

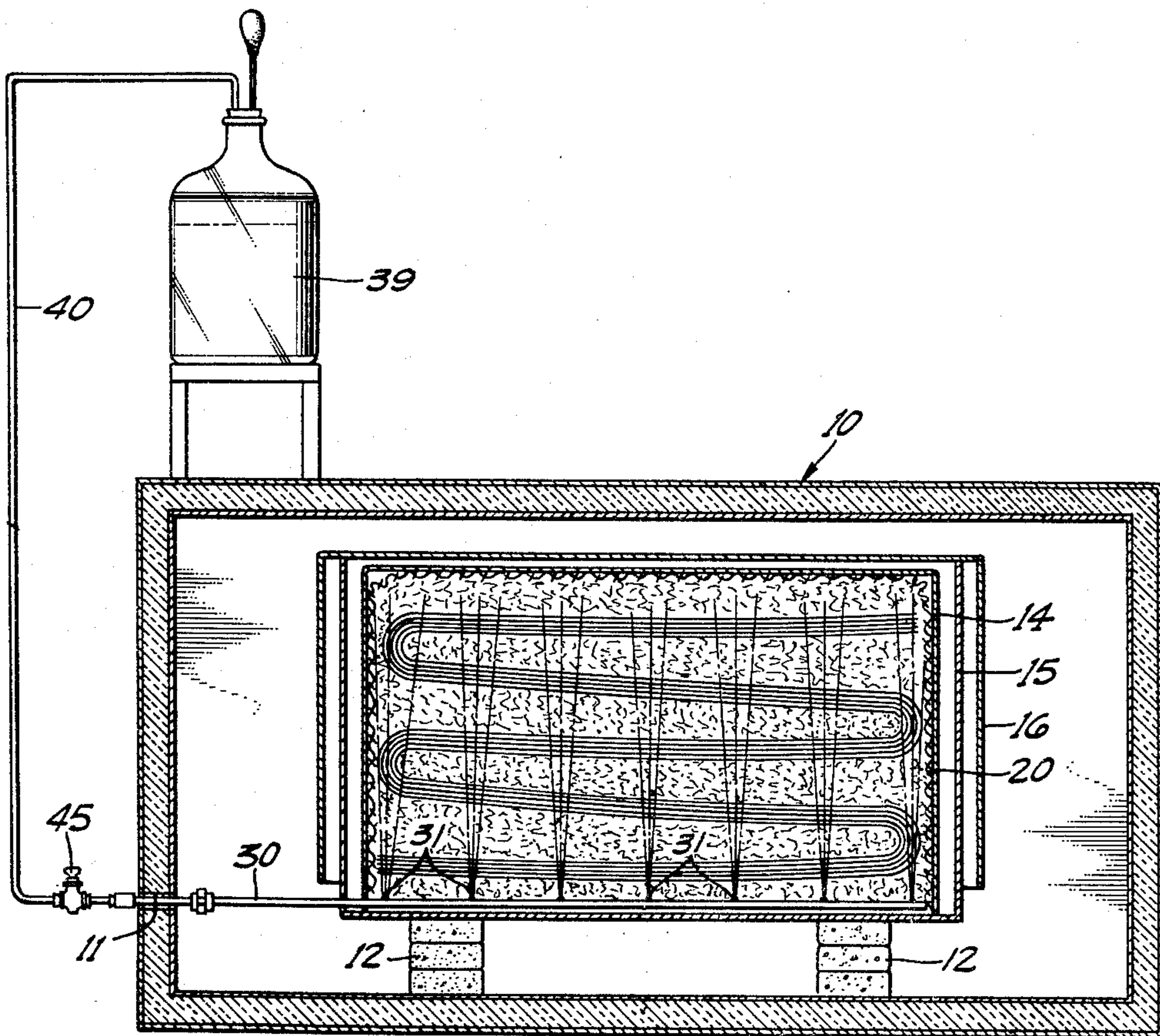
Sept. 11, 1962

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3,053,775

METHOD FOR CARBONIZING FIBERS

Filed Nov. 12, 1959



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3,053,775

METHOD FOR CARBONIZING FIBERS

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Filed Nov. 12, 1959, Ser. No. 852,580

8 Claims. (Cl. 252-421)

This application is a continuation-in-part of my prior, co-pending application Serial No. 569,391, filed March 5, 1956, entitled Method for Carbonizing Fibers, and Articles Produced Therefrom, now abandoned.

