United States Patent [19]

Leeds

[11] **3,716,332**

[45] **Feb. 13, 1973**

[54] **CARBONIZATION OF WOOL**

[75] Inventor: **Donald H. Leeds**, Rolling Hills, Calif.

[73] Assignee: **Ducommun Incorporated**

[22] Filed: **July 27, 1970**

[21] Appl. No.: **58,232**

[52] **U.S. Cl** 423/447, 264/29

[51] **Int. Cl.** **C01b 31/07**

[58] **Field of Search** 23/209.1; 264/29; 8/128, 140

[56] **References Cited**

UNITED STATES PATENTS

3,107,152	10/1963	Ford et al.	23/209.2
3,285,696	11/1966	Tsunoda	23/209.1
3,297,405	1/1967	Sperk et al.	23/209.1
3,305,315	2/1967	Bacon et al.	23/209.1
3,533,741	10/1970	Higgins	23/209.1

Primary Examiner—Edward J. Meros

Attorney—Whann and McManigal

[57] **ABSTRACT**

A fibrous carbon product is produced by subjecting a body of wool fibers in a furnace to a reduced pressure to remove essentially all of the oxygen from the furnace and thereafter heating said body of wool fibers at a reduced pressure in the absence of any appreciable oxygen to a temperature of at least about 800°F at which carbonization will occur. An inert gas such as nitrogen is preferably passed over the body during carbonization to remove reaction products.

