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CONTINUOUS PROCESS FOR PREPARING ELECTRICALLY CONDUCTIVE CARBONACEOUS FIBERS

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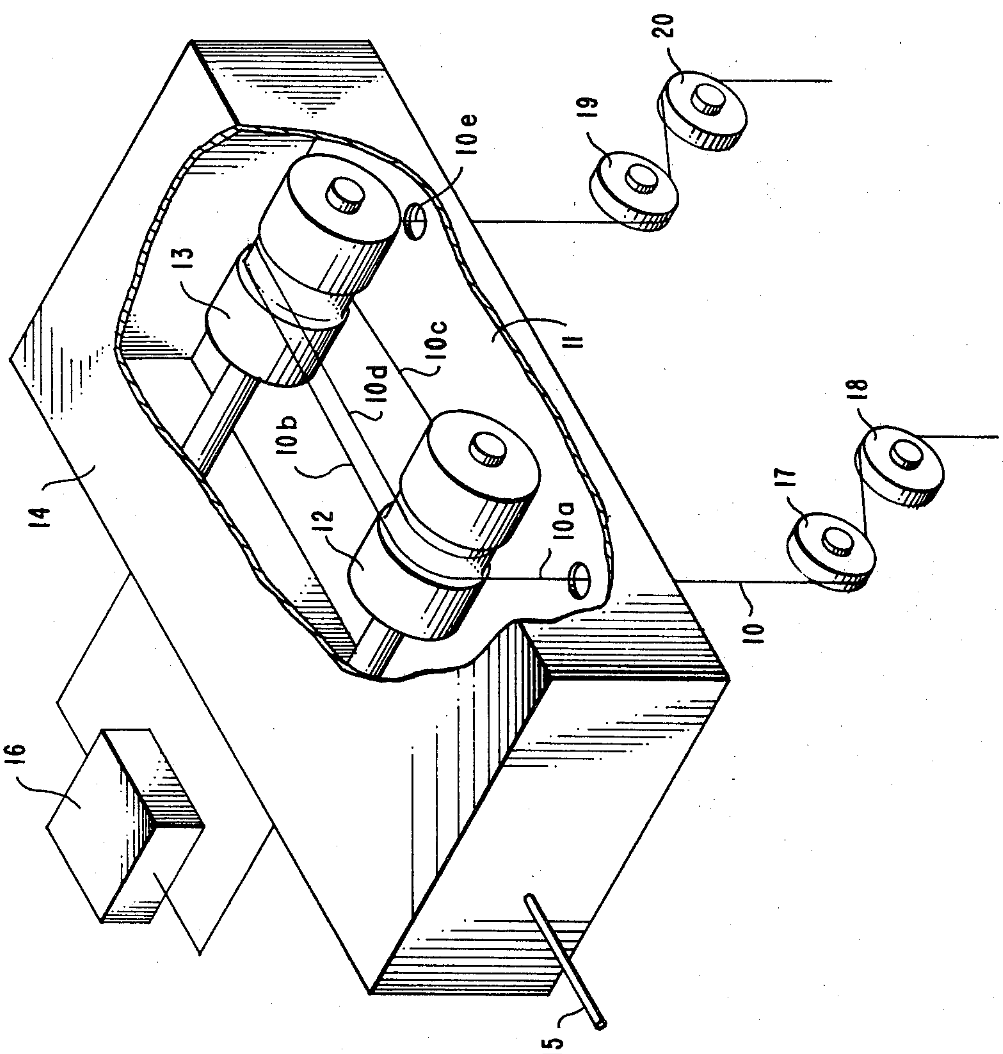



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# CONTINUOUS PROCESS FOR PREPARING ELECTRICALLY CONDUCTIVE CARBONACEOUS FIBERS

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## ABSTRACT OF THE DISCLOSURE

Electrically conductive carbonaceous fibers are prepared directly from non-conductive fibers by continuously radiantly heating a short strand of the non-conductive fiber by passing a current through an adjacent conductive carbon fiber strand. In a continuous process adjacent conductive and non-conductive strands are passed between a pair of relatively closely spaced electrodes which resistively heat the conductive strand which, in turn, radiantly heats the non-conductive strand to raise its carbon content and render it conductive.

