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METHOD OF CARBONIZING FIBROUS CELLULOSIC MATERIALS

Carlos L. Gutzeit, Long Beach, Calif., assignor to Hitco, a corporation of California

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ABSTRACT OF THE DISCLOSURE

An improved method of carbonizing fibrous cellulosic materials comprises impregnating the fibrous material with a selected hydrate-forming, hygroscopic halide capable of increasing the yield of carbon fiber, initially carbonizing the impregnated material at a temperature not in excess of about 50° F. higher than the minimum initial carbonizing temperature and thereafter increasing the temperature to at least about 600° F. until carbonization is substantially completed.

The present invention generally relates to carbonization and more particularly relates to an improved method of carbonizing fibrous cellulosic materials.

Amorphous and semigraphitic carbon products are becoming increasingly important in various application, for example in the space industry where thermally insulating ablation-resistant materials are required. Heretofore, carbon products have been prepared by a wide variety of techniques in monolithic and fibrous forms. The fibrous forms are newer and present special production problems. They include amorphous carbon and so-called "graphite" carbon products which, in reality, are partly amorphous and partly crystalline. It will be understood that, unless otherwise specified, reference herein to fibrous carbon products is intended to include those fibrous carbon products which are essentially amorphous and also those fibrous carbon products which are essentially crystalline, as well as fibrous carbon products which are mixtures of amorphous and crystalline carbon. Fibrous carbon products have been prepared for commercial use in the form of textiles, rovings, extended filaments, cords, tapes and the like. Moreover, various techniques have been developed for laminating these fibrous carbon products in the fabrication of such composite structures as nose cones, heat shields, exhaust nozzles, etc.

Whereas strong monolithic forms of carbon can be fabricated rather simply by well-known resin binding and hot-pressing techniques, fibrous forms of carbon do not lend themselves to such fabrication techniques. Instead, time consuming procedures have had to be utilized in order to convert starting materials such as cellulosic fibers to carbonized fibrous products while preserving to some extent the strength and flexibility of the fibrous starting materials. However, present commercial techniques are subject to several major deficiencies. Thus, they still result in substantial losses in initial strength, flexibility and durability of the fibers during carbonization. In many instances, the physical integrity of the fibers is seriously impaired. Moreover, those commercial carbon fiber products which are currently available usually vary considerably from lot to lot in strength, flexibility, durability and other important physical characteristics. Another major drawback of present commercial techniques for the preparation of fibrous carbon products from fibrous cellulosic material is their low yield of usable product. Thus, the usual commercial method results in a recovery of only about 18–20 weight percent of carbon fiber product, as opposed to a theoretical yield of about 44.4 weight percent of carbon, in the case of rayon, cotton and the like, based upon the amount of carbon in the starting material.

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A still further serious drawback of standard commercial carbonizing methods is the relatively great length of time required to produced an acceptable product. Thus, for example, many commercial carbonizing methods require five to ten days in order to convert fibrous cellulosic material to finished carbonized fiber products. Accordingly, such products are relatively expensive. This makes any substantial improvement in yield of high quality product doubly important. Another difficulty of commercial processes in that they are not well adapted to provide carbon products having preselected variations in characteristics such as surface area, etc. It would be desirable in certain applications to provide fibrous carbon products having greatly reduced surface area in contrast to the usual commercial fibrous carbon products.

In still other applications it would be desirable to provide fibrous carbon products having extremely high surface areas, as for example, in applications where the product is to be used as an adsorptive medium. However, existing commercial methods of preparation of carbon fibers are not sufficiently flexible as to be able to produce without difficulty carbon fiber products of preselected and controlled surface area.

In view of the foregoing, it would be desirable to provide an improved method of carbonizing fibrous cellulosic materials, which method should be capable of resulting in substantially improved yields of uniformly high quality carbon products exhibiting high strength, flexibility and durability. Preferably, the method should be adapted to the production of both amorphous and semicrystalline ("graphitic") carbon products in fibrous form. The method should also be well adapted to provide fibrous carbon products within various preselected ranges of surface area, the tensile strength and other characteristics without requiring major or expensive changes in the method. It would also be desirable if the method could be carried out in a relatively short period of time so as to minimize the cost of the method.

Accordingly, it is a principal object of the present invention to provide an improved carbonization method.

It is also an object of the present invention to provide a simple, relatively rapid and inexpensive method of carbonizing cellulosic fiber materials to fibrous carbon products.

It is a further object of the present invention to provide an improved method of carbonizing fibrous cellulosic materials to fibrous carbon products having preselected and controlled characteristics, for example, tensile strength, flexibility, durability and, particularly, surface area.

It is a still further object of the present invention to provide an improved carbonization method capable of producing fibrous carbon products of uniformly high quality in substantially improved yield.

These and other objects are accomplished in accordance with the present invention by providing an improved carbonization method. The method comprises carbonizing fibrous cellulosic materials at relatively low temperature after impregnation of the materials with selected neutral or slightly acidic hygroscopic salts capable of catalyzing the carbonization so as to substantially improve the yield. In one embodiment, the carbonization is also carried out in the presence of a selected depolymerization inhibitor, which results in a low surface area product of high strength. In another embodiment, final carbonization occurs in the presence of an agent capable of substantially increasing the surface area of the product.

The present method is extremely rapid and efficient and yet is very simple. Moreover, it results in the production of uniformly high quality fibrous material of controlled surface area and other physical characteristics in a yield heretofore unobtainable. Thus, yields as high as 38 weight percent or more are obtained, in contrast to con-

ventional 18-20 weight percent yields. The carbon fiber product is, according to a preferred embodiment of the method, fired at a suitable high temperature in excess of about 1600° F. for a short period of time sufficient to provide a high purity, heat shrunk finished product.

In another embodiment of the method, the catalytic salt is removed from the carbonized product before firing, as by aqueous acid extraction. This can also be accomplished by initially using or converting the catalytic salt to bromide or iodide and firing at a temperature sufficiently high to assure rapid vaporization thereof. In yet another embodiment, the catalytic salt vaporizes during final carbonization. If desired, the carbonized fibrous product can be graphitized, with or without a separate firing step, so as to provide a finished graphitized fiber product in improved yield and having improved properties.

As a specific example, clean rayon cloth was immersed in a 1 M aqueous solution of calcium chloride for one minute, then withdrawn, drained and patted dry on a towel. It was then dried in an oven at 250° F. for 10 minutes, after which it was passed directly into a helium-containing carbonizing zone comprising a mullite tube at 320° F. and maintained therein for 20 minutes, then passed directly to a second helium-containing mullite tube, heated to 650° F. and maintained therein for 30 minutes. It was then passed directly to a firing furnace and brought to 1800° F. in 15 minutes and held at that temperature for 15 more minutes. The furnace contained helium. It was then allowed to cool to below 300° F. in helium and then removed from the furnace and allowed to cool to ambient temperature in air, and subsequently examined. The product was 99%, by weight, purity, high strength (20,000+ p.s.i.) fibrous carbon cloth of high flexibility and quality. The yield was 36 weight percent, and the overall process time was less than 2 hours, including cooling to ambient temperature. The B.E.T. (Brunauer, Emmett and Teller nitrogen adsorption test) surface area was about 100 m.²/gm.

Accordingly, the present method is relatively simple, inexpensive and rapid and provides a final fibrous carbon product of uniformly high quality in unexpectedly high yield. The product has high tensile strength, flexibility and durability and has controlled surface area. The method is adapted for batch, semicontinuous or continuous operation. Further advantages of the present invention will be apparent from a study of the following detailed description.

Now referring more particularly to the present method, carbonization of fibrous cellulosic materials is initiated in the presence of selected hydrate-forming, hygroscopic, preferably water-soluble halide salt, which catalyzes the carbonization reaction to provide the fibrous carbon product an improved yield. The salt is neutral or slightly acidic and may comprise, for example, a halide or alkali metal or alkaline earth metal, for example calcium chloride, magnesium chloride, etc., or a halide of a metal such as aluminum or higher atomic weight metal such as titanium, manganese, zirconium, or thorium. Thus, group I-A through III-A metals are preferred, along with the indicated higher molecular weight metals. Selection of suitable salts is within the skill of one versed in the art, in view of the foregoing criteria.

The salt may also be an ammonium or a low molecular weight alkyl ammonium halide. In this regard, ammonium chloride, ammonium bromide and ammonium iodide are suitable as well as methyl ammonium chloride, methyl ammonium bromide, methyl ammonium iodide, ethyl ammonium chloride, dimethyl ammonium chloride, methyl ethyl ammonium bromide, isopropyl ammonium chloride, diisopropyl ammonium bromide, methyl ethyl ammonium iodide, diethyl ammonium chloride and the like. Among those selected salts, those which are acidic and highly hygroscopic are preferred, for example calcium chloride, aluminum chloride and magnesium

chloride. They result in the greatest improvement in yield. Sodium chloride and potassium chloride, which are neutral salts and only slightly hygroscopic, provide less improvement in yield and, accordingly, are not preferred. Whatever halide salt is selected, it must, as previously indicated, be hydrate-forming, hygroscopic, neutral or slightly acidic and be capable of catalyzing or otherwise facilitating the carbonization so as to result in the desired improvement in yield of the fibrous carbon product without depreciating desired characteristics of the product.

In one preferred embodiment of the invention, a depolymerization inhibitor is employed during carbonization, together with the yield-improving catalytic salt. The depolymerization inhibitor has the effect of preventing loss of carbon from the structure, as by depolymerization and dissipation as carbon oxides, etc. Accordingly, this agent greatly reduces the surface deterioration of the carbon fibers so that the surface area of the carbonized fibrous product is kept very low. Moreover, in some instances at least, this agent further improves the yield and/or tensile strength of the product. The depolymerization inhibitor comprises ammonia, an alkyl amine or an ammonium halide, or alkyl ammonium halide. It will be noted that in the latter two instances, the depolymerization inhibitor is the catalytic salt. In the case of the ammonia or alkyl amine, the depolymerization inhibitor can be present in the form of an atmosphere during carbonizing. For example, ammonia or an alkyl amine can be added to or completely substituted for an inert gas in the carbonizing zone. Obviously, the alkyl amine must be of sufficiently low molecular weight and high volatility to be in gaseous form at carbonizing temperatures of about 300° F. and above. Inasmuch as, for most purposes, it is desired that the surface area of the carbon fiber product be very low, it is preferred in most instances to employ the depolymerization inhibitor as or with the catalytic salt during carbonization.

The neutral or slightly acidic salt (which optionally may incorporate the depolymerization inhibitor) is employed by impregnating the starting material therewith. The starting material comprises fibrous cellulosic material, such as rayon, cotton or the like. It may be natural or artificial, i.e. reconstituted, and in woven or unwoven fibrous form. Moreover, it may be carded or uncarded, chopped, felted or the like. In many instances, woven textiles are used as the starting materials, because of their inherently greater utility. In any event, the starting material should be substantially devoid of foreign matter, including finishes, coatings and the like, which may materially interfere with the desired carbonization. Preferably, the starting material is also essentially free of non-interfering foreign matter. If desired, various conventional washing operations, solvent treating steps or the like can be carried out on the starting material to bring it to a desired state of purity. Such steps are not required, however, so long as the starting material is initially essentially free of foreign matter which would interfere with the desired carbonization and/or reduce the purity of the final product, and so long as the foreign matter which is present in the starting material can be removed easily from the carbonized product.

Impregnation of cellulosic starting material of sufficiently purified form, for example rayon textile which has been treated to remove finishing agents, is accomplished by contacting the starting material in any suitable manner, as by spraying, etc., with the selected salt in a sufficient concentration so as to materially increase the yield of product. Usually, the selected salt is soluble or at least readily dispersible in water and, accordingly, is used in an aqueous solution or dispersion into which the starting material is immersed. Alcohol or other suitable solvents or dispersants compatible with the starting material can be used, if desired.

It has been found that concentrations of less than about

0.1 mol of the selected salt in solution or dispersion may be insufficient to provide a substantial effect on yield of product. However, this somewhat depends on the salt. Accordingly, a concentration of 0.1 mol or more of the salt is characteristically employed, and is usually about 0.5 mol or more. The impregnation of the starting material with the selected salt can be carried out for any suitable contact time, for example about 1–5 minutes, after which the impregnated starting material can be passed to the carbonization zone wet (containing solvent or dispersant) or dry (essentially free of solvent or dispersant), preferably the latter.

Drying of the impregnated starting material can be carried out in any suitable manner, for example by heating in air to below carbonizing temperature. For example, impregnated rayon cloth with calcium chloride in aqueous solution has been dried by heating the drained cloth in air to about 250° F. and holding it at that temperature for, for example, about 15 minutes. The initial minimal carbonization point for calcium chloride-impregnated rayon cloth is about 300° F., so that the 250° F. drying temperature does not effect carbonization of the rayon. Carbonization of the impregnated starting material is then initiated by increasing the temperature of the impregnated starting material. During such carbonization, the cellulosic material constituting hexose units is converted to carbon by removal of the hydrogen and oxygen. Although the exact mechanism of carbonization is not fully understood, it is believed that carbonization under the conditions of the present method involves stripping off of hydrogen and hydroxyl radicals from the hexose units by formation of water molecules. Accordingly, such carbonization appears to proceed, in part at least, by dehydration. It will be understood that regardless of the accuracy or inaccuracy of the theory detailed below, the present method is reproducible and is not to be limited by such theory. Referring again to the theory, apparently the catalytic salt, alone or with the depolymerization inhibitor, increases carbon recovery by controlling the sequence of dehydration and hydration reactions which appear to be necessary to convert the glucose units of the cellulosic starting material to carbon and water. It appears to be essential to minimize, as much as possible, the formation of volatile carbon-oxygen compounds, such as carbon monoxide and carbon dioxide, which ordinarily tend to polymerize to tars and, instead, to further the hydration of the oxygen linkages to hydroxyl groups and then eliminate those groups in the form of water by combination of the hydroxyl groups with adjacent hydrogen atoms.

It is further believed, although again the present invention is not limited to such theory, that the specific mode of action of the catalytic salt is to adsorb moisture, the product of dehydration, thus removing it from physical contact with the decomposing cellulosic structure, during carbonization, thereby facilitating further dehydration of the cellulosic structure. This immediate adsorption or removal of the moisture from the reaction appears to aid in driving the reaction rapidly towards complete carbonization without the substantial loss of carbon in the form of carbon monoxide, carbon dioxide and tars. Instead, the carbonization appears to proceed, in the presence of the selected salt, in a more orderly, rapid and regular manner to provide a carbon product essentially free of other materials and while retaining most of the carbon in the fibrous product.

It is important that initial carbonization of the impregnated starting material be carried out at a controlled temperature, in accordance with the following. This controlled temperature should not be more than about 50° F. higher than the minimum carbonization temperature for the particular system. In the case of selected catalyst salts used in the *absence* of depolymerization inhibitor, the minimum carbonization temperature is usually about 300° F. In the case of selected catalyst salts which are also depolymerization inhibitors or are used therewith,

that is in the presence thereof, the minimum carbonization temperature is usually somewhat higher, for example about 350° F. The indicated controlled temperature should be maintained for at least about 15 minutes. Preferably, an about 30 minute time period is employed at this temperature. It will be understood that various temperatures not exceeding by more than 50° F. the minimum carbonization temperature can be used during that period of time, if desired. Thus, for example, the impregnated material can be held at a fixed temperature, or can be continuously increased in temperature or can be incrementally increased in temperature, so long as the 50° F. upper limit is observed. The indicated upper temperature limit for initial carbonization is required because higher temperatures promote too rapid a carbonization reaction which, in turn, materially increases the risk of impairment of fiber integrity. This initial carbonization reaction is exothermic and must be carefully controlled in order to avoid temperature excursions which would damage desired physical characteristics of the brous carbon product.

By the end of a 15 minute period, however, most of the carbonization which can take place at the indicated temperature has taken place. Usually, obvious elaboration of moisture has diminished or stopped. Accordingly, the temperature of the carbonizing material is thereafter raised to a temperature sufficient to permit completion of carbonization within a reasonably short period of time. It has been found that a temperature of at least about 600° F. should be employed for the final carbonization and that, in any event, temperatures in excess of about 900° F. are never required. Suitable temperatures can be selected within the about 600–900° F. range, with lower temperatures within that range being adequate where no depolymerization inhibitor is present and higher temperatures in that range being used when depolymerization inhibitor is present.

The final carbonization should be carried out until the carbon product has the desired carbon content, i.e., until carbonization is substantially complete. This usually occurs in a minimum of about 15 minutes, although a period of about 30 minutes or more is preferred. It will be understood that the final carbonization can be carried out on an isothermal basis, or on a variable temperature basis, as in the case of initial carbonization. For example, the carbonizing material can be continuously increased in temperature, or incrementally increased in temperature, or the like. Whatever the technique employed, the minimum temperature limit is observed and the upper temperature need not be exceeded regardless of the particular selected salt and depolymerization inhibitor.

During carbonization, both initial and final, a suitable environment is maintained around the carbonizing material. Although vacuum could be used, this is usually impractical for commercial purposes. Instead, an inert gas, with or without additional gases hereinafter described, is usually employed. The inert gas may be, for example, argon, xenon, krypton, helium, nitrogen or the like gas nonreactive under the conditions pertaining in the present system. Preferably, the inert gas is employed as a moving purge stream, rather than a static volume. This is not so important in the second dehydrating step, that is during final carbonization, because only a limited amount of dehydration and carbonization take place therein. Accordingly, a static volume of environmental gas is frequently employed during final carbonizing at the indicated elevated temperatures. However, it is preferred that initial carbonization take place in a manner which facilitates the rapid removal of moisture from contact with the carbonizing material in the carbonizing zone. Thus, it is desired to keep the moisture concentration of the environment in contact with the starting material in the carbonizing zone below about 1%, by weight (or volume), since free moisture does interfere with the dehydration reaction, slowing the same and, in some instances, impairing the

physical integrity of the fiber. Accordingly, it is preferred that a purge stream of the environment gas surrounding the starting material be used during initial carbonization. Such purge stream preferably maintains the moisture content in the carbonization zone below the indicated 1% level. Alternatively, initial carbonization can be advantageously carried out in a carbonization zone which has a very large volume in proportion to the volume of the impregnated cellulosic material so that the volume of static gas surrounding such starting material is large in relation to the starting material, thereby assuring adequate dilution of the moisture elaborated from the starting material.

In addition to or in substitution for the inert gas, a basic gas which acts as a depolymerization inhibitor can be used during carbonization, preferably at least during initial carbonization, and more preferably throughout carbonization, if it is desired to reduce the total surface area of the ultimate carbon fiber product as low as possible. For example, the total surface area may be reduced to, for example, 10 to less than 1 m.²/gm. (B.E.T.). This basic gas comprises ammonia or an alkyl amine in a suitable concentration of, for example, 1 to about 20 volume percent in a suitable inert gas, such as argon, neon, krypton, xenon, nitrogen or the like. Alternatively, as previously indicated, the depolymerization inhibitor may be a suitable ammonium-containing catalytic salt, which has the same effect as the basic gas in reducing the surface area of the ultimate carbon fiber product.

In one embodiment of the present method, the catalytic salt is employed without depolymerization inhibitor so as to produce a moderate surface area carbon fiber product of the order of about 25–100 m.²/gm. (B.E.T.) or more, for example. The surface area may be further increased to as high as about 300–600 m.²/gm. (B.E.T.) or more by effecting the final carbonization in the presence of a selected halide or halogen gas, such as hydrogen iodide, hydrogen bromide, hydrogen chloride, bromine, iodine or chlorine or the like, alone or in admixture with inert gas, for example in a concentration of 1–20 volume percent in the inert gas. The selected gas is not used in the initial carbonization, but is limited to use in the final carbonization during which temperature excursions can be more easily controlled. Moreover, the gas has the indicated effect on surface area even when it is employed to only a limited extent during final carbonization, that is only during a portion of the total time devoted to final carbonization.

If desired, a catalytic salt can be employed which is a bromide or iodide, or is converted to the same during final carbonization, as by the use of a described selected halide or halogen (surface area-increasing) gas, which is bromine, iodine, hydrogen bromide or hydrogen iodide or a mixture thereof, diluted or undiluted with inert gas. In any event, prior to termination of carbonization, in the indicated embodiment, the catalytic salt is in bromide or iodide form so that it can be readily vaporized from the carbon fiber during firing at a temperature below that at which substantial depreciation of the thermal insulative value of the carbon fiber occurs. In such an event, it is not necessary to remove the metallic cation of the catalytic salt from the carbonized fiber product (in order to purify the same) by a separate washing step or the like. Instead, the cation is removed as low-boiling bromide or iodide during the firing operation at a temperature of between about 1800 and about 2000° F. If, however, the salt is a chloride, in order to strip it from the carbonized fiber during firing, temperatures of at least about 2200° F. and usually substantially above are required. In such instances, depreciation of the thermal insulative value of the carbon fiber may occur. Accordingly, it is usually desirable to remove chloride salts from the carbon fiber product by other means than by elevated temperature, as by washing the fiber product with a dilute acid, such as hydrochloric acid or other mineral acid followed by water washing and

drying, after which the firing operation, if desired, can be carried out at a temperature of less than about 2200° F.

Accordingly, the metallic catalytic salt can be removed from the fully carbonized fibrous product in any one or more of a number of ways. Thus, the product can be washed with dilute acid, such as hydrochloric acid, sulfuric acid or the like, then water washed and subsequently dried (and fired, if desired). Alternatively, bromide or iodide metallic catalytic salt can be used, and the carbon product can be fired at about 1600–2200° F. to heat shrink the fiber and boil off such salt along with other volatiles. Another alternative is to employ nonmetallic, low-boiling, nonresidue forming catalytic salt, such as ammonium chloride, methyl amine hydrochloride (methyl ammonium chloride) and the like, so that the problem of metallic impurities is avoided. In this regard, the ammonium chloride volatilizes during final carbonization. In such an instance, the starting material may be purified before carbonization, as previously described, to assure a high purity final product.

In some instances, however, it is desirable to "load" the carbon fiber product with a high molecular weight metal, such as thorium, lanthanum or the like. Accordingly, the catalyst in such instance can include thorium halide, lanthanum halide or the like, this salt being left in the carbonized fiber, even after firing at elevated temperature.

As a further optional step which is usually employed, the firing previously referred to is carried out in an inert atmosphere, such as that previously described, or in a vacuum, at at least about 1600° F. and usually not more than about 2200° F. Temperatures above about 2200° F. are undesirable, since some depreciation in the thermal insulative value of the fiber occurs. Accordingly, it is usually desirable to fire at temperatures below about 2100° F.–2200° F. Usually, about 1800–1900° F. is preferred, and for a time sufficient to substantially eliminate volatile impurities and heat shrink the fiber. For example, the exposure time at above 1600° F. can be from about 1 minute and usually is about 5–20 minutes or the like.

It will be understood that the carbon fiber products provided by the described method are basically turbostratic carbon fiber products. They can be easily converted to high quality graphitic products, in accordance with the method, that is products comprising a mixture of amorphous carbon and crystalline carbon with up to about 100% crystalline carbon, by heating them in an inert atmosphere or vacuum to graphitization temperature, for example to about 4000–4500° F. or more, and maintaining them at graphitization temperature for a suitable interval of time, for example from a few minutes to one or more hours. The graphitization can be carried out as an extension of, in substitution for or in addition to the firing step previously described. During graphitization, the essentially amorphous carbon material is partially, substantially or even essentially completely converted to crystalline carbon, that is graphite, depending upon the particular graphitizing parameters. These products are known as graphitic fibrous products because they exhibit certain graphite properties in varying degree, depending upon their extent of graphitization.

It will be understood that whatever the treatment or sequence thereof employed in accordance with the present method, the carbonizable and carbonized materials are not exposed to an oxygen-containing atmosphere above about 300° F. This is to avoid combustion thereof. Heating and cooling are effected sufficiently slowly so as to avoid unduly stressing the fibers.

The following examples further illustrate certain features of the present invention:

EXAMPLE I

Carbonization of a plurality of samples of various types of rayon was carried out in accordance with the following procedure:

In each instance, approximately 2 grams of the rayon, either in cloth or strand form, were dried overnight at

about 190–200° F., cooled in a desiccator and accurately weighed. Each sample was then immersed in a large volume of aqueous solution of selected salt catalyst, in accordance with the present invention, for a period of a few (1–5) minutes, then removed and allowed to drain free of the aqueous solution. After a period of about 5 minutes, the sample was then pressed gently with a paper towel and then placed in a zircon crucible for carbonization.

Up to 8 zircon crucibles, each containing a sample, were processed together by placing the same in the center of a horizontal mullite tube approximately 40 inches long and about 4 inches in diameter, which tube was mounted in a refractory furnace. While purging the furnace with helium or ammonia, depending upon the particular samples run, at a rate sufficient to keep the gas moisture content below 1 volume percent, the mullite tube was externally heated for one hour at 120° C. (248° F.) to remove the solvent, i.e., the water, from the sample. Then while maintaining a stream of the same inert gas or ammonia, the mullite tube was gradually heated to 300° C. (572° F.) over a 1½ hour period. Thereafter, each sample was cooled to ambient temperature. The samples were then removed from the crucibles, and each sample was extracted with 0.1 M aqueous HCl to remove salts remaining in the carbonized sample, after which the samples were water washed and then returned to the zircon crucibles and mullite tube in the furnace. Up to 8 of the washed, carbonized samples were then heated in helium to 1000° C. (1832° F.) over 30–45 minutes and maintained at this temperature for the remainder of an hour, that is for 15–30 minutes. After this firing treatment, the samples were then cooled in helium to 120° C. (248° F.), then quickly removed from the crucibles to a desiccator and cooled to room temperature. After weighing the samples to determine the amount of carbon, each sample was ignited in air at 1000° C. to determine the small ash residue, and the carbon yield was then corrected by subtraction therefrom of this ash residue. The results of the parallel tests on a plurality of samples are set forth in Table I below:

