Sept. 5, 1972 P. A. SMUDSKI 3,689,220

PROCESS FOR CARBONIZING FIBROUS CELLULOSIC MATERIAL

Filed June 30, 1971 3 Sheets-Sheet 1

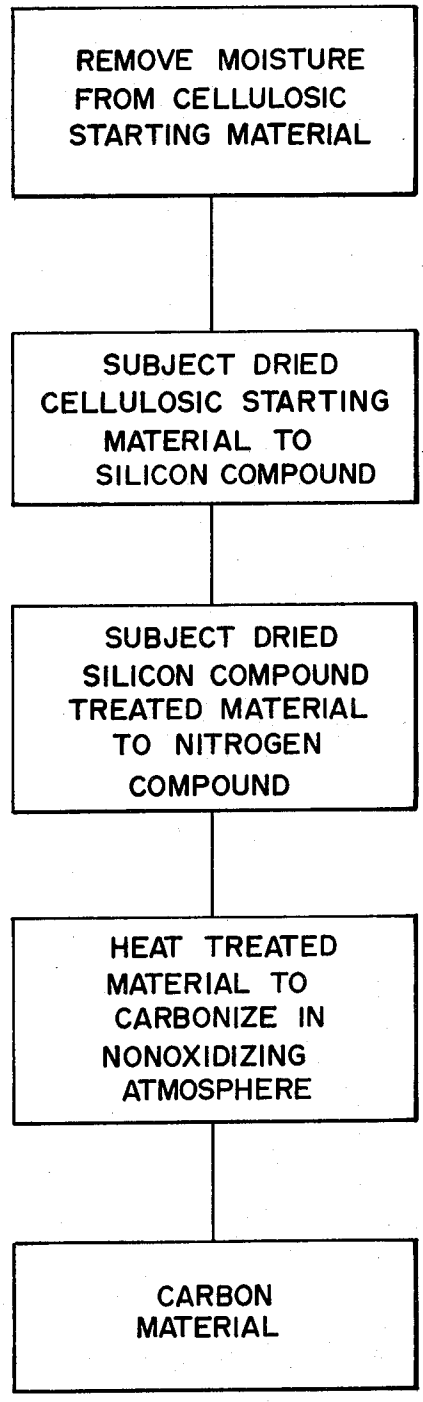

FIG. 1

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PROCESS FOR CARBONIZING FIBROUS CELLULOSIC MATERIAL

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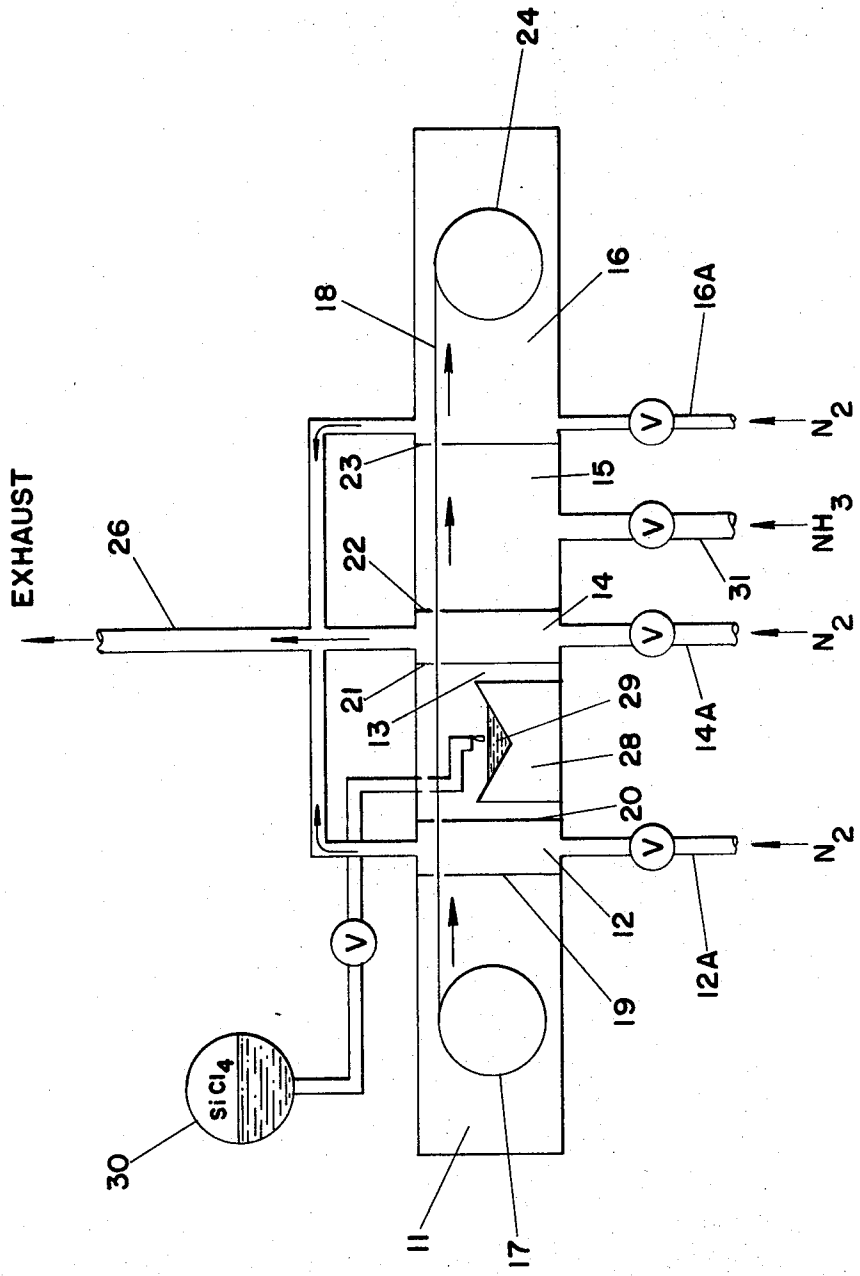

