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[54] CARBONACEOUS FABRIC LAMINATE

[75] Inventors: Theodore Ralph Wessendorf, Florence, Ky.; John Michael Criscione, Broadview Heights, Ohio

[73] Assignee: Union Carbide Corporation, New York, N.Y.

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Related U.S. Application Data

[63] Continuation of Ser. No. 846,252, July 30, 1969, abandoned.

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[51] Int. Cl. B32b 11/10

[58] Field of Search 161/182, 156; 252/502; 23/209.1

[56] References Cited

UNITED STATES PATENTS

2,764,539	9/1956	Horvitz	204/67
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Primary Examiner—George F. Lesmes
Assistant Examiner—Patricia C. Ives
Attorney, Agent, or Firm—John S. Piscitello

[57] ABSTRACT

A lightweight refractory thermal insulator is provided. Superposed layers of carbonaceous fabric are cemented together to form a laminate which, because of its low weight, structural integrity, and excellent thermal resistance, is useful as thermal insulation in a variety of applications. If desired, a thin uniform film or coating of carbon black may be interspersed between the layers of carbonaceous fabric in order to impart improved thermal properties to the laminate.

8 Claims, No Drawings

CARBONACEOUS FABRIC LAMINATE

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation of application Ser. No. 846,252, filed July 30, 1969, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to refractory materials for use as thermal insulation and more particularly to laminated carbonaceous articles comprising superposed layers of carbonaceous fabric.

2. Description of the Prior Art

The continuing and accelerating technological advance brought about by research on materials for use in space vehicles has resulted in the development of a large number of materials. Despite all this research, however, the materials developed to date as backings for reentry heat shields in space vehicles have not proven entirely satisfactory in that they are either too heavy for their intended purpose, have poor structural integrity, or have been found not to possess maximum insulating properties under the wide variety of conditions in which space vehicles operate. Consequently, efforts have continued in the search for an improved heat shield backing. Such a material should be lightweight, possess good structural integrity, and act as a thermal insulator over a wide range of temperatures. In addition to heat shield applications, a material having such properties would find wide use in a variety of applications where such combination of properties is desirable.

The primary object of this invention, therefore, is to provide an article with good structural properties which is an excellent thermal insulator over a wide temperature range and yet is lightweight and of a low density so that it may be readily employed as a heat shield backing and in other applications.

SUMMARY OF THE INVENTION

Broadly, the object of the invention is accomplished by providing a laminate structure formed by bonding superposed sheets of a carbonaceous fabric which may be either a nonwoven carbon or graphite fibrous material such as felt or batting, or a woven fabric such as carbon or graphite cloth. The term "carbonaceous" as used throughout this specification is intended to include both the graphitic and non-graphitic forms of carbon.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The laminated articles of the instant invention are formed by cementing together layers of carbonaceous fabric. From five to fifteen sheets of carbonaceous fabric cemented together has been found to provide an excellent article having low thermal conductivity and diffusivity as well as excellent structural properties. If desired, a thin uniform film or coating of carbon black may be interspersed between the sheets of carbonaceous fabric in order to impart improved thermal properties to the laminate.

The carbonaceous fabric preferably employed in the instant invention is prepared by processing carbon or graphite fibers by any method, either wet or dry, which effects the disposition of such fibers in intimately contacting relation in a non-woven fibrous body. Air laying operations such as carding and garnetting which effect a relatively oriented disposition of fibers into a felted sheet are suitable for this purpose. When a more random deposition of fibers is desired, such as in the production of battings, conventional textile devices which effect the air laying of fibers in a random webbing can be employed.

Felt is the preferred fabric for use in the invention. Most preferably, the felt is prepared by water laying short carbon or graphite fibers using conventional paper making techniques. The paper-thin felt sheets which can be prepared in this manner are the most preferred form of fabric for use in preparing the laminated articles of this invention.

When preparing felt or "paper" by the water laying of carbon or graphite fibers, the fibers are first cut or chopped to a size suitable for processing, e.g., about one-fourth inch in length; homogeneously intermixed with water and a suitable binder, such as starch or other well known binder, to form an aqueous slurry; and then deposited from the slurry on a substrate to form a sheet. This sheet is then processed by conventional paper making techniques to produce the final carbonaceous product.

