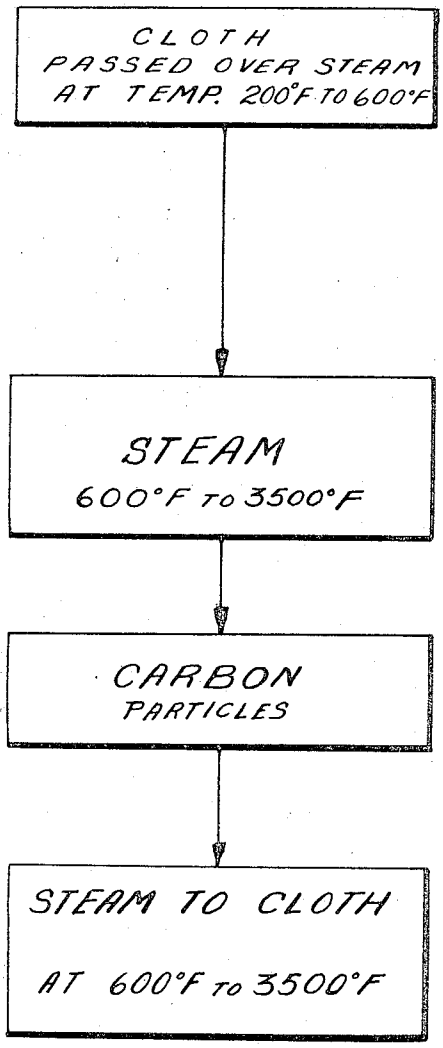
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PROCESS FOR CARBONIZING FIBROUS CELLULOSIC MATERIALS

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PROCESS FOR CARBONIZING FIBROUS CELLULOSIC MATERIALS

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ABSTRACT OF THE DISCLOSURE

A process for the preparation of carbon fibers by pyrolyzing cellulosic fibers, preferably in fabric form, in a non-oxidizing gaseous atmosphere containing a predominant amount of steam.

This invention relates to the preparation of carbon fibers.

Previous proposals for making carbon fibers from cellulosic materials frequently have suffered from the disadvantage of requiring relatively expensive types of inert atmosphere and/or difficulties in controlling the rate of carbonization to prevent too rapid a devolatilization during the early critical stages.

It is an object of the present invention to prepare good quality carbon fibers from regenerated cellulose, e.g. in the form of yarn, cloth individual fibers or the like, with reproducible results.

Another object is to devise an improved procedure for forming carbon fibers from regenerated cellulose.

An additional object is to employ an economical atmosphere in forming carbon from cellulose fibers.

A further object is to moderate the rate of carbonization by preventing too rapid a devolitalization in converting cellulosic fibers to carbon.

Yet another object is to provide a desirable reducing atmosphere during carbonization.

A mere specific object is to prepare improved carbon fibers, e.g. in the form of cloth, from viscose rayon.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by pyrolyzing cellulosic fibers, preferably in fabric form, to carbon using steam as such or steam which has been partially decomposed over hot carbon as the purging medium.

The present invention is suitable for conversion of various forms of cellulosic fibers into carbon fibers. Thus it can be employed with cotton fibers, cotton linters, cotton cloth, flax or other cellulosic fibers. Preferably, however, regenerated cellulose fibers are employed, most preferably in the form of cloth. As used in the present specification and claims the term "regenerated cellulose" is intended to embrace fibers of viscose rayon, cuprammonium rayon and saponified cellulose ester rayon, e.g. saponified cellulose acetate rayon.

The regenerated cellulose can be employed in the form of cord, yarn, cloth or the like, but preferably is in the form of cloth.

The invention will be best understood with reference to the accompanying drawing which is a diagrammatic illustration of one form of the invention.

The carbonization is carried out in a non-oxidizing atmosphere.

Steam can be used by itself or it can be diluted with an inert gas such as nitrogen, helium or argon or it can be diluted with a reducing gas such as hydrogen, deuterium or carbon monoxide when employed in pyrolyzing the cellulose in the temperature range of 200 to 700° F., preferably not over about 600° F. The steam is 20 to 100% of the gas by mol percent.