FIG. 2

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Filed June 30, 1971 3 Sheets-Sheet 3

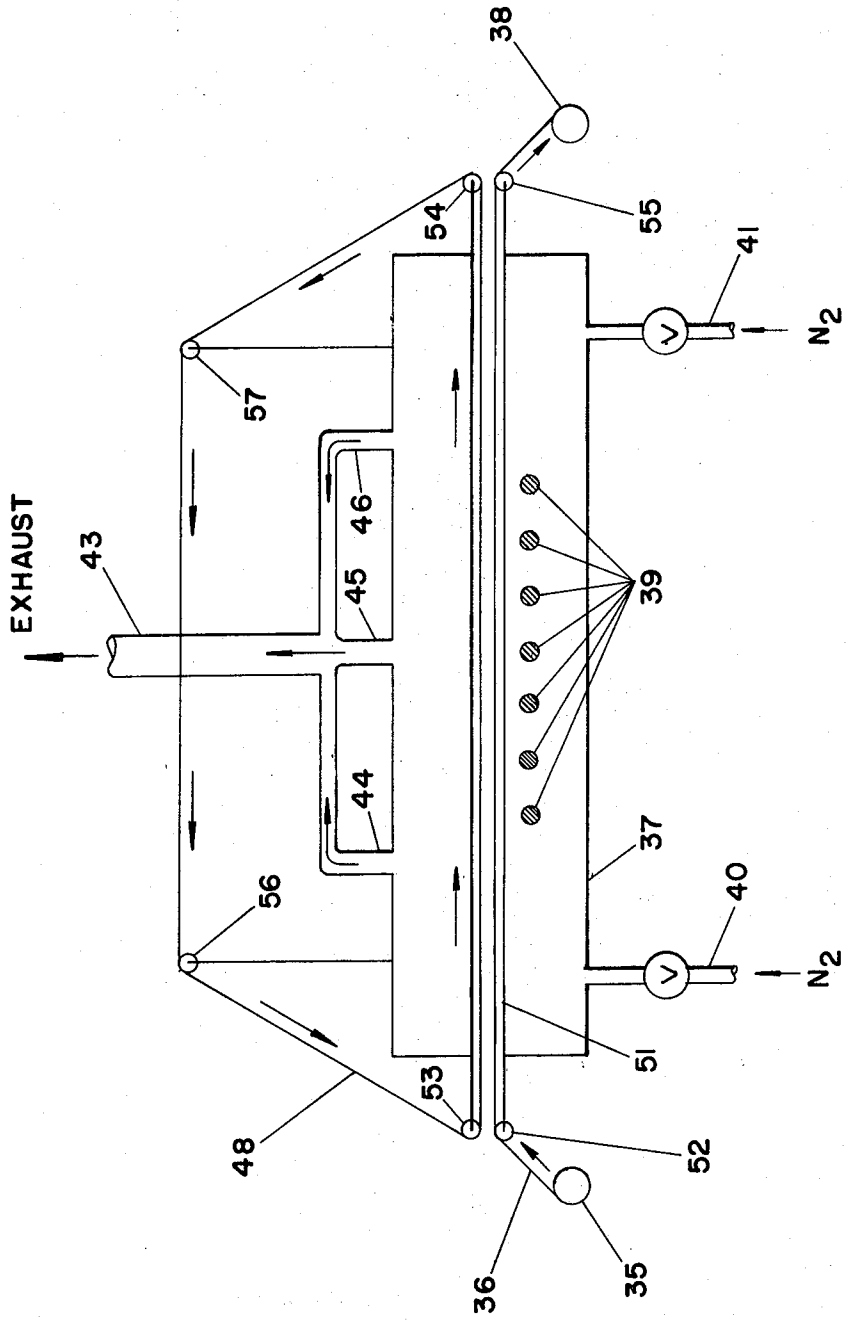

FIG. 3

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United States Patent Office 3,689,220 Patented Sept. 5, 1972

3,689,220

PROCESS FOR CARBONIZING FIBROUS CELLULOSIC MATERIAL

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Filed June 30, 1971, Ser. No. 158,355
Int. Cl. C01b 31/09
U.S. Cl. 423—447 11 Claims

ABSTRACT OF THE DISCLOSURE

Cellulosic material in fibrous form (for example, rayon cloth) is converted to carbon by subjecting the cellulosic material to a silicon compound, such as silicon tetrachloride; subsequently, subjecting the silicon compound treated cellulosic material to a nitrogen compound, such as ammonia; and finally subjecting the silicon compound treated, nitrogen compound treated cellulosic material to thermal degradation in a nonoxidizing atmosphere. This process can be utilized to yield carbon in fibrous form of quality comparable to that produced by other processes, to increase the yield of carbon produced from the cellulosic material, and most significantly to substantially reduce the time required for thermal degradation of the cellulosic material. The material being processed possesses sufficient strength at all stages of processing to be self-supporting, permitting processing to occur in a semi-continuous fashion, with each step of processing being accomplished by passing the material to be processed from one roll through the processing apparatus, and onto a second roll.

BACKGROUND OF THE INVENTION

Because of its refractoriness, electrical conductivity, thermal conductivity, resistance to corrosion, and reinforcing properties, carbon (including graphitized carbon commonly called graphite) in fibrous form such as yarns, fabrics and filaments is finding increasing acceptance in technical applications of commercial importance. Carbon and graphite felts are used as insulation and heat shields in high temperature induction