PROCESS FOR THE MANUFACTURE OF CARBON TEXTILES

Rostislav Didchenko, Cleveland, Ohio, assignor to Union Carbide Corporation, a corporation of New York
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ABSTRACT OF THE DISCLOSURE

An improved process for producing carbon textiles from cellulosic textiles is provided which comprises heating a cellulosic textile to a temperature up to about 400° C. in an atmosphere which contains a strongly hydroscopic reactive Lewis acid-type gas which chemically modifies the starting cellulosic textile following by carbonizing the so-modified textile in an inert atmosphere to produce a substantially all carbon textile.

This invention relates to carbon textiles and more particularly to an improved method for manufacturing the same. As used herein and in the appended claims "carbon" includes both the non-graphitic and graphitic forms of carbon.

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 said 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 carbont 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. 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 in said patent comprises heating a cellulosic textile in an inert atmosphere at a progressively higher temperature until substantial carbonization of said textile occurs. The resultant product possesses the chemical and physical attributes evidenced 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. Patent 3,107,152, which issued to C. E. Ford and C. V. Mitchell on Oct. 15, 1965. 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.

In all thermal processes for the production of carbon textiles from cellulose, the most critical part of the process takes place during the low temperature pyrolysis phase of the carbonization treatment, i.e., while it is being heated at temperatures up to about 300° to 400° C. In this temperature range, the mechanism by which cellulose is converted into a carbonaceous char determines not only the amount of undesirable tarry by-products formed, and, therefore, the yield of carbon residue, but it also has a great influence on the physical properties of the final product.

In the past, the first stages in the carbonization of cellulose usually have been conducted either under inert or vacuum conditions. Carbon textiles produced by these techniques possess highly desirable chemical and physical properties, however the yield of carbon obtained is generally about 40 percent of theoretical. This low yield is due to the formation of volatile by-products such as carbon dioxide, carbon monoxide, formaldehyde, glacial and heavy tar fractions which vaporize and remove carbon from the basic cellulosic unit or structure.

Accordingly, it is the principal object of the invention to provide a method for producing carbon textiles from cellulosic textiles in near theoretical yields.

An additional object of the invention is to provide a process for producing carbon textiles which have improved physical properties.

A still further object of the invention is to provide a process for producing carbon textiles wherein the amount of volatile by-products formed during the pyrolysis of the cellulosic starting material is substantially reduced.

Broadly stated, the objects of the invention are accomplished by a process which comprises heating a cellulosic textile in the temperature range of from ambient temperature to about 400° C. and in the course of said heating subjecting it to a reactive gas containing atmosphere followed by further heating of the resultant chemically modified cellulosic product in an essentially inert atmosphere to a temperature sufficient to produce a substantially all carbon textile.

In the practice of the invention, cellulose in any textile form may be employed as a starting material, i.e., it may be in the form of felt, cloth, tow, yarn, or the like.

Suitable reactive gas forming materials are volatile acid anhydrides and their derivatives and salts which act as Lewis acids or bases. These gases are introduced into the atmosphere in which the pyrolysis takes place, which may be a partial vacuum, air or an inert gas, such as argon or nitrogen. The reactive gases employed must be strongly hydroscopic and react with cellulose as a dehydrating agent to form cellulosic intermediates which upon subsequent carbonization yield close to theoretical amounts of carbon in a form which still retains the textile characteristic of the starting material, such as hand and drape.

Some specific reactive materials which have been evaluated and found to be readily amenable to the practice of the invention are: phosphorus pentachloride, phosphorous trichloride, ammonium chloride, ammonia bromide, phosphorus pentoxide, phosphorous trichloride, phosphorous oxychloride, sulfur oxychloride and hydrochloric acid.

The temperature at which reactive gaseous materials may effectively be employed ranges from ambient to about 400° C. This is due to the fact that the reactive gas must be brought into contact with the cellulosic textile before

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it has been substantially thermally converted to carbon.
The reactive gaseous material may be introduced into the
atmosphere in which the pyrolysis takes place as a
gas directly, with or without a carrier gas, or it may be
introduced indirectly, i.e., by vaporizing a volatile liquid
or solid. When the latter technique is used, a carrier gas
is also usually employed. The partial vapor pressure of
the reactive gaseous material in the pyrolysis zone can
range from a few to several hundred torr. However, a
partial vapor pressure above about 200 torr should be
avoided as the structure of the starting textile can be
punctured if the initial reaction between it and the reac-
tive material is allowed to occur too vigorously.

