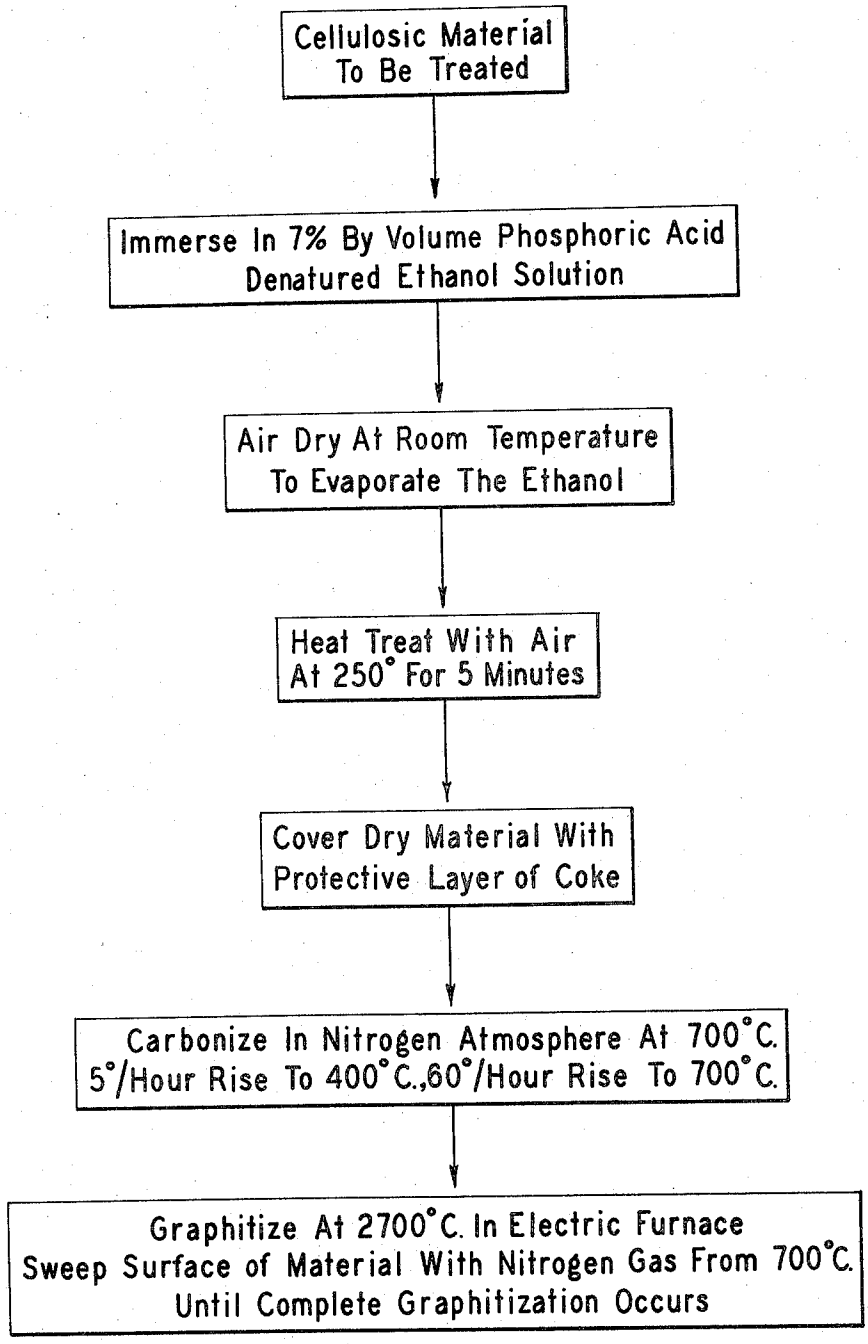
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PROCESS FOR MANUFACTURING FLEXIBLE CARBONACEOUS TEXTILE MATERIAL

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PROCESS FOR MANUFACTURING FLEXIBLE CARBONACEOUS TEXTILE MATERIAL

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This invention relates to manufactured carbonaceous materials which possess textile characteristics, and more particularly, to an improved process for manufacturing the same.

The prior art has provided carbonaceous filaments for use in incandescent lighting. Thomas A. Edison prepared carbonized filaments for incandescent lighting purposes by dissolving clean commercial cotton or other natural cellulose in a solution of zinc chloride and squirting the resulting mass through a fluid hardener. The resulting filament was dried and carbonized by heating out of contact with air. Others taught immersing the filaments of Edison in a hydrocarbon or carbon containing vapor and subsequently passing an electric current therethrough to raise it to a temperature sufficient to cause decomposition of the hydrocarbon or carbon compound and deposition of carbon on the filament. W. R. Whitney improved such filaments by heating them at extreme temperatures in order to graphitize the deposit on the base filament. These filaments were, however, rather inflexible, and did not retain the textile characteristics of of the cellulosic starting material.