When the steam is employed in pyrolyzing at temperatures above 700° F., it is first passed over a bed of reactive carbon to prevent loss by the water gas reaction of the carbon fibers in the cloth being carbonized. Preferably the bed of reactive carbon is maintained at a temperature equal to or above the temperature of the cloth being carbonized. If desired it is also possible to use steam which has thus been partially broken down into carbon monoxide and hydrogen in the earlier and critical pyrolysis of the cellulosic fibers at temperatures of 700° F. or below.

If desired small amounts of additional reagents can be introduced with the steam. Thus for example, steam volatile acid catalysts such as acetic acid, hydrochloric acid, formic acid, oxalic acid, propionic acid, malonic acid can be introduced into the liquid water being vaporized to generate the steam which is to be passed through the carbonization chamber. These acids can be added to the water so that there is 0.05 to 2 mol percent of acid based on the volume of steam being passed into the carbonization chamber. Such acids help to neutralize any alkali which may still be present in the cellulose, e.g. regenerated cellulose.

The cellulosic material is purified in conventional fashion prior to initiation of the carbonization treatment. Thus there can be used commercial viscose or other regenerated cellulose which has a sodium content below 25 p.p.m. or if the cellulose has above 25 p.p.m. of sodium it can be reduced below 25 p.p.m. by washing with water or dilute acid. There can also be used cellulosic fibers having a sodium content above 25 p.p.m. but for most consistent results the sodium content should be below 25 p.p.m.

The cellulose, e.g. regenerated cellulose fabric is heated in the atmosphere of steam, with or without non-oxidizing diluting gases as indicated above, to a temperature of 200 to 400° F. The heating to the upper end of this range can be either rapid or slow and the time is not critical. It is critical, however, that the heating in the temperature range of 400 to 550° F. be quite slow. Thus the heating up to 380° F. can be accomplished in 2 minutes but the heating in the range of 300 to 550° F., most preferably 400 to 550° F., should be for at least one-half hour and preferably is at least 2 hours and can be much longer, e.g. 12 hours or even a week. The product is then gradually heated to a temperature of from 550 to 800° F. for 1½ to 24 hours or longer, usually 4 to 12 hours, next the temperature is raised from 800 to 1500° F. or above over a period of 2 to 18 hours. At a top temperature of 1500° F. the product has 94% carbon, at a top temperature of 1800 F., the product has 96.5 to 97.5% carbon, and at a top temperature of 2000° F. the product contains 98 to 99% carbon. If the final temperature is elevated to 3500° F. or above, e.g. 5000° F., the product is converted into graphite fibers or cloth.

It has been found desirable to use a final temperature of 1800° F. because the resulting fiber product, whether in the form of cord, yarn or cloth is very strong.

A preferred heating schedule comprises a slow heating rate of 18° F. to 90° F. rise per hour from a temperature of 212° F. to 750° F. followed by a heating rate of up to 215° F. per hour to a temperature of 1650° F. fol-

lowed by further heating at a rate up to 5400° F. per hour until the desired maximum temperature is reached.

It has been found that the steam is considerably more economical to use than other gaseous media for the pyrolysis. Steam also has a moderating effect on the rate of carbonization preventing too rapid a devolatilization during the critical heating stages. Steam also has desirable heat capacity and heat transfer characteristics. When steam is partially decomposed in a water gas reaction ahead of the carbonization chamber, a desirable reducing atmosphere is provided.

Unless otherwise indicated all percentages are mol percent.

Example 1

Painesville White heavy duty viscose rayon cloth was heated from about 200° F. to 550° F. in the presence of a current of steam. (The Painesville White rayon had 3400 filaments in the yarn and 20 x 20 threads per square inch). The heating to a temperature of about 400° F. was quite rapid. The rate of heating was controlled to provide a uniform temperature in the cloth and to avoid unduly rapid generation of volatiles in the pyrolysis temperature range of 400° to 550° F. A total of 3 hours was required to pass through the 400° F. to 550° F. temperature range.

The thus pyrolyzed cloth was ready for further heating in conventional fashion, e.g. with an inert gas such as nitrogen, argon, helium or using a vacuum, e.g. .001 mm. or employing a reducing gas such as hydrogen or carbon monoxide. Thus in one example the cloth was placed in a nitrogen atmosphere and heated from 550° F to 800° F. over a period of 6 hours and finally heated at a temperature increasing from 800 to 1800° F., over 6 hours to obtain a carbon cloth having a carbon content over 97%.