This invention relates to fibrous materials and has particular reference to a process for carbonizing fibers and to articles produced therefrom.

One of the primary objects of this invention is to provide a process for the production of carbon in fibrous form having a high intrinsic fiber density and good tensile strength. While fibers of carbon are not basically new, carbon fibers heretofore produced have been so weak in structure that they could not resist even slight mechanical forces without breakage or disintegration. The present invention provides for the first time fibers substantially of carbon which are sufficiently strong to retain their fibrous form upon being subjected to mechanical forces.

Another object of this invention is to provide a hard, high density carbon in the form of fine fibers, the fibers being clean and strong because of the high density, yet flexible and resilient due to the small diameter of the fibers.

Another object of this invention is to provide a process for the production of carbon fibers having a wide range of fiber diameter and other characteristics for use in varied specific applications.

Another object of this invention is to provide a carbon fiber which is capable of being activated to a high level while still retaining a considerable part of its original strength, the activated fiber having adsorption characteristics equal on a weight basis to conventional activated carbon in granular form. Granular activated carbon is well known in industrial applications, but is limited to use applications which provide means to contain the carbon granules. Activated carbon fibers of the present invention extend the use of carbon to clothing, masks, and filters of fiber construction.

Other objects and advantages of the invention, it is believed, will be readily apparent from the following detailed description of preferred embodiments thereof when read in connection with the accompanying drawings.

In the drawings:

The single FIGURE is a diagrammatic view illustrating the apparatus required to carry out the process of this invention on a small scale.

Briefly, this invention comprehends within its scope the discovery that certain synthetic fibers may be carbonized by carefully controlled thermal decomposition to produce a dense, strong carbon fiber. The choice of raw materials is limited to synthetic fibers of the non-thermoplastic type, which do not tend to melt or flow on heating and hence retain the fibrous form when heated to the decomposition point.

Natural fibers, such as cotton, for example, are not suitable for the purpose of this invention. Although such fibers may be carbonized, they are weak and therefore are unsatisfactory for practical use in the form of carbon fibers.

It has been found that a regenerated cellulose fiber, such as viscose rayon, cuprammonium rayon and saponified acetate rayon, is a particularly suitable raw material for accomplishing the ends of the present invention.

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The present process comprises heating the raw fiber material in an inert, oxygen-free atmosphere to a temperature sufficiently high to bring about substantially complete thermal decomposition of the non-carbon constituents of the material, great care being taken to control the rate of temperature rise so that gasification is slow to prevent fiber rupture by rapid decomposition.

It has been discovered that a critical temperature range of from about 250° to about 500° F. exists for the desired carbonization of the raw regenerated cellulose fibers. It is in this range that the major part of the carbonization takes place. It is extremely important that the rate of temperature rise through this temperature range be controlled so that the weight yield of carbon fiber will be greater, preferably, than 45 percent of the carbon content of the original raw regenerated cellulose, and so that the tensile strength of the resultant carbon fiber will be at least 5,000 p.s.i. The temperature rise through this range for a single fiber, for example, should take place uniformly in not less than 8 minutes and preferably over a period of one hour so as to prevent excessively fast gasification, such as would otherwise damage the fiber. In actual practice, utilizing a mass of fibers, the time required to raise the temperature of the entire mass of fibers through this range will exceed the time required for an individual fiber according to the heat transfer characteristics of the particular equipment employed and the volume of the mass of fibers.