Once the cellulosic textile has been exposed to and
reacted with the reactive gaseous atmosphere, the system
is then usually purged with an inert gas to remove any
remaining reactive material which might still be present
in said system. The partially chemically modified cel-
losic textile is then subjected to further heating in an
inert atmosphere until substantial carbonization occurs,
and is then heated to a temperature of around 700-900 C.

This product can then be subjected to further heating to
temperatures of the order of 2000-2500 C. and oxygen,
so as to produce a graphite textile product.

It should also be noted that it is often not essential that
the reactive gaseous atmosphere be removed from the
system while the chemically modified cellulosic interme-
tiate is being heated to carbonizing temperatures. This is
due to the fact that at temperatures above about 400 C, the
"reactive gaseous materials" do not react with or attack
the resulting essentially all carbon structure. However,
when air or an oxygen containing gas is utilized as a
carrier, it is necessary to remove it from the carbonizing
system at temperatures in excess of about 450 C. as in-
cipient oxidation of carbon occurs at about this tem-
perature.

In addition, it should be mentioned that some reactive
compounds may be reduced to their elemental compo-
nents if they are allowed to remain in the system as the
chemically modified cellulosic material is carbonized.
Upon cooling, these elemental components might be
deposited in or on the resulting carbon textile. Accord-
ingly, if the presence of such components in the end prod-
uct is undesirable, the reactive materials from which they
are produced should be purged from the carbonizing ap-
paratus prior to the carbonization treatment.

In accordance with the teachings of the invention, car-
bon textiles were produced as described in the following
examples:

**EXAMPLE I**

A six by four centimeter rectangular piece of viscose
rayon cloth weighing 1.45 grams was wrapped around a
quartz mandrel and positioned inside of a cylindrical
quartz reaction tube which in turn was horizontally
mounted in the center of an electric tube furnace. The
quartz reaction tube was provided with ports at its ends
for the ingress and egress of gases. A thermocouple
was located within the interior of the quartz reaction tube
to monitor the temperature of the atmosphere therein. The
Ingress port was connected to an auxiliary preheater
furnace where the reactive gas was generated by heating
a boat containing about 2 grams of phosphorous pentac-
chloride. A continuous stream of dry air, as a carrier gas,
was introduced into the preheater furnace by a suitable
means at a rate of about 250 ml. per minute. This gas
was continuously flowed over the boat to pick up the
leaving phosphorus pentachloride vapors. The resulting
gaseous mixture was then flowed over the cloth sample
while both furnaces were heated to 100°C. in 25 min-
utes. The preheater furnace was held at this temperature
in order to continuously produce about 10 mm. partial
carrier vapor pressure of phosphorous pentachloride in the
system at the temperature of the reaction furnace and, ac-
cordingly, the sample therein was uniformly raised to
300°C. in about 45 minutes. At this point, the flow of

phosphorous pentachloride was terminated and the air in
the system was replaced with nitrogen. The sample
was then completely carbonized by heating it in the exist-
ing inert atmosphere to a temperature of about 975°C.

The resultant carbonized cloth weighed 0.62 gram
(corresponding to a weight yield of approximately 96
percent of theoretical) and had the dimensions of 4.5 x
3.3 cm. (corresponding to a linear shrinkage of about
20 percent).

**EXAMPLE II**

A six by five centimeter piece of rayon cloth weighing
2.00 grams was positioned in an apparatus essentially
identical to that described in Example I except that said
apparatus was provided with a means for continuously
delivering about 30 mm. vapor pressure of phosphorous
pentachloride to the system. This was accomplished by hold-
ing phosphorous tribromide in an in-line trap at 70-75°C.
and allowing the resultant vapors to flow into the
preheater assembly. The reactive gas was then mixed
with dry air and flowed through the system while the pre-
heater and reaction furnaces were simultaneously heated
to 300°C. in about one hour. The carbonizing step was
then accomplished by heating to 975°C. in a nitrogen
atmosphere as described in Example I.

