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PREPARATION OF CARBON TEXTILES FROM POLYACRYLONITRILE BASE TEXTILES

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ABSTRACT OF THE DISCLOSURE

A process is provided for producing a high weight yield of carbon textiles from thermoplastic polyacrylonitrile base textiles. This process comprises converting a thermoplastic polyacrylonitrile textile starting material to a thermoset polyacrylonitrile base textile material by subjecting it to the action of a chemical oxidizing agent selected from the oxygen containing compounds of the metallic transition elements and then carbonizing the resultant thermoset polyacrylonitrile textile by heating it in an inert atmosphere to a temperature in excess of about 700° C. for a time sufficient to produce a substantially all-carbon base textile which retains the physical characteristics of the starting textile material, such as hand and drape.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to an improved process for the production of carbon textiles from polyacrylonitrile base textiles. As used herein and in the appended claims, the term carbon is intended to include both the non-graphitic and graphitic forms of carbon.

Description of prior art

Carbon is an element which possesses many interesting and useful chemical and physical properties. It is a material which both can be found in nature and produced synthetically. Carbon is a readily processable material and can be fashioned into almost any intricate shape or pattern. Today, the uses of carbon in commerce and industry are myriad.

Presently, most of the carbon articles used in industry are produced by a process which comprises mixing non-graphitic carbon particles with a carbonizable binder, extruding or molding the so-produced mixture into the desired shape or article and, subsequently, heating it to a temperature sufficient to carbonize the binder phase. If, during this heating the maximum temperature which the resultant article experiences is of the order of 700–900° C., it is said to be a non-graphitic all carbon article. However, if the article is further heated to a temperature of the order of 2000–2500° C. and higher, it is said to be converted to a graphitic form of carbon and is generally called graphite.

Recently, there has been introduced to the carbon art carbon in the form of a textile. This form of carbon is unique in that it possesses the flexibility of a textile while at the same time is characterized by the electrical and chemical properties associated with conventionally formed carbon articles.

United States Patent 3,011,981 which issued Dec. 5, 1961 to W. T. Soltes describes and claims a method for manufacturing carbon in a textile form. Briefly, the process disclosed therein comprises heating a cellulosic textile in an inert atmosphere at a progressively higher temperature until substantial carbonization of the textile occurs. The resultant product possesses the chemical and physical attributes exhibited by conventionally formed carbon articles while it retains the flexibility and other

physical characteristics associated with the textile starting material, such as hand and drape.

A textile form of fibrous graphite is disclosed and claimed in United States Patent 3,107,152, which issued to C. E. Ford and C. V. Mitchell on Oct. 15, 1963. Broadly stated, the process for producing fibrous graphite disclosed therein comprises heating a cellulosic starting material in an inert atmosphere at progressively higher temperatures for various times until a temperature of about 900° C. is achieved followed by further heating in a suitable protective atmosphere at still higher temperatures until substantial graphitization occurs. The product produced by this process exhibits the chemical and physical properties generally associated with conventionally fabricated graphite while, at the same time, it retains the textile characteristics of the starting material.

In addition to the foregoing methods for producing carbon textiles, recently there has been introduced to the carbon art a method for producing carbon textiles from polyacrylonitrile base textiles. Briefly, this method comprises heating a thermoplastic polyacrylonitrile base textile in an atmosphere which contains uncombined gaseous oxygen to convert it to a thermoset material which can then be subjected to a carbonizing treatment without destroying the textile structure evidenced by the starting material. However, since untreated polyacrylonitrile base textiles soften and fuse and then start to disintegrate into a powder at temperatures in excess of about 300° C., this temperature must not be exceeded during the foregoing treatment. In actual practice, a temperature in excess of about 250° C. has been found to be undesirable. When a temperature much in excess of about 250° C. is employed, the final carbonized product tends to be rather fragile and embrittled, i.e., it commences to lose its textile characteristics. When a temperature much below 250° C. is utilized, the time required to convert the thermoplastic polyacrylonitrile base material to a thermoset product is exceptionally long and commercially impractical. In fact, even at the optimum temperature of 250° C. the oxidation treatment must be continued for from 2 to 3 hours in order to obtain, on subsequent pyrolysis, a carbon fiber in reasonable yields which exhibits adequate physical properties.

The foregoing disadvantages are readily overcome by the practice of applicant's process for producing carbon textiles from polyacrylonitrile base textiles. The benefits obtained from the use of his invention will be discussed later in more detail. However, it should be noted at this time that by the use of applicant's technique for producing carbon textiles from polyacrylonitrile textiles it is possible to reduce the time required to convert a thermoplastic polyacrylonitrile base textile material to a carbonizable thermoset polyacrylonitrile base textile material from about 120 minutes to about 5 minutes.

Summary

Briefly, the subject invention is accomplished by a process which comprises the steps of subjecting a thermoplastic polyacrylonitrile base textile material to the action of a chemical oxidizing reagent selected from the oxygen containing compounds of the metallic transition elements to convert the thermoplastic polyacrylonitrile textile material to an essentially thermoset material which can then be converted to a carbon textile material by heating it in a non-oxidizing atmosphere to a temperature in excess of 700° C.

The principal advantage of the instant invention is that it eliminates the lengthy and uneconomical gaseous oxidation treatment heretofore required to be employed when one is desirous of converting polyacrylonitrile base textiles to a textile form of carbon.

Description of the preferred embodiments of the invention

Polyacrylonitrile base textiles contemplated by the present invention as the starting materials for the production of carbon textiles are prepared by conventional fiber spinning techniques from polyacrylonitrile homopolymers, copolymers, interpolymers, terpolymers, graft copolymers, and the like, which contain at least about 85 percent by weight of polyacrylonitrile. The molecular weight of these polymers can be as low as about 15,000 and as high as about 300,000. The carbon content of the polymer is also important. For purposes of the present invention the carbon content should be at least about 57.5 percent by weight. This latter requirement differentiates in one aspect the synthetic starting materials of the present invention from the cellulosic materials employed in the prior art processes for making carbonaceous filaments since such cellulosic materials, for example, cellulose, rayon, etc., have carbon content of only about 45 percent by weight and less.

Illustrative of the aforementioned polyacrylonitrile-derived base textiles are polyacrylonitrile homopolymers, and copolymers, graft copolymers, interpolymers and terpolymers of acrylonitrile with other polymerizable ethylenically unsaturated compounds such as vinyl compounds, i.e., vinyl alcohol, vinyl chloride, vinyl pyridine, acrolein, acrolein diacetate, acrylic acid, 1-hexene, methacrolein, methacrylonitrile, methylvinylpolysiloxane, methacrylamide, and the like, esters, i.e., allyl acetate, the methacrylates, methyl acrylate, ethyl acrylate, methyl cinnamate, and the like; styrenes, i.e., iso-propenyl-toluene, α-methylstyrene, α-acetoxystyrene, styrene, stilbene, o-chlorostyrene, and the like; dienes, i.e., 1-acetoxybutadiene, butadiene, 2-chlorobutadiene, 2-methylbutadiene, and the like.

Any chemical oxidizing agent or solution which contains an oxygenated compound of the metallic transition elements is suitable for the practice of the invention. However, best results are obtained when the transition metal element is selected from the group consisting of titanium, vanadium, chromium, molybdenum, manganese, tungsten, cobalt, platinum, and palladium. The preferred oxidizing reagents or compounds are those which contain a transition metal in its highest oxidation state. In particular, two chemical reagents which have been found to be especially suited to the practice of the invention are potassium dichromate and potassium permanganate.

Preferably, the oxidizing agent which contains the transition metal element is applied to the polyacrylonitrile base textiles in solution form, i.e., it is dissolved in a suitable vehicle. In practice, this vehicle may be acidic, basic or neutral. All that is required is that it does not react with the transition metal dissolved therein so as to destroy its effectiveness as a reagent which can convert a thermoplastic polyacrylonitrile base material to a thermoset polyacrylonitrile base material which will carbonize without losing its original textile characteristics.

In addition to the foregoing technique for practicing the instant invention, it should be noted that it is oftentimes desirable to employ the transition metal containing oxidizing agent in the melt or vapor state for all that is required is that it be brought into direct physical contact with the material being treated.

The temperature at which a polyacrylonitrile base textile material may be advantageously subjected to the action of a transition metal-oxide containing reagent according to the teachings of the instant invention varies from below room temperature to over 200° C. The effect of increasing the treatment temperature is the usual one of increasing the rate of reaction. It should again be noted that the invention is most efficiently and effectively carried out when the transition metal element in the transition metal-oxide containing reagent is present in its highest oxidation state. For example, potassium permanganate is much more effective than manganese dioxide since in potassium permanganate the manganese is in the +7 oxidation state and a much better oxidizing agent than in the +4 state as is the case of manganese dioxide.

The present invention will now be described in greater detail in the following examples.

Example I

Approximately 1 gram of a single ply thermoplastic homopolymer polyacrylonitrile base yarn having a denier of 200 and consisting of 50 monofilaments was placed into an isopropanol bath for about 10 minutes in order to remove the lubricating finish therefrom. The washed yarn was then vacuum dried for approximately 30 minutes at room temperature to remove the isopropanol solvent. The so-cleansed yarn was then placed into a vessel which contained an alkaline (0.317 N) potassium permanganate solution. The alkalinity of the solution was achieved by adding 2 moles of sodium carbonate for each 3 moles of potassium permanganate in the solution. The temperature of the potassium permanganate solution was maintained at about 85° C. The thermoplastic polyacrylonitrile base yarn was allowed to remain in the heated potassium permanganate solution for about 5 minutes in order to convert it to an essentially thermoset material, i.e., a material which could be carbonized without fusing. The resultant yarn was removed from the reagent containing bath, washed with distilled water and vacuum dried for one hour at 60° C. The oxidized yarn was then carbonized by heating it (at a rate of 60° C. per hour) to a temperature of about 1000° C. followed by a 1 hour hold at this temperature. Yarn so-produced exhibited the chemical and physical properties of carbon while retaining its original textile characteristics, such as hand and drape. The weight yield of the so-treated and carbonized yarn was 42.8 percent.

