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THERMAL INSULATION

Filed July 20, 1962

FIG. 2

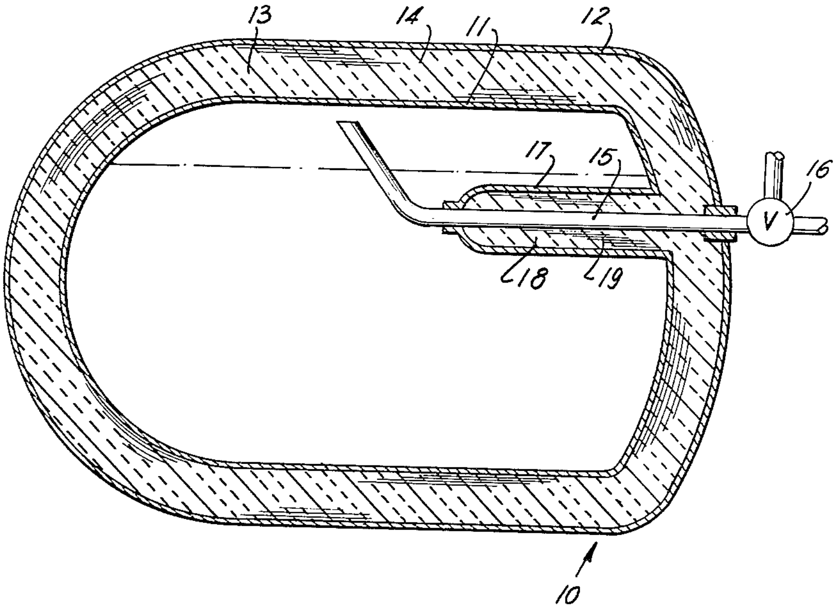
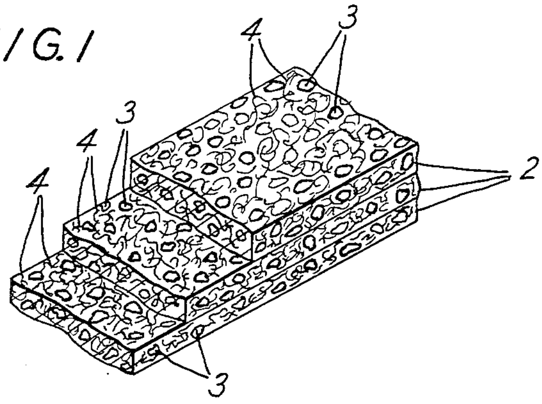


FIG. 1



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3,199,714

THERMAL INSULATION

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This invention relates to an improved composite multi-layered insulation for use in a vacuum space between warm and cold boundaries, as for example the inner vessel and the outer casing of a double-walled container for low-boiling liquefied gases such as oxygen, helium and hydrogen.

In U.S. Patent No. 3,007,596, issued November 7, 1961 to L. C. Matsch, there is described an alternate-layer insulation employing thin metallic foils separated by sheets of low-conductive fibrous material. U.S. Patent No. 3,009,600, issued November 21, 1961 in the name of L. C. Matsch, describes a preferred low-conductive material for use in this multi-layered insulation, namely permanently precompacted paper composed of unbonded fibers having diameters less than about 5 microns and lengths of less than about 0.5 inch. The paper is preferably formed of glass fibers.

The superlative performance of these insulating systems is well known. Occasionally, however, special requirements are encountered which present problems in their use. One problem is met when heat flows through the insulation system from two directions. The effectiveness of the insulation is largely confined to obstructing heat flow in a direction essentially normal to foil orientation. In cases where a substantial temperature difference exists in the insulation system in a direction parallel to the foil orientation, large amounts of heat can be transported along the reflective shields which are usually composed of a highly conductive metal.

Another problem is encountered when multi-layer insulations containing continuous shields are required to conform to complex curvatures, such as spheres or the end closures of cylindrical vessels. Indiscriminate folding or crumping of the insulation layers may result in shorting circuits developing between the shield layers, thereby nullifying the effectiveness of the insulation between such short-circuited shields. The thin shield may also be torn during the folding step, thereby exposing radiation windows through the insulation. Usually the techniques necessary to prevent such occurrences are expensive and time consuming. Often the corrective measures require individual handling and arrangement of the foil layers, so that the problems are intensified as the total number of shields is increased.

A third problem encountered with alternate-layer foil and fiber insulations is spiral conduction. This problem is most apt to appear in small diameter cylinders insulated with only a few spiral layers of material. The total length of the spirally wound foil from the warm outermost layer to the cold inner layer is relatively short in such cases, and the heat conduction by the highly conductive metallic foil can become a significant factor.

There exists a long-standing need for a high quality insulation which is thermally homogeneous, in the sense that it would exhibit high resistance to heat flow in all directions and by all modes of heat transfer. Such an insulation should help alleviate the above-mentioned problems of two-directional heat flow and short circuiting.

An example of one such homogeneous material is the opacified powder disclosed in U.S. Patent No. 2,967,152 issued to L. C. Matsch et al. on January 3, 1961. Thermal conductivities on the order of 0.3×10^{-3} B.t.u./hr. ° F., sq. ft./ft. are readily obtained by proper compositions of this type. Although the conductivity of such insulation is generally an order of magnitude greater than those of U.S.P. 3,007,596, the opacified powder is nevertheless a reasonable approach to a solution of the above-described problems encountered with alternate-layer insulations. It is not necessary to employ the opacified powder throughout the entire insulation system since its use may be limited to those parts of the system which are difficult to cover with alternate-layer material, due to the curvature of surfaces or the existence of pipes and connections.

Nevertheless, the use of opacified powders to any extent in the insulation system is a less-than-ideal solution to the problem. In order that the admixture of powders will remain homogeneous, the low-conductive component must be of extreme fineness and such materials are usually quite expensive. The powder mixture must also be prepared in the dry state, and it is difficult and expensive to obtain complete homogeneity in the preparation. The extremely fine metallic particles are also subject to oxidation, which is highly detrimental to satisfactory performance of opacified powder materials. In general, powders are more difficult to evacuate than are fiber materials, due at least in part to the very high adsorptive power of the fine powders. Special provisions are usually required to prevent carry-over of powder from the insulation system to the evacuation equipment. Finally, powder material exhibits strong settling tendencies and as settling occurs, the surfaces in the uppermost parts of the insulation system may be exposed, or at least be covered by inadequate thickness of insulation.

It is therefore an important object of the present invention to provide an improved vacuum-insulation system for reducing heat transmission by all modes of heat transfer to values well below that of any known thermally homogeneous insulating systems, particularly for minimizing heat inleak to very low-boiling liquefied gases such as helium and hydrogen.

Another object is to provide such an improved composite multi-layered insulation system in which heat transfer is reduced in a direction parallel to the layers.

A further object is to provide such an improved composite multi-layered insulation which may be readily conformed to complex curved surfaces.

Still another object is to provide an improved composite multi-layered insulation in which heat transfer by spiral conduction is reduced.

Further objects and advantages of this invention will be apparent from the ensuing disclosure and the appended claims.

In the drawings:

FIG. 1 is an isometric view of a composite insulating material embodiment of the invention shown in a flattened position with parts broken away to expose underlying layers.

FIG. 2 is an elevation view taken in cross-section of a double-walled liquefied gas container employing the insulation of FIG. 1.

According to the present invention, a composite multi-layered insulation is provided for use in a vacuum space between warm and cold boundaries. The insulation comprises permanently precompacted low-conductive layers of 10 fibers having diameters less than about 20 microns for reducing heat transfer by conduction, being oriented substantially perpendicular to the direction of heat inleak across the vacuum space. Finely-divided radiant heat reflecting bodies of sizes less than about 500 microns are incorporated in and uniformly dispersed through the fibers composing the permanently precompacted layers in an amount between about 10% and 60% by weight of the composite. A binder is provided for cementing the heat reflecting bodies to the fibers. Less than about 10% by weight reflecting bodies does not achieve a significant opacifying effect whereas greater than 60% reflecting bodies produces bridging of such bodies through and along the composite surface. The latter results in a solid conductive path.

The term "vacuum," as used herein, is intended to apply to sub-atmospheric absolute pressure conditions not substantially greater than 500 microns of mercury, and preferably below 100 microns of mercury. For superior quality results, the pressure should preferably be below 25 microns of mercury.

The reflecting body-containing permanently precompacted composite may, for example, be formed on standard paper-making machines in the following manner, using a binder such as colloidal silica. The latter is preferably provided in the form of a colloidal silica aqueous sol, or alternatively as the hydrolyzed form of a compound such as tetraethylsilicate. First, the composite fibers and the reflecting bodies are thoroughly admixed in the desired proportions to form a defibered, substantially homogeneous aqueous dispersion in a papermill beater or mixing device. The binder, i.e. colloidal silica, is also preferably added to the dispersion in quantities of about 2 to 20% by weight of the fiber-reflecting body mixture. With colloidal silica the binder preferably comprises about 10 to 20% by weight of the composite sheet, while 2 to 10% by weight is preferred when organic binders are used.

The homogeneous aqueous dispersion is fed into the headbox of the paper-making machine while simultaneously introducing therewith a solution of a cationic agent. The latter should be added in an amount of about 0.5 to 10.0 percent by weight of the fiber-reflecting body-binder mixture, and preferably is about 1 to 3% by weight of the mixture. Cationic starches such as the amine-modified materials are suitable cationic agents. Exemplary of such amine-modified starches are Cato 8 (a modified cornstarch), and Cato Amylon (a hybrid starch containing 55–60% amylose), both sold by National Starch and Chemical Corporation of Plainfield, New Jersey.

The pH of the headbox dispersion is preferably maintained in the range of about 2.7–6. For fibers of glass, quartz and mineral wool, the pH is preferably maintained in the range of about 2.8–4. Ceramic fibers preferably utilize a pH of about 4–6. Prior to the headbox, the pH of the dispersion should also be maintained in the same ranges. The adjustment of the pH can be readily attained by the addition of acids such as sulfuric.

The dispersion containing the defibered material, the reflecting bodies, the binder and the cationic agent is deposited upon the wire of the paper-making machine to form the reflecting body-containing composite, then compacted by, for example, compression rolls or by vacuum and finally dried in accordance with conventional practice in the art.

Instead of inorganic binders such as colloidal silica, organic binders may be used separately or in combination with inorganics in the preparation of reflective body-containing composite. These include polyvinylidene chloride, polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol, cellulosic compounds such as carana gum or guar gum, acrylic resins as methylmethacrylate, formaldehyde resins and epoxy resins (in the emulsified form). Certain silicones such as the phenyl methyl compounds are also suitable. When organic binders are employed, the fibers are dispersed in an acid medium as previously described, but the dispersion may be neutralized or even made basic prior to introduction of the binder. A suitable medium for raising the pH of the dispersion is ammonium hydroxide, the residual ammonia being driven off during the sheet drying step.

The fibers may, for example, be formed of glass, ceramic, quartz, or potassium titanate, depending on the temperatures to which the composite multi-layered insulation will be exposed. For example, at temperatures below about 900° F. glass fibers are preferred but at higher temperatures glass tends to soften and the other enumerated materials are more suitable. When glass fibers are used they are preferably of less than 5 microns diameter, while a fiber diameter range of 0.2 to 3.8 microns gives best results. The above range represents a preferred balance between increasing frailness and cost of relatively small diameter fibers, and increased conductance and gas pressure sensitivity of relatively large diameter fibers. Glass fibers having diameters in the range of 0.2 to 0.5 micron such as those commercially designated as 104 or AAAA fiber, and fibers designated as 106 or AAA fiber having diameters in the range of 0.5 to 0.75 micron are normally available as papers, and are especially suitable for practicing this invention. Glass fibers as large as those designated class B fibers having diameters between 2.5 and 3.8 microns can also be employed satisfactorily with an appropriate binder.

Certain organic compositions may be used as the low conductive fibrous sheet material of the present invention, as for example the viscose material known commercially as rayon, the polyamide known as nylon, the condensation product of dimethyl terephthalate and ethylene glycol which is known commercially as Dacron, the vinyl chloride-acrylonitrile copolymer known as Dynel, and cotton.

The finely-divided radiant heat reflecting bodies may, for example, be formed of aluminum, copper, nickel and molybdenum. Again the selection of the reflecting body is influenced by the operating temperature of the insulating composite. Aluminum is stable at temperatures below about 900° F., and is preferred in this range. Copper is a practical alternative to aluminum at below 900° F., and is the preferred reflecting body at temperatures between 900° F. and about 1,730° F., its melting point being 1,981° F. The 1,730° F. temperature limitation is based on maintaining the copper vapor pressure below 0.01 micron Hg molybdenum has an extremely high melting point of 4,750° F., but to maintain its vapor pressure below 0.01 micron Hg, the practical range for use of molybdenum is limited to temperatures below about 3,490° F. Nickel is an attractive reflecting material for temperatures between about 1740° F. (limit for copper) and 2110° F. The upper limit of 2110° F. is considerably below its melting point (2,650° F.) and again is established by the requirement that the vapor pressure of the metal be maintained below 0.01 micron Hg. It should be recognized that considerations other than the thermal softening point may be determining in the selection of the radiant heat reflecting body. For example, safety factors may preclude the use of a readily oxidizable material such as aluminum in an insulation for liquid oxygen.

Best results are obtained when the radiant heat reflecting bodies are relatively small, with particle sizes of less than 50 microns as the major dimension. Aluminum and copper paint pigment flakes of less than 0.5 micron thickness are especially suitable for relatively low-temperature systems. Any lubricant used for grinding the flakes to the desired size is preferably removed prior to admixing with fibers and binder. For example, one commercially available aluminum flake is a polished, low-residual-grease powder with a 98% passage through a 325 mesh screen (44 microns). An electron microscopic particle size determination of this powder indicates the majority of particles are between 2 and 14 microns size.

The following examples describe the specific preparation of the novel insulations used in the succeeding thermal and electrical conductivity tests.

EXAMPLE ONE

In this example, 78 pounds of AAA glass fiber (diameter of 0.5 to 0.75 micron and length predominantly about $\frac{1}{32}$–$\frac{1}{4}$ inch) was added to a papermill beater or mixing device, along with 12.5 pounds of A glass fiber (diameter of 1.5 to 2.5 microns and same length as AAA fiber). One quart of commercial hydrochloric acid and 1200 gallons of water were also added to the beater, resulting in a pH of approximately 3.0. This mixture was initially defibered in the beater for ten minutes with the roll of the beater raised off from the bed plate and then lightly brushed to separate the fibers for ten minutes.

At the end of the brushing operation 50 pounds of a colloidal silica aqueous sol containing 30 percent solids and 4.75 pounds of $\frac{1}{4}$ inch glass rovings were added to the beater and mixed with the fibers for twelve minutes. Lastly, 50 pounds of below 50 micron particle sized aluminum flakes were added and the mixture defibered in the beater for ten minutes.

A solution of cationic agent was prepared by mixing 15 pounