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(54) **Densified carbonaceous fiber structures.**

(57) A fibrous structure comprising a multiplicity of nonflammable, nonlinear, substantially irreversibly heat-set, first carbonaceous polymeric fibers, and at least one second nonflammable carbonaceous polymeric fiber, yarn or tow in an interlocking relationship with said first fibers; the fibrous structure is preferably densified and has a bulk density of from 4.8 to 32 kg/m^3, and a process for producing the interlocked, fibrous structure useful as a thermal insulating and/or sound absorbing structure.

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DENSIFIED CARBONACEOUS FIBER STRUCTURES

The present invention relates to a process for making a fibrous structure from a multiplicity of first, nonflammable, nonlinear, resilient, elongatable, substantially irreversibly heat-set, carbonaceous polymeric fibers by locking together the fibers with second fibers of a carbonaceous polymeric precursor material, and then heat treating the entire structure to heat-set the second fibers.

The fibrous structure of the present invention has utility in thermal and/or sound insulation applications and in filtration. The structures are preferably densified and are characterized by having good shape and volume retention and are structurally stable to numerous compression and unloading cycles. Those structures having a relatively high densification (as compared to undensified structures) surprisingly have a felt-like appearance and few broken fibers.

A multiplicity of the carbonaceous fibers are used to form a wool-like fluff, felt, web, blanket, batting, or the like, and are hereinafter, for reasons of brevity, generally referred to as a "fibrous structure". Where the fibrous structure is densified as by implantation with a second fiber, the structure is generally referred to herein as a "densified fibrous structure" or simply as a "densified structure".

The term "implanting" used herein generally refers to a method of entangling, intermingling or interlocking of fibers. Preferably, the fibrous structure of first fibers is densified by stitch locking the fibrous structure with the second fiber.

For many high temperature insulation applications, it is desirable to make a fibrous structure, i.e., a wool-like fluff, or batting, of a higher densification such that it will retain its integrity and its densified structure over prolonged periods of exposure to high temperatures. Densified structures are usable at temperatures greater than 400° C and will maintain their good mechanical and physical characteristics.

Nonflammable, nonlinear, resilient carbonaceous fibers that are suitable for making the fibrous structures of the invention are described in European Patent Publication No. 0199567, published October 29, 1986, entitled "Carbonaceous Fibers with Spring-Like Reversible Deflection and Method of Manufacture," by McCullough et al. Prior to the present invention, it has not been possible to permanently densify a fibrous structure of the aforementioned nonlinear carbonaceous fibers and to maintain the integrity of the densified fibrous structure at temperatures higher than 400° C.

At temperatures greater than 400° C, fibers made from the above-mentioned carbonaceous polymeric material (including non-flammable p-aramid fibers) decompose and, accordingly, the fibrous structure loses its integrity. It is therefore of considerable advantage to be able to permanently densify and lock a fibrous structure together with a polymeric fiber which does not lose its physical properties at elevated temperatures.

U.S. Patent No. 4,628,846 to Vives discloses an apparatus which may be utilized to prepare the fibrous structures of the invention.

The present invention is directed to a fibrous structure comprising a multiplicity of nonflammable, nonlinear, substantially irreversibly heat-set, first carbonaceous polymeric fibers, wherein the first fibers are resilient, shape reforming, and elongatable, and have a reversible deflection ratio of greater than 1.2:1 and an aspect ratio greater than 10:1, and at least one second nonflammable, substantially irreversibly heat-set, carbonaceous polymeric fiber, yarn or tow implanted in an interlocking relationship with said first fibers for forming an interlocked fibrous structure.

Preferably, the present invention resides in a fibrous structure, wherein the first carbonaceous fibers have a sinusoidal or coil-like configuration and the fibrous structure is in the form of at least one layer of a nonwoven, wool-like fluff, batting or webbing, and said second carbonaceous fiber, yarn or tow has a linear or nonlinear configuration and a higher denier than said first carbonaceous fibers.

Advantageously, the second interlocking carbonaceous fibers are chemically similar or identical to the first carbonaceous fibers of the fibrous structure.

The invention further relates to a densified fibrous structure having a bulk density of from 4.8 to 32 kg/m³.

The present invention also relates to a method for forming a fibrous structure of a multiplicity of nonflammable, nonlinear, substantially irreversibly heat-set, first carbonaceous polymeric fibers, comprising the steps of implanting into the first fibers at least one non-heat-set second carbonaceous polymeric fiber, yarn or tow in an interlocking relationship with said first fibers, and then heat treating the fibrous structure in an inert atmosphere to heat-set said interlocking second fiber, yarn or tow.