The resultant carbon textile weight 0.80 gram (corre-
sponding to a weight yield of approximately 90.0 percent
of theoretical) and had the dimensions of 4.4 by 3.7 cm.
(corresponding to a linear shrinkage of about 26 percent).

While the foregoing examples have described only one
species of apparatus suitable for the practice of the
invention, it will be readily appreciated by those skilled
in the art that many other equipment variants may also
be employed to realize the benefits afforded by the inven-
tion. One of these is described in Example III.

**EXAMPLE III**

A mixture, by weight, of 3 parts of ammonium chlor-
ide to one part ammonium bromide was suitably posi-
tioned in a conventional carbonizing furnace along with
a six by four centimeter piece of rayon cloth weighing
1.75 grams. The amount of salt mixture, 0.5 gram, was
completely evaporated as the furnace was heated to a
temperature of about 500°C. in 2 hours. The chemically
modified rayon cloth sample therein was then carbonized
by heating it in said furnace to a temperature of 975°C.

The resultant carbon textile weighed 0.72 gram (corre-
sponding to a weight yield of approximately 92 percent
of theoretical) and had the dimensions of 4.2 by 2.8 cm.
(corresponding to a linear shrinkage of about 30 percent).

In addition to the specific reactants recited in the fore-
ground examples, viscose rayon specimens were also ben-
eficially converted to carbon textiles by employing the
reactants listed in the following table.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Reactant</th>
<th>Carrier gas</th>
<th>Yield, in percent per (775°) C.</th>
<th>Yield, in percent of theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscose rayon</td>
<td>None</td>
<td>N_{2}</td>
<td>16.0</td>
<td>26.2</td>
</tr>
<tr>
<td>Do</td>
<td>PCl_{5}</td>
<td>N_{2}</td>
<td>12.5</td>
<td>43.2</td>
</tr>
<tr>
<td>Do</td>
<td>POCl_{3}</td>
<td>N_{2}</td>
<td>10.0</td>
<td>57.9</td>
</tr>
<tr>
<td>Do</td>
<td>SOCl_{2}</td>
<td>N_{2}</td>
<td>26.8</td>
<td>61.7</td>
</tr>
<tr>
<td>Do</td>
<td>HOCl</td>
<td>N_{2}</td>
<td>27.0</td>
<td>60.7</td>
</tr>
<tr>
<td>Do</td>
<td>HOCl</td>
<td>Air</td>
<td>26.5</td>
<td>51.2</td>
</tr>
<tr>
<td>Do</td>
<td>HCl</td>
<td>N_{2}</td>
<td>33.3</td>
<td>85.8</td>
</tr>
<tr>
<td>Do</td>
<td>NBrCl</td>
<td>N_{2}</td>
<td>25.6</td>
<td>55.2</td>
</tr>
</tbody>
</table>

What is claimed is:

1. A process for the production of carbon textiles from
   cellulose textiles comprising heating a cellulose textile
   in the temperature range of from about 300° to 1000° C.
   and in the course of said heating subjecting said textile
to the action of at least one reactive gaseous material of
   the Lewis acid-base type selected from the group
   consisting of phosphorous pentachloride, phosphorous tri-
   bromide, ammonium chloride, ammonium bromide, phos-
   phorous trichloride, phosphorous oxychloride and sulfur
   oxychloride, with said reactive gaseous material having

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5 a partial vapor pressure below about 200 torr to form a chemically modified cellulosic intermediate, and further heating said cellulosic intermediate in an inert atmosphere to a temperature in excess of 700° C. to carbonize said cellulosic intermediate.

2. The process of claim 1 wherein said reactive material is vaporized phosphorous pentachloride.

3. The process of claim 1 wherein said reactive material is vaporized phosphorous tribromide.

4. The process of claim 1 wherein said reactive material is vaporized ammonium chloride.

5. The process of claim 1 wherein said reactive material is a mixture of ammonium chloride and ammonium bromide vapors.

6. The process of claim 1 wherein said reactive material is phosphorous trichloride.

7. The process of claim 1 wherein said cellulosic textile is rayon.

8. The process of claim 1 wherein said cellulosic textile is viscose rayon.

9. The process of claim 1 wherein said carbon textile is heated to graphitizing temperature.

References Cited

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