## BACKGROUND OF THE INVENTION

Carbonaceous fibers have been known for some time to be especially useful for their high temperature properties. Carbon fibers are quite stable and maintain their integrity at high temperatures under inert atmosphere because of their high carbon contents. The non-crystalline and crystalline forms of carbon do not melt but ultimately sublime at extremely high temperatures. They have great resistance to thermal shock, and can have various degrees of thermal and electrical conductivity. These factors, together with the chemically inert nature of the fibers has led to their usage in a wide variety of protective, insulative and structural applications for severe temperature and corrosive environments.

In preparing carbon fibers, cellulosic materials such as cotton, rayon and the like are heated under controlled conditions at successively elevated temperatures to carbonize the cellulosic structures. Volatile components and compounds are driven off as gases while the basic integrity of the fibers is maintained. Such pyrolysis has been used in preparing carbon and graphite materials in the form of fabrics, tapes, yarns and the like, and is disclosed, for example, in U.S. Pat. No. 3,294,489. Although the methods of achieving conductive carbon fibers having carbon contents of above about 90% utilized heretofore have resulted in satisfactory fibers, a number of disadvantages have resulted. Such methods have comprised gradually heating the cellulosic materials in ovens under non-oxidizing conditions until the desired carbonization level is attained. However, the heating times have been relatively long, e.g. up to 24 hours or more in order to insure thorough and uniform heating. The cost of processing is thereby increased, because the dwell time within a furnace must be accomplished either by extending the furnace length or decreasing the feed rate or both. Methods used heretofore have also required preheating or firing of the fibers at temperatures of about 1000° to 1200° C. during or following their pyrolysis in order to attain desired percentages of carbon. It would be generally preferable to attain the desired final properties by processes that are faster, less costly and involve less handling.

## SUMMARY OF THE INVENTION

The present invention provides a method for preparing carbon fibers which comprises continuously and radiantly heating a short length of moving non-conductive carbonaceous fiber strand by resistively heating a conductive carbon fiber strand which is adjacent to or in intimate contact with the non-conductive strand. The non-conductive strand is radiantly heated to at least about 800° C. whereby the non-carbon volatiles are driven off and the carbon content brought up to at least about 85%. The non-conductive strand portion is thereby rendered electrically conductive. In the continuous process the conductive portion of the strand is returned to pass between the electrodes where it is resistively heated and in turn radiantly heats another portion of the advancing non-conductive strand.



The apparatus used in accordance with the invention comprises at least one pair of conductive electrodes which are relatively close together, preferably of the roller type and a power supply.

## BRIEF DESCRIPTION OF THE DRAWING

A better understanding of the invention may be had by reference to the following description, taken in conjunction with the accompanying drawing which represents a simplified perspective, partially broken away, of a form of apparatus for continuously fabricating carbonaceous materials in accordance with the invention.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises passing a non-conductive amorphous carbon fiber strand between a pair of electrodes which are in contact with a conductive carbon fiber strand adjacent to the non-conductive strand. A potential is applied to the electrodes whereby the conductive strand is resistively heated to a temperature sufficient to radiantly heat the adjacent non-conductive strand to render it conductive. The heating process may be carried on continuously by utilizing an apparatus as shown in the drawing. The portion of the strand which has been converted to a conductive state is passed between the electrodes again and is resistively heated and in turn radiantly heats an adjacent non-conductive portion of the continuously arriving carbon fiber strand. The carbon fibers are heated essentially instantaneously, uniformly and for a short period of time substantially throughout the length of strand that is between the electrodes.

The heating process as described herein, whereby the fiber strands are heated between electrodes, is carried out in an inert or reducing atmosphere. By the term inert atmosphere is meant a gaseous composition, the components of which will not react or otherwise degradate the fibers. Specifically, a non-oxidizing atmosphere, such as nitrogen, helium, argon and the like should be used and in such a manner as to eliminate excess volatiles from concentrating in the vicinity of the heating fiber strands. Alternatively a reducing gaseous medium may be used such as hydrogen, methane, etc. It is preferred to carry out the process within a closed or covered vessel with the inert atmosphere being continuously changed so as to remove the volatiles which tend to build up and could cause undesirable fiber degradation.