The gaseous decomposition products given off during the heating operation can themselves provide the inert, oxygen-free atmosphere if properly contained. In order to avoid brittleness in the product, the fiber diameter of the raw materials should be less than about 200 microns. Preferably, the fiber diameter is less than 100 microns.

The raw materials may be treated in the form of continuous mono-filaments, in the form of short-length or staple fibers, in the form of yarn or woven webs, or in any other suitable fiber form. Continuous mono-filaments or yarns are preferred, since they can be continuously treated by passage through a suitable furnace or other heating apparatus.

The continuous process may be carried out in a tunnel furnace having a preheat section followed by an atmospheric trap, a carbonizing section and a cooling section, through which the fiber is drawn. The rollers for the fiber should be of ceramic material, and the fibrous material is preferably supported and guided through the furnace on a guide belt or belts of quartz glass cloth. Inasmuch as the fibers undergo shrinkage of from 20 to 35% during carbonization, provision must be made for such shrinkage by providing for multiple drive of the quartz belts in the carbonization zone. The cooling section may comprise water jacketed heat transfer plates.

The process may also be carried out batch-wise in a suitable furnace provided with adequate temperature control means.

Products produced by the above-described thermal decomposition process have a wide scope of industrial uses. The carbon fibers are strong, yet highly flexible and may be readily fabricated into the desired form or assembled with other components for use. Thus, continuous carbon filaments may be woven into yarn and/or cloth for thermal insulation, filtration applications and the like. The yarn, cloth, or staple carbon fibers, having sufficient strength to provide a self-supporting mass of fibers, may be formed into mats or pads for similar uses. Also, the carbon fibers in yarn or staple form may be used as a catalyst or catalyst carrier, and as a caulking material for specialized applications. Other industrial applications will readily present themselves to those skilled in the art.

If desired, the fibrous raw material may be formed before carbonization into mats, pads, or continuous webs of low bulk density and having a high degree of shape retention by bonding the fibers together with a suitable thermosetting resin such as urea formaldehyde. The resin should be applied at a low viscosity such that cross-fiber cementing occurs without the deposition of excessive or thick resin masses. Any extensive thickening of the fiber diameters or the formation of nodules of resin on the fibers is undesirable and produces brittle sections in the finished product. Preferably, the resin bond film is of the same order of magnitude as the fiber diameter. The cured, resin-bonded fiber mats or pads are carbonized in accordance with the above-described process to produce carbon-bonded, carbon fiber mats or pads suitable for use in air filters, as thermal insulation and the like.

It is within the scope of this invention to provide the carbon fibers with coatings of various types, applied either before or after carbonization. Such coatings may include oxides for various purposes, i.e., MgO , ZnO , etc., for improved fireproofing, to minimize the need to protect the material from oxidizing atmospheres when used as a thermal insulation; Fe_2O_3 , Cr_2O_3 , Al_2O_3 , as catalyst surfaces for catalytic reactions utilizing the carbon fiber as the carrier; CuO , Cu_2O , etc., for inversion of the selective adsorption characteristics to provide specific adsorption properties; and appropriate oxides to change the black color of the carbon fibers.

The above and other surface coating materials may be introduced prior to or during regeneration and fiber formation. This simplifies the coating process and produces more thorough and uniform coatings, more impervious coatings, and coatings with a greater degree of bond to the fiber.

It has been found that during the carbonization process the raw material undergoes a change from an electrical insulating material to a conducting material. It has been further found that a semi-conductive product may be produced by partial carbonization as by not permitting the temperature to rise above $500^\circ F.$ during the carbonization. By proper control of the temperature, the product may be made to exhibit variable specific resistance. Such materials are useful in electronic applications such as in making sensing elements, transducers, conductivity devices, and the like.