The process of the invention also permits the blending of the fibrous structure of the first fibers with larger diameter second carbonaceous polymeric precursor fibers which have greater shear resistance in the implantation, e.g., needle punching operation. Carbonaceous fibers having a relatively larger denier may also be provided for greater mechanical strength.

In accordance with a preferred embodiment of the invention, a fibrous structure of the first heat-set, nonlinear, carbonaceous polymeric fibers is implanted by needle punching with the second fiber, yarn or tow made from a carbonaceous precursor material to increase the bulk density and mechanical strength of the fibrous structure. The needle punching causes the second fibers to form loops in the fibrous structure.

The heat treatment of the fibrous structure then hooks in the looped stitch. A high degree of needle punching can be used to produce a densified structure which, after heat treatment, has a felt-like feel and appearance.

In accordance with a further embodiment of the invention two or more fibrous structures, such as battings, may be joined together. The fibers of one batting can be utilized as the interlocking fibers for the other batting.

The first carbonaceous fibers preferably possess a sinusoidal or a coil-like configuration or a more complicated structural combination of the two. These first fibers may also include linear, heat-set, carbonaceous polymeric fibers.

The carbonaceous fibers that are employed in the present invention have a carbon content of at least 65 percent and a nitrogen content of from 5 to 35 percent. These fibers are particularly identified by their degree of carbonization and/or their degree of electrical conductivity in the determination of the particular use for which they are most suited.

The first carbonaceous fibers, or matrix fibers, are prepared by heat treating a suitable stabilized carbonaceous polymeric precursor material such as that derived from stabilized polyacrylonitrile (PAN) based materials or pitch based materials, i.e., materials derived from petroleum or coal tar pitch, or other polymeric materials which can be converted into carbonaceous fibers or fiber structures which are nonflammable and thermally stable.

For example, in the case of PAN based fibers, the fibers are formed by melt or wet spinning a suitable fluid of a precursor material and having a nominal diameter of from 4 to 25 micrometers. The fibers are collected as an assembly of a multiplicity of continuous filaments in tows and stabilized by oxidation, in the case of PAN based fibers, in the conventional manner. The stabilized fibers, tows or staple yarn (made from chopped or stretch broken fiber staple) are thereafter formed into a coil-like and/or sinusoidal form by knitting the fiber, tow or yarn into a fabric or cloth (recognizing that other fabric forming and coil forming methods can be employed).

The so-formed fabric or cloth is thereafter heat treated, in a relaxed and unstressed condition, at a temperature of from 525°C to 750°C, in an inert atmosphere, for a period of time to produce a heat induced thermoset reaction wherein additional cross-linking and/or a cross-chain cyclization reaction occurs between the original polymer chain. At the lower temperature range of from 150°C to 525°C, the fibers are provided with a varying degree of temporary to permanent set while in the upper range of temperatures of 525°C to 750°C, the fibers are provided with a substantially permanent or irreversible heat-set configuration. What is meant by "permanent" or "irreversible heat-set" is that the carbonaceous fibers possess a degree of irreversibility where the nonlinear fibers, when stretched to a substantially linear shape, without exceeding their internal tensile strength, will revert to their nonlinear configuration once the stress on the fiber is released. Fibers that are heat treated in accordance with the above procedure can be stretched to a substantially linear configuration and upon release will revert to their unstressed nonlinear configuration. Such stretching of the fiber can be conducted over many cycles without breaking the fiber, such being the case even if additional tension (without exceeding the fibers tensile strength) is applied to the fiber once the fiber is in a substantially linear configuration.

It is, of course, to be understood that the fibers may be initially heat treated at the higher range of temperatures, provided that the heat treatment is conducted while the coil-like and/or sinusoidal fibers are in a relaxed or unstressed state and under an inert, nonoxidizing atmosphere. As a result of the higher temperature treatment of from 525°C to 750°C, a permanently set, sinusoidal or coil-like configuration is imparted to the fibers, tow or yarn. The resulting fibers, tow or yarn, having the nonlinear structural configurations, which may be derived by deknitting a knitted cloth, are subjected to other methods of treatment, known in the art, to create an opening, a procedure in which the tow or the fibers of the cloth are separated into an entangled, wool-like fluffy material in which the individual fibers retain their coil-like or sinusoidal configuration, yielding a fibrous structure of considerable loft.