The carbon fibers which may be used in the process of the invention are those which have been initially heated preferably in an inert atmosphere at temperatures of up to about 400° C. and which have carbon contents of about 50% and above and preferably above about 60%. Fibers having carbon contents below about 50% when quickly and radiantly heated by the process often do not retain their original strength. That is because of the rapid out-gasing caused by rapid pyrolysis on materials which have not previously been sufficiently carbonized. On the other hand, fibers having carbon contents above about 90%–95% are themselves electrically conductive enough so that the radiant heat treatment is not necessary. Such fibers may be directly resistively heated and fired between electrodes as set forth in co-pending application Ser. No. 617,187, filed Feb. 20, 1967. Thus the non-conductive fibers utilized in the present process are those having carbon contents between about 50% and about 85% and preferably 60%–85%. The fibers may be those prepared from cellulosic or other materials that yield carbonaceous fibers on pyrolysis. Suitable starting materials include cotton, rayon, viscose rayon, as well as wool, polyacrylonitrile, polyvinyl chloride and the like.

Coating materials may be used in order to reduce the friction of the fiber strand passing through the process and to substantially eliminate abrasion of the strands as they enter into the system. The coatings may comprise suitable polymeric materials which do not otherwise inhibit or affect the process. Suitable polymers include fluoroethylene polymers, such as polytetrafluoroethylene (Teflon) and its copolymers, and high molecular weight polyethers, such as polyethylene glycols, etc. Strand and web materials may be coated with the polymers any time prior to introduction into the process of the invention. These coating materials may also be used to protect the finished strands or webs upon completion of the process described above.

Carbon fiber filaments, strands and webs that also may be utilized to advantage in the process of the present invention are those prepared by impregnating a fibrous cellulosic material with a hydrate-forming hygroscopic halide such as an ammonium, alkali or alkaline earth metal halide and thereafter heated to a temperature not more than about 50° F. higher than the minimum carbonization temperature of the impregnated material. Such fibers and methods of preparation as disclosed in co-pending application Ser. No. 517,951, filed Jan. 3, 1966, assigned to the assignee of the present invention have outstanding properties for some purposes when treated according to the present invention because they approach the theoretical maximum in carbon yield.

The length of the short span heating between the electrodes depends upon the feed rate of the strand or web, the voltage applied to the electrodes, and the heating period desired. Heating temperature is regulated by varying the current passed through the conductive carbon fiber strand. The temperature of the non-conductive strand portion depends on the proximity or distance between it and the conductive strand. It is preferred to use a strand or web span of between about one-fourth and about six inches and preferably about one-half and about four inches. Suitable driving rates for the strands or webs are of between about two and about 100 feet per minute and preferably between about five and 80 feet per minute. At such process rates, the overall heating time of any given point on the short heated span is between about $\frac{1}{50}$ and about ten seconds. The times involved in the process are significantly shorter than times utilized heretofore to prepare conductive carbon fibers.

Although the invention has been generally described as heating single strands or portions of the carbonaceous strands or webs, it should be appreciated that one or more spans may be used in each heating phase. Additionally, more than one strand may be processed in the same apparatus at one time.

As set forth above, the radiant heat from the adjacent resistively heated conductive carbon fiber strand will drive off non-carbonaceous materials and volatiles from the non-conducting carbon strand. The carbon content of the non-conductive strand is thereby raised from between about 50% and about 85% to above 85% to render it conductive. The temperature to which the non-conductive strand must be heated is at least about 800° C. The adjacent conductive carbon fiber strand will have a carbon content of above about 90%. Sufficient current is passed through the conductive strand to heat it to



at least 1000° C. up to about 3200° C. or higher. In the continuous process, not only is the high temperature of resistant heating of the conductive strand advantageous to the adjacent non-conductive strand, but the conductive portion is itself improved. Such high temperatures actually fire the strand in a very uniform manner thereby vaporizing or otherwise eliminating residual non-carbon materials from the fiber. The purity of the conductive strand is improved by practically instantaneously heating throughout the length and cross-section of the portion of the fiber between the electrodes. Carbon contents are increased up to as high as 99% or more. At temperatures above about 2400° C. the carbon within the strand becomes crystalline.

In order to more clearly illustrate the process, reference is made to the drawing which represents a cutaway of apparatus used in the heating method of the invention. The strand of non-conductive carbon fiber **10** is fed into a closed chamber **11** which is filled with an inert or reducing atmosphere. A conduit **15** in the housing **14** is connected to a positive pressure source of nitrogen or other inert gas in order to purge the environment and maintain it essentially free of oxygen. A pair of electrode rollers **12** and **13** are rotatably mounted on a wall of the housing **14**. The rollers **12** and **13** are made of a highly electrically conductive material such as copper, although they may also be fabricated of brass, aluminum, graphite or other similar materials. It may be desirable to use grooved or center slanted rollers in order to maintain the conductive and non-conductive strand portions in close proximity to each other although other means such as a Godet-type guide may also be used. Each electrode roller is coupled to an adjustable power source **16** which may provide alternating or direct current.