Carbon fibers produced by the present carbonization method have very low adsorption capacity. These same fibers may, however, be activated to provide saturation adsorption capacities for carbon tetrachloride, for example, of 30–50% by weight of the activated carbon fiber, while still retaining a high proportion of the strength properties of the unactivated carbonized fiber. It has been found that the unactivated carbonized fibers may be activated by reaction with steam at temperatures from 1200° to $1800^\circ F.$ This is the well known activation process which has heretofore been applied to granular carbon materials.

The activation process may be carried out continuously on continuous filaments by introducing a steam reaction chamber immediately prior to the cooling section of the tunnel furnace described above. In the case of the batch process, steam apparatus is added to the furnace for use after carbonization. The activation may be accomplished prior to cooling following carbonization, or it may be carried out on the cooled, finished carbon fiber product.

The following is a specific example of the process as carried out on a small-scale batch operation, but it is to be understood that the invention is not to be limited to the details set forth:

Example 1

The apparatus is shown diagrammatically in the drawing, and includes a 4-burner, gas-fired box kiln furnace 10 provided with a side port 11. Mounted inside the fur-

nace on ceramic blocks 12 was a set of three rectangular iron pans 14, 15 and 16 of progressively increasing size. The pan 14 measured 19" in length, 10" in width and 6" in depth; the pan 15 measured 20" x 11" x 6½"; and the pan 16 measured 21" x 11½" x 7". The pan 14 was provided with quartz cloth insulation 20 on the sides and bottom thereof to insulate the fibers from the iron of the pan.

In carrying out this example, 40 feet of "tow" type viscose rayon (American Viscose Co., 245M denier; fil., 1.5; qual., "A"; type, brt. tow; fin., soft unbl.; sym., TN339) was then layered into pan 14 between 1-inch thick layers of "fluffy" type viscose rayon fibers (American Viscose Co., 5.5 denier; length, 5"–7"; qual., "A"; type, var. reg.; lustre, brt.; sym., 1432) to prevent packing. Pan 14 was then covered with pan 15 and the two pans inverted and then covered with pan 16. The furnace was preheated to $300^\circ F.$ for about 15 minutes and the assembly of the three pans put into the center of the furnace on ceramic blocking to permit uniform movement of air. The furnace and contents were then heated slowly through the gasification stage (300° – $500^\circ F.$) for 2¼ hours. The temperature was then allowed to rise to $1000^\circ F.$ to drive off the gases, the furnace then turned off and the batch allowed to cool for 18¼ hours.

The carbon fibers produced had a tensile strength of 10,000 p.s.i. and a weight yield of 52% of the carbon content of the raw regenerated cellulose fibers.

The following example describes the production of activated carbon wool fibers by the batch method:

Example 2

The apparatus described in Example 1 was utilized with the addition of a length of ¼-inch steel tubing 30 welded through one end of the pan 15 and to the bottom, the tubing being provided with a plurality (about 6 in this case) of ⅛-inch holes 31 equally spaced inside the pan length. The tubing passed through the furnace port 11. A 5-gallon bottle 39 of distilled water was positioned on top of the furnace and provided with a supply tube 40 connected to the tubing 30. A stop-cock 45 was also provided in the tube 40.

The carbonization step of this example was identical to that of Example 1, except that here, following the 2¼-hour carbonization step, the temperature of the carbon fibers was raised to $1450^\circ F.$, and maintained there for about 2 hours, during which time about 5 gallons of distilled water from the bottle 39 was slowly fed by gravity into the tubing 30. Steam was thus forced out of the holes 31 and through the carbonized fibers to activate the same. At the end of the two-hour period, the batch was dried by lowering the temperature to about $500^\circ F.$ for about 15 minutes. The furnace was then allowed to cool for about 18¼ hours as in Example 1. The activated carbon fibers thus produced had a carbon tetrachloride saturation activity of 35% by weight.