The stabilized fibers which are permanently set into their desired structural configuration e.g., by knitting and thereafter heating at a temperature of greater than 525°C in a relaxed and unstressed condition, retain their resilient and reversible deflection characteristics. It is to be understood that higher temperatures may be employed of up to about 1500°C, but the most flexible fibers and the smallest loss of fiber breakage, when carding the fibers to produce the fluff, is found in those fibers which are heat treated to a temperature from 525°C to 750°C.

The second carbonaceous fibers that are used in the present invention include fibers that are capable of interlocking with the first fibers of the fibrous structure described above and that are capable of withstanding the high temperatures disclosed. The second fibers may be derived from a separate thread, may be fibers of an adjacent batting, or may be blended into the first fibers forming the wool-like fluff or batting and used for densification.

Preferably, the interlocking second fibers may be prepared from the same or a similar stabilized carbonaceous polymeric precursor material as the first fibers. For example, a suitable stabilized precursor material can be selected from PAN or pitch based materials (i.e., petroleum or coal tar), or other polymeric materials that are thermally stable at the high temperature of interest as described above such as, for example, aramid fibers, particularly the aromatic polyaramides, e.g., KEVLAR™ (a trademark of E. I. du Pont de Nemours & Co., Inc.).

PAN based fibers can be collected as an assembly of a multiplicity of continuous filaments in tows and stabilized by oxidation in a conventional manner. The stabilized second fibers, tows or staple yarn (made from chopped or stretch broken fiber staple) are thereafter, in accordance with the present invention, implanted into the first carbonaceous fiber structure to form the fibrous structure or a densified structure.

When implanted into the fibrous structure, the second carbonaceous fibers may be incorporated into the structure as a linear or nonlinear fiber before permanently heat-setting the second fibers.

The second, nonlinear fibers can be prepared in a similar manner as the first fibers, by imparting to the fibers a temporary set by heat treating these fibers in a relaxed and unstressed condition at a temperature range of from 150 °C to 525 °C in an inert atmosphere. The fibers are provided with a varying degree of temporary to permanent set with an increase in temperature in the specified temperature range. The fibers are then permanently set by a chemical treatment or by heat treating the fibrous structure after the interlocking step. Preferably, the heat treatment is at a temperature of 525 °C and above such that the fibers are provided with a permanent set.

When the second carbonaceous fibers are permanently heat-set, integrity and handleability is imparted to the fibrous structure comprising the combination of the first and second carbonaceous fibers.

As with the first fibers, temperatures of up to about 1500 °C may be employed to impart a permanent set to the second fibers, but the most flexible and smallest loss of fiber breakage is found in those fibers that are heat treated to a temperature of from 525 °C to 750 °C.

The interlocked fibrous structure is utilized in high temperature thermal insulating and sound absorbing structures and may be classified into three groups depending upon the particular use and the environment that the structures in which they are incorporated are placed.

In a first group, the carbonaceous fibers used in the fibrous structure of the present invention are electrically nonconductive. The term nonconductive applies to a resistance of greater than 4 x 106 ohms/cm when measured on a 6K tow of fibers each having a diameter of from 7 to 20 microns. The specific resistivity of each fiber is greater than about 10^2 ohms/cm.

In a second group, the carbonaceous fibers used in the fibrous structure of the present invention are classified as being partially electrically conductive (i.e., having a low electrical conductivity) and have a carbon content of less than 85 percent. When the precursor stabilized fiber is an acrylic fiber, i.e., a PAN based fiber, the percentage nitrogen content is from 5 to 35 percent, preferably, from 16 to 20 percent. These partially conductive fibers are excellent for use as insulation for aerospace vehicles as well as insulation in areas where public safety is a concern. The structures formed therefrom are lightweight, have low moisture absorbency, good abrasive strength together with good appearance and handle.

The larger the amount of carbon content in the carbonaceous fibers, the higher the degree of electrical conductivity. Such fibers still retain a wool-like appearance when formed into a densified structure, especially when the majority of the fibers are nonlinear, e.g., coil-like. Also, the greater the percentage of coil-like fibers in the structure, the greater is the resiliency of the structure. As a result of the greater carbon content, structures prepared with these partially conductive fibers also have greater sound absorbing properties and result in a more effective thermal barrier at higher temperatures. These fibers have an electrical resistance of from 4 x 10^6 to 4 x 10^3 ohms/cm when measured on a 6K tow of fibers, wherein each fiber has a diameter of from 7 to 20 micrometers.