The non-conductive carbon fiber strand **10** is passed from a suitable supply source such as a reel, spindle, spool, etc. and over guide rollers **17** and **18** to the pair of electrodes **12** and **13**. As mentioned above, the guide rollers may be of the Godet-type to keep the strand portions passing over the electrodes in close relation to one another. The strand is passed around the pair of electrodes **12** and **13** once to form a complete loop and on to a takeup reel or spool via guide rollers **19** and **20**.

For the purpose of explanation of the effect of the heating of the strand **10** at the different phases of the process, it will be referred to as strand portions **10*a***, **10*b***, **10*c***, **10*d*** and **10*e***. The arriving strand portion **10*a*** is a non-electrically conductive carbon fiber having a carbon content of between about 50% and 85%. As the strand portion **10*b*** passes between the electrode rollers **12** and **13** it is adjacent to conductive strand portion **10*d*** which is resistively heated to between about 1000° and 3200° C. Strand portion **10*b*** thereby is radiantly heated to at least 800° C. and pyrolyzed to drive off non-carbonaceous materials and raise its carbon content to above 85%.

It will be appreciated that the temperature and concomitant pyrolysis of the advancing strand portion **10*b*** will increase as it travels toward electrode roller **13**. The specific temperature of the strand portion **10*b*** at any given point between the electrode rollers **12** and **13** will depend on the temperature of the conductive strand portions **10*d*** and its proximity to strand portion **10*b*** as well as the speed at which the strand portions are advancing. However, according to the invention, at least by the time the strand portion **10*b*** contacts electrode roller **13** it will have been pyrolyzed to such an extent that it is electrically conductive. In fact where the strand portions **10*b*** and **10*d*** are in such proximity as to be physically in contact with one another or almost so, the temperature of strand portion **10*b*** may be the same or substantially the same as that of strand portion **10*d*** by the time it contacts the electrode roller **13**. Although it has been stated that strand portion **10*d*** may be heated to about 3200° C.

or higher, it is preferred to maintain its temperature between about 1800° and about 2800° C. where strand portion **10***b* is in close proximity or in contact with strand portion **10***d* since extremely high temperatures may tend to cause undesired fiber degradation of radiantly heated strand portion **10***b*, especially where its initial carbon content is relatively low, i.e. below about 75%. As the strand **10** is guided or looped around electrode roller **13** and passes toward electrode **12**, strand potrion **10***c* which is electrically conductive due to its carbon content becomes resistively heated. The specific temperature at which it is resistively heated will, of course, depend on the current passing through it, rate of advance, cross-section, etc. Temperatures above about 1000° C. will be produced however, since the current passing through the strand portion **10***c* is essentially the same as that passing through strand portion **10***d*, which, according to the invention, is heated to at least about 1000° C. and since both of those portions are similarly conductive. The initial carbon content of strand portion **10***c* must be at least 85% and preferably above about 90% and will be further increased to as high as 99% or above by the time it reaches electrode roller **12**. However, where strand portion **10***b* has been heated radiantly to a temperature of about 2000° C. or so, the initial carbon content of strand portion **10***c* may be of the order of about 95% or more. The resistive heating of strand portion **10***c* is uniform and essentially instantaneous between the electrode rollers and the fiber is further improved by the removal of additional volatile materials. As strand **10** loops around electrode roller **12** and toward electrode roller **13**, strand portion **10***d* is resistively heated as set forth above and in turn radiantly heats nonconductive strand portion **10***b* and so on in a continuous manner. It will be appreciated that strand portion **10***d* may also be improved by further removal of volatiles especially where its initial carbon content is below about 95%–97% due to lower temperature heating or very fast strand advance rates.

In conjunction with the above-described process, a starter strand may also be employed and passed along the strand path in such a manner that it is sufficiently adjacent to the non-conductive strand portion **10***b* at the start of the continuous operation. The starter strand must be sufficiently electrically conductive so that it will become resistively heated and, in turn, radiantly heat the non-conductive strand portion **10***b* to render it conductive. The starter strand may be any conductive material and is preferably a conductive carbon fiber. Once the continuous process has begun, the starter strand is unnecessary and may be removed from the process. Alternatively the starter strand may be used in the form of a leader, tied on to the leading end of the non-conductive strand utilizing a small knot.