Example 3

Utilizing the same apparatus as described in Example 1, a 2.0 pound batch of 3 denier, 3"–5" length fibers of cuprammonium rayon, was carbonized by slowly heating the same through a temperature range of $250^\circ F.$ to $500^\circ F.$ for 2½ hours. The temperature was then raised to $1000^\circ F.$ to drive off gases from the furnace. The batch of carbonized fibers was then permitted to cool to room temperatures over a period of approximately 18 hours.

The carbon fibers thus produced were tested and revealed a tensile strength of 8,000 p.s.i. and a weight yield equal to 50.4% of the carbon content of the raw cuprammonium rayon fibers.

Example 4

Again, utilizing the apparatus described in connection with Example 1, a 1.5 pound batch of 1 denier saponified acetate rayon fibers was carbonized by slowly heating the same through a temperature range of $250^\circ F.$ to $500^\circ F.$

for 2½ hours. The temperature was then raised to 1000° F. and the batch allowed to cool to room temperature over an 18 hour period. The resultant carbonized fibers were tested and revealed a tensile strength of 11,200 p.s.i. and a weight yield equal to 51.7% of the carbon content of the original saponified acetate rayon fibers.

Further tests and experiments in connection with single fibers or mono-filaments of these materials reveal that the rate of increase in temperature through the critical range of from about 250° F. to about 500° F. should be accurately controlled, so that the increase in temperature from 250° F. to 500° F. will consume a period of time of at least 8 minutes. If the temperature rise is attained in a time shorter than 8 minutes, the tensile strength and weight yield of the resultant carbonized fiber will be materially reduced.

Having fully described my invention, it is to be understood that I do not wish to be limited to the details set forth, but my invention is of the full scope of the appended claims.

Having thus described my invention, what I claim is:

1. A process for the production of a carbon fiber comprising the steps of heating viscose rayon fiber in an inert atmosphere through a temperature range of from about 300° F. to about 500° F., said heating requiring at least 30 minutes to attain said 500° F. temperature.

2. A process for the production of a carbon fiber comprising the steps of heating viscose rayon fiber in an inert atmosphere through a temperature range of from about 300° F. to about 500° F., said heating requiring about two hours to attain said 500° F. temperature.

3. A process for the production of a carbon fiber comprising the steps of heating viscose rayon fiber in an inert atmosphere through a temperature range of from about 300° F. to about 500° F., said heating requiring at least 30 minutes to attain said 500° F. temperature, and subjecting the fiber thus produced to the action of steam at an elevated temperature to activate the same.

4. A process for the production of a carbon fiber com-

prising the steps of heating viscose rayon fiber in an inert atmosphere through a temperature range of from about 300° F. to about 500° F., said heating requiring about two hours to attain said 500° F. temperature, and subjecting the fiber thus produced to the action of steam at an elevated temperature to activate the same.

5. The method of making a carbon fiber which comprises heating a non-thermoplastic, regenerated cellulose fiber in an inert atmosphere through a temperature range of from approximately 250° F. to approximately 500° F., said heating requiring at least 8 minutes to attain said 500° F. temperature.

6. The method of making a carbon fiber which comprises heating a non-thermoplastic, regenerated cellulose fiber in an inert atmosphere through a temperature range of from approximately 250° F. to approximately 500° F. in a time period of not less than 8 minutes; and subjecting the fiber thus produced to the action of steam at an elevated temperature to activate the same.

7. The method of making a carbon fiber having a tensile strength of at least 5,000 p.s.i. which comprises heating in an inert atmosphere a regenerated cellulose fiber selected from the class consisting of viscose rayon, cuprammonium rayon and saponified acetate rayon, through a temperature range of from about 250° F. to about 500° F., the increase in temperature from about 250° F. to about 500° F. being accomplished in not less than 8 minutes.

8. The method defined in claim 7 including the further step of subjecting the thus heat-treated fiber to the action of steam at a further elevated temperature to activate the same.

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