Converting the fiber slurry into sheets of felt or "paper" involves three general steps, or modifications of these, by which all commercial-base papers are made:

1. The arrangement of the fibers in the slurry into a wet sheet;

2. The removal of a portion of the free water from the wet sheet by wet pressing - this is reflected by improved physical characteristics of the paper;

3. The progressive removal of additional water by heat. In principle, a wet sheet is generally formed either by running a dilute suspension of fibers evenly onto the surface of a moving endless belt of wire cloth, through which excess water may be drained, or by running an endless belt of wire cloth through a suspension of fibers. In the first case - the Fourdrinier process - a part of the water drains off by gravity, a part is taken from the sheet by suction, and a part is removed by pressure; in the second case, a vacuum is maintained below the stock level in the cylinder in which the wire cloth is rotating and the sheet forms on the wire by suction much as does a cake on a vacuum filter. Most paper grades are formed by the first process; very lightweight tissues and many grades of paperboard are made by the second. In either case, the thickness of the sheet is controlled by the speed of travel of the machine, by the consistency (ratio of fiber to water) of the suspension, or by the amount of stock allowed to flow onto the machine.

Woven carbonaceous fabrics such as carbon and graphite cloth are also suitable for use in the instant invention. These materials are available commercially and are generally produced by the techniques described in U.S. Pat. Nos. 3,011,981, 3,107,152 and 3,116,675.

After the carbonaceous fabric sheets have been prepared they are assembled in the desired configuration in a laminated assembly. Best results are achieved employing carbonaceous "paper" from 0.006 to 0.012 inches thick. Greater or lesser thickness dimensions, however, will also provide excellent results.

Prior to being assembled in a laminate, the sheets of carbonaceous fabric are lightly coated with a carbonizable resin in an amount sufficient to securely bond them together. The carbonizable resins which can be used are any binders or cements commonly used for bonding carbon or graphite and include, among others, coal tar pitches, phenolics, epoxies, furanes and the like. In order to insure an even distribution of resin on the carbonaceous fabric, the resin is preferably dissolved in a suitable solvent and the carbonaceous fabric is soaked in the solution. The carbonaceous fabric is then removed from the solution and the solvent evaporated, leaving a uniform coating of resin on the fabric. If desired, the sheets may then be coated with a thin uniform layer of carbon black flour.

Once assembled, the laminate is placed in a press and a suitable compressive pressure, e.g., from about 500 psi. to about 1500 psi., is applied while the press platen temperature is raised, if necessary, to a temperature sufficiently elevated to cure the resin. Heating is continued until the resin is cured. The assembly is then baked to effect carbonization of the resin, e.g., at a temperature of from about 500°C. to about 2200°C., preferably from about 700°C. to about 1000°C. When the laminate is prepared from the preferred form of carbonaceous fabric sheets, i.e., from carbonaceous "paper" having a thickness of 0.006 to 0.012 inches, and compressive pressures in the amount stated above are applied to form the laminate, the carbonaceous "paper" employed is generally reduced in thickness to from 0.001 to 0.003 inches as a result of the pressure applied.

Any inert liquid solvent capable of dissolving the carbonizable resin employed and vaporizable at a temperature lower than that at which the resin reacts (i.e., the temperature at which the resin cures or carbonizes) can be employed in preparing the laminate structures of the instant invention. Generally, the carbonizable resin is present in the solution in an amount of from about 5 per cent by weight to about 75 per cent by weight, preferably from about 10 per cent by weight to about 25 per cent by weight. Suitable solvents include, among others, saturated aliphatic hydrocarbons such as hexane, heptane, pentane, isooctane, purified kerosene, and the like; saturated cycloaliphatic hydrocarbons such as cyclopentane, cyclohexane, methylcyclopentane, dimethylcyclopentane, and the like; aromatic hydrocarbons such as benzene, toluene, xylene, and the like; and ketones such as acetone, and the like.

If desired, after the solvent has been evaporated from the carbonaceous fabric sheets, the sheets may be "dusted" with a thin uniform layer of carbon black flour prior to being assembled in the desired laminate configuration and baked. This results in a laminate structure having layers of carbon black interspersed between the carbonaceous fabric sheets. The carbon black film disrupts the contact between the sheets of carbonaceous fabric and thereby provides a more effective thermal barrier. For this reason, laminate structures wherein the carbonaceous fabric sheets have been dusted with carbon black are the preferred embodiment of the invention.

Any form of carbon black, e.g., gas blacks, furnace combustion blacks, furnace thermal blacks, lampblacks, may be employed to dust the resin coated sheets of carbonaceous fabric. The carbon black flour is preferably applied to the surface of the carbonaceous sheets to a thickness of less than 0.001 inch, but can be applied in greater thicknesses, e.g., from 0.001 inch to about 0.002 inch.

The carbon black flour may be applied to the resin coated carbonaceous fabric sheets in any suitable manner, e.g., by suspending the carbon black in a suitable gaseous vehicle and spraying the mixture on the substrate to the desired thickness, e.g., by means of a conventional air gun. Air is the preferred gas because it is inexpensive and readily available, but any inert gas which will not react with the carbon black particles, carbonaceous fabric sheets, and resin binder employed can also be used, e.g., inert gases such as nitrogen, carbon dioxide, argon, krypton, xenon, and the like, are suitable.

