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(54) Title: MINERAL COMPOSITE VACUUM INSULATION PANEL SHEETS

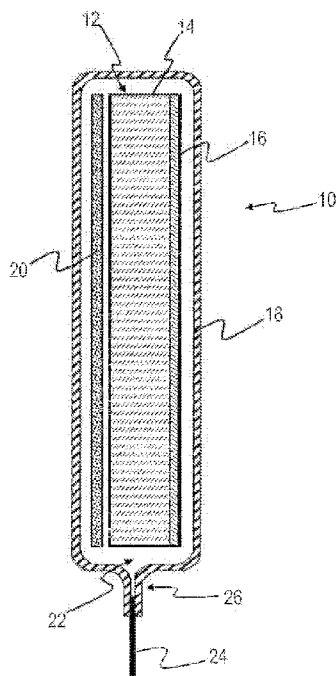


FIG. 1

(57) Abstract: A composite core material for use in vacuum insulation panels may include a fibrous insulating material and an inorganic particulate material. A method of making a composite core material for use in vacuum insulation panels may include depositing a layer of fibrous insulating material to form a fibrous core, and applying an inorganic particulate material to the fibrous core to form the composite core material. A vacuum insulation panel may include a composite core material including a fibrous insulating material and an inorganic particulate material. The vacuum insulation panel may have an R-value greater than or equal to about 30 per inch of thickness of the composite core material and may have a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>. The fibrous insulating material may include fiberglass or mineral wool fibers. The inorganic particulate material may include diatomaceous earth, perlite, or silica.

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**MINERAL COMPOSITE VACUUM INSULATION PANEL SHEETS****CLAIM FOR PRIORITY**

[0001] This PCT International Application claims the benefit of priority of U.S. Provisional Patent Application No. 62/000,742, filed May 20, 2014, the subject matter of which is incorporated herein by reference in its entirety.

**DESCRIPTION OF THE DISCLOSURE****Field of the Disclosure**

[0002] The present disclosure relates to a mineral composite vacuum insulation panel sheets. The present disclosure also relates to methods for making mineral composite vacuum insulation panel sheets.

**Background**

[0003] Vacuum insulation panels may be used to insulate and regulate the temperature of buildings and temperature-sensitive equipment, such as cryogenic storage tanks. Vacuum insulation panels may include fiberglass cores; however, obtaining a desired thermal resistance (R-value) may require many layers of fiberglass, making the fiberglass cores expensive to produce. Fiberglass panels may also lack mechanical strength because relatively short fiber lengths do not entangle sufficiently to withstand applications of force. Long fiber lengths may also lack good mechanical strength because voids in the entangled fibers may compress and allow for deformation of the fiberglass panels. These voids may also compress over time, which may result in decreased thermal performance.

[0004] Metallic films and foils may be used to increase the mechanical strength of a vacuum insulation panel; however, metallic films act as heat conductors through the panel. At metal film thicknesses sufficient to obtain good mechanical properties, the heat transfer properties of the films may significantly reduce the effectiveness of the fiberglass core.

[0005] It may be desirable to produce a fiber-based insulation panel, such as a vacuum insulation panel, having improved mechanical properties. It may also be desirable to provide a vacuum insulation panel with improved thermal resistance properties at a lower cost. It may also be desirable to provide a core material for vacuum insulation panels having improved thermal resistance and improved mechanical properties, such as density.

### **SUMMARY**

[0006] In the following description, certain aspects and embodiments will become evident. It should be understood that the aspects and embodiments, in their broadest sense, could be practiced without having one or more features of these aspects and embodiments. It should be understood that these aspects and embodiments are merely exemplary.

[0007] According to one aspect of this disclosure, a composite core material for use in vacuum insulation panels may include a fibrous insulating material and an inorganic particulate material.

[0008] According to another aspect, a method of making a composite core material for use in vacuum insulation panels may include depositing a layer of fibrous

insulating material to form a fibrous core, and applying an inorganic particulate material to the fibrous core to form the composite core material.

[0009] According to another aspect, a vacuum insulation panel may include a composite core material including a fibrous insulating material and an inorganic particulate material. The vacuum insulation panel may have an R-value greater than or equal to about 30 per inch of thickness and a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>.

[0010] According to a further aspect, the fibrous insulating material may include at least one of fiberglass and mineral wool fibers.

[0011] According to another aspect, the inorganic particulate material may include at least one of diatomaceous earth, perlite (including expanded perlite), talc, kaolin, calcined kaolin, vermiculite, mica, feldspar, palygorskite, nepheline syenite, silica, attapulgite clay, bentonite, or an alkali earth metal carbonate (e.g., calcium carbonate, barium carbonate, or magnesium carbonate). The silica may include natural silica, such as, for example, natural amorphous silica.

[0012] According to yet another aspect, the fibrous insulating material may be a first layer of the composite core material, and the inorganic particulate material may be a second layer of the composite core material overlaying the first layer. The second layer may be a spray-coated layer sprayed over the first layer.

[0013] According to still another aspect, the inorganic particulate material may be dispersed within the fibrous insulating material. For example, the fibrous insulating material and the inorganic particulate material may be deposited at

substantially the same time, such that the inorganic particulate material is dispersed throughout the fibrous insulating material.

[0014] According to another aspect, the method may include hydropulping the fibrous insulating material.

[0015] According to still another aspect, the composite core material may be enclosed in a film enclosure. The film enclosure may be evacuated. The evacuated film enclosure may be sealed to form a vacuum insulation panel.

[0016] According to yet another aspect, the vacuum insulation panel may have a thermal resistance, or R-value, greater than or equal to about 30 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr. For example, the vacuum insulation panel may have an R-value greater than or equal to about 35 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, greater than or equal to about 40 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, greater than or equal to about 45 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, or greater than or equal to about 47 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

[0017] According to a further aspect, the inorganic particulate material may have a top particle size ( $d_{90}$ ) of less than or equal to about 100  $\mu\text{m}$ , such as, for example, less than or equal to about 80  $\mu\text{m}$ , less than or equal to about 70  $\mu\text{m}$ , less than or equal to about 60  $\mu\text{m}$ , less than or equal to about 55  $\mu\text{m}$ , less than or equal to about 50  $\mu\text{m}$ , less than or equal to about 45  $\mu\text{m}$ , less than or equal to about 40  $\mu\text{m}$ , less than or equal to about 35  $\mu\text{m}$ , less than or equal to about 30  $\mu\text{m}$ , less than or equal to about 25  $\mu\text{m}$ , or less than or equal to about 20  $\mu\text{m}$ .

[0018] According to yet another aspect, the inorganic particulate material may have a median particle size ( $d_{50}$ ) of less than or equal to about 50  $\mu\text{m}$ , such as, for example, less than or equal to about 40  $\mu\text{m}$ , less than or equal to about 30  $\mu\text{m}$ , less than or equal to about 25  $\mu\text{m}$ , less than or equal to about 20  $\mu\text{m}$ , less than or equal to about 15  $\mu\text{m}$ , less than or equal to about 10  $\mu\text{m}$ , less than or equal to about 5  $\mu\text{m}$ , or less than or equal to about 3  $\mu\text{m}$ . According to a further aspect, the inorganic particulate material may have a  $d_{50}$  ranging from about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ , such as, for example, from about 5  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ , or from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ .

[0019] According to another aspect, the inorganic particulate material may have a bottom particle size ( $d_{10}$ ) of less than or equal to about 20  $\mu\text{m}$ , such as, for example, less than or equal to about 15  $\mu\text{m}$ , less than or equal to about 10  $\mu\text{m}$ , less than or equal to about 5  $\mu\text{m}$ , less than or equal to about 3  $\mu\text{m}$ , less than or equal to about 1  $\mu\text{m}$ , or less than or equal to about 0.5  $\mu\text{m}$ . According to some aspects, the inorganic particulate material may have a bottom particle size ( $d_{10}$ ) ranging from about 0.5  $\mu\text{m}$  to about 20  $\mu\text{m}$ , such as, for example, from about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 0.5  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 0.5  $\mu\text{m}$  to about 3  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , or from about 0.5  $\mu\text{m}$  to about 1  $\mu\text{m}$ .

[0020] According to another aspect, the inorganic particulate material may include a porous inorganic particulate material. According to a further aspect, the inorganic particulate material may have a median pore diameter less than or equal to about 5  $\mu\text{m}$ , such as, for example, less than or equal to about 3  $\mu\text{m}$ , less than or equal to about 2  $\mu\text{m}$ , or less than or equal to about 1  $\mu\text{m}$ . According to another aspect, the particulate inorganic material may have a pore volume of less than or equal to about 5 ml/g, such as, for example, less than or equal to about 4 ml/g, less than or equal to about 3 ml/g, or less than or equal to about 2 ml/g.

[0021] According to yet another aspect, the inorganic particulate material may have a water absorption greater than or equal to about 100% by weight of the dry inorganic particulate material. For example, the inorganic particulate material may have a water absorption greater than or equal to about 125%, greater than or equal to about 150%, greater than or equal to about 175%, greater than or equal to about 200%, greater than or equal to about 225%, or greater than or equal to about 250%.

[0022] According to still a further aspect, the vacuum insulation panel may have a density after evacuation of less than or equal to about 18 lbs/ft<sup>3</sup>, such as, for example, less than or equal to about 17 lbs/ft<sup>3</sup>, less than or equal to about 16 lbs/ft<sup>3</sup>, less than or equal to about 15 lbs/ft<sup>3</sup>, less than or equal to about 14 lbs/ft<sup>3</sup>, less than or equal to about 12 lbs/ft<sup>3</sup>, less than or equal to about 11 lbs/ft<sup>3</sup>, or less than or equal to about 10 lbs/ft<sup>3</sup>. According to still another aspect, the vacuum insulation panel may have a density before evacuation of less than 10 lbs/ft<sup>3</sup>.

[0023] According to another aspect, the inorganic particulate material may have a density less than or equal to about 10 lbs/ft<sup>3</sup>, such as, for example, less than or



equal to about 9 lbs/ft<sup>3</sup>, less than or equal to about 8 lbs/ft<sup>3</sup>, less than or equal to about 7 lbs/ft<sup>3</sup>, less than or equal to about 6 lbs/ft<sup>3</sup>, less than or equal to about 5 lbs/ft<sup>3</sup>, or less than or equal to about 4 lbs/ft<sup>3</sup>.

[0024] According to another aspect, the ratio of fibrous insulating material to inorganic particulate material may be greater than or equal to about 50:50 by weight. For example, the ratio of fibrous insulating material to inorganic particulate material may be greater than or equal to about 70:30 by weight, greater than or equal to about 75:25 by weight, greater than or equal to about 80:20 by weight, greater than or equal to about 85:15 by weight, or greater than or equal to about 90:10 by weight.

[0025] According to still another aspect, the inorganic particulate material may act as a "getter" material. For example, the inorganic particulate material may adsorb gasses or vapors in the vacuum insulation panel, such as, for example, water vapor, oxygen, and nitrogen.

[0026] According to another aspect, the R-value of the vacuum insulation panel having a composite core material may increase over time. For example, the R-value of the vacuum insulation panel having a composite core material may increase by greater than or equal to about 10% 44 days after evacuation, by greater than or equal to about 20% 44 days after evacuation, or by greater than or equal to about 30% 44 days after evacuation.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0027] FIG. 1 shows an exemplary vacuum insulation panel including a composite core material.

[0028] FIG. 2 shows the R-value of exemplary vacuum insulation panels having composite core materials.

[0029] FIG. 3 shows the density of exemplary vacuum insulation panels having composite core materials.

[0030] FIG. 4 shows the change in R-value over time of exemplary vacuum insulation panels having composite core materials.

### **DESCRIPTION OF EXEMPLARY EMBODIMENTS**

[0031] According to some embodiments, a fiberglass-mineral composite may be used to form a core for vacuum insulation panels. According to some embodiments, a composite core material for use in vacuum insulation panels includes a fibrous insulating material and an inorganic particulate material.

[0032] According to some embodiments, a method of making a composite core material for use in vacuum insulation panels may include depositing a layer of fibrous insulating material to form a fibrous core, and applying an inorganic particulate material to the fibrous core to form the composite core material.

[0033] According to some embodiments, a vacuum insulation panel may include a composite core material including a fibrous insulating material and an inorganic particulate material. The vacuum insulation panel may have an R-value greater than or equal to about 30 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr and a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>.

[0034] According to some embodiments, the fibrous insulating material may include at least one of fiberglass and mineral wool fibers.

[0035] Although certain embodiments may be described in terms of fiberglass, it is understood that other fibrous insulating materials, such as, for example, mineral wool, glass wool, stone wool, ceramic wool, or fibers derived from mineral wool, glass wool, stone wool, or ceramic wool may be used. Accordingly, any insulating fiber may be used as the fibrous insulating material, such as, for example, inorganic fiber or inorganic wool materials.

[0036] The fiberglass may include either short fibers or longer fibers, such as, for example, glass wool fibers. Long fibers may be reduced to relatively shorter fibers, such as, for example, by hydropulping. Hydropulping machines may be used to reduce the length of glass fibers by using spinning blades to cut the fibers. The relative length of the fibers used in the composite core materials of this disclosure may determine the degree of entanglement of the fibers (e.g., greater fiber lengths may have greater entanglement) and the laminarity of the glass-fiber containing layers.

[0037] According to some embodiments, the fibrous insulating material may be formed into a sheet or ply using a "wet process." In an exemplary wet process, a slurry of the fibrous material is formed with a slurry agent, such as water. The slurry may then be passed through a hydropulping machine to shorten the fiber length or to achieve a desired consistency of the slurry. A fibrous sheet or ply may be formed using techniques similar to conventional paper-forming techniques, such as, for example, draining the slurry through a headbox to create a ply of the entangled glass fibers. According to some embodiments, the sheet or ply may be drained through a mold to achieve a desired shape of the sheet or ply. According to some embodiments, a binder

or matrix, such as a resin or polymer matrix, may be added to adhere the fibers together.