Very recently, manufactured carbonaceous materials, which possess all of natural carbonaceous materials attendant unique electrical, chemical, and mechanical properties, have become commercially available in the form of textile materials, such as carbonaceous yarns and cloths. These materials possess the unique properties of carbonaceous materials in combination with textile properties, such as drape and hand, and are useful in countless applications.

United States Patent 3,011,981 issued December 5, 1961 to W. T. Soltes discloses a method for manufacturing textile carbon by the thermal conversion of fibrous and substantially pure cellulosic materials, such as strands, skeins, ropes, cloths, fabrics and batting pads. The textile carbon product is stated to be electrically conductive while retaining the flexibility and other physical characteristics of the textile starting material.

Electrically conductive graphite in a flexible fiber and fabric form is reported in Metal Progress, May 1959, pp. 115–116, and is commercially available in any textile form such as yarns, braids, felts, and woven or knit fabrics, such as cloth.

Research into the problem of thermally converting cellulosic textile materials into carbonaceous materials which retain all the original textile characteristics has led to the discovery of many critical areas in the processing of the material.

One such area evolves from the fact that cellulosic fibers normally contain about 5 percent to 20 percent absorbed water which is in equilibrium with the ambient humidity. The fibers may be dehydrated by heating, but unfortunately upon cooling, the moisture is re-absorbed in a very short time interval. In fact, absorption is so rapid that it can be observed while weighing a dried sample of cloth on an analytical balance.

It has been determined that this absorbed moisture interferes with the production of flexible carbonaceous textile material in that it encourages the formation of tarry surface deposits on the individual filaments of the textile material. Upon further pyrolysis these tarry deposits will decompose. As a result, the individual filaments will stick to one another, particularly at any cross connections. Accordingly, a brittle, weak product results.

It has been proposed to avoid the above problem by thoroughly drying the cellulosic material to be treated for a long period of time and immediately thereafter carbonizing the dried material in the same oven, thereby preventing any re-absorption of moisture. While this procedure has been very successful, unfortunately it is not always possible or practical with the equipment at hand.

Accordingly, the principal object of this invention is to provide an improved process for the production of carbonaceous textile material from cellulosic material wherein the carbonization may be done at any time after an initial dehydration treatment has been performed on the cellulosic starting material.

A concurrent object of the invention is to provide a process for the manufacture of textile carbonaceous materials from textile cellulosic starting materials which is particularly adaptable to a continuous operation.

Broadly stated, the objects of the invention are accomplished by an initial treatment cycle which is performed on a cellulosic textile starting material and which imparts a permanent dehydration thereto.

The treatment consists of driving off a certain percent of the volatiles of the cellulosic starting material in order to obtain a permanently dehydrated material which hereinafter shall be referred to as "heat treated" material. Heat treated material may be provided by a thermal treatment alone or in combination with a chemical treatment such as the use of acid. The time, temperature, acid concentration and the vehicle for the acid are all critical in the successful practice of the invention and will be detailed in full. However, it will be appreciated that the optimum processing conditions will vary depending upon the particular type of cellulosic textile material that is being treated.

Initially, it will be appreciated that in the manufacture of carbonaceous textile filaments, fibers, yarns and fabrics, the transformed material must not melt or become a powdery at any time between the starting cellulosic stage and the finished carbonaceous stage if the characteristic textile attributes of the starting material are to be retained by the finished carbonaceous material. This restriction is unique in the art of manufactured carbonaceous materials. Conventional carbonaceous materials either start with a mixture of carbon and a semi-fluid tar or pitch binder or a binder which becomes semi-fluid at some intermediate thermal stage.

It is known that cellulose will thermally decompose to a mixture of smaller molecules in a given time interval. If this conversion is permitted to occur uniformly, the result would be a powdery and perhaps semi-fluid mass which is unacceptable for the purposes of this invention. Accordingly, it will be appreciated that close control of the treatment of the cellulosic starting material is very important.

More specifically, the permanently dehydrated heat treated material of the invention may be defined as a non-flammable, non-fusible, strong and flexible material of cellulosic origin, which has undergone an approximate weight loss based on the starting cellulosic material in the range of from about 20% to about 50% and which has a volatile content of approximately 45% to 70%. Such heat treated material after being carbonized by a standard procedure (ASTM–D 189–61 "Standard Method of Test for Conradson Carbon Residues of Petroleum Products"), will have a fixed carbon content of approximately 30% to 55% by weight.