The laminates prepared by dusting the resin coated carbonaceous fabric sheets with carbon black generally contain, after carbonization, from about 3 per cent by weight to about 40 per cent by weight, preferably from about 10 per cent by weight to about 25 per cent by weight, of carbon black; from about 15 per cent by weight to about 67 per cent by weight, preferably from about 35 per cent by weight to about 55 per cent by weight, of carbonaceous fabric; and from about 30 per cent by weight to about 45 per cent by weight, preferably from about 35 per cent by weight to about 40 per cent by weight, of carbonized binder.

The laminates which have not been dusted with carbon black generally contain, after carbonization, from about 25 per cent by weight to about 80 per cent by weight, preferably from about 65 per cent by weight to about 75 per cent by weight, of carbonaceous fabric; and from about 20 per cent by weight to about 75 per cent by weight, preferably from about 25 per cent by weight to about 35 per cent by weight, of carbonized binder.

The laminate structures of the instant invention may be prepared in various sizes and shapes. Thus, for example, flat plate laminates up to 0.04 inches thick have been prepared as well as frustrum shaped bodies 20 inches long with a major diameter of 8 inches and a 6 degree half angle. Composites have also been laid up in a concentric layer pattern and in an inter-leaf ply pattern.

In order to test the effectiveness of the laminate structures of the invention as thermal insulators, a number of laminates were fabricated and tested for thermal diffusivity and thermal conductivity. Thus, carbon paper laminates were fabricated from 4 × 4 × 0.010 inches sheets of carbon paper. The sheets of carbon paper were immersed in a solution of acetone containing 20 weight per cent of a phenolic resin of the novolac type together with a hardening agent therefor, allowed to stand until the acetone evaporated, and then assembled into a laminate structure by stacking 10 sheets in a parallel fashion on top of one another. A sheet of aluminum foil was placed on the top and bottom of the stack and the assembly was placed in a press and a compressive pressure of 1000 psi. was applied while the press platen temperature was raised to 120°C. to cure the resin. Heating was continued for about 2 hours. The laminate was then placed between two graphite plates, packed in coke, and heated to 800°C. at a rate of 5° – 10°C./hour to carbonize the resin.

The thermal diffusivity, thermal conductivity and short beam shear strengths of a number of laminates so prepared are listed in Table 1 below along with the val-

ues obtained for a laminate containing ten sheets of carbon paper interspersed with nine layers of carbon black. The latter laminate was prepared in the manner described above except that after evaporation of the acetone, the impregnated paper sheets were sprayed with an air stream containing suspended microparticles of carbon black (Thermax) about 0.3 microns in diameter. The air stream was uniformly directed at the paper surface for a sufficient period of time to deposit the desired quantity of particles. Excess or loose particles were brushed from the coated surface. The sheets of prepared material were then lamainated, cured, and pyrolized as described above.

In order to measure the effect of high temperature on the laminate structures of the invention, a number of composites were prepared in the manner described above and tested for thermal diffusivity and thermal conductivity at elevated temperatures. The data obtained is shown in Table 2. It is apparent from Table 2 that the laminates of the invention are not substantially affected by being subjected to high temperatures such as 2000°C. As shown therein, thermal conductivity increases slightly at higher temperatures, but still is significantly low, particularly in view of the low density which is maintained throughout the temperature cycle.

TABLE 1

Room Temperature Thermal Properties [1] and Short Beam Shear Strengths [2] of Laminate Insulators

Sample [3]	Thermal Diffusivity cm^2/sec	Thermal Conductivity BTU-ft / ft^2-hr-°F	Shear Strength psi
(1) Carbon "paper" laminate	0.0022	0.070	390
(2) Carbon "paper" laminate	0.0024	0.077	—
(3) Carbon "paper" — carbon black laminate	0.0015	0.06	310

Notes:

[1] The samples were evaluated by the laser pulse technique.

[2] 4/1 span-to-depth, measured parallel to laminate.

[3] The carbon "paper" of the laminates after compression was from 0.001 to 0.003 inches thick. Sample (1) contained ten sheets of carbon "paper" bonded together with 33 weight percent of carbonized resin (based on the weight of the entire composite). Sample (2) contained ten sheets of carbon "paper" bonded together with 38 weight percent of carbonized resin (based on the weight of the entire composite). Sample (3) contained ten sheets of carbon "paper" interspersed with nine layers of carbon black, each layer of carbon black having a thickness of less than 0.001 inches, with the total weight of the carbon black being 20 percent of the total weight of the entire composite and the total weight of the carbonized resin being 30 percent of the total weight of the entire composite.