and resistance furnaces. Graphite cloth heating elements are used for temperatures up to 2500° C. in vacuum and inert gas furnaces for metal working. At lower temperatures, graphite cloth is used in a variety of ways as an electric heat source. Aircraft de-icers, water heaters, and heaters for softening sheets of plastics are typical applications. Graphite yarn is braided into packings for pumps and valves. Carbon fiber reinforced plastic ablation materials for thermal protection in reentry and rocket propulsion systems constitute a most important use of these materials. A presently developing application of immense commercial potential is the use of carbon fiber reinforced carbon bodies as brake linings for jet aircraft. For these purposes, the cost of carbon fiber and the time necessary to produce the carbon fiber, which is a major contributor to the cost of the carbon fiber, become of great importance.

Carbon fibers and fabrics can be made from any fibrous raw material which, upon being subjected to thermal degradation, pyrolizes without going through a fusion stage to yield a carbon residue, while maintaining the integrity of the fiber. Cellulosic materials are well suited for this use, and one of the most commonly used raw materials is rayon. Methods for converting rayon and

other cellulosic materials to carbon cloth are based on the carefully controlled thermal degradation of the cellulosic material. Two general approaches are employed. According to one method, cellulosic material is degraded in a nonoxidizing gaseous environment by raising the temperature of the cellulosic material very slowly. Typical speeds of heating are as follows: 10 to 50° C./hour, up to about 400 or 500° C.; about 100° C./hour up to about 1000° C.; and from 1000° C. up to about 1800° C. (2800° C. if graphite cloth is desired) at a much faster rate, perhaps 3000° C./hour. Further details of such processes are given, for example, in W. T. Soltes, U.S. Pat. No. 3,011,981; and in C. E. Ford et al., U.S. Pat. No. 3,107,152.