Example 2

The procedure of Example 1 was carried out except that the heating at 400 to 550° F. was carried out over a period of 6 hours.

Example 3

Viscose rayon cloth having 3400 filaments in the yarn and having 20 x 20 threads per square inch and a sodium content of 7 p.p.m. was heated from about 200 to 550° F. in a current of steam and nitrogen containing 80 mol percent steam and the balance being nitrogen. The rate of heating was such that it took 4 hours to pass through the 400° F. to 550° F. temperature range. The temperature of the cloth was raised to a temperature of 400° F. in about 5 minutes.

The thus pyrolyzed cloth was then heated from 550° F. to 800° F., over a period of 5 hours and finally heated at a temperature increasing from 800 to 1800° F. over 6½ hours to obtain carbon cloth having a carbon content over 97%.

Example 4

Painesville White viscose rayon cloth was heated from 212° F. to 550° F. in the presence of a current of steam. The heating to a temperature of 380° F. was quite rapid (less than 5 minutes), the rate of heating was then controlled so that the temperature rose from 380° F. to 550° F. over a period of 4 hours. The thus pyrolyzed cloth was then heated gradually from 550° F. to 1800° F. over a period of 12 hours in the presence of steam which had previously been passed over a bed of reactive carbon particles. The steam was passed over the carbon bed at a temperature 100° F. above that at which it was used as an atmosphere for the heating of the partially pyrolyzed cloth and then was cooled to the indicated pyrolyzing temperatures. Thus as the pyrolyzing temperature was gradually increased from 550° F. to 1800° F. the steam employed was passed over the carbon bed

at a temperature gradually increased from 650° to 1900° F.

Example 5

The procedure of Example 4 was repeated except that the steam employed in heating the cloth from 212 to 550° F. was steam that had been passed over a bed of reactive carbon particles at a temperature which was gradually increased from 300 to 650° F. The steam was cooled to the requisite temperature of 212 to 550° F. prior to introduction into the chamber containing the cloth to be pyrolyzed.

Example 6

The procedure of Example 4 was repeated except that hydrogen chloride vapor in an amount of 0.2 mol percent of the steam was introduced into the steam prior to passage through the carbonization chamber at 212 to 550° F.

It is also possible to add a minor amount of nitrogen, argon, helium or other nonoxidizing gas to the steam partially decomposed by the water gas reaction prior to introducing the thus decomposed steam to the cloth or other fiber to be carbonized.

What is claimed is:

1. In a process of preparing carbon fibers from cellulosic fibers the improvement comprising carrying out the pyrolysis of partially carbonized cellulosic fibers at a temperature of above 700° F. in the presence of steam which has carbon monoxide and hydrogen therein as a result of having been passed over reactive carbon at a temperature at least equal to the pyrolysis temperature prior to treatment of the partially carbonized fibers therewith.

2. A process according to claim 1 wherein the cellulosic fibers are regenerated cellulose fibers.

3. A process according to claim 2 wherein the atmosphere consists of at least 20 mol percent of steam and the balance other nonoxidizing gases.

4. A process according to claim 3 wherein the nonoxidizing gases are inert gases.

5. A process according to claim 2 wherein the regenerated cellulose fibers are in the form of cloth.

6. In a process of preparing carbon fibers from cellulosic fibers the steps comprising carrying out the pyrolysis of the cellulosic fibers in the range of 400 to 700° F. in a nonoxidizing atmosphere comprising a predominant amount of steam to form partially carbonized fibers and carrying out the pyrolysis of the partially carbonized fibers at a temperature above 700° F. in a nonoxidizing atmosphere which is predominantly a mixture of steam, carbon monoxide and hydrogen resulting from the partial decomposition of the steam by passing the same over reactive carbon at a temperature at least equal to the pyrolysis temperature.

7. A process according to claim 6 wherein the cellulosic fibers are in the form of regenerated cellulose cloth.

8. A process according to claim 1 including a small amount of a volatile nonoxidizing acid in the steam.

9. A process according to claim 1 wherein the cellulosic fibers are viscose rayon cloth.

10. A process according to claim 6 wherein the cellulosic fibers are viscose rayon cloth.

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