TABLE I

Sample:	Rayon Type	Impregnating Solution	Gas Stream	Carbon Recovery, Wt. percent of Dried Rayon
1	Cloth A	Blank	Helium	24
2	do	0.1 M CaCl ₂	do	31
3	do	0.5 M CaCl ₂	do	33½
4	do	1.0 M CaCl ₂	do	38
5	Cloth B	Blank	do	15
6	do	0.5 M CaCl ₂	do	35½
7	Cloth A	0.1 M MgCl ₂	do	31½
8	do	0.5 M MgCl ₂	do	35½
9	Cloth B	0.1 M MgCl ₂	do	30½
10	do	0.5 M MgCl ₂	do	34
11	Strands C	Blank	Ammonia	22
12	do	0.5 M CaCl ₂	do	33½
13	do	0.33 M AlCl ₃	do	35
14	Strands D	0.5 M CaCl ₂	do	33½
15	do	0.33 M AlCl ₃	do	35

Table I clearly indicates that the carbon yield obtained through the use of the calcium, magnesium, and aluminum chloride was large. Moreover, the yield increased with increasing salt concentrations within the range indicated in Table I. However, in separate parallel tests it was found that higher salt concentrations effected only slight further improvements in carbon recovery. Moreover, those higher salt concentrations made the carbonized fibers more difficult to purify during extraction with acid to remove the salt residue.

In further parallel tests it was discovered that results obtained through the use of other halide salts, including bromides and iodides, were comparable to the results obtained through the use of the chloride salts indicated in Table I. So also were parallel tests utilizing cotton in place of rayon.

Table I further illustrates that the ammonia depolymerization inhibitor gas stream provided the same results in terms of yield as did the helium. The product (carbon fiber) yield, whether helium or ammonia was used, was substantially higher than previously obtainable by conventional methods. Thus, with the blank samples 1 and 5, carbon recovery was approximately 24–25 weight percent, but this yield substantially increased through the use of the catalytic salt even in a concentration at low as 0.1 mol, as shown in sample 2, wherein the yield was increased from 24 weight percent to 31 weight percent. This yield was further increased up to 38 weight percent through the use of higher concentrations of calcium chloride, for example about 1 mol, as in sample 4.

Accordingly, the present method has been demonstrated to provide a substantial improvement in the yield of carbon fiber products from cellulosic starting materials. The products obtained through the use of the method specified above were also tested for tensile strength, durability, appearance and flexibility and found to be uniformly high quality products having a tensile strength at least comparable to conventional carbonized fiber products, a high degree of flexibility and durability, and an attractive uniform appearance. They were found to be highly useful for a wide variety of applications, including abrasive, high temperature use in nose cones.

EXAMPLE II

A series of parallel tests were carried out to determine the effect of the depolymerization inhibitor upon surface area of the products produced in accordance with the method. The method set forth in Example I was carried out, using, however, only rayon strands as the starting material. The drying, weighing, impregnating, draining and carbonization steps were as set forth in Example I, including the water removal step preliminary to carbonization. However, after carbonization up to a maximum temperature of 572° F. over a 1½ hour period, the samples were then rapidly heated to 1000° C. in helium and maintained at this temperature for 15–20 minutes. No intervening washing step was carried out to remove salts. The results are as set forth in Table II below:

TABLE II

Sample:	Impregnating Solution	Gas Stream	Surface Area, m. ² /gm. (B.E.T.)
16	Blank	Helium	191
17	1.0 M CaCl ₂	do	55
18	1.0 M CaCl ₂	Ammonia	0.8
19	1.0 M MgCl ₂	Helium	25.5
20	1.0 M MgCl ₂	Ammonia	3.5
21	1.0 M ZrCl ₄	Helium	43

Table II clearly illustrates that the use of ammonia instead of helium, that is the use of depolymerization inhibitor instead of inert gas, has the effect during carbonization of substantially reducing the surface area of the carbonized product. Extremely low surface areas were obtained when ammonia was substituted for the helium, for example 0.8 m.²/gm. in sample 18, in contrast to 191 m.²/gm. in sample 16.

The opposite effect was achieved in a parallel series of tests using an acidic halogen or halide gas in place of helium during final carbonization at temperatures above 600° F. Surface areas were of the order of magnitude of 300 m.²/gm. and above, in contrast to blank samples exhibiting surface areas of 50–150 m.²/gm. In several of those tests, hydrogen bromide, bromine, iodine, and hydrogen iodine were reacted with chloride catalytic salts during final carbonization to convert the catalytic salts to bromides and iodides, which were volatilized free of the fully carbonized product at 1100° C. and below during firing over a period of 30 minutes. A separate acid

treatment and washing step to dissolve out such salts thereby was obviated. High purity carbon fiber products of very large surface area were obtained.

EXAMPLE III

In a series of tests to determine the effect of catalytic salt which comprises depolymerization inhibitor, a plurality of samples of rayon in strand and cloth form were impregnated with either ammonium chloride or methyl amine hydrochloride (methyl ammonium chloride) by immersion in aqueous solutions containing the same in 0.1–1.0 M concentration. No separate product purification step was employed following carbonization. Instead, in order to insure high purity carbon fiber products, purification of the starting material was carried out by washing the same with a dilute (0.1 M) aqueous HCl solution, followed by washing away of the acid with deionized water, neutralization of the fiber with dilute alkali (0.1 M aqueous ammonium hydroxide) and subsequent water washing.