A second approach comprises the low temperature degradation of cellulosic material in a liquid environment, typically at temperatures ranging from about 150 to 400° C., followed by a second degradation at higher temperatures in a gaseous environment. Like the first approach, very low rates of heating are employed. Further details of the second process are described in M. T. Cory, U.S. Pat. No. 3,508,871.

According to either of the above approaches, if cellulosic material is degraded too rapidly, the resultant carbon cloth is weak. Thus, it is an object of the present invention to provide a process for producing carbonized cellulosic material such that the carbonization can proceed at a more rapid rate than has heretofore been feasible.

SUMMARY OF THE INVENTION

According to the present invention, fibrous cellulosic material (preferably dried of substantially all free water) is converted to carbon material by first subjecting the fibrous cellulosic material to an environment of a silicon compound selected from the group consisting of silicon tetrachloride ($SiCl_4$) and organohalosilanes such as silicon tetrachloride substituted with from 1 to 3 lower alkyl groups; secondly subjecting the silicon compound treated material to an environment of a nitrogen compound selected from the group consisting of ammonia, and primary and secondary lower alkyl amines (i.e., ammonia substituted with 1 or 2 lower alkyl groups) in an amount at least sufficient to neutralize the unreacted chlorine in said material; and finally heating the cellulosic material which has been treated with both the silicon compound and the nitrogen compound to a temperature of at least about 1600° C. in a nonoxidizing atmosphere, whereby to produce a carbon material from the cellulosic material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart which illustrates the process of the present invention in its various steps, including the preferred preliminary drying step.

FIG. 2 is a schematic representation of an apparatus which can be utilized to subject the cellulosic material to successive environments of silicon and nitrogen compounds, prior to carbonization.

FIG. 3 is a schematic representation of a furnace which can be utilized to carbonize the treated cellulosic material.

DETAILED DESCRIPTION

Cellulosic fibers which can be utilized in the present invention include seed fibers, woody fibers, bast fibers, and

leaf fibers, as well as regenerated cellulose, i.e., rayon. Rayon is the preferred cellulosic material because it is essentially pure cellulose, and because it is readily available in continuous filament form.

The initial chemical treatment with the silicon compound is preferably accomplished with silicon tetrachloride. Treatment can occur with the silicon tetrachloride in the vapor phase, or by passing the untreated cellulosic material through liquid silicon tetrachloride. Various other chloro-silicon compounds can also be utilized, such as organohalosilanes, and in particular, lower alkyl substituted silicon tetrachloride. "Lower alkyl" as used herein indicates alkyl groups having from 1 to about 3 carbon atoms. Silicon tetrachloride is the preferred silicon compound for use in the present invention, and the next favored compound is methyltrichlorosilane.

It is not essential that the cellulosic material be dried prior to its chemical treatment, but it is usually preferred to remove substantially all free water from the cellulosic material prior to its treatment with the silicon compound. This can be accomplished, for example, by drying the cellulosic material at a temperature ranging from about 100 to 120° C. for about 1 to 7 days under an absolute pressure of less than about 150 mm. of mercury. Removal of water from the cellulosic material prior to treatment with the silicon compound is usually desirable since it reduces the amount of silicon compound which is consumed in the process, which in turn reduces the amount of silicon compounds left on the carbon cloth produced. Excessive water in the cellulosic material to be carbonized also results in decreased strength of the carbon cloth produced. If the amount of silicon compounds used or remaining in the cloth after carbonization and the strength of the carbon cloth are not matters of concern, the treatment of cellulosic material containing water does have the positive effect of reducing weight loss and shrinkage during carbonization.

The preferred rate of utilization of the silicon compound is less than 1 liter, preferably from about 0.1 to about 0.5 liter, of liquid silicon compound per 100 kg. of uncarbonized cellulosic material. If a gaseous silicon compound is used, an equivalent amount should be used. The rate of silicon compound utilization can be varied by maintaining a pool of the liquid material for evaporation. The rate of evaporation, and therefore of utilization, is proportional to the surface area on the top of the liquid pool. Silicon compound use can therefore be controlled by varying this surface area.

The amount of the nitrogen compound utilized is not highly critical, but at least enough should be used to neutralize the unreacted chlorine in the cellulosic material. This can be determined by the cessation of noticeable white cloud formation or by the change of odor from that characteristic of the silicon compound used, or of hydrochloric acid, to that characteristic of the nitrogen compound used.

Referring now to the drawings:

FIG. 1 is a flow chart which illustrates the various steps of the process of the present invention. The first drying step is optional, although highly preferred, and can be accomplished with existing conventional machinery. The second and third steps of subjecting the cellulosic starting material to a silicon compound and subsequently to a nitrogen compound can conveniently be accomplished in apparatus such as that illustrated in FIG. 2.

FIG. 2 illustrates a chemical treatment apparatus divided into six chambers **11–16**. Chamber **11** contains feed roll **17** which is the source of cellulosic starting material **18**. Cellulosic material **18** is fed from feed chamber **11** through first purge chamber **12**, silicon compound treatment chamber **13**, second purge chamber **14**, nitrogen compound treatment chamber **15**, to collection chamber **16**. Each two adjacent chambers are separated by walls **19–23**, each wall containing a narrow slit which allows the passage of cellulosic material **18**. The cellulosic material which is to be treated in the apparatus of FIG. 2 is preferably in the form of a bolt of cellulosic cloth, such as rayon cloth, but the apparatus can also be used to treat cellulosic material in fiber form. Regardless whether in fiber form or cloth form, the cellulosic material upon reaching collection chamber **16** is rolled up upon take-up roll **24**. Purge chambers **12** and **14** and collection chamber **16** are provided with purge gas inlets **12A**, **14A** and **16A**, respectively. Through these purge gas inlets, **12A**, **14A** and **16A** there is provided a suitable purge gas, preferably nitrogen, which prevents the silicon compound and nitrogen compound from getting into the wrong locations within the apparatus. This purge gas, together with vapors from chambers **13** and **15**, is exhausted from the apparatus through exhaust outlet **26**.

Silicon compound treatment chamber **13** is provided with silicon compound reservoir **28** containing pool **29** of the silicon compound to be utilized for treating the cellulosic material **18**. By utilizing a reservoir **28** which has a wedge-shaped cross section, such as that shown in FIG. 2, the surface area of the silicon compound available for evaporation can be varied by merely varying the depth to which silicon compound reservoir **28** is filled. This is desirable in order to vary the amount of silicon compound which is available for treating cellulosic material **18** so that excessive amounts of silicon compound is not utilized to treat the cellulosic material. After determining the proper depth to fill reservoir **28** in order to maintain the proper amount of evaporation, taking into account the rate of feed of cellulosic material **18** through silicon compound treatment chamber **13**, the pool **29** in reservoir **28** is maintained at a constant level by replenishment from silicon compound source **30**. In utilizing this mode of treatment, it is necessary to utilize a silicon compound which is liquid at the pressure (usually atmospheric) within the chemical treatment apparatus. As noted above, silicon tetrachloride is preferred for this purpose. If gaseous silicon compounds are utilized, silicon compound treatment chamber **13** can be outfitted with a silicon compound inlet analogous to nitrogen compound inlet **31**, to be described below. Alternatively, the cellulosic material **18** traveling through silicon compound treatment chamber **13** can be passed through a pool of the liquid silicon compound itself.

After passage through silicon compound treatment chamber **13**, cellulosic material **18** is passed through purge chamber **14** and into nitrogen compound treatment chamber **15**. Nitrogen compound treatment chamber **15** is provided with a nitrogen compound inlet **31**, through which a gaseous nitrogen compound such as ammonia is fed. If it is desired to utilize a liquid nitrogen compound, apparatus analogous to that utilized in silicon compound treatment chamber **13** can be provided in nitrogen compound treatment chamber **15**. As mentioned above, the amount of nitrogen compound utilized is not highly critical; it is only necessary to utilize sufficient nitrogen compound to neutralize any unreacted chlorine in cellulosic material **18**.