[0038] According to some embodiments, an inorganic particulate material may be added to the fibrous insulating material to form a composite core material containing both the fibrous insulating material and the inorganic particulate material. The inorganic particulate material may include at least one of natural silica, diatomaceous earth, perlite (including expanded perlite), talc, kaolin, calcined kaolin, vermiculite, mica, feldspar, palygorskite, nepheline syenite, silica, attapulgite clay, bentonite, or an alkali earth metal carbonate (e.g., calcium carbonate, barium carbonate, or magnesium carbonate). Clay or hydrous materials, such as, for example, kaolin, vermiculite, or attapulgite clay, may be dried, calcined, or dehydrated prior to being added to the composite core material. The silica may include natural silica, such as, for example, natural amorphous silica. Natural amorphous silica may include processed or modified amorphous silica, such as, for example, described in U.S. Patent Application Publication No. 2012/0048145 A1, assigned to the same assignee as the present disclosure, the disclosure of which is hereby incorporated by reference in its entirety.

[0039] Particle size characteristics described herein may be measured by a Microtrac laser particle size distribution analyzer. The Microtrac laser particle size distribution analyzer provides measurements and a plot of the cumulative percentage by weight of particles having a size, referred to in the art as the "equivalent spherical diameter," or "esd."

[0040] According to some embodiments, the inorganic particulate material may have a top particle size ( $d_{90}$ ) of less than or equal to about 100  $\mu\text{m}$ , such as, for example, less than or equal to about 80  $\mu\text{m}$ , less than or equal to about 70  $\mu\text{m}$ , less than or equal to about 60  $\mu\text{m}$ , less than or equal to about 55  $\mu\text{m}$ , less than or equal to about 50  $\mu\text{m}$ , less than or equal to about 45  $\mu\text{m}$ , less than or equal to about 40  $\mu\text{m}$ , less than or equal to about 35  $\mu\text{m}$ , less than or equal to about 30  $\mu\text{m}$ , less than or equal to about 25  $\mu\text{m}$ , or less than or equal to about 20  $\mu\text{m}$ .

[0041] According to some embodiments, the inorganic particulate material may have a median particle size ( $d_{50}$ ) of less than or equal to about 50  $\mu\text{m}$ , such as, for example, less than or equal to about 40  $\mu\text{m}$ , less than or equal to about 30  $\mu\text{m}$ , less than or equal to about 25  $\mu\text{m}$ , less than or equal to about 20  $\mu\text{m}$ , less than or equal to about 15  $\mu\text{m}$ , less than or equal to about 10  $\mu\text{m}$ , less than or equal to about 5  $\mu\text{m}$ , or less than or equal to about 3  $\mu\text{m}$ . According to some embodiments, the inorganic particulate material may have a median particle size ( $d_{50}$ ) ranging from about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ , such as, for example, from about 5  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 30  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ , or from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ .

[0042] According to some embodiments, the inorganic particulate material may have a bottom particle size ( $d_{10}$ ) of less than or equal to about 20  $\mu\text{m}$ , such as, for example, less than or equal to about 15  $\mu\text{m}$ , less than or equal to about 10  $\mu\text{m}$ , less than or equal to about 5  $\mu\text{m}$ , less than or equal to about 3  $\mu\text{m}$ , less than or equal to

about 1  $\mu\text{m}$ , or less than or equal to about 0.5  $\mu\text{m}$ . According to some embodiments, the inorganic particulate material may have a bottom particle size ( $d_{10}$ ) ranging from about 0.5  $\mu\text{m}$  to about 20  $\mu\text{m}$ , such as, for example, from about 10  $\mu\text{m}$  to about 20  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 15  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , from about 0.5  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 0.5  $\mu\text{m}$  to about 3  $\mu\text{m}$ , from about 3  $\mu\text{m}$  to about 5  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ , or from about 0.5  $\mu\text{m}$  to about 1  $\mu\text{m}$ .

[0043] According to some embodiments, the inorganic particulate material may include a porous inorganic particulate material. According to some embodiments, the inorganic particulate material may have a median pore diameter less than or equal to about 5  $\mu\text{m}$ , such as, for example, less than or equal to about 3  $\mu\text{m}$ , less than or equal to about 2  $\mu\text{m}$ , or less than or equal to about 1  $\mu\text{m}$ . According to some embodiments, the particulate inorganic material may have a pore volume of less than or equal to about 5 ml/g, such as, for example, less than about or equal to about 4 ml/g, less than or equal to about 3 ml/g, or less than or equal to about 2 ml/g.

[0044] According to some embodiments, the inorganic particulate material may have a water absorption of greater than or equal to about 100% by weight of the dry inorganic particulate material, such as, for example, greater than or equal to about 130%, greater than or equal to about 150%, greater than or equal to about 200%, or greater than or equal to about 250%.

[0045] According to some embodiments, the fibrous insulating material may have a fiber diameter less than or equal to about 20  $\mu\text{m}$ , such as, for example, less than or equal to about 10  $\mu\text{m}$ , less than or equal to about 8  $\mu\text{m}$ , less than or equal to

about 5  $\mu\text{m}$ , less than or equal to about 3  $\mu\text{m}$ , less than or equal to about 2  $\mu\text{m}$ , or less than or equal to about 1  $\mu\text{m}$ .

[0046] According to some embodiments, the inorganic particulate material may be applied to the fibrous insulating material using a spray method. For example, the inorganic particulate material may be applied by spraying a layer of the inorganic particulate material onto the fiberglass, such as by spray-coating the layer of inorganic particulate material over the fibrous core. According to some embodiments, the inorganic particulate material may be applied to the fiberglass by spraying a solution containing the inorganic particulate material onto a fiberglass web. Spraying a solution of inorganic particulate material may promote intermixing of the fiberglass and the inorganic particulate material. According to some embodiments, the inorganic particulate material may be applied as part of a slurry that is used to create a fiberglass ply or sheet. Use of a solution of inorganic particulate material or applying the inorganic particulate material at substantially the same time as the fibrous insulating material may promote dispersion of the inorganic particulate material throughout the fibrous insulating material. As a result, the inorganic particulate material may be coextensive with some or all of the fibrous insulating material layer.

[0047] The inorganic particulate material may, in some embodiments, include a binder. The binder may facilitate adhesion between the inorganic particulate material and the fibrous insulating material. For example, binders may include, but are not limited to, silicone-based binders, inorganic binders, and organic binders. According to some embodiments, the inorganic binder may be a silicate-based binder, such as, for example, sodium silicate or potassium silicate. Use of an inorganic binder may prevent

the formation of volatile organic compounds after the composite core material is sealed in a vacuum insulation panel. Formation of volatile organic compounds may reduce the vacuum level of the vacuum insulation panel, thereby decreasing its effectiveness over time.

[0048] The composite core material may be dried prior to sealing the core in a vacuum insulation panel. Drying the composite core material may facilitate evaporation and release of water vapor, volatile organic compounds, and other gasses from the composite core material prior to sealing the composite core material in a film enclosure. If the composite core is not dried to remove water and other compounds that could form vapors or gasses within the vacuum insulation panel, the R-value of the vacuum insulation panel may be reduced because of the decreased vacuum created by the vapor.