In a third group are carbonaceous fibers having a carbon content of at least 85 percent. These fibers, as a result of their high carbon content, have superior thermal insulating and sound absorbing characteristics. The coil-like or sinusoidal shape of the fibers in the fibrous structure provides an insulation which has good compressibility and resiliency while maintaining improved thermal insulating efficiency. The fibrous structure prepared with the third group of fibers has particular utility in the insulation of furnaces and in areas of high heat and noise.

Preferably, the third group of fibers which are utilized are derived from stabilized acrylic fibers and have a nitrogen content of less than 10 percent. As a result of the still higher carbon content, the fibrous structures are more electrically conductive. That is, the electrical resistance is less than 4 x 10^3 ohms/cm when measured by a 6K tow of fibers, wherein each fiber has a diameter of from 7 to 20 micrometers.

The precursor stabilized acrylic fibers which are advantageously utilized in preparing the fibrous structures are selected from acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers. The copolymers preferably contain at least about 85 mole percent of acrylonitrile units and up to 15 mole percent of one or more monovinyl units copolymerized with styrene, methylacrylate, methyl methacrylate, vinyl chloride, vinylidene chloride, vinyl pyridine and the like. Also the acrylic filaments may comprise terpolymers wherein the acrylonitrile units are preferably at least about 85 mole percent.

It is to be further understood that carbonaceous precursor starting materials may have imparted to them an electrically conductivity property on the order of that of metallic conductors by heating a fibrous structure to a temperature above about 1000°C in a nonoxidizing atmosphere. The electroconductive property may be obtained from selected starting materials such as pitch (petroleum or coal tar), polyacetylene, acrylonitrile based materials, e.g., a polyacrylonitrile copolymer (PANOXTM or GRAFIL-01TM polyphenylene, polyvinylidene chloride (SARANTM trademark of The Dow Chemical Company), and the like.

In accordance with a feature of the invention antistatic fibers, i.e., fibers that have the ability to dissipate an electrostatic charge, can be inserted into the fibrous structure which also serve as the interlocking and densifying fibers.

Preferred precursor materials are prepared by melt spinning or wet spinning the precursor materials in a known manner to yield a monofilament fiber or multifilament tow. The fibers, yarn or tow are then made into a woven fabric or knitted cloth by any of a number of commercially available techniques. The fabric or cloth is then heated to a temperature above 525°C, preferably above 550°C, and thereafter deknitted and carded to produce the wool-like fluff that is employed in the fibrous structure of the invention.

If desired, the densified fibrous structure can be heat treated to form carbon or graphite structures. The present process permits the preparation of carbon or graphite structures without complicated knitting operations.

It is understood that all percentages as herein utilized are based on weight percent.

Particular embodiments of the present invention are set forth in the following examples:

Example 1

A. A nonlinear carbonaceous fiber tow which had been heat treated to 550°C was opened on a Shirley opener and was blended with 25 percent dogbone shaped larger denier OPF (oxidized PAN fiber) obtained from RK Carbon Fibers, Inc. of Philadelphia, Pennsylvania. The dogbone OPF had a temporary crimp which was set at a temperature of 200°C prior to blending. Battings were combined and run through a needle punch machine and densified from a thickness of 7.5 cm to 1.8 cm with the same precursor fibers.

B. The resulting densified batting or felt from Part A, which contained the dogbone OPF lock stitches, was heat treated at 700°C under a nitrogen atmosphere for 60 minutes. The resulting densified batting or felt had good permanent integrity and was stable to a temperature greater than 400°C.

Example 2

Following the procedure of Example 1A, a densified batting was formed. The resulting batting was then heat treated at a temperature of 1500°C for 60 minutes to produce a uniform carbon structure which was suitable as sound and thermal insulation.

Claims

1. A fibrous structure comprising a multiplicity of nonflammable, nonlinear, substantially irreversibly heat-set, first carbonaceous polymeric fibers, wherein the first fibers are resilient, shape reforming, and elongatable and have a reversible deflection ratio of greater than 1.2:1 and an aspect ratio greater than 10:1, and at least one second nonflammable, substantially irreversibly heat-set, carbonaceous polymeric fiber, yarn or tow implanted in an interlocking relationship with said first fibers for forming an interlocked fibrous structure.

2. The structure of Claim 1, wherein said interlocking fibrous structure is densified and has a bulk density of from 4.8 to 32 kg/m^3.