After passage through silicon compound treatment chamber **13** and nitrogen compound treatment chamber **15**, the cellulosic material is wound up on take-up roll **24**, to await the next step of processing, carbonization. Alternatively, the treated cloth can be fed directly into the carbonization furnace.

FIG. 3 illustrates a carbonization furnace which can be utilized to carry out the thermal degradation necessary for carbonizing the treated cellulosic material obtained from the apparatus of FIG. 2. Feed roll **35**, which in reality can be the same roll as take-up roll **24** of the apparatus of FIG. 2, provides treated cellulosic material **36** which is fed through furnace **37** to take-up roll **38**. Furnace **37** is provided with a number of heating elements **39**, which are maintained at differing temperatures in order to provide a temperature gradient within furnace **37**. By correlating the temperature gradient maintained within furnace **37**

and the feed rate of treated cellulosic material **36** through furnace **37**, the rate of heating of treated cellulosic material **36** can be closely controlled.

Since it is desired to carry out the carbonization in a non-oxidizing atmosphere, furnace **37** is provided with inlets **40** and **41** for nonoxidizing gas, such as nitrogen. Since the carbonization process yields a number of volatile materials, including the degradation products of the cellulosic material as well as the products from the treatment process carried out in the apparatus of FIG. 2, the nonoxidizing gas together with these degradation products is carried off through exhaust outlet **43**. Since a temperature gradient is maintained within furnace **37**, it is possible that volatile materials which are driven off from the cellulosic material **36** at the hotter (right hand as illustrated in FIG. 3) end of furnace **37** can be condensed in the cooler (left hand) end of the furnace **37**. Should these vapors condense on cellulosic material **36**, they can cause harm to the quality of the carbon cloth. Two steps are utilized in order to minimize the chance of this occurring. First, a plurality of exhaust tubes **44–46** are utilized, all feeding into exhaust outlet **43**. More important, however, cellulosic material **36** is provided with protective means, such as protective cloth **48**, to protect the cellulosic material from condensed vapors produced from the carbonization process. The protective cloth approach, if used, preferably utilizes a carbon cloth which will not undergo any further degradation throughout the carbonization process. Other heat resistant materials can also be utilized, however. As an alternative to utilizing protective cloth **48**, cellulosic material **36** can be protected by a permanent cover (not shown) which is provided within furnace **37** immediately over cellulosic material **36**.

Support table **51**, within furnace **37**, as well as rollers **52–55**, are utilized in order to maintain cellulosic material **36** in a flat position as it is traveling through furnace **37**. Rollers **56** and **57** supplement rollers **52–55** in supporting protective cloth **48**, if it is used.

Both of the above operations, i.e., chemical treatment with the silicon compound and the nitrogen compound, as well as the carbonization operation, can be performed in a batch operation if desired. Batch processing is preferred if the piece of cellulosic material to be converted to carbon material is relatively small, and semicontinuous processing, such as that illustrated in FIGS. 2 and 3, is preferred if the piece of cellulosic material to be converted into carbon is relatively large. In either batch processing or semicontinuous processing, it has been found preferable to carbonize the cellulosic material in a two-step process. The first step is accomplished by passing the cellulosic material through a furnace having a temperature gradient and a speed of passage of the cellulosic material which results in a temperature rise of between about 600 and about 700° C./hour, for example, culminating in a maximum temperature of about 800° C. After the first passage of the material through the furnace, it can be stored for further carbonization, or it can be passed directly to a second furnace with a greater temperature gradient. In either event, the second carbonization can proceed under conditions of temperature gradient and speed of travel such that the rate of increase of temperature in the carbon cloth is much greater, for example, from about 5000 to about 6000° C./hour, culminating in a maximum temperature of about 1650° C., in the event that ordinary carbon cloth is desired, or on the order of about 2800° C. in the event that graphite cloth is desired.

The invention will now be illustrated with several examples.

EXAMPLE 1

Six pieces of rayon about 4 feet long and 5 inches wide were exposed to a silicon compound, as set forth in Table 1. Four different methods of exposure were utilized, as follows:

Method 1: The rayon cloth was pulled through a beaker containing vapor of the silicon compound. About 8 inches of the cloth could be contained conveniently in the beaker at one time. This section of cloth was allowed to sit in the vapor for the indicated time period, and a new 8-inch section was drawn in and the treated section was moved to a beaker containing ammonia vapor where the cloth was accumulated until the whole strip was treated.

Method 2: Strips were treated by folding them up end over end so that the whole strip could be contained in the beaker. Otherwise, method 2 was similar to method 1.

Method 3: The strip was processed according to method 2, and then the strip was removed and refolded in the opposite direction for additional exposure to the silicon compound.

Method 4: Strips were drawn quickly through the liquid silicon compound, the exposure time being just long enough to wet the cloth. The strips were then placed in a beaker containing ammonia vapor, prior to carbonization.

Strips processed as above were then subjected to a carbonization operation, by placing the strips in graphite boats 3 feet long and 5 inches in internal diameter. It was necessary to fold the strips once, end over end, to get them into the boats. The boats were then pushed through a furnace under an atmosphere of nitrogen at a rate of about 1 inch per minute. The furnace contained a hot zone at a temperature of about 1600° C., which extended for about 3 feet in length. Prior to reaching the hot zone, the rayon passed through a temperature gradient wherein the rayon was gradually increased from room temperature to the 1600° C. temperature of the hot zone. The length of the temperature gradient was about 12 feet, so that the increase in temperature for the carbon cloth was about 650 to 675° C./hour. The percent warp shrinkage and carbon yield were measured for each sample, as was the average strength of the carbon cloth produced. The results are set out in Table 1.

TABLE 1

Sample	Silicon compound	Exposure method	Exposure time, minutes	Percent warp shrinkage	Carbon yield, percent	Average strength, lbs./strand
1	CH_3SiCl_3	1	2	30	23	3.86
2	CH_3SiCl_3	2	5	30	24	2.87
3	CH_3SiCl_3	2	10	30	24	1.66
4	CH_3SiCl_3	3	4	30	25	3.50
5	CH_3SiCl_3	4	(1)	30	23	.15
6	$SiCl_4$	4	(1)	20	29	1.28

[1] Few seconds.

It was noted that a curvature remained in the cloth at the place where folding occurred, but the strength of the cloth was unimpaired at this point.

EXAMPLE 2

Pieces of rayon cloth about 20 cm. x 35 cm. were carbonized according to the present example. The rayon samples were exposed to silicon tetrachloride vapor for various lengths of time as set out in Table 2. The silicon tetrachloride treated rayon was then exposed to ammonia. The pieces of treated rayon were then carbonized in two steps, the first step having varying conditions as set out in Table 2. The initial heating conditions listed are the time required for the initial heating, and the maximum temperature attained during that heating process. In the second step of carbonization, the treated rayon samples were subjected to a baking at 1650° C., the heating taking place at a much more rapid rate than the first step. The percentage of shrinkage, carbon yield and average strength were measured for all of the samples; and five of the samples were analyzed for carbon content, silicon content, nitrogen content, and chlorine content. The results of these tests are set out in Table 2.

TABLE 2

Sample	$SiCl_4$ exposure, mins.	Initial heating conditions		Percent shrinkage	Carbon yield	Average strength, lbs./strand	Analysis, percent			
		Hrs.	° C.				C	Si	N	Cl
7	1	1	600	12	30	1.66				
8	1	4	1,000	22	20	2.09	98.96	.06	Nil	.05
9	2	4	1,000	20	28	0.57	98.99	.054	Nil	.05
10	3	4	1,000	21	30	2.57	99.77	1.04	.14	.05
11	2	4	1,000	20	28	0.57	98.99	0.54	Nil	.05
12	2	6	1,200	17	31	0.69				
13	2	9	1,400	21	27	1.31	99.43	.07	.22	.05

The variations in percent shrinkage, carbon yield and strength for the various samples of this example are believed to be due to variable amounts of moisture allowed to enter the cloth, the unknown water content of the rayon prior to treatment with silicon tetrachloride, and the like.

EXAMPLE 3

In this example, rolls of rayon cloth were converted to carbon in a semicontinuous manner, i.e., the rayon was fed from one roll to another in a continuous fashion until the rayon material was used up.

