyl units copolymerized therewith.

11. A process according to claim 8 in which said acrylic fibrous material is an acrylonitrile homopolymer.

12. A process according to claim 11 in which said acrylonitrile homopolymer possesses a single filament tenacity of at least about 5 grams per denier prior to stabilization.

13. A process for the stabilization of a continuous length of a fibrous material consisting of an acrylonitrile homopolymer comprising passing said material through an oxygen containing atmosphere having a temperature of about 260° C. to 290° C. until said material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, and subsequently passing the resulting material through an oxygen containing atmosphere having a temperature from about 310° C. to 350° C. for at least about one minute to form a stabilized product capable of undergoing carbonization which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame.

14. A process according to claim 13 in which said continuous length of fibrous material is an acrylonitrile homopolymer yarn.

15. A process according to claim 13 in which said continuous length of fibrous material is an acrylonitrile homopolymer continuous filament.

16. A process according to claim 13 in which said oxygen containing atmosphere is air.

17. A process for the carbonization of an acrylic fibrous material comprising heating a fibrous material consisting primarily of recurring acrylonitrile units in an oxygen containing atmosphere at a temperature from about 10° C. to 100° C. below its critical temperature until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, subsequently subjecting the resulting fibrous material to an oxygen containing atmosphere at a temperature ranging from about the critical temperature of the starting material up to about 50° C. in excess of the critical temperature of the starting material for at least about one minute to form a stabilized fibrous product which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame, and subsequently heating said stabilized fibrous product at a temperature of about 900° C. to 3000° C. in an inert atmosphere until a carbonized fibrous product is formed.

18. A process according to claim 17 in which said acrylic fibrous material is an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith.

19. A process according to claim 17 in which said acrylic fibrous material is 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.

20. A process according to claim 17 in which said acrylic fibrous material is an acrylonitrile homopolymer.

21. A process according to claim 17 in which said acrylic fibrous material possesses a single filament tenacity of at least about 5 grams per denier prior to stabilization.

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22. A process according to claim 17 in which said acrylic fibrous material is a yarn.

23. A process for the carbonization of an acrylic fibrous material comprising heating a fibrous material consisting primarily of recurring acrylonitrile units in an oxygen containing atmosphere at a temperature from about 10° C. to 40° C. below its critical temperature until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, subsequently subjecting the resulting fibrous material to an oxygen containing atmosphere at a temperature ranging from about the critical temperature of the starting material up to about 30° C. in excess of the critical temperature of the starting material for at least about one minute to form a stabilized fibrous product which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame, and subsequently heating said stabilized fibrous product at a temperature of about 900° C. to 3000° C. in an inert atmosphere until a carbonized fibrous product is formed.

24. A process according to claim 23 in which said acrylic fibrous material is a yarn.

25. A process according to claim 23 in which said acrylic fibrous material is an acrylonitrile copolymer which contains at least about 99 mol percent of acrylonitrile units and up to about 1 mol percent of one or more monovinyl units copolymerized therewith.

26. A process according to claim 23 in which said acrylic fibrous material is an acrylonitrile homopolymer.

27. A process according to claim 26 in which said acrylonitrile homopolymer possesses a single filament tenacity of at least about 5 grams per denier prior to stabilization.

28. A process according to claim 23 in which said stabilized fibrous product is heated to a maximum temperature of about 2000° C. to 3000° C. in an inert atmosphere where it is maintained until substantial graphitization has occurred.

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29. A process for the carbonization of a continuous length of a fibrous material composed of an acrylonitrile homopolymer comprising passing said material through an oxygen containing atmosphere having a temperature of about 260° C. to 290° C. until said fibrous material contains at least about 5 percent oxygen by weight while retaining its original fibrous configuration essentially intact, subsequently passing the resulting fibrous material through an oxygen containing atmosphere having a temperature from about 310° C. to 350° C. for at least about one minute to form a stabilized fibrous product which retains its original fibrous configuration essentially intact and which is non-burning when subjected to an ordinary match flame, and subsequently heating said stabilized fibrous product at a temperature of about 900° C. to 3000° C. in an inert atmosphere until a carbonized fibrous product is formed.

30. A process according to claim 29 in which said stabilized fibrous product is heated to a maximum temperature of about 2000° C. to 3000° C. in an inert atmosphere where it is maintained until substantial graphitization has occurred.

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EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

40 8—115.5; 23—209.4

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,539,295

Dated November 10, 1970

Inventor(s) Michael J. Ram

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

Column 2, line 5, correct "requires" to read --requirements--.
Column 3, line 24, correct "t.pi." to read --t.p.i.--.
Column 4, line 48, correct "recation" to read --reaction--.
Column 5, line 10, correct "commended" to read --commenced--;
line 42, correct "efficiences" to read --efficiencies--;
line 51, correct "hat" to read --that--.
Column 6, line 29, delete "was" and insert --may--.
Column 7, line 5, correct "80" to read --800--;
line 18, delete "of";
line 40, correct "1" to read --10--.
line 49, correct "equidisant" to read --equidistant--.
Column 9, line 37, correct "essentialy" to read --essentially--.

Signed and sealed this 30th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents