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[54] **PROCESS FOR PRODUCING CARBON FIBERS HAVING A HIGH YOUNG'S MODULUS OF ELASTICITY**


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**Related U.S. Application Data**

[63] Continuation of Ser. No. 610,789, Jan. 23, 1967, abandoned.

[52] **U.S. Cl** .....**423/447**
[51] **Int. Cl.** .....**C01b 31/07**
[58] **Field of Search**....23/209.1, 209.2, 209.4, 209.3; 264/29; 8/116



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[57] **ABSTRACT**

Carbon fibers having a high Young's modulus are produced by a process which comprises longitudinally stressing partially carbonized cellulosic base fibers by means of an applied tensional force while concurrently subjecting them to a carbonizing treatment. The resultant stress carbonized fibers can then be subjected to a stress graphitizing treatment, if desired.


**7 Claims, No Drawings**

# PROCESS FOR PRODUCING CARBON FIBERS HAVING A HIGH YOUNG'S MODULUS OF ELASTICITY

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of application Ser. No. 610,789, filed Jan. 23, 1967, now abandoned.

## BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improved process for producing carbon fibers from cellulosic materials and to the fibers so produced. As used herein and in the appended claims, carbon is intended to include both the non-graphitic and graphitic forms of carbon.

2. Description of the 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 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.

U.S. Pat. No. 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 at the same time 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 U.S. Pat. No. 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 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.

Recently, a high modulus, high strength form of graphite fiber has become commercially available. Briefly, this material is produced by a process which comprises stretching a substantially all carbon fiber while it is being heated to graphitizing temperatures.

Although this improved form of graphite fiber possesses properties which are unobtained in graphite fibers produced via the methods disclosed by both Soltes and Ford, et al, the method of producing it suffers from at least one serious processing difficulty. Namely, the high force necessary to achieve both maximum strength and a high Young's modulus is a limiting factor during the stress graphitization of the already carbonized fiber. That is, in order to obtain optimum strength and modulus values, the amount of stress required is dangerously close to the breaking stress of the carbon fiber. Needless to say, such close limits are not conducive to a successful commercial operation.

## SUMMARY

Briefly, the subject invention is accomplished by a process which comprises concurrently longitudinally stressing a partially carbonized cellulosic base fiber while subjecting it to a carbonizing temperature in the range of from about 250° to 900°C. so that a given length of the resultant, stretched fiber is at least 5 percent longer than it would have been had it been carbonized in a stress-free manner. The so-produced non-graphitic carbon fiber exhibits a higher Young's modulus of elasticity than heretofore obtainable in non-graphitic carbon fibers produced by conventional techniques. In addition, the non-graphitic carbon fiber so-produced is especially amenable to conventional stress graphitizing treatments. For example, non-graphitic carbon fibers stress carbonized by the technique of the instant invention which were subsequently stress graphitized at a force of 400 grams per two ply exhibited a Young's modulus and breaking strength of 52 $\times 10^6$ lb/in$^2$ and 280,000 lb/in$^2$, respectively, while fibers produced by the practice of the prior art, i.e., by stress graphitizing a conventionally carbonized fiber, required a force of 1300 grams per 2 ply to duplicate these physical properties.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

Fibers suitable for the practice of the invention are those which upon carbonization do not melt or fuse but which when so heat treated tend to lose their inherent orientation. Specifically, fibers suitable for the practice of the invention are fibers of either natural or regenerated cellulosic origin which have been subjected to a pre-heat treatment to convert them to partially carbonized carbonaceous fibers. This is accomplished by first heating the raw cellulosic base fibers in either an inert or oxidizing atmosphere to a temperature in the range of from about 100° to about 350°C. for fibers which have been treated with a carbonizing aid, such as phosphoric acid, or from about 150° to about 350°C. for fibers which are untreated, until the fibers have undergone an approximate weight loss

based on the starting cellulosic material in the range of from about 20 percent to about 50 percent. Both of these techniques are described in detail in Ser. No. 224,989, filed Sept. 20, 1962, now U. S. Pat. No. 3,305,313, issued Feb. 21, 1967, which has been assigned to the same assignee as the instant application.

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

## EXAMPLE I

An apparatus was constructed for stretching carbonaceous fibers, preferably in yarn form, at elevated temperatures. This apparatus consisted of a vertically positioned, electric resistance heated hollow tube furnace having a length of approximately 2 feet and a diameter of 2 inches; a graphite rod positioned across the top of the tube furnace; and an atmosphere control system for regulating the atmosphere in the hot zone of the furnace. A partially pre-carbonized yarn prepared by heating a 1650 denier, 720 filament, 1 ply rayon yarn to a temperature of about 250°C. was doubled over the support rod and passed through the apparatus. The yarn was joined together at the two ends and the desired weight (see Table 1) was attached thereto which thereby put the yarn under a longitudinally applied tension or stress. The fibers in the furnace were then gradually heated to carbonizing temperatures. The heating schedule was 600°C./hr. from room temperature to 900°C. followed by an immediate cooling at an initial rate of approximately 400°C./hr. The 400°C./hr. cool-off rate rapidly decayed so that the approximate time from 900°C. to room temperature was about 16 hours. An argon atmosphere was maintained in the furnace both while the yarn was being heated and cooled. The amount of stretch which the yarn experienced during the stress carbonization was measured with a precision cathetometer.

It should be noted here that the partially carbonized cellulosic starting material inherently shrinks while it is being completely carbonized. Accordingly, the per cent of effective stretch reported in Table 1 below is determined by measuring the difference in length between a unit length of stress carbonized material and a similar unit length of material carbonized in a stress-free manner and dividing that value by the length of the stress-free carbonized material followed by multiplying the obtained value by 100. The foregoing is the meaning to be applied to the term "percent effective stretch" when used herein and in the appended claims.

Table 1 presents data which illustrates the resultant properties of carbon fibers stress carbonized by the foregoing technique.

Table 1

| Sample No. | Force on Fibers (gm/2 ply) | Percent Effective Stretch | Young's Modulus ($10^6$ lb/in$^2$) | Tensile Strength (lb/in$^2$) |
|---|---|---|---|---|
| 1 | 5 | 0.05 | 5.8 | 73,000 |
| 2 | 250 | 20 | 8.0 | 62,000 |
| 3 | 400 | 35 | 10.1 | 83,000 |
| 4 | 500 | 50 | 10.4 | 71,000 |

Note: the 5 gm/2 ply force applied to sample 1 was simply to align the fiber within the furnace during its carbonization. It is believed that this force did not exert any significant stress on the yarn as it was being carbonized. Accordingly, the Young's modulus and tensile strength figures evidenced by sample number 1 represent those properties which are obtained by carbonizing a rayon yarn by conventional techniques.

Although not included in Table 1 additional experimental data indicates that an effective stretch of at least 5 percent must be achieved during the stress carbonizing procedure to insure that so-treated fibers will exhibit significantly improved properties. An effective stretch of 5 percent has been found to produce fibers which have a Young's modulus of elasticity of at least $6.2 \times 10^6$ lb/in$^2$.

## EXAMPLE II

Using the same technique, apparatus and type of starting fiber as described in Example 1, fibers were stress carbonized by applying a tensional force of 400 gm/2 ply while concurrently heating them to a temperature of approximately 900°C. These stress carbonized fibers were then graphitized by heating them to 2800°C. under essentially no load conditions. The properties of the fibers so-produced are presented in Table II. In order to produce graphite fibers exhibiting similar properties by conventional stress graphitizing techniques, it was necessary to employ a stressing force which was twice as great as that required by the stress carbonizing method. For comparison, properties of fibers produced by the technique of the instant invention and by the prior art method are presented in Table II.

Table II

| Method | Force on fibers (gm/2 ply) | Effective temp. range over which force was applied (°C) | Young's Modulus ($10^6$ lb/in$^2$) | Tensile Strength |
|---|---|---|---|---|
| Stress Carbonizing (followed by stress free graphitization to 2800°C.) | 400 | 250–900 | 23.4 | 180,000 |
| Stress Graphitizing (prior art) | 800 | 100–2800 | 23.0 | 175,000 |

From the foregoing data, it is clear that the instant invention provides a method for producing high modulus fibers without requiring that they be subjected to high stresses during their subsequent graphitization.

## EXAMPLE III

Using the same apparatus, technique and type of starting fiber as described in Example 1, fibers were stress carbonized by applying a tensional force of 450 gm/2 ply while concurrently heating them to a temperature of approximately 900°C. These stress carbonized fibers were then stress graphitized by applying a tensional force of 400 gm/2 ply while concurrently heating them to a temperature of approximately 2900°C. The properties of fibers so-produced are presented in Table III. For comparison, the properties of graphite fibers produced by conventional stress graphitizing techniques are also reported in Table III.

Table III

| | Effective temp. range |
|---|---|

| Method | Force on fibers gm/2 ply | over which force was applied (°C.) | Young's Modulus ($10^6$ lb /in$^2$) | Tensile Strength (lb /in$^2$) |
|---|---|---|---|---|
| Stress Carbonized (and subsequently) Stress Graphitized | 450 | 250–900 | | |
| Stress Graphitized (prior art) | 400 | 900–2900 | 52 | 280,000 |
| | 1300 | 1000–2800 | 55 | 290,000 |

From a review of the date presented in Table III, it is seen that stress carbonizing reduces the amount of stressing required to produce high modulus, high strength, fibers by stress graphitizing already carbonized fibers.

What is claimed is:

1. A process for producing a high Young's modulus of elasticity non-graphitic carbon fiber which comprises:

a. heating a partially carbonized carbonaceous fiber at a temperature of from about 250°C. to about 900°C. to substantially completely carbonize said fiber , said partially carbonized carbonaceous fiber having been produced by the heat treatment of a cellulosic fiber at a temperature in the range of from about 100°C. to about 350°C. until the fiber has undergone an approximate weight loss based on the starting cellulosic material in the range of from about 20 percent to about 50 percent, while;

b. concurrently stretching said fiber by means of an applied tensional force an amount sufficient to achieve a percent effective stretch of at least 5 percent.

2. The process of claim 1 wherein said partially carbonized carbonaceous fiber is substantially completely carbonized in an inert atmosphere.

3. The process of claim 1 wherein said partially carbonized carbonaceous fiber is produced by heating a cellulosic fiber at a temperature in the range of from about 150 to about 350°C.

4. The process of claim 1 wherein said partially carbonized carbonaceous fiber is produced by heating a cellulosic fiber which has been treated with phosphoric acid to a temperature in the range of from about 100° to about 350°C.

5. The process of claim 1 wherein said non-graphitic carbon fiber is graphitized by heating it to a temperature in excess of 2000°C.

6. The process of claim 1 wherein said non-graphitic carbon fiber is stress graphitized by heating said fiber to a temperature of about 2800°C. while applying a stressing force thereto sufficient to permanently stretch said fiber.

7. The process of claim 1 wherein said partially carbonized carbonaceous fiber is in yarn form.

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