[0049] The composite core material may, according to some embodiments, include a more than one layer of fibrous insulating material, more than one layer of inorganic particulate material, or both. For example, a first layer of inorganic particulate material may be applied over a first layer of fibrous insulating material. A second layer of fibrous insulating material may then be applied over the first layer of inorganic particulate material, and a second layer of inorganic particulate material may be applied over the second layer of fibrous insulating material. According to some embodiments, the inorganic particulate material may be applied to one face of the layer of fibrous insulating material or to both faces of the fibrous insulating material.

[0050] According to some embodiments, the inorganic particulate material may have a density less than or equal to about 10 lbs/ft<sup>3</sup>, such as, for example, less



than or equal to about 9 lbs/ft<sup>3</sup>, less than or equal to about 8 lbs/ft<sup>3</sup>, less than or equal to about 7 lbs/ft<sup>3</sup>, less than or equal to about 6 lbs/ft<sup>3</sup>, less than or equal to about 5 lbs/ft<sup>3</sup>, or less than or equal to about 4 lbs/ft<sup>3</sup>.

[0051] According to some embodiments, the inorganic particulate material may act as a "getter" material. For example, the inorganic particulate material may adsorb gasses or vapors in the vacuum insulation panel, such as, for example, water vapor, oxygen, and nitrogen.

[0052] According to some embodiments, the R-value of the vacuum insulation panel having a composite core material may increase over time. For example, the R-value of the vacuum insulation panel may increase by greater than or equal to about 10% 44 days after evacuation, by greater than or equal to about 20% 44 days after evacuation, or by greater than or equal to about 30% 44 days after evacuation.

[0053] According to some embodiments, the composite core material may be incorporated into a vacuum insulation panel, as shown in FIG. 1. An exemplary vacuum insulation panel 10 may include one or more composite core materials 12 having, for example, a fiberglass layer 14 and an inorganic particulate material layer 16. According to some embodiments, inorganic particulate material 16 may be deposited onto, incorporated into, or intermixed with fiberglass material 14. Composite core material 12 may be placed inside a film enclosure 18, for example, a polymer or metallic film enclosure. Film enclosure 18 may also be a multi-layer enclosure containing more than one film layer, such as, for example, one or more metallic layer and one or more

polymer layer, two or more metallic layers, or two or more polymer layers. The multi-layer film may include a laminated structure.

[0054] Suitable polymer films may include, but are not limited to, tetraphthalate polyester films, polytetrafluoroethylene films, polyimide films, fluorinated ethylene propylene films, polyvinylidene chloride films, polyethylene films, or copolymer films containing one or more of the listed polymers. Suitable metal films may include aluminum films, silver films, gold films, chromium films, nickel films, stainless steel films, or alloy metal films containing one or more of aluminum, silver, gold, chromium, iron, or nickel.

[0055] According to some embodiments, the thickness of a polymer film may range from about 10  $\mu\text{m}$  to about 1500  $\mu\text{m}$ , for example, from about 25  $\mu\text{m}$  to about 500  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 250  $\mu\text{m}$ , or from about 50  $\mu\text{m}$  to about 100  $\mu\text{m}$ . According to some embodiments, the thickness of the metal film may range from about 0.01  $\mu\text{m}$  to about 0.2  $\mu\text{m}$ , for example, from about 0.2  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , from about 0.3  $\mu\text{m}$  to about 0.7  $\mu\text{m}$ , or from about 0.3  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ .

[0056] According to some embodiments, vacuum insulation panel 10 may also include an adsorbent material or adsorbent layer 20 to adsorb gasses that may be released from composite core material 12 or that permeate through film enclosure 18, such as through pinholes in film enclosure 18. For example, adsorbent material 20 may adsorb water vapor or volatile organic compounds. Adsorbent material 20 may include, for example, a molecular sieve material, such as a hydrophobic molecular sieve. Various oxides, such as, for example, palladium oxide, may also be used to reduce outgassing of hydrogen and other gasses that may develop during processing of the

vacuum insulation panel, such as, for example, during sealing of the film enclosure.

According to some embodiments, adsorbent material 20 may instead be an absorbent material capable of absorbing gasses or liquids in vacuum panel enclosure 10.

Adsorbent material 20 may also have both adsorbent and absorbent properties, depending on the composition of adsorbent material 20 and the gasses or vapors within film enclosure 18.

[0057] Film enclosure 18 of the exemplary vacuum insulation panel 10 may be evacuated and sealed with an airtight seal to maintain the vacuum. Depending on the composition of film enclosure 18, film enclosure 18 may be sealed by, for example, heat sealing, hot melting, laser welding or sealing, by use of an adhesive, or combinations thereof. Any method of sealing film enclosure 18 may be used, including other methods known in the art.

[0058] Prior to complete sealing of film enclosure 18, cavity 22 containing composite core material 12 and any other materials (e.g., adsorbent material 20), may be evacuated using, for example, evacuation tube 24. Once the desired vacuum pressure is obtained, the remainder of film enclosure 18 between evacuation tube 24 and cavity 22 may be sealed, for example, at location 26 prior to extraction of evacuation tube 24. Sealing film enclosure 18 prior to extracting evacuation tube 24 can help retain the vacuum in vacuum insulation panel 10.

[0059] According to some embodiments, the vacuum insulation panel having a composite core material may have a thermal resistance, or R-value, greater than or equal to about 30 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr. For example, the vacuum insulation panel may have an R-value greater than or

equal to about 35 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, greater than or equal to about 40 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, greater than or equal to about 45 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, or greater than or equal to about 47 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

[0060] According to some embodiments, the vacuum insulation panel may have a density after evacuation of less than or equal to about 18 lbs/ft<sup>3</sup>, such as, for example, less than or equal to about 17 lbs/ft<sup>3</sup>, less than or equal to about 16 lbs/ft<sup>3</sup>, less than or equal to about 15 lbs/ft<sup>3</sup>, less than or equal to about 14 lbs/ft<sup>3</sup>, less than or equal to about 12 lbs/ft<sup>3</sup>, less than or equal to about 11 lbs/ft<sup>3</sup>, or less than or equal to about 10 lbs/ft<sup>3</sup>.

[0061] The addition of an inorganic particulate material to the fibrous insulating material may improve the thermal and mechanical properties of core materials for vacuum insulation panels. For example, the addition of inorganic particulate materials may reduce the amount of fiberglass or other fibrous insulating material required to achieve a desired R-value. A reduction in the amount of fibrous insulating material may lower the manufacturing cost of the composite core material, and may also reduce the overall weight of the vacuum insulation panel. The inorganic particulate material may also improve the mechanical properties of the core material by, for example, increasing the density of the core material. Furthermore, the inorganic particulate material may improve the properties of the core material and corresponding vacuum insulation panel by coating the fibrous insulating material to provide a relatively smoother interface between the fibers and a film enclosure. The inorganic particulate

material may mitigate protrusion of the ends of the fibers, which can pierce the film enclosure and create holes in the film that allow gasses to enter the insulation panel and weaken the vacuum over time. Weakening of the vacuum may also decrease R-value of the vacuum insulation panel and degrade its effectiveness over time.

[0062] According to some embodiments, the inorganic particulate material may act as a "getter" material to adsorb gasses or vapors in the vacuum insulation panel, such as, for example, nitrogen, water vapor, or oxygen. When the inorganic particulate material also acts as a getter material, the need for an additional adsorption material may be reduced or eliminated. This may simplify the construction of the vacuum insulation panel. The use of a particulate inorganic material that acts as a getter material may also reduce the cost of the vacuum insulation panel. When the particulate inorganic material also functions as a getter material, the overall weight and density of the vacuum insulation panel may be reduced.

[0063] According to some embodiments, the inorganic particulate material may increase the R-value of the vacuum insulation panel through aging. For example, the R-value of a vacuum insulation panel having a composite core material may increase by greater than or equal to about 10% 44 days after evacuation. For example, the R-value of the vacuum insulation panel may increase by greater than or equal to about 15%, greater than or equal to about 20%, greater than or equal to about 25%, or greater than or equal to about 30% 44 days after evacuation.

#### EXAMPLES

[0064] Samples A-C of composite core materials were prepared by spray-coating various minerals onto a layer of fiberglass sheet substrates. Sample A included

a layer of natural amorphous AF silica (ECOFLAT™) having a mean particle size of about 3 µm. Sample B included a layer of perlite (HARBORLITE® 200) having a median particle size of 17 µm. Sample C included a layer of diatomaceous earth (CELITE® NPP™). For the control samples, 600 g deionized water was used with no mineral addition.

[0065] Table 1 below shows the material properties of the inorganic particulate materials used to prepare each of samples A-C. The particle size distribution was measured using a Microtrac laser particle size distribution analyzer. The pore diameter and pore volume were measured by mercury intrusion porosimetry using a Micromeritics AutoPore porosimeter and following the methodology set forth in the instrument instruction manual.

[0066] Water absorption of the inorganic particulate materials was measured by Celite test method no. LO-412-351, "Water Absorption (Dry End Point)." To measure the water absorption, 5 grams of dry AF silica (Sample A) and dry perlite (Sample B), and 10 grams of diatomaceous earth (Sample C) were placed in 500 ml porcelain dishes. Distilled water was added from a burette at a rate of 1 drop per second. The samples were stirred during the addition of the water using a spatula having a 4 inch blade so that each drop of water fell on a dry portion of the material. As the sample particles became wet, they coalesced and formed small lumps of paste. The lumps were kept distributed throughout the mass by stirring, with care not to use pressure in the mixing. As the absorption progressed, larger lumps were formed, which formed balls of paste. At this point, the rate and quantity of water added was decreased, as set forth in the method. The added water then struck the wet balls of

material, which were stirred to bring them into contact with the remaining dry sample. When all of the dry sample was wet and the resulting paste tended to smear on the sides and bottom of the dish, no more water was added. The amount of water used during the process was determined, and the weight percent of water absorbed was calculated as set forth in the method.

| Mineral       | Density<br>(lb/ft <sup>3</sup> ) | Pore<br>Diameter<br>(μm) | Pore<br>Volume<br>(mL/g) | d <sub>10</sub><br>(μm) | d <sub>50</sub><br>(μm) | d <sub>90</sub><br>(μm) | Water<br>Absorption<br>(%) |
|---------------|----------------------------------|--------------------------|--------------------------|-------------------------|-------------------------|-------------------------|----------------------------|
| A (AF Silica) | 8.5                              | 1.45                     | 2.05                     | 1.92                    | 6.23                    | 17.14                   | 130                        |
| B (Perlite)   | 6.0                              | 2.54                     | 3.15                     | 5.49                    | 16.49                   | 44.99                   | 250                        |
| C (DE)        | 4.8                              | 2.45                     | 4.89                     | 3.83                    | 11.49                   | 24.87                   | 100                        |

TABLE 1

[0067] The composite core materials were prepared from fiberglass sheet substrates composed of ten layers of fiberglass sheets measuring 11 inches by 11 inches, having a total weight of 243 g and a total thickness of about 1 inch. Solutions of the inorganic particulate minerals were prepared by placing 81 g of the sample minerals (e.g., AF Silica, perlite, or diatomaceous earth) in glass beakers with 600 g of deionized water and stirring for 10 minutes. Each mineral solution was then transferred to a bottle sprayer and was sprayed onto the rough surface side of fiberglass sheet substrates.

[0068] The spray-coated sheets were then dried in the oven overnight at 120 °C. A control sample was also prepared by spraying the fiberglass layer with water. Samples A-C and the control sample were dried in the oven at 120 °C overnight.

[0069] Table 2 shows the relative ratios by weight of the compositions of the composite core material for each of samples A-C and the control.

| Sample  | Fiberglass<br>(wt%) | AF Silica<br>(wt%) | Perlite<br>(wt%) | Diatomaceous<br>Earth (wt%) |
|---------|---------------------|--------------------|------------------|-----------------------------|
| Control | 100                 | 0                  | 0                | 0                           |
| A       | 74                  | 26                 | 0                | 0                           |
| B       | 77                  | 0                  | 23               | 0                           |
| C       | 77                  | 0                  | 0                | 23                          |

TABLE 2

[0070] Before panel fabrication, the composite core sheets were dried in the oven again. The dried composite core sheets were then encased in a barrier film. The encased panels were evacuated and sealed at a vacuum pressure of  $2.0 \times 10^{-2}$  Torr at room temperature. The panels were then aged by sitting at room temperature for 24 hours.

[0071] After aging, thermal conductivity was measured using the test method similar to ASTM C1667-09, "Standard Test Method for Using Heat Flow Meter Apparatus to Measure the Center-of-Panel Thermal Resistivity of Vacuum Panels." The thermal conductivity testing apparatus consisted of a 6.35 mm thick aluminum plate with full coverage electrical heaters under plate. The plate with the heaters rested on 51 mm thick foam insulation. The plate temperature was measured using a calibrated thermocouple. Digital DC power to the heaters was adjusted to obtain and maintain the desired temperature of the plate.

[0072] The density in vacuum was determined by measuring the dimensions and weight of the evacuated panels.

[0073] The results of the R-value and density measurements are shown in FIGS. 2 and 3, respectively, and in Table 3 below.



[0074] Table 3 below also shows the R-values and densities of samples A-C as compared to the control sample, which are also shown in FIGS. 2 and 3, respectively.

| Sample  | R per inch<br>at $2 \times 10^{-2}$ Torr | Density (lb/ft <sup>3</sup> )<br>at $2 \times 10^{-2}$ Torr |
|---------|------------------------------------------|-------------------------------------------------------------|
| Control | 37.6                                     | 10.9                                                        |
| A       | 36.9                                     | 16.9                                                        |
| B       | 40.3                                     | 13.9                                                        |
| C       | 36.7                                     | 14.3                                                        |

TABLE 3

[0075] As demonstrated in FIG. 2 and Table 3, each of samples A-C have R values greater than 30 per inch of thickness. Sample B has an R-value comparable to the control sample, and sample A exhibits an R-value greater than the control sample.

[0076] FIG. 3 and Table 3 show the densities of samples A-C and the control sample in a vacuum of about  $2 \times 10^{-2}$  Torr. The densities of the composite samples A-C are greater than the density of the control sample.

[0077] As shown in FIGS. 2 and 3, and Table 3, composite samples for vacuum insulation panels can be created by adding a mineral layer to a fiberglass layer. The composite vacuum insulation core panels may have R-values comparable to fiberglass panels, but may have increased densities. The increased densities may provide better mechanical properties for the composite panels, such as, for example, increased mechanical strength or impact resistance. The composite panels may also decrease manufacturing costs by reducing the amount of fiberglass needed to obtain the same thermal properties, such as R-value, which may also lower the overall weight of the finished vacuum insulation panel.

[0078] Table 4 shows a comparison of the R-values of samples A-C and the control sample over various aging periods at room temperature. As shown in Table 4, the R-value of the vacuum insulation panels containing AF silica (Sample A) and perlite (Sample B) increased with aging time, whereas the R-value of the control sample and diatomaceous earth sample (Sample C) decreased with aging.

| Sample   | R-Value (inch <sup>-1</sup> ) After Aging |         |         |
|----------|-------------------------------------------|---------|---------|
|          | 1 day                                     | 14 days | 44 days |
| Control  | 37.6                                      | 32.2    | 29.6    |
| Sample A | 36.9                                      | 43.0    | 47.7    |
| Sample B | 40.3                                      | 41.12   | 44.7    |
| Sample C | 36.7                                      | 34.3    | 33.7    |

TABLE 4

[0079] A plot of the data in Table 4 is shown in FIG. 4. As shown in Table 4 and FIG. 4, the R-value of the control sample decreased over the 44-day aging period. The R-value of sample C also decreased over the same period. However, the R-value of sample C decreased significantly less than the control sample. After 14 days, the R-value of sample C, although less than the R-value after 1 day of aging, was actually greater than the R-value of the control sample. Surprisingly, the R-value of samples A and B increased over the 44-day period by about 30% and about 10%, respectively, as compared to the R-value after 1 day of aging.

[0080] Without wishing to be bound to a particular theory, it is believed that the inorganic particulate materials added to the composite core material may act as “getters” to scavenge gasses or vapors, such as, for example, nitrogen, oxygen, or

water vapor, over time. This vapor or gas scavenging may occur as a chemical or physical interaction with the surface or pores of the inorganic particulate material. The action to scavenge a gas or vapor may help maintain or improve the vacuum of the vacuum insulation panel, thereby maintaining or improving the R-value over time. For example, while samples A and B improve the R-value over time, sample C appears to maintain the R-value when compared to the control sample. Thus, although sample C may have an R-value that is initially lower than the control sample, after a relatively short period of time, the R-value of sample C was actually greater than the control sample, which may make the vacuum insulation panel more effective over the life of the panel.

[0081] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the exemplary embodiments disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

## WHAT IS CLAIMED IS:

1. A composite core material for use in a vacuum insulation panel, the composite core material comprising:
  - a fibrous insulating material; and
  - an inorganic particulate material.
2. The composite core material of claim 1, wherein the fibrous insulating material comprises at least one of fiberglass and mineral wool fibers.
3. The composite core material of claim 1, wherein the inorganic particulate material comprises at least one of natural silica, diatomaceous earth, perlite, talc, kaolin, calcined kaolin, vermiculite, mica, feldspar, palygorskite, nepheline syenite, silica, attapulgite clay, bentonite, or an alkali earth metal carbonate.
4. The composite core material of claim 1, wherein
  - the fibrous insulating material comprises a first layer; and
  - the inorganic particulate material comprises a second layer overlaying the first layer.
5. The composite core material of claim 4, wherein the second layer comprises a spray-coated layer sprayed over the first layer.

6. The composite core material of claim 1, wherein the composite core material is enclosed in a vacuum insulation panel at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

7. The composite core material of claim 6, wherein the vacuum insulation panel has an R-value greater than or equal to about 30 per inch of thickness.

8. The composite core material of claim 6, wherein the vacuum insulation panel has an R-value greater than or equal to about 40 per inch of thickness.

9. The composite core material of claim 6, wherein the vacuum insulation panel has an R-value greater than or equal to about 47 per inch of thickness.

10. The composite core material of claim 1, wherein the inorganic particulate material has a median particle size less than about 20  $\mu\text{m}$ .

11. The composite core material of claim 6, wherein the vacuum insulation panel has a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>.

12. The composite core material of claim 6, wherein the vacuum insulation panel has a density after evacuation of less than or equal to about 12 lbs/ft<sup>3</sup>.

13. The composite core material of claim 1, wherein the inorganic particulate material has a density less than or equal to about 9 lbs/ft<sup>3</sup>.

14. The composite core material of claim 1, wherein the inorganic particulate material has a density less than or equal to about 5 lbs/ft<sup>3</sup>.

15. The composite core material of claim 1, wherein the inorganic particulate material has a median pore diameter less than or equal to about 3  $\mu$ m.

16. The composite core material of claim 1, wherein the inorganic particulate material has a pore volume less than or equal to about 5 ml/g.

17. The composite core material of claim 1, wherein the ratio of fibrous insulating material to inorganic particulate material is greater than or equal to about 50:50 by weight.

18. The composite core material of claim 1, wherein the ratio of fibrous insulating material to inorganic particulate material is greater than or equal to about 70:30 by weight.

19. The composite core material of claim 1, wherein the inorganic particulate material has a water absorption greater than or equal to about 130% by weight of the dry inorganic particulate material.

20. The composite core material of claim 1, wherein the inorganic particulate material is a getter material.

21. The composite core material of claim 6, wherein the R-value of the vacuum insulation panel is greater than or equal to 10% larger 44 days after evacuation of the vacuum insulation panel.

22. The composite core material of claim 6, wherein the R-value of the vacuum insulation panel is greater than or equal to 30% larger 44 days after evacuation of the vacuum insulation panel.

23. A method of making a composite core material for use in a vacuum insulation panel, the method comprising:

depositing a layer of fibrous insulating material to form a fibrous core; and  
applying an inorganic particulate material to the fibrous core to form the composite core material.

24. The method of claim 23, wherein the fibrous insulating material comprises at least one of fiberglass and mineral wool fibers.

25. The method of claim 23, wherein the inorganic particulate material comprises at least one of natural silica, diatomaceous earth, perlite, talc, kaolin,

calcined kaolin, vermiculite, mica, feldspar, palygorskite, nepheline syenite, silica, attapulgite clay, bentonite, or an alkali earth metal carbonate.

26. The method of claim 23, wherein applying the inorganic particulate material comprises spray-coating the fibrous core with the inorganic particulate material.

27. The method of claim 26, wherein spray-coating the fibrous core comprises spray-coating the fibrous core with a solution containing the inorganic particulate material.

28. The method of claim 23, further comprising:  
hydropulping the fibrous insulating material prior to depositing the layer of fibrous insulating material.

29. The method of claim 23, wherein depositing the layer of fibrous insulating material and applying the inorganic particulate material occur at substantially the same time, such that the inorganic particulate material is dispersed throughout the layer of fibrous insulating material.

30. The method of claim 23, further comprising:  
enclosing the composite core material in a film enclosure;  
evacuating the film enclosure; and  
sealing the evacuated film enclosure to form a vacuum insulation panel.



31. The method of claim 30, wherein the vacuum insulation panel has an R-value greater than or equal to about 30 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

32. The method of claim 30, wherein the vacuum insulation panel has an R-value greater than or equal to about 40 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

33. The method of claim 30, wherein the vacuum insulation panel has an R-value greater than or equal to about 47 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

34. The method of claim 23, wherein the inorganic particulate material has a median particle size less than about 50  $\mu\text{m}$ .

35. The method of claim 23, wherein the inorganic particulate material has a median particle size less than about 5  $\mu\text{m}$ .

36. The method of claim 30, wherein the vacuum insulation panel has a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>.

37. The method of claim 30, wherein the vacuum insulation panel has a density after evacuation of less than or equal to about 12 lbs/ft<sup>3</sup>.

38. The method of claim 23, wherein the inorganic particulate material has a density less than or equal to about 9 lbs/ft<sup>3</sup>.

39. The method of claim 23, wherein the inorganic particulate material has a density less than or equal to about 5 lbs/ft<sup>3</sup>.

40. The method of claim 23, wherein the ratio of fibrous insulating material to inorganic particulate material is greater than or equal to about 50:50 by weight.

41. The method of claim 23, wherein the ratio of fibrous insulating material to inorganic particulate material is greater than or equal to about 70:30 by weight.

42. The method of claim 23, wherein the inorganic particulate material has a water absorption greater than or equal to about 130% by weight of the dry inorganic particulate material.

43. The method of claim 23, wherein the inorganic particulate material is a getter material.

44. The method of claim 30, further comprising:

aging the vacuum insulation panel, wherein the R-value of the aged vacuum insulation panel is greater than or equal to 10% larger 44 days after evacuation of the vacuum insulation panel.

45. A vacuum insulation panel comprising:

a composite core material including a fibrous insulating material and an inorganic particulate material,

wherein the vacuum insulation panel has an R-value greater than or equal to about 30 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr, and a density after evacuation of less than or equal to about 17 lbs/ft<sup>3</sup>.

46. The vacuum insulation panel of claim 45, wherein the fibrous insulating material comprises at least one of fiberglass and mineral wool fibers.

47. The vacuum insulation panel of claim 45, wherein the inorganic particulate material comprises at least one of natural silica, diatomaceous earth, perlite, talc, kaolin, calcined kaolin, vermiculite, mica, feldspar, palygorskite, nepheline syenite, silica, attapulgite clay, bentonite, or an alkali earth metal carbonate.

48. The vacuum insulation panel of claim 45, wherein  
the fibrous insulating material comprises a first layer; and  
the inorganic particulate material comprises a second layer overlaying the first layer.

49. The vacuum insulation panel of claim 45, wherein the inorganic particulate material is dispersed within the fibrous insulating material.

50. The vacuum insulation panel of claim 45, wherein the vacuum insulation panel has an R-value greater than about 47 per inch of thickness at a vacuum pressure of about  $2 \times 10^{-2}$  Torr.

51. The vacuum insulation panel of claim 45, wherein the inorganic particulate material has a median particle size less than about 20  $\mu\text{m}$ .

52. The vacuum insulation panel of claim 45, wherein the inorganic particulate material has a density less than or equal to about 9 lbs/ft<sup>3</sup>.

53. The vacuum insulation panel of claim 45, wherein the ratio of fibrous insulating material to inorganic particulate material is greater than or equal to about 50:50 by weight.

54. The vacuum insulation panel of claim 45, wherein the inorganic particulate material has a median pore diameter less than or equal to about 3  $\mu\text{m}$ .

55. The vacuum insulation panel of claim 45, wherein the inorganic particulate material has a pore volume less than or equal to about 5 ml/g.

56. The vacuum insulation panel of claim 45, wherein the inorganic particulate material has a water absorption greater than or equal to about 130% by weight of the dry inorganic particulate material.

57. The vacuum insulation panel of claim 45, wherein the inorganic particulate material is a getter material.

58. The vacuum insulation panel of claim 45, wherein the R-value of the vacuum insulation panel is greater than or equal to 30% larger 44 days after evacuation of the vacuum insulation panel.

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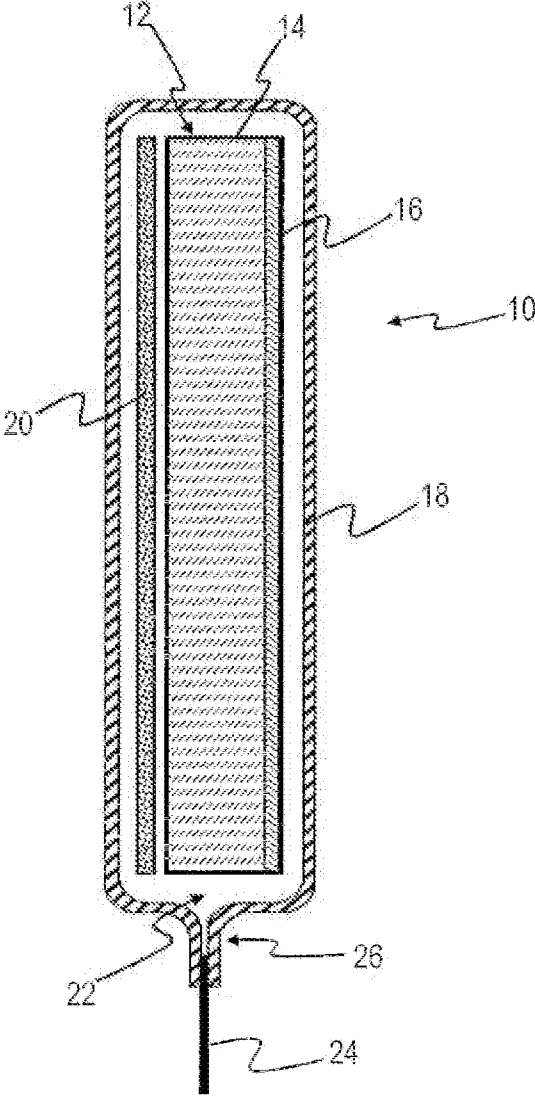
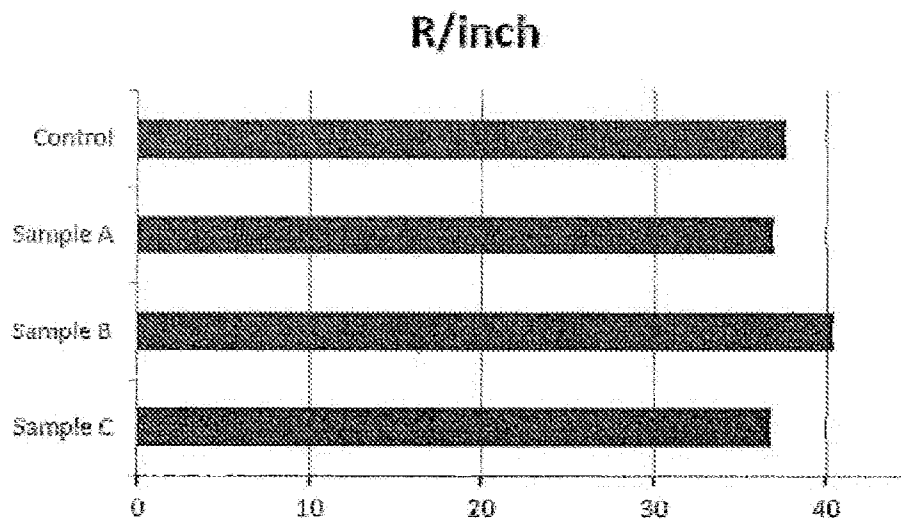
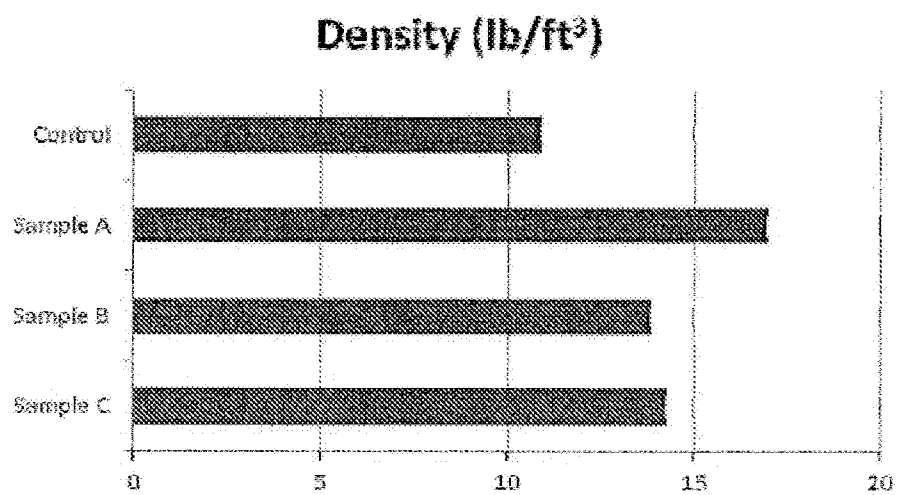
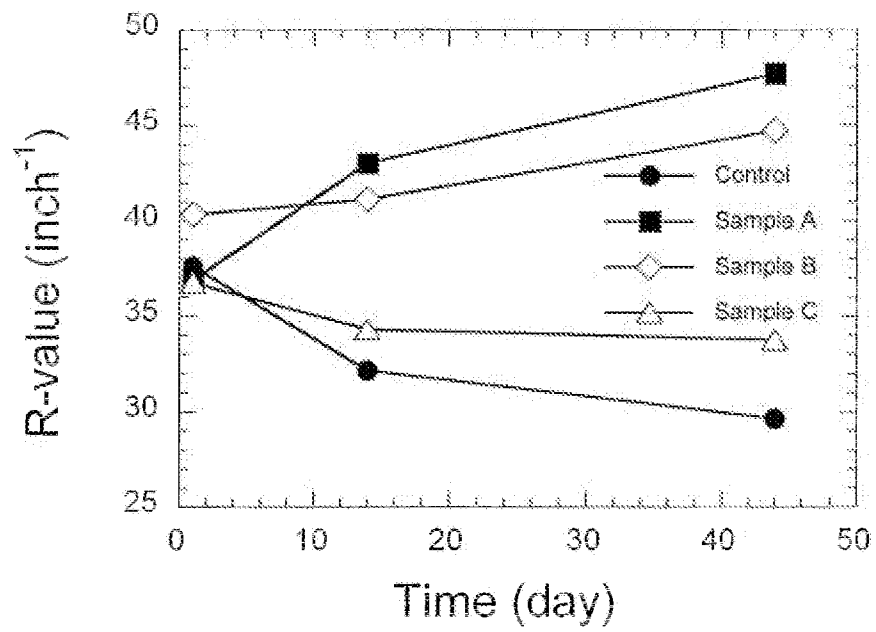


FIG. 1

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FIG. 2FIG. 3

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FIG. 4



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/30961

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC(8) - B32B 17/06; E04B 1/80; F16L 59/065 (2015.01)<br>CPC - B32B 17/068; E04B 1/803; F16L 59/065<br>According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                      |                                                                                                                                    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC(8): B23P 17/04, 17/06; B32B 3/18, 5/02, 7/04, 7/08, 7/10, 15/14, 17/02, 17/06; E04B 1/62, 1/74, 1/76, 1/78, 1/80; F16L 59/065 (2015.01); CPC: B23P 17/04, 17/06; E04B 1/62, 1/74, 1/76, 1/78, 1/80, 1/803; B32B 3/18, 5/02, 7/04, 7/08, 7/10, 15/14, 17/02, 17/06<br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google; Google Scholar; ProQuest; KEYWORDS: composite core material vacuum insulation panel fibrous insulating material inorganic particulate material fiberglass mineral wool layer pressure R-value                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                      |                                                                                                                                    |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                      |                                                                                                                                    |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Citation of document, with indication, where appropriate, of the relevant passages                                   | Relevant to claim No.                                                                                                              |
| X<br>---<br>Y<br>---<br>A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | US 2012/0009376 A1 (RUSEK, S.) January 12, 2012; figure 1A; paragraphs [0048-0052, 0069-0077, 0094]; claims 1 and 21 | 1-4, 6-9, 11-12, 20, 23-25, 28-33, 36-37, 43, 45-50, 57<br>---<br>5, 10, 13-19, 26-27, 34-35, 38-42, 51-56<br>---<br>21-22, 44, 58 |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | US 5,837,621 A (KAJANDER, R.) November 17, 1998; column 6, lines 21-33; claims 1 and 9                               | 5, 17-18, 26-27, 40-41, 53                                                                                                         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | US 2013/0116107 A1 (WANG, B.) May 9, 2013; paragraphs [0006, 0028, 0032-0033, 0048]                                  | 10, 13-15, 34-35, 38-39, 51-52, 54                                                                                                 |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | US 2011/0265654 A1 (EISENHARDT, A. et al.) November 3, 2011; paragraph [0084]                                        | 16, 55                                                                                                                             |
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| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                      |                                                                                                                                    |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier application or patent but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or, which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>"&" document member of the same patent family |                                                                                                                      |                                                                                                                                    |
| Date of the actual completion of the international search<br>04 August 2015 (04.08.2015)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                      | Date of mailing of the international search report<br><b>18 AUG 2015</b>                                                           |
| Name and mailing address of the ISA/<br>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, Virginia 22313-1450<br>Facsimile No. 571-273-8300                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                      | Authorized officer<br>Shane Thomas<br>PCT Helpdesk: 571-272-4300<br>PCT OSP: 571-272-7774                                          |