Where it is desired to increase the modulus strength of the strand or other fibrous form of carbonaceous material according to another feature of the invention, stress may be applied to the strand portion **10***e* thereby stretching the strand to a certain extent. Suitable stretching means include the use of a weight placed on the strand before its final takeup or takeup that is faster than the rate at which the strand is fed into the system.

In order to illustrate the improvement and advantages of the process of the invention the following example is provided. It is to be understood that the conditions used in the example are for the purpose of illustration only and are not intended to be limiting.

## EXAMPLE

A carbonized rayon cord of 1650 denier, 720 fil and 7-ply which had been oven heated to a temperature of about 310° C. and has a carbon content of about 73% by weight was introduced into an apparatus similar to that shown in the drawing. The cord had an average break strength of 15 pounds. The rate of advance of the cord through the apparatus was 15 feet per minute and the distance between the center of the electrodes was 1.4 inches. The electrical power supplied to the electrodes was 30–35 volts at 20 amps. A conductive starter strand was utilized until a conductive portion of the cord was obtained after which the starter strand was eliminated. The process was run under a nitrogen atmosphere. The temperature of the conductive strand portion corresponding to **10***d* of the drawing was maintained at between about 2200°–2400° C. while the corresponding strand portion **10***c* was between about 2100° and 2300° C. The finished cord was found to contain 99.98% carbon by weight and had an average break strength of 19 pounds.



Strand and web processing apparatus in accordance with the invention may take a variety of different forms, inasmuch as they may be varied in particular details to provide different characteristics for different types of products being operated upon. For example, it may be desired to optimize physical characteristics, or to optimize production rates while providing improved but not optimum physical characteristics. The state of the starting material provided is significant, inasmuch as the starting material may have the greater or lesser percentage of carbon, dependent upon the prior treatment. Generally, the material being processed will be in strand form, the term "strand" applying generally to filaments, yarns, cordage and the like. It is also feasible, however, to process web materials, including tape, sleeving and similar forms. Various mechanisms and apparatus are illustrated and described for different purposes, but it will be appreciated that these are provided by way of example only and that a number of modifications and variations may be used in accordance with the inventive concept.

What is claimed is:

**1.** A method for improving carbonaceous materials comprising: in the presence of a non-oxidizing atmosphere continuously passing a non-conductive strand portion of carbonaceous material from a first electrode to a second electrode while simultaneously passing an electrically conductive strand portion of carbonaceous material from the first electrode to the second electrode the conductive strand portion being adjacent the non-conductive strand portion and supplying current to the electrodes whereby the conductive strand portion is resistively heated thereby radiantly heating the non-conductive strand portion.

**2.** The method of claim **1** wherein the respective strand portions are portions of an initially non-conductive continuous carbonaceous strand.

**3.** The method of claim **1** wherein the initial carbon content of non-conductive strand portion is between about 50% and about 85% by weight.

**4.** The method of claim **1** wherein the carbonaceous material is cellulosic in origin.

**5.** The method of claim **1** wherein the non-conductive strand portion is radiantly heated to a temperature of at least about 800° C.

**6.** A method for improving a non-conductive carbonaceous strand which comprises:

(a) continuously passing an advancing initially non-conductive strand portion of carbonaceous material from a first electrode to a second electrode which electrodes have a potential therebetween;

(b) simultaneously with step (a) continuously passing an advancing conductive carbonaceous strand portion from the first electrode to the second electrode whereupon the conductive strand portion is resistively heated to an extent to radiantly heat the non-conductive strand portion which is adjacent thereto to render it conductive by the time it reaches the second electrode;

(c) continuously returning the advancing strand portion which has been rendered conductive according to step (b) to the first electrode from the second electrode whereby the strand portion is resistively heated;

(d) continuously returning the advancing conductive strand portion of step (c) from the first electrode to the second electrode in such a manner that it is adjacent to and radiantly heats the non-conductive strand portion of step (a) to render it conductive according to step (b); wherein the steps (a)–(d) are carried out within a non-oxidizing atmosphere and

(e) guiding the advancing strand portion of step (d) to a takeup means after it passes over the second electrode.

7. The method of claim 6 wherein the strand portion passing over the second electrode according to step (e) is subjected to tensile stress after leaving the second electrode.




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