3. The structure of Claim 1, wherein said first and second carbonaceous fibers are derived from stabilized polymeric precursor fibers or pitch based precursor fibers having a diameter of from 4 to 25 micrometers.

4. The structure of Claim 3, wherein said polymeric precursor fibers are acrylic fibers selected from acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers, wherein said copolymers and terpolymers contain at least

85 mole percent acrylic units and up to 15 mole percent of one or more monovinyl units copolymerized with another polymer.

5. The structure of any one of the preceding claims, wherein said carbonaceous fibers have a carbon content of greater than 65 percent and an LOI value of greater than 40.

6. The structure of Claim 5, wherein said carbonaceous fibers are electrically conductive and have a carbon content of at least 85 percent and an electrical resistance of less than 4 x 10^3 ohms/cm when measured on a 6K tow of fibers in which each fiber has a nominal diameter of from 7 to 20 micrometers.

7. The structure of Claim 5, wherein said carbonaceous fibers are electrically nonconductive or do not possess any electrostatic dissipating characteristics, have a carbon content of less than 85 percent, and an electrical resistance of greater than 4 x 10^3 ohms/cm when measured on a 6K tow of fibers in which each fiber has a nominal diameter of from 7 to 20 micrometers.

8. The structure of Claim 5, wherein said carbonaceous fibers have a low electrical conductivity and electrostatic dissipating characteristics, a carbon content of less than 85 percent, and an electrical resistance of from 4 x 10^6 to 4 x 10^3 ohms/cm when measured on a 6K tow of fibers in which each fiber has a nominal diameter of from 7 to 20 micrometers.

9. The structure of any one of the preceding claims, wherein the first carbonaceous fibers have a sinusoidal or coil-like configuration and the fibrous structure is in the form of a nonwoven, wool-like fluff, batting or web, and said second carbonaceous fiber has a linear or nonlinear configuration and a higher denier than said first carbonaceous fibers.

10. A process for forming a fibrous structure of a multiplicity of nonflammable, nonlinear, substantially irreversibly heat-set, first carbonaceous polymeric fibers, comprising the steps of implanting into the first fibers at least one non-heat-set second carbonaceous polymeric fiber, yarn or tow in an interlocking relationship with said first fibers, and then heat treating the fibrous structure in an inert atmosphere to heat-set said interlocking second fiber, yarn or tow.

11. The process of Claim 10, wherein the second fiber, yarn or tow is made from a precursor carbonaceous polymeric material capable of being irreversibly heat-set to form a carbonaceous fiber, yarn or tow which is similar or identical in composition to said first heat-set carbonaceous fibers.

12. The process of Claim 10 or 11, wherein said fibers are acrylic fibers, and including the step of heat treating the fibrous structure containing the second non-heat-set interlocking fibers at a temperature above 525°C in an inert atmosphere to impart a permanent set to the second fiber, yarn or tow.

13. The process of Claims 10, 11 or 12, wherein the fibrous structure is in the form of a wool-like fluff, matting, felting or batting, and said second fiber, yarn or tow is present in said fibrous structure to densify the structure to a bulk density of from 4.8 to 32 kg/m^3 to provide integrity and handleability to the structure.

14. The process of any one of Claims 10 to 13, wherein the implementation of the second fibers into the first fibers is accomplished by needle-punching.

15. The process of any one of Claims 10 to 14, wherein said second carbonaceous fibers are selected from fibers that are of the same or a different composition from said first carbonaceous fibers.

16. The process of any one of Claims 10 to 15, wherein said implanted second fiber is derived from a batting.

17. The process of any one of Claims 10 to 16, wherein the second fiber is a linear or a nonlinear fiber.

18. The process of any one of Claims 10 to 17, wherein the fibrous structure comprises a plurality of battings.

19. The process of Claim 18, wherein at least one said batting comprises carbonaceous fibers having a carbon content of at least 85 percent.

20. The process of Claim 18, wherein at least one of said batting includes linear fibers.

21. A method of forming a multi-plied batting structure comprising the steps of providing a first batting of a first nonlinear, resilient, shape reforming, elongatable, nonflammable, heat-set carbonaceous fiber derived from oxidized polyacrylonitrile, said fibers having a reversible deflection ratio of greater than 1.2:1, an aspect ratio greater than 10:1 and a limited oxygen index value greater than 40, superimposing at least one second batting of polyacrylonitrile fibers on said first batting, interlocking the polyacrylonitrile fiber from said second batting with the heat-set fibers of said first batting, and then heat treating the entire densified structure to substantially permanently heat-set said second batting.