Example II

Another 1 gram sample of single ply thermoplastic homopolymer polyacrylonitrile base yarn having a denier of 200 consisting of 50 monofilaments was processed as described in Example I except that the lubricating finish was not removed from the yarn prior to its being oxidized with the alkaline potassium permanganate solution. The resulting carbonized yarn retained its original textile characteristics and exhibited a weight yield of 42.4 percent.

Example III

The experiment described in Example I was repeated with the only difference being that the yarn was treated in the oxidizing potassium permanganate solution for 30 minutes instead of 5 minutes. Upon subsequent carbonization, the resultant carbon yarn exhibited excellent textile characteristics and a weight yield of 41.6 percent.

Example IV

The procedure set forth in Example III was essentially repeated with the only significant difference being that an acidified 1 percent potassium dichromate solution was employed as the oxidizing reagent instead of an alkaline potassium permanganate solution. The resultant 1000° C. carbonized carbon yarn exhibited excellent textile characteristics, such as hand and drape, and a weight yield of 38.6 percent.

Example V

An approximately .26 gram specimen of a single ply thermoplastic, homopolymer polyacrylonitrile base yarn having a denier of 200 and consisting of 50 monofilaments was positioned inside of a reaction vessel and exposed under reflux conditions to the oxidizing action of vaporized chromyl chloride. The temperature of the chromyl chloride vapor was approximately 118° C. The duration of the oxidation treatment was about 15 minutes after which the oxidized fibers in yarn form were withdrawn from the reflux apparatus and washed in distilled water to remove any residual chromyl chloride. These fibers were then vacuum dried at 60° C. for one hour.

The resultant oxidized thermoset fibers were then carbonized by heating them under non-oxidizing conditions at a rate of 60° C. per hour to 1000° C. followed by a hold at this temperature for 1 hour. Fibers so-produced exhibited the chemical and physical properties of carbon while retaining their original textile characteristics such as hand and drape. The weight yield of the so-treated and carbonized fibers was 34.7 percent.

While the foregoing examples all concern the use of a homopolymer polyacrylonitrile base yarn, which is preferred, it will be readily appreciated by those skilled in the art that other yarns containing less than 100 percent polyacrylonitrile material, as hereinbefore described, are also amenable to the practice of the invention. In addition, it has been discovered that superior results are obtained when the filaments which make up the textile used in the practice of the invention have an extremely small cross section or diameter and are free of any surface finish. Also, it has been observed that highly desirable results are achieved when one uses a dilute solution of a strong oxidizing reagent such as potassium dichromate or potassium permanganate as opposed to a highly concentrated one. The preferred oxidizing temperature in the practice of the invention is that at which only a few minutes residence time in the oxidizing solution is required to effect the transformation of polyacrylonitrile from a thermoplastic to a thermoset material which is amenable to carbonization at elevated temperatures without fusing and losing its original textile characteristics.

The foregoing information and examples are presented herein for illustrative purposes only and are not intended to unduly limit the scope of the invention.

What is claimed is:

1. A process for the manufacture of a carbon textile from a thermoplastic polyacrylonitrile base textile comprising the steps of:

(a) oxidizing said thermoplastic polyacrylonitrile base textile by contacting it with an oxygen containing compound of the transition metal elements for a time sufficient to convert said thermoplastic polyacrylonitrile base textile to an essentially thermoset polyacrylonitrile base textile; and

(b) heating said thermoset polyacrylonitrile base textile in a non-oxidizing atmosphere to a temperature in excess of 700° C. for a time sufficient to convert said polyacrylonitrile base textile to a substantially carbon base textile which substantially retains the physical characteristics of the textile starting material.

2. The process of claim **1** wherein said oxygen containing compound is in solution form.

3. The process of claim **1** wherein said thermoplastic polyacrylonitrile base textile consists essentially of a homopolymer of acrylonitrile.

4. The process of claim **2** wherein said solution contains a compound selected from the group consisting of potassium permanganate and potassium dichromate.

5. The process of claim **4** wherein the duration of said oxidizing step (a) is from 5 to 30 minutes.

6. The process of claim **4** wherein said oxidizing step (a) is carried out at a temperature of about 85° C.

7. The process of claim **1** wherein the transition metal in said oxygen containing compound of the transition metal elements is selected from the group consisting of titanium, vanadium, chromium, molybdenum, manganese, tungsten, cobalt, platinum and palladium.

8. The process of claim **1** wherein said polyacrylonitrile base textile is in the form of a yarn.

9. The process of claim **8** wherein the surface of said yarn has been treated to remove any lubricant therefrom.

10. The process of claim **1** wherein the transition metal in said oxygen containing compound of the transition metal elements is in its highest oxidation state.

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