The heat treated material of the invention is extremely useful for making resin-bonded laminates which either in use, or prior to use, are to be carbonized by being subjected to elevated temperatures. By proper control of the heat treating process and environment, a heat treated fabric may be produced with a residual shrinkage most compatible with that of the resin used in laminating so that in the subsequent carbonizing treatment differential shrinkage and accompanying stresses would be minimized. In addition, heat treated material would be immediately useful as a thermal insulator and as a filter for corrosive liquids and vapors. Of course, it also readily lends itself to subsequent carbonization and graphitization in that since it is permanently dehydrated no special precautions must be taken to avoid the readsorption of moisture. Furthermore, the heat treated material has undergone an initial shrinkage during conversion from raw cellulose. This characteristic permits large rolls of cellulosic material, after heat treatment, to be treated as a unit. Thus, it is possible to set-up a continuous operation which can supply flexible carbonized or graphitized textile material of cellulosic origin in any length.

Heat treating itself is the controlled partial and selective decomposition of cellulosic material by means of heat, preferably in conjunction with oxidation and/or chemical decomposition. The chemical decomposition, when employed, would normally consist of an acid treatment which consists of soaking the cellulosic material in an acid solution prior to subsequent heating in an oxidizing or non-oxidizing atmosphere. Alternatively, the cellulosic material may be subjected to the acid treatment by conventional vacuum impregnation techniques. The process of heat treating should be distinguished on the one-hand from a simple drying and on the other from a coking or carbonizing step. True heat treating within the scope of this invention commences with the initial decomposition of the cellulose molecule involving rupture of carbon-oxygen and carbon-hydrogen bonds with the evolution of water, and ends at a point just prior to the scission of the main cellulosic molecule, the rupture of carbon-carbon bonds, and the evolution of hydrogen.

Heat treatment may vary in time from less than one minute to many hours at a temperature or schedule of temperatures not less than 100° C. or more than 350° C., the specific time and temperature depending primarily on acid concentration, which may vary from none to 50%, and the atmosphere in which the heating is being conducted, and secondarily on the vehicle for the acid and the specific textile form which is being treated.

General observations which may be made in regard to heat treating include the following:

(1) Lower temperatures require longer heating times.

(2) The use of acid moves the entire heat treating process to lower temperature levels and/or shorter heat treating time, as does the use of an oxidizing atmosphere which is at all times preferred. For example, the conversion of rayon cloth to heat treated material without the use of acid requires about 10 hours of heating in air at a temperature of 250° C. The same rayon material which has been soaked in a 6% acid solution may be converted in 6 minutes in air at 235° C.

(3) Acid when used may be present in either an aqueous or non-aqueous solution. An aqueous solution has been found preferable for heat treating cellulosic yarns, and a non-aqueous solution is preferred for cellulosic textile materials such as sheets of cloth. Generally speaking, the more compacted are the individual celluosic filaments, such as in tightly woven cloth as compared to yarns or loose woven goods, the more a non-aqueous solution is preferred.

(4) If an acid treatment is employed in conjunction with heat treating, a temperature above about 100° C. and below 350° C. is required for the successful conversion of cellulosic textile materials to heat treated materials.

However, if the heat treating is accomplished by thermal means alone, a temperature above 180° C. and below 350° C. is employed. In either case, for ease of processing, a temperature between about 200° C. and 300° C. is preferred.

(5) Acid concentration may vary from none to 50% and a range of from 2 to 10% is preferred, the exact optimum depending on the particular form of textile starting material. A higher acid concentration is preferred for woven and knitted fabrics than for felts and a higher acid concentration is preferred for felts than for fibers, filaments or batting. An acid concentration of about 7% is preferred for cloth and about a 3% concentration is preferred for yarn.

(6) When no acid is employed, the average time required to convert a cellulosic textile material to a heat treated material in an oxidizing atmosphere is as follows:

at 180° C.—time in excess of 48 hours
at 250° C.—about 10 hours
at 350° C.—less than 1 minute

(7) When an acid concentration of 7% is employed, the average time required to convert a cellulosic cloth material to a heat treated cloth material in an oxidizing atmosphere is as follows:

at 180° C.—about 4 hours
at 230° C.—about 2 hours
at 250° C.—about 6 minutes
at 350° C.—from under 2 minutes to less than a few seconds

The entire process of the invention, the individual steps of which will be discussed separately below, will be more readily understood by reference to the accompanying drawing wherein the single figure is a flow sheet of the preferred embodiment of the invention.