The first step of this example was drying the rayon cloth. A charge of approximately 60 lbs. (just under 60 sq. yards) was placed in an oven maintained at a temperature of 100° C. for 7 days. The pressure maintained within this oven varied from about 35 to about 125 mm. of mercury absolute. Successive charges of rayon subjected to this vacuum-heating technique showed weight losses ranging from about 8 to about 10%.

Rolls of rayon cloth, after having been dried as described above, were passed through a chemical treatment apparatus where the rayon cloth was subjected successively to silicon tetrachloride vapors and ammonia vapors. The treated cloth was then run through a furnace in two successive stages, the first stage having a maximum temperature of about 800° C. and the second stage having a maximum temperature of about 1650° C. The furnace had a temperature gradient about 6 feet in length, and the cloth was processed through the furnace at speeds of approximately 1 inch per minute and 4 inches per minute, respectively, for the 800 and 1650° C. carbonization steps. Accordingly, the rates of heating of the rayon cloth were about 650° C./hour and about 5500° C./hour, respectively, for the first and second stages of carbonization. Five rolls of cloth processed in the above manner had average tensile strengths as indicated in Table 3.

TABLE 3

Sample	Direction	Average tensile strength, lbs./strand
14	Warp	1.48
	Fill	0.89
15	Warp	1.22
	Fill	0.64
16	Warp	0.74
	Fill	0.55
17	Warp	2.18
	Fill	0.85
18	Warp	0.54
	Fill	0.64

I claim:

1. A process for producing carbonized fibrous cellulosic material, comprising the steps of

(1) subjecting the fibrous cellulosic material to be carbonized to an environment of a silicon compound selected from the group consisting of silicon tetrachloride and silicon tetrachloride substituted with from 1 to 3 lower alkyl groups, whereby to form a silicon compound treated material;

(2) subjecting the silicon compound treated material to an environment of a nitrogen compound selected from the group consisting of ammonia and ammonia substituted with from 1 to 2 lower alkyl groups in an amount at least sufficient to neutralize the unreacted chlorine in said material, whereby to form a silicon compound treated, nitrogen compound treated cellulosic material; and

(3) heating the silicon compound treated, nitrogen compound treated cellulosic material to a temperature of at least about 1600° C., in a nonoxidizing atmosphere.

2. A process according to claim 1, wherein the cellulosic material is rayon.

3. A process according to claim 1, comprising in addition the step of drying the cellulosic material to remove substantially all free water, prior to the step of subjecting the cellulosic material to an environment of a silicon compound.

4. A process according to claim 3, wherein the drying is accomplished by subjecting the cellulosic material to a temperature ranging from about 100 to about 120° C., for a period of from about 1 to about 7 days, under an absolute pressure of less than about 150 mm. of mercury.

5. A process according to claim 1, wherein the silicon compound is selected from the group consisting of silicon tetrachloride and methyltrichlorosilane.

6. A process according to claim 2, wherein the silicon compound is silicon tetrachloride in a gaseous phase.

7. A process according to claim 6, wherein the gaseous silicon tetrachloride is utilized at a rate equivalent to from about 0.1 to about 0.5 liter of liquid silicon tetrachloride per 100 kg. of dried cellulosic material.

8. A process according to claim 1, wherein the silicon compound treated, nitrogen compound treated cellulosic material is fed through a carbonization furnace in which a temperature gradient is maintained, the carbonization furnace being provided with means for protecting the cellulosic material within the furnace from condensed vapors produced by the carbonization process.

9. A process according to claim 8, wherein the cellulosic material is protected by a supplementary layer of cloth fed through the carbonization furnace in conjunction with the cellulosic material to be carbonized.

10. A process according to claim 8, wherein the cellulosic material is protected by a permanent covering means within the carbonization furnace.

11. A process according to claim 1, wherein the cellulosic material is carbonized in two steps, the first step comprising passing the cellulosic material through a furnace having a temperature gradient and a speed of passage of the cellulosic material which results in a temperature rise of between about 600 and about 700° C./hour, culminating in a maximum temperature of about 800° C.; and the second step comprising passing the cellulosic material through a furnace having a temperature gradient and a speed of passage of the cellulosic material

which results in a temperature rise of between about 5000 and about 6000° C./hour, culminating in a maximum temperature of at least about 1600° C.

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EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

264—29; 423—449