8 Claims, 3 Drawing Figures

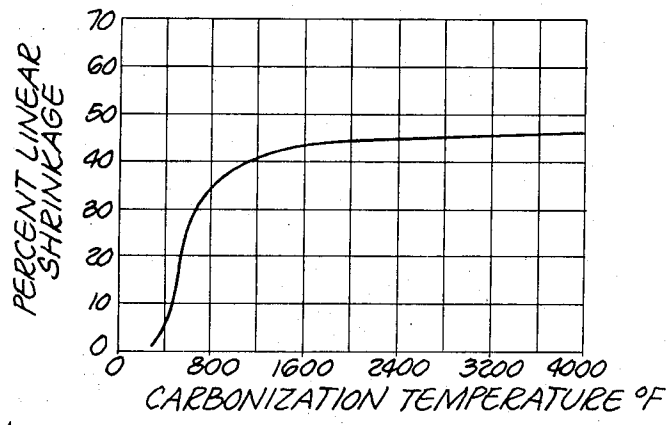


FIG. 1. EFFECT OF TEMPERATURE ON LINEAR SHRINKAGE OF WOOL DURING CARBONIZATION

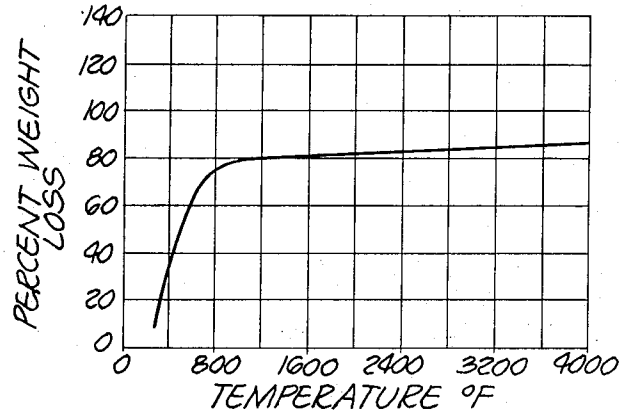


FIG. 2. EFFECT OF TEMPERATURE ON WEIGHT LOSS OF WOOL DURING CARBONIZATION

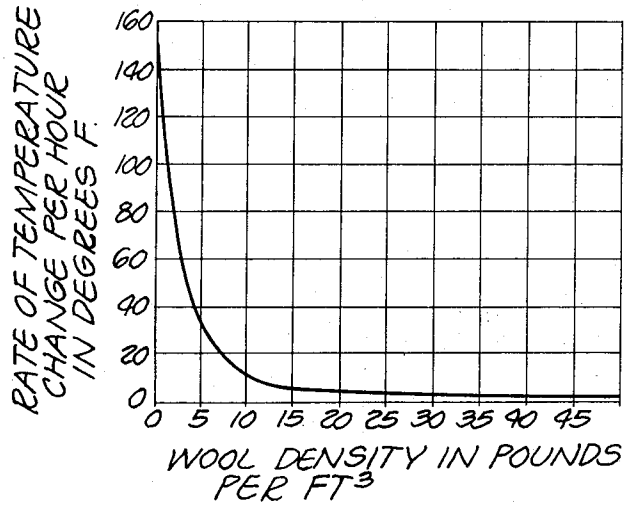


FIG. 3. EFFECT OF WOOL DENSITY ON HEAT TREATING RATE

DONALD H. LEEDS
INVENTOR
WHANN & McMANIGAL
Attorneys for Applicant
BY

CARBONIZATION OF WOOL

BACKGROUND OF INVENTION AND PRIOR ART

An urgent need for superior refractory materials arises in connection with NASA-AEC-USAF re-entry vehicles, advanced military aircraft, high energy braking systems, turbines, nuclear reactor technology and other instances.

In the past rayon fibers have been used as a substrate material for products of this type. In my invention I use raw wool which I carbonize in a particular manner as hereafter set forth; and I am able to form a material which is two to five times stronger for re-entry vehicle heat shields than current rayon based carbonized materials at a given density.

In my invention the thermal conductivity of such a structure is one-third to one-fifth that of a rayon based material. Also, I am able to carbonize the wool fibers so that they have sufficient strength to permit the carbonized body to be rough-machined without the necessity, as is the case with rayon based materials, of performing a carbon infiltration step in order to build up the carbon content and increase the strength of the material so that it can be handled.

The product of my invention may be utilized as a stiff product which can be machined and used "as is," or may be used as a carbonized substrate in connection with which infiltration steps can be performed in order to increase its density.

Others in the art have attempted to carbonize wool but have either failed or produced an inferior unuseable material. Some of the difficulties involved in the attempted carbonization of wool fibers is the fact that the wool fibers apparently go through higher and higher carbon content organics before finally forming the carbon fibers typical of their carbonized condition. In at least one of these stages the fiber condition approximates a viscous liquid capable of fusing to other fibers and losing its scaley surface form and being blown into a froth by volatiles evolved during a too-rapid heating cycle.

It is an object of my invention to provide a process in which a vacuum is imposed on the raw wool body in order to remove all oxygen in order that during the process oxygen will not combine with the wool fibers and erode their surfaces, and which during the carbonizing steps all reaction products are removed from the presence of the wool body, this being done, for example, by passing an inert gas such as nitrogen over the body to remove such reaction products.

It is another object of my invention to carry the temperature of the wool body through a critical temperature stage whereby superior results in the forming of the carbonized body may be accomplished. I have found that it is critical when passing the wool body through a temperature range of about 375°F. to about 800°or 900°F. to change the temperature from the low figure to the high figure at a rate of about 3° per hour. I have varied this temperature change from 2° to 5° per hour, but find superior high density tensile and flexure strength results are attained at a 3° per hour rate of temperature change.

Rayon precursor carbon felt composites in the past exhibited an anisotropy ratio of 2.5 to 1 in flexure strength and 3.5 to 1 in tensile strength. The *a–b* direction in these composites was always the strongest. The tensile strength of wool precursor carbon and graphite felt composites appears to be isotropic within experimental precision. The *a–b* direction flexure strength of the wool based composite is double that of the *a–b* direction strength of the same density rayon based composite. The tensile strength of the wool is also almost double that of the rayon *a–b*. Additionally, the wool based carbon material is five times stronger than the rayon based carbon composite in the *c* direction. This high isotropic tensile strength, and particularly the high *c* direction or interlaminar tensile strength of wool based composites is believed exceptionally good in comparison with other carbon-carbon composite fabrication techniques. These other techniques include flat laminate or filament winding construction and other materials such as high modulus carbon fibers. The "interlaminar" tensile, or shear properties of these alternatives are lower in comparison. Even the excellent properties of "3–D" constructions are bought at the horrendous price of fabrication complexity and cost. It is postulated that there is an inherent solution possible in the isotropic-fiber-orientation of the felt approach to the disturbing real-life problem of off-axis (off-orthogonal axes) stress loading in the use environment.