In the discussion of the invention which follows hereafter, the conversion of the starting cellulosic material to heat treated material which is subsequently carbonized and/or graphitized, will be limited to the preferred process which employs acid as well as heat controlled decomposition in an oxidizing atmosphere. Further, for ease of understanding, the discussion will be generally limited to tthe treatment of cellulosic cloth. It will be appreciated, that this is in no way intended to be in limitation of the foregoing discussion of the preparation of the permanently dehydrated heat treated material which forms one part of the subject invention.

More specifically, this preferred process comprises immersing the cellulosic material to be carbonized into an acid aqueous or non-aqueous solution, removing said solvent by evaporation, and finally heat treating said dried material at a temperature in the range of from about 100° C. to 350° C. thereby imparting a permanent dehydration to the material. The thus treated material may subsequently be carbonized and graphitized, if desired, at convenience in a conventional manner.

Any acid source of hydrogen ion is suitable and this includes, among others, acids such as phosphoric, sulfuric, hydrochloric and nitric acids, and acid salts such as diammonium phosphate and diethyl chloro phosphate.

When a non-aqueous solvent is employed, such as would be the case in the conversion of starting cellulosic cloth into a heat treated carbonaceous cloth which retains the textile characteristics of the cellulosic cloth, suitable solvents include the alcohols and ketonic non-aqueous solvents such as methyl ethyl ketone.

After the material to be carbonized is treated with the acid solution it is preferably air-dried, suitably at room temperatures. The air drying removes the alcohol and leaves the acid evenly distributed on the material. Without removal, the alcohol could possibly be a fire hazard upon subsequent heat treatment.

Upon completion of air drying, the material is heat treated preferably in an oxidizing atmosphere at a tem-

perature between 100° C. and 350° C. and preferably between 200° C. and 300° C. as set forth above.

The treated material may now be conventionally carbonized at convenience and, if desired, subsequently graphitized.

A specific example of the invention is the following:

A large roll of cellulosic cloth was immersed in a 7% by volume phosphoric acid (75% commercial food grade), 93% denatured ethanol solution. The treated cloth was dried in loose folds by high velocity air at room temperature. Thereafter the dried cloth was subjected to hot circulating air at a temperature of 250° C. for 5 minutes. The thus permanently dehydrated heat treated material was subsequently carbonized in a baking oven at 700° C. at a rate of 5° C. per hour to 400° C. and 60° C. per hour to 700° C., using a protective layer of coke and an atmosphere of nitrogen gas for oxidation protection. The thus carbonized material was graphitized in a conventional electric furnace at 2700° C. while the furnace was purged with nitrogen gas.

Some typical properties for cellulosic material which has been treated as above, are set forth in the below table. These properties illustrate the basic differences between the heat treated, the carbonized, and the graphitized material. The percentages are based on the amount which is remaining to be lost upon conventional graphitization.

TABLE

Treatment Undergone	Volatile Content, Percent	Linear Shrinkage, Percent	Temperature Required for 1% weight loss in 8 hours, ° C.
Graphitized	0	0	500
Carbonized	15	6	350
Heat Treated	50	18	100

It has been interestingly noted that the heat treated yarns of this invention may be conveniently and rapidly raised to graphitizing temperatures without providing a separate intermediate carbonizing bake. While a distinct carbonizing step may also be eliminated in manufacturing graphite cloth, the raising of heat treated cloth to graphitizing temperature must be done very slowly during the period of heating to 700° C.

The term cellulosic material as used herein and in the appended claims refers to all natural cellulosic forms (cotton, linen, jute, etc.) and all regenerated cellulosic forms such as rayon.

We claim:

1. A process for the production of a permanently dehydrated heat treated material from a cellulosic textile material wherein the heat treated material substantially retains the characteristic physical textile attributes of the unheat treated cellulosic starting material, said process comprising subjecting said cellulosic material to a controlled partial and selective decomposition of the cellulosic molecule by immersing said cellulosic material in an acid solution to wet said material therewith, removing said wet material from said solution, drying said material to remove the solvent therefrom, and heat treating said dried material in an oxidizing atmosphere, whereby said decomposition involves a rupture of carbon-oxygen and carbon-hydrogen bonds and the evolution of water, but falling just short of the scission of the main cellulose molecule, the rupture of the carbon-carbon bonds and the evolution of hydrogen.

