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3,488,151

PREPARATION OF CARBON FIBERS FROM POLY-VINYL ALCOHOL BASE FIBERS

William J. Noss, Marshallville, Ohio, assignor to Union Carbide Corporation, a corporation of New York
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ABSTRACT OF THE DISCLOSURE

A process is provided for producing a high weight yield of carbon fibers, preferably in a textile form, from thermoplastic polyvinyl alcohol base fibers. This process comprises converting a thermoplastic polyvinyl alcohol base fibrous starting material to a thermoset polyvinyl alcohol base fibrous 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 fibrous polyvinyl alcohol base material 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 fibrous product which retains the physical characteristics of the starting fibrous 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 fibers, preferably in textile form, from polyvinyl alcohol base fibers and 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 processible 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 a fibrous form of carbon. This form of carbon is unique in that it possesses the flexibility of a fibrous material while at the same time is characterized by the electrical and chemical properties associated with conventionally formed carbon articles.

United States Patents 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 polyvinyl alcohol base textiles. Briefly, this method comprises heating a thermoplastic polyvinyl alcohol 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, when this technique is employed the time required to convert the thermoplastic polyvinyl alcohol base material to a thermoset product is exceptionally long and commercially impractical. In fact, even at the optimum temperature of 200° C. the gaseous oxidation treatment must be continued for from 16 to 24 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 polyvinyl alcohol 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 it is possible to reduce the time required to convert a thermoplastic polyvinyl alcohol base textile material to a carbonizable thermoset polyvinyl alcohol base textile material from in excess of 16 hours to less than about 0.5 hour.

SUMMARY

Briefly, the subject invention is accomplished by a process which comprises the steps of subjecting a thermoplastic polyvinyl alcohol base fibrous material, preferably in textile form, to the action of a chemical oxidizing reagent selected from the oxygen containing compounds of the metallic transition elements for a time sufficient to convert the thermoplastic polyvinyl alcohol base fibrous material to an essentially thermoset material which can then be converted to a carbon fibrous material by heating it in a non-oxidizing atmosphere at 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 polyvinyl alcohol base fibers and textiles to a fibrous form of carbon.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

Polyvinyl alcohol base fibers and textiles contemplated for use as starting materials in the practice of the present invention are those which have been fashioned from polyvinyl alcohol base polymers that have been either chemically treated or cross-linked to render them insoluble in

water. One well known technique for controlling the solubility of polyvinyl alcohol base polymers is to react them with materials such as formaldehyde; another is to cross-link the polyvinyl alcohol structure by heating such polymers to a temperature of about 250° C.

Illustrative of the type of polyvinyl alcohol base polymeric materials which may be employed in the practice of the present invention are homopolymers of polyvinyl alcohol; copolymers of vinyl alcohol and vinyl acetate; terpolymers of vinyl alcohol, vinyl acetate and maleic anhydride. It is not intended to limit the present invention to the foregoing types of polyvinyl alcohol base polymers for other well known polyvinyl alcohol base polymeric materials will be readily apparent to the skilled artisan.

Any chemical oxidizing agent or solution containing 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 chromium trioxide.

Preferably, the transition metal containing oxidizing agent is applied to the polyvinyl alcohol base fibers and/or 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 polyvinyl alcohol base material to a thermoset polyvinyl alcohol 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 contact with the material being treated.

The temperature at which a polyvinyl alcohol base textile material may be advantageously subjected to the action of a transition metal-oxygen 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-oxygen containing solution 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 +4 in the manganese dioxide.

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

Example I

An approximately 1 gram batch of homopolymer polyvinyl alcohol base fibers in yarn was washed in a solution of trifluoro-trichloroethane for about 10 minutes to remove any surface finish therefrom. In their manufacture, these fibers had been treated with a formaldehyde solution to render them insoluble in water. The yarn was then removed from the cleansing solution and vacuum dried for 20 minutes at 30° C. The so-cleansed yarn consisting of 36 monofilaments, each having a denier of about 6.7, was placed into a vessel which contained an acidified 1 percent solution of chromium trioxide. This solution was prepared by adding 1 gram of chromium trioxide to 98 ml. of a .05 molar aqueous solution of sulfuric acid. The temperature of the oxidizing solution was maintained at

approximately 85° C. The thermoplastic polyvinyl alcohol homopolymer base yarn was allowed to remain in the heated chromium trioxide containing oxidizing solution for 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 oxidizing bath, washed with water for 10 minutes, re-washed with a 5 percent solution of sodium hydrosulfite until free from residual oxidizing material and, subsequently, vacuum dried for about 1 hour at 60° C. The oxidized yarn was then carbonized in an argon atmosphere at a rate of 60° C. per hour to 1000° C., followed by a 1 hour hold at this temperature. The resulting weight yield of carbon was 31.5 percent. The average tensile strength of the yarn monofilaments was 26,800 pounds per square inch. The Young's modulus of elasticity was 2.7×10^6 pounds per square inch. The resultant carbonized yarn exhibited the typical chemical and physical properties of non-graphitic carbon while it retained its original textile characteristics, such as hand and drape.

Example II

The procedure described in Example I was repeated except that approximately 1 gram of chromium trioxide was dissolved in 98 ml. of an aqueous. 1 M nitric acid solution and the duration of the oxidation treatment therein changed to 10 minutes. Upon carbonization, the resulting weight yield of carbon was 30.1 percent. The average tensile strength of the yarn monofilaments was 31,000 pounds per square inch. The Young's modulus of elasticity was 2.3×10^6 pounds per square inch. The resultant non-graphitic carbon yarn exhibited the typical chemical and physical properties of non-graphitic carbon while it retained its original textile characteristics, such as hand and drape.

Example III

The procedure described in Example I was repeated except that the oxidizing solution was prepared by dissolving 1 gram of potassium dichromate in 98 ml. of .05 M aqueous sulfuric acid solution. After carbonization, the resulting weight yield of carbon was 29.8 percent. The average tensile strength of the yarn monofilaments was 16,600 pounds per square inch and the Young's modulus of elasticity was 2.7×10^6 pounds per square inch. The resultant non-graphitic carbon yarn exhibited the typical chemical and physical properties of non-graphitic carbon while it retained its original textile characteristics, such as hand and drape.

Example IV

A .9056 gram polyvinyl alcohol yarn specimen was positioned inside of a reaction vessel and exposed under refluxing conditions to the oxidizing action of vaporized chromyl chloride. The temperature of the vapor was approximately 118° C. The duration of the oxidation treatment was about 15 minutes after which the yarn was withdrawn from the apparatus and water washed to remove any residual chromyl chloride. The yarn was then vacuum dried at 60° C. for one hour. The resultant oxidized thermoset yarn was carbonized by heating it 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. The yarn so-produced exhibited the chemical and physical properties of carbon while it retained its original textile characteristics such as hand and drape. The weight yield of the so-treated and carbonized fibers was 15.1 percent.

While the foregoing examples all concern the use of a polyvinyl alcohol homopolymer base yarn, which is preferred, it will be readily appreciated by those skilled in the art that other yarns and textiles containing less than 100 percent vinyl alcohol 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 yarn or 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 chromium trioxide 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 polyvinyl alcohol base material from a thermoplastic to a thermoset material which is amenable to carbonization at elevated temperatures without losing its original textile characteristics. It will be appreciated by those skilled in the art that the lower the bath temperature and the more dilute the oxidizing solution, the longer will be the residence time required to produce the necessary degree of fiber oxidation.

In addition, it should be noted that if a non-aqueous oxidizing solution is employed, the polyvinyl alcohol base fibers must be such that they are not soluble in the non-aqueous media. Polyvinyl alcohol base fibers of this type are well known in the art and are readily available commercially.

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 fiber from a thermoplastic polyvinyl alcohol base-fiber comprising the steps of:

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

(b) heating said thermoset polyvinyl alcohol base fiber in a non-oxidizing atmosphere to a temperature in excess of 700° C. for a time sufficient to convert said polyvinyl alcohol base fiber 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 polyvinyl alcohol base fiber consists essentially of a homopolymer of vinyl alcohol.

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

5. The process of claim 4 wherein the duration of said oxidizing step (a) is from 5 to 10 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 polyvinyl alcohol base fiber 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 finish 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.

11. The process of claim 1 wherein said polyvinyl alcohol fiber is in textile form.

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EDWARD J. MEROS, Primary Examiner

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