THE PRESENT INVENTION

It performing the process of my invention I start with wool as a precursor material. By the term "wool" I have reference to wool in its natural state except cleaned from shorn sheep, wherein it normally exists in fibers of the order of 10 to 50 microns (0.00042 to 0.0021 inch) in diameter by one-eighth to 2 to 3 inches long. It may be mixture of the fibers containing noils which are one-half inch long and less and tops which are longer than one-half inch. Worsted yarn, for example, is made by twisting tops after the noils are combed out. The size of the fibers depends mainly on the mixture of wool on hand supplied from France (or Belgium) which contains the shortest noils to Australian, Argentinian, Schlumberger and Noble, which contain the longest noils.

The wool may take the form of a felt or it may be in the form of textiles, such as cloths, tufted and needled fabrics, 3–D constructions, worsted and/or noils, as well as monofilament and multi-ply filament windings and constructions.

As an initial step in my process I prefer to take the wool material, wool felt, for example, and shape it to the general form that the product will take. As an example, a felt body may be formed into large truncated cones four to five feet tall with a wall thickness of one-half inch. Also, plates up to four inches thick and a foot by a foot and a half wide may be formed. This general shape, after carbonization, can, in my process, be rough-machined to substantially the required dimensions without the necessity of an infiltration step as is required where rayon is used as the precursor material.

I then place the wool body or shape into a furnace where the additional process steps are performed. I find that furnaces of the following general character are among those satisfactory for my use:

The furnaces I have used are essentially water cooled steel vessels vacuum sealable in construction. Just in-

side the outer jacket is a water cooled copper coil with suitable electrical connections which exit the outer jacket. Within the coil is a graphite cylinder which is capable of inductively suscepting, that is, converting electrical energy into thermal energy and heating the chamber. Within this graphite cylinder in the vacuum chamber is the useable hearth volume for carbonization, infiltration, etc. Gas is introduced centrally at the bottom and exhaust is pumped out at the top after the incoming gas has had the chance to traverse the full height of the furnace. The graphite cylinder heats the internal volume.

The furnaces I have used for wool carbonization have useable volumes 10 inches in diameter by 14 inches high, 17 inches in diameter by 34 inches high and 38 inches in diameter by 72 inches high. These furnaces, specified by the diameter of the outer steel shells as 3 foot, 4 foot and 7 foot furnaces have all been used to carbonize wool.

Temperature is controlled in these furnaces through power input to the induction coil. Temperature is monitored by thermocouples located in the susceptor, in a block of carbonizing material in a support shelf, and in the air space above the load. It is also monitored by Ray-O-Tube recording radiation pyrometry and with manual optical pyrometry. Pressure is also monitored manually and automatically.

The first step in the process is a pump-down step in which pressure within the furnace and around the wool product is reduced to a pressure of approximately 1 to 2 millimeters of mercury. In the following Table 1 I have given the factors involved in five of many processes which I have performed. In these examples the wool body was of a density of approximately 15 pounds to 45 pounds per cubic foot and the minimum thickness of its minimum dimension was greater than one-half inch.

TABLE 1

Run No.	Oper. No.	Time to/at temp., hrs.	Temp., ° F.	Pump down, Hrs.	Sequential press, mm. Hg	N_2CFH, percent	(1) Remarks
41-339	1				.10		
	2	4.5	57-375		1.20	10	
	3	175	375-900	16	1.00-4.00-1.00	15-0	3°/hr.
	4	4.25	900-1,200		av. 1.5	5-1	
	5	4	1,200-1,800		av. 1.5	1-0	
	6	2	1,800		1.10	0	
31-244	1				.18		
	2	4.5	55-375		1.10	4	
	3	146.5	375-800	20	av. 2.5	5-13-0	3°/hr.
	4	5.5	800-1,200		av. 5.0	0	
	5	4.5	1,200-1,700		av. 1.5	0	
	6	2	1,700-2,033		av. 1.5	0	
43-186	1				.23		
	2	14.5	70-635	16	1.00	27.5±5	Fast cycle.
	3	37	1,750		1.20	20	
	4	3	1,750		av. 6.8	20	
43-187	1				.24		
	2	166.5	70-1,725	19	.90	30	Slow cycle.
	3	3	~2,000		1.00	30	
43-188	1				.07		
	2	24	70-4,100	2.25	1.00	45	Bakeout.
	3	2	4,100	2.25	1.20	45	

Referring to the Table, the first column is the run number, the second column indicates the operation number of the process, the next column is the time to or at temperature in hours, the next column is the temperature in degrees F., the next column is pump-down hours, the next column is sequential pressure in mm Hg, the next column is nitrogen rate through the furnace in cubic feet per hour, and the last column is remarks.