After this purification procedure, the samples were then impregnated with aqueous 0.1–1.0 M ammonium chloride or methyl amine hydrochloride by immersion therein for 1–5 minutes. After removal from the solutions, the samples were allowed to drain, then were dried at about 250° F. for about one half hour, after which they were gradually increased in temperature to approximately 752° F., i.e., 400° C., over a period of approximately 1½ hours while in helium. Certain of the samples were then tested to determine their ash residue, and it was determined that essentially no nonvolatile residue remained in the samples, and that the samples were essentially high purity carbon fibers. Some of the samples were subjected to a firing operation in helium at about 1600° F. for approximately 15 minutes' residence time, having been heated to that temperature over a period of approximately one half hour. The fired samples were found to have high tensile strength on the order of about 19,000 p.s.i., were very flexible, and were found to have unimpaired fiber form. The yield of product was approximately 40 weight percent from both the cloth and the strand samples or approximately 90% of the theoretical value of 44 weight percent. The best recoveries were obtained when 2 M ammonium chloride or 2 M methyl ammonium chloride aqueous solution was used for impregnating. Similar recoveries were obtained when the firing step was carried out at about 1900° F. and when ethyl ammonium chloride, isopropyl ammonium iodide and dimethyl ammonium bromide were used as the catalytic salts.

EXAMPLE IV

A continuous technique for the production of carbonized cellulosic fiber was demonstrated by the following tests.

Parallel tests were performed on rayon cloth samples, each of which had been subjected to an aqueous (0.1 M) HCl wash, followed by aqueous wash and then followed by impregnation with either aqueous 2 M ammonium chloride, aqueous 2 M methyl ammonium chloride, aqueous 2 M dimethyl ammonium chloride, aqueous 2 M ammonium chloride containing 1 weight percent $\text{Mn}(\text{OOCCH}_3)_2$ or aqueous 2 M ammonium chloride containing 1 weight percent titanium trichloride. In parallel tests the environment was either helium or ammonia. In each of the parallel tests, the impregnated rayon cloth was passed upwardly through a 40 inch long heating zone with a total residence time within the zone of about one hour, and with the average temperature of the first 10 inches of the zone at 365° F., and the average temperature of the last or top 10 inches of the zone at 680° F. There was a graduated increase in temperature between those two areas from the bottom of the zone to the top of the zone. The operation was carried out on a continuous basis, the cloth having first been drawn through the acid purification bath, then the water, then

a basic neutralizing bath of ammonia (0.1 M aqueous), followed by a second water wash, then impregnating solution, and then directly into the carbonizing zone as part of the continuous carbonizing process. During carbonizing within the carbonizing zone, helium or ammonia was passed concurrently with the sample up through the zone to remove moisture, so as to keep the moisture content below 1 volume percent.

In a separate parallel series of tests, the same results as with the sharp temperature gradient 40 inch heating zone were obtained by following the same procedure except to compartmentalize the heating zone to avoid moisture accumulation and pass the sample down sequentially through 3 separate heating compartments of the zone operating at successively higher temperatures, the first compartment, for example, about 300° F., the second compartment, for example, about 350° F., the third zone at, for example, 400° F. The carbonized product then passed upward through a fourth heating compartment of the zone at the maximum heating temperature, for example, about 680° F. Each heating compartment had a separate inlet and outlet for sweeping the sample with helium or ammonia.

The carbonized samples were then heated in helium to 1700–2100° F. over a 20 minute period and maintained at that temperature for 15 minutes to fire the same, then cooled to ambient temperature in helium and tested.

The ammonium chloride, methyl ammonium chloride, dimethyl ammonium chloride, ammonium chloride containing manganese diacetate and the ammonium chloride containing titanium trichloride all produced comparable results in that the yield of product was approximately 35–40 weight percent. In each instance, carbonization was essentially complete and each product exhibited high quality, including high tensile strength, extreme flexibility, durability and a suitable appearance. All samples exhibited extremely low surface area on the order of about 1–10 m.²/gm.

The preceding examples clearly illustrate that the present method is simple, highly efficient, inexpensive and rapid and provides a high yield of uniformly high quality carbon fiber product. Such products have high flexibility, tensile strength and durability and have surface areas which can be controlled so as to be substantially larger than, comparable to or substantially smaller than those of conventionally prepared carbon fiber products. Moreover, the yields of the carbon fiber products have been greatly increased to approximately 30–40 weight percent or up to about 90% of the theoretical value of 44.4 weight percent, in contrast to 18–20 weight percent obtained in conventional processes. Despite the use of salts in the present method, a highly purified product can be obtained in which the salt or ash residue is extremely small. The product can have a purity of 98% or more, and usually such purity is in excess of 99 weight percent. The purity can be obtained, if desired, without the use of a separate washing step subsequent to carbonization. The method is adaptable to batch, semi-continuous and continuous production of carbon fiber in cloth, strand, cord or other forms at a rate which approaches an overall treating period of as little as 1–2 hours, in contrast to conventional processes which may be as long as 10 days or more. Various other advantages are as set forth in the foregoing.