TABLE 2

High Temperature Thermal Properties[1] of Laminate Insulators

Density Sample[2]	Initial (g/cc)	Final[3] (g/cc)	Temperature Avg.[4] (°C)	Temperature Differ.[5] (°C)	Thermal Diffusivity (cm^2/sec)	Thermal Conductivity BTU - ft / ft^2-hr-°F
(1) Carbon "paper" laminate	0.71	0.52	2025	1150	0.0050	0.31
	—	0.65	1995	970	0.0057	0.45
	—	0.75	1795	670	0.0061	0.56
(2) Carbon "paper" laminate	0.81	0.73	1670	760	0.0039	0.34
	—	—	1960	940	0.0050	0.45
(3) Carbon "paper" — carbon black laminate	0.93	—	1520	120	0.0022	0.24
	—	0.89	2020	540	0.0027	0.32
(4) Carbon "paper" — carbon black laminate	0.67	—	1358	495	<0.0033	0.25
	—	—	1595	610	<0.0041	0.31
	—	0.64	2005	770	0.0022	0.17
	—	0.64	1978	976	0.0037	0.29

Notes:

[1] Thermal properties of Samples 1 and 2 were determined using the arc image 360° cyclic phase shift method in argon atmosphere. Thermal properties of Sample 3 were determined using the arc image 180° cyclic phase shift method with quadratic correction in argon atmosphere. The first three determinations of thermal properties of Sample 4 (at 1358°C., 1595°C., and 2005°C. average temperatures, respectively), were made using the arc image 180° cyclic phase shift method, with quadratic correction in argon atmosphere being made for the third determination. The fourth determination of thermal properties of Sample 4 (at 1978°C. average temperature) was made using the arc image 360° cyclic phase shift method in argon atmosphere. Each value represents the average of two sample determinations.

[2] The carbon "paper" of the laminates after compression was from 0.001 to 0.003 inches thick. Sample 1 contained ten sheets of carbon "paper" bonded together with 30 weight percent of carbonized resin (based on the weight of the entire composite) while Sample 2 contained ten sheets of carbon "paper" bonded together with 38 weight percent of carbonized resin (based on the weight of the entire composite). Sample 3 contained ten sheets of carbon "paper" interspersed with nine layers of carbon black, each layer of carbon black having a thickness of less than 0.001 inches with the total weight of the carbon black being 20 percent of the total weight of the entire composite and the total weight of the carbonized resin being 30% of the total weight of the entire composite. Sample 4 contained ten sheets of carbon "paper" interspersed with nine layers of carbon black, each layer of carbon black having a thickness of less than 0.001 inches, with the total weight of carbon black being 5 percent of the total weight of the entire composite and the total weight of the carbonized resin being 30% of the total weight of the entire composite.

[3] Final density measured after exposure to maximum temperature.

[4] Temperature average of front and back faces of laminate.

[5] Temperature difference between back and front faces.

What is claimed is:

1. A laminate structure having a thermal conductivity no greater than 0.077 BTU-ft./ft.²-hr.-°F. and a thermal diffusivity no greater than 0.0024 cm.²/second at room temperature, as measured by the laser pulse technique, comprising a plurality of superposed layers of non-woven paper-thin felt made from carbon fibers, wherein each layer of paper-thin felt is from 0.001 to 0.003 inches thick, bonded together with a carbonized binder.

2. A laminate structure as in claim 1 in which the carbon fibers of the paper-thin felt layers are about one-fourth inch in length.

3. A laminate structure as in claim 1 having from five to 15 layers of paper-thin felt.

4. A laminate structure as in claim 3 in which the carbon fibers of the paper-thin felt layers are about 1/4 inch in length.

5. A laminate structure having a thermal conductivity no greater than 0.077 BTU-ft./ft.²-hr.-°F. and a thermal diffusivity no greater than 0.0024 cm.²/second at room temperature, as measured by the laser pulse technique, comprising a plurality of superposed layers of non-woven paper-thin felt made from carbon fibers, wherein each layer of paper-thin felt is from 0.001 to 0.003 inches thick and is interspersed with thin uniform layers of carbon black, each layer of carbon black being less than 0.001 inches thick, and bonded together with a carbonizable binder.

6. A laminate structure as in claim 5 in which the carbon fibers of the paper-thin felt layers are about 1/4 inch in length.

7. A laminate structure as in claim 5 having from five to 15 layers of paper-thin felt.

8. A laminate structure as in claim 7 in which the carbon fibers of the paper-thin felt layers are about one-fourth inch in length.

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