Taking Run No. 41-339, as an example, the pump-down time was 16 hours and the pressure was 0.10 mm Hg. The purpose of this pump-down step is to limit the oxygen content of the atmosphere of the furnace to a harmless level. The object, of course, is to exclude oxygen for the reason that its presence during the heating process would reduce yield by combining with some of the "meat" of the fiber diameter. Also, the presence of oxygen during the process may make a soft carbonized material which would be undesirable.

It is my object to obtain maximum material yield since obviously the higher the "as carbonized" density the less infiltration furnace time will be required where the product of my invention is later to be infiltrated.

The pump-down step will dehydrate the fiber body and success is obtained where outgassing pressures will normally register above one to two mms. until such gas vapors have been removed by pumping.

A further object in pumping-down and continuing the operation of the exhaust pump is a precaution in the event that there may be a furnace air leak. It normally takes 16 to 19 hours to void any chemisorbed interstitials in the wool, such as water vapors.

The second step is performed for 4½ hours and during this period of time the temperature is raised from 57° to 375° F. at a pressure of 1.20 mm. At this time an inert gas, such as nitrogen, is fed into the furnace and in Run No. 41-339 the amount of nitrogen was 10% of the nitrogen flow meter for the given furnace size (4 feet) in cubic feet per hour. Nitrogen is used to poison the vacuum to adjust the downstream pressure (toward the pump) in the carbonization chamber of the furnace, to purge the chamber of carbonization gases and/or adjust the pressure therein and to increase the cooling rate of the carbonized product after completion of the heating cycle. Other inert gases, such as argon or helium, could be substituted but with increased expense. Also, as indicated in Run No. 31-244, the inert gas may be completely eliminated in the majority of the process. In practice, this initial step may be performed anywhere from about one hour to 4.5 hours. The rate of temperature change in this step is not critical.

In step No. 3 the temperature is raised from 375° to 900° F. over a period of 175 hours at a closely controlled rate of temperature change of 3° per hour. I have in instances varied the rate of temperature change from 2° to 5° per hour. However, the best results are where the temperature change is at about 3° per hour. This is the critical temperature range and time and rate of temperature increase is important. Where I have varied from the rates as given I have had unsuccessful runs which resulted in frothed fused wool where appreciable mass concentration of wool fibers was

present since the carbonization reaction is exothermic. Where low mass concentration of fibers is present faster rates are possible. If I depart from the approximately 2° to 5° per hour temperature change with high mass concentration in this critical range carbon fibers may be fused. Distorted blocks of carbonized composites may occur and quality control is lost.

The rate of temperature change above the temperature range of about 800° to 900° F. is not critical and faster increases in temperature may be used for economic reasons.

It will be noted in Run 41–339 that in operation number 3 the pressure has varied between 1 to 4 millimeters and back to 1 millimeter and that the nitrogen flow has varied from 15 percent to 0 percent.

Step four was conducted in 4.25 hours and the temperature has been increased from 900° to 1,200° F. The average pressure was 1.5 millimeters and the rate of flow of nitrogen varied from 5 percent to 1 percent.

Step five was accomplished in four hours, whereby the temperature was increased from 1,200° to 1,800° F. and an average of 1.5 mm of mercury pressure was obtained with 1 percent to 0 percent nitrogen.

Following this step the temperature was maintained for two hours at 1,800°F. at a pressure of 1.10 millimeters of mercury and 0 percent nitrogen.

This final 2 hours "soak" period at maximum temperature is to insure driving-off all material volatizable in the wool char at the indicated temperature.

I have performed a similar process in which steps four and five were combined and operated for a period of 2 to 8 hours in which the temperature was raised from 900° to 1,800° F.

In some instances I have found it desirable to increase the temperature from 1,800° to 1,950° F., which is the temperature at which infiltration of a carbonaceous gas, such as methane, would be used should it thereafter be desired to increase the density of the carbonized product or substrate.

In Run No. 43–186, which is a fast cycle, the microstructure of the material shows the fibers completely fused to each other at their cross-overs. It also showed that the fibers had lost their scale structure and that the surfaces had been fused to form smooth carbon fibers. The material "as carbonized" (and without performing any additional infiltration step) had a flexure strength of 4,000 psi as compared with the material of the slow cycle run, which is Run No. 43–184, which showed a flexure strength of 400 to 800 psi. The additional strength I attribute to the fusion of fibers at the cross-overs. I found, however, that the "as carbonized" strength advantage is not maintained where the material is later infiltrated to higher densities.

The flexure strength of the resulting char I have found varies from 350 pounds per square inch to 4,000 pounds per square inch, depending upon how fast I carbonize the material. In slow carbonization, such as in Runs 41–339 or 31–242, where the temperature is maintained in the critical range from 146 to 175 hours, I am able to preserve the fiber surface structure of the wool. It remains scaly and the fibers remain individual. Where fast carbonization occurs, as previously explained, the scaly surface and its advantageous characteristics at higher densities are lost.

Where the density of the wool felt is 24 pounds per cubic foot (0.38 g/cc) during carbonization there is an average increase of approximately 8 percent to 26 pounds per cubic foot (0.41 g/cc).

Low density wool felts increase an average of 47 percent in density on carbonization and low density felts shrink 87 percent by volume (43 percent linear), whereas the higher density felts, such as the 24 pounds per cubic foot felt mentioned above, shrink 81 percent by volume (41 percent linear).

In the accompanying drawing the chart, FIG. 1, shows the effect of temperature on linear shrinkage of the wool during the performance of my process. FIG. 2 is a chart which shows the effect of temperature on weight loss of wool during carbonization.

The effect of the density of the wool on heat treating rate is shown in FIG. 3. Where the density of the wool body is from approximately one-half to 5 pounds per cubic foot or less the temperature change may range between approximately 33° to 150° F. per hour. Where the density of the wool body is from approximately 5 to approximately 15 pounds per cubic foot the temperature change may range between approximately 5° to 33° F. per hour. Where the density of the wool is above 15 pounds per cubic foot the temperature change may vary at a rate of between approximately 2° F. to approximately 5° per hour. This is true where the minimum dimension is one-half inch or greater. Where the minimum dimension is less than one-half inch the rate of temperature change per hour may be increased, and in some cases this increase may be to a range of 33° to 150° F.

I claim:

1. A process of forming a carbonized body, including:
   a. subjecting a body of wool fibers in a furnace to a reduced pressure to remove essentially all of the oxygen from the furnace;
   b. heating said body of wool fibers in an inert atmosphere at a reduced pressure in the absence of any appreciable oxygen through the temperature range of 375° to 800° F. at a rate dependent upon the density of said body and to a temperature at which carbonization will occur.

2. A process as defined in claim 1, in which the rate of temperature increase in said temperature range is at the rate of 2° to 5° F. per hour when the compacted density of said body is approximately 15 pounds per cubic foot or greater and the minimum dimension in one direction is greater than approximately one-half inch.

3. A process as defined in claim 1, in which the rate of temperature increase in said temperature range is approximately 33° to 150° F. per hour for wool fiber bodies in the density range of approximately 5 pounds per cubic foot or less.

4. A process as defined in claim 1, in which the rate of temperature increase in said temperature range is approximately 5° to 33° F. per hour for wool bodies in the density range of approximately 6 to 14 pounds per cubic foot.

5. A process as defined in claim 1, in which the rate of temperature increase in said temperature range is approximately 33° to 150° F. per hour for wool fiber bodies where the minimum dimension in one direction is less than one-half inch.

6. A process as defined in claim 1 which also includes flowing an inert gas around said body at least during a part of said heating stage.

7. A process as defined in claim 1 which includes the step of heating said body of wool fibers to a temperature of at least 1,800°F.

8. A process as defined in claim 1 in which the pressure is maintained below about 6.8 mm Hg during the heating stage.

* * * * *