2. A process for the production of a permanently dehydrated heat treated material from a cellulosic textile material wherein the heat treated material substantially retains the characteristic physical textile attributes of the unheat treated cellulosic starting material, said process comprising subjecting said starting material to the action of an acid solution of up to 50% concentration prior to said heating then subjecting in an oxidizing atmosphere

said starting material to a temperature in the range of from about 100° C. to about 350° C. for a time sufficient to cause said starting material to realize an approximate weight loss based on the starting material in the range of from about 20% to about 50% and to have a volatile content in the range of from about 45% to about 70%.

3. A process for the production of a permanently dehydrated heat treated material from a cellulosic textile material wherein the heat treated material substantially retains the characteristic physical textile attributes of the unheat treated cellulosic starting material, said process comprising subjecting said starting material to action of an acid solution of up to 50% concentration prior to said heating, then subjecting said starting material to a temperature in the range of from about 100° C. to about 350° C. for a time sufficient to cause said starting material to realize an approximate weight loss based on the starting material in the range of from about 20% to about 50% and to have a volatile content in the range of from about 45% to about 70%.

4. The process of claim 2 wherein the acid concentration of said solution is in the range of from 2 to 10%.

5. The process of claim 4 wherein said cellulosic starting material is chosen from the group consisting of fibers, filaments, yarns and battings, the solvent for said acid solution is water, and said acid concentration is approximately 3%.

6. The process of claim 4 wherein said cellulosic starting material is a cloth textile material, the solvent for said acid solution is non-aqueous and said acid concentration is approximately 7%.

7. The process for the production of a permanently dehydrated heat treated cloth material from a rayon cloth material wherein the heat treated material substantially retains the characteristic physical attributes of the rayon material, said process comprising soaking said rayon cloth in an approximate 6% acid solution and thereafter subjecting said cloth to a temperature of about 235° C. for about 6 minutes in an oxidizing atmosphere.

8. A process for the production of a permanently dehydrated heat treated material from a cellulosic textile material wherein the heat treated material substantially retains the characteristic physical textile attributes of the unheat treated cellulosic starting material, said process comprising treating said cellulosic material with an approximate 7% acid solution and thereafter subjecting said cellulosic material to a temperature between about 230° C. and 250° C. for a time between about 6 minutes and two hours in an oxidizing atmosphere.

9. The process of claim 4 wherein said acid ingredient of said solution is chosen from the group consisting of the acids of phosphoric acid, sulfuric acid, hydrochloric acid, and nitric acid, and the acid salts of diammonium phosphate and diethyl chloro phosphate.

10. The process of claim 9 wherein the solvent for said acid is chosen from the group consisting of alcohol and ketonic non-aqueous solvents.

11. A process for the carbonization of cellulosic material which comprises immersing said cellulosic material in an acid solution to wet said material therewith; removing said wet material from said solution; drying said material to remove the solvent therefrom; heat treating said dried material in an oxidizing atmosphere at a temperature in the range of from about 100° C. to 350° C. to impart a permanent dehydration thereto, and subsequently carbonizing said material by heating said material to a carbonizing temperature while protecting said material from oxidation.

12. The process of claim 11 wherein said carbonized material is subsequently graphitized in an electric furnace by heating said material to a graphitizing temperature while said furnace is being purged with nitrogen gas.

13. A process for imparting a permanent dehydration to cellulosic textile material which comprises immersing said cellulosic material into a non-aqueous acid solution to

wet said material; removing said wet material from said solution, drying said material and subsequently heat treating said dried material in an oxidizing atmosphere at a temperature in the range of from about 100° to 350° C. for a time sufficient to cause said starting material to realize an approximate weight loss based on the starting material in the range of from about 20% to about 50% and to have a volatile content in the range of from about 45% to 70%.

14. The process of claim **13** wherein said acid ingredient of said solution is chosen from the group consisting of the acids of phosphoric acid, sulfuric acid, hydrochloric acid and nitric acid and the acid salts of diammonium phosphate and diethyl chloro phosphate, and said non-aqueous ingredient of said solution is chosen from the group consisting of alcohol and ketonic non-aqueous solvents.

15. A process for imparting a permanent dehydration to cellulosic textile material which comprises immersing said cellulosic material into a 7% by volume phosphoric acid (75% commercial food grade), 93% denatured ethanol solution to wet said material, removing said wet material from said solution, air-drying said material at room temperature to remove said denatured ethanol and subsequently heat treating said dried material with hot circulating air at a temperature of 250° C. for 5 minutes.

16. The process of claim **15** wherein said cellulosic material is a roll of cloth.

17. The process of claim **5** wherein said heat treated material is heated rapidly to a graphitizing temperature of the order of 2700° C. in an electric furnace which is being purged with nitrogen gas.

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