Various changes, modifications, alterations and substitutions can be made in the present method, its steps and parameters and in the equipment for carrying out the steps. All such changes, modifications, alterations and substitutions as are within the scope of the appended claims form a part of the present invention.

What is claimed is:

1. An improved method of carbonizing fibrous cellulosic material, which method comprises impregnating fibrous cellulosic material with selected hydrate-forming hygroscopic metal halide salt capable of increasing the yield of carbon fiber, said salt being present in the im-

pregnated fibrous cellulosic material in an amount sufficient to substantially increase said yield, thereafter initially carbonizing the impregnated fibrous cellulosic material in the presence of a nonoxygen containing atmosphere comprising basic depolymerization inhibitor gas selected from the group consisting of monoalkyl amine, dialkyl amine and inert gaseous mixtures thereof, at a temperature not in excess of about 50° F. higher than the minimum initial carbonizing temperature for said material impregnated with said salt and for a period of at least about 15 minutes, and thereafter increasing the temperature of said impregnated carbonizing material to at least about 600° F. for a period of at least about 15 minutes under a nonoxygen containing atmosphere until carbonization of said material is substantially completed, whereby an improved yield of fibrous carbon product is obtained.

2. The method of claim 1 wherein said carbonizing at least about 600° F. is carried out in an environment selected from the group consisting of vacuum, inert gas, said depolymerization inhibitor gas, a mixture of inert gas and said depolymerization inhibitor gas, acidic surface-area increasing gas selected from the group consisting of a halogen and hydrogen halide, and said acidic surface-area increasing gas and inert gas mixture.

3. The method of claim 1 wherein the metal of said halide salt is selected from the group consisting of an alkaline earth metal, an alkali metal, aluminum, titanium, manganese, zirconium and thorium.

4. An improved method of carbonizing fibrous cellulosic material, which method comprises impregnating fibrous cellulosic material with selected hydrate-forming, hygroscopic metal halide salt capable of increasing the yield of carbon fiber, said salt being present in the impregnated fibrous cellulosic material in an amount sufficient to substantially increase said yield, initially carbonizing the impregnated fibrous cellulosic material in the presence of a nonoxygen containing atmosphere comprising basic depolymerization inhibitor gas selected from the group consisting of ammonia, monoalkyl amine, dialkyl amine and inert gaseous mixtures thereof, at a temperature not in excess of about 50° F. higher than the minimum initial carbonizing temperature for said material impregnated with said salt and for a period of at least about 15 minutes, thereafter increasing the temperature of said impregnated carbonizing material to at least about 600° F. and maintaining said material at at least about 600° F. for a period of at least about 15 minutes under a nonoxygen containing atmosphere until carbonization of said material is substantially completed, removing said salt from the carbonized fibrous material and thereafter firing said material at a temperature of at least

about 1600° F. for a time sufficient to substantially remove remaining volatiles and heat shrink the product.

5. The method of claim 4 wherein said salt is removed by contacting the carbonized fibrous material with an aqueous acid solution, thereby dissolving said salt from said material, after which said firing is carried out.

6. The method of claim 4 wherein said salt comprises salt selected from the group consisting of bromides and iodides, wherein said salt is removed from said carbonized fibrous material during firing at a temperature above the vaporization point for said salts but below a temperature which substantially decreases the thermally insulative value of said carbonized fibrous material, and wherein during carbonizing at at least 600° F. an acidic atmosphere containing gas selected from the group consisting of hydrogen bromide, bromine, hydrogen iodide and iodine is provided in contact with the carbonizing fibrous cellulosic material, whereby the surface area thereof is substantially increased.

7. The method of claim 4 wherein said carbonizing is carried out on a continuous basis by continuously passing said impregnated fibrous cellulosic material through a carbonizing zone and maintaining a temperature gradient in said zone increasing from the inlet end of said zone to the outlet end of said zone, wherein an overall residence time of at least about 30 minutes is provided for said impregnated fibrous cellulosic material in said zone, and wherein the carbonized product is continuously passed from the carbonizing zone and into and through a firing furnace and subjected therein to a temperature of at least about 1600° F. for a time sufficient to substantially remove remaining volatiles and heat shrink the product.

8. The method of claim 7 wherein before said carbonizing the starting fibrous cellulosic material is continuously passed, in sequence, through an aqueous acid impurity-removing bath, a water wash and an impregnating solution of said salt.

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EDWARD J. MEROS, Primary Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,479,151

November 18, 1969

Carlos L. Gutzeit

It is certified that error appears in the above identified
patent and that said Letters Patent are hereby corrected as
shown below:

Column 1, line 27, "application" should read -- applications --; line 33, "amrophous" should read -- amorphous --. Column 2, line 3, "produced" should read -- produce --; line 10, "in" should read -- is --; line 67, "ripid" should read -- rapid --. Column 5, line 5, "characterically" should read -- characteristically --. Column 6, line 20, "brous" should read -- fibrous --. Column 9, Table I, Sample 5, under "Carbon Recovery, Wt. percent of Dried Rayon" "15" should read -- 25 --. Column 10, line 71, "iodine" should read -- iodide --. Column 12, line 5, "carbonizinz" should read -- carbonizing --; lines 56 and 57, after "carbonization" insert a period. Column 13, line 48, after "least" and before "600° F." insert -- about --.

Signed and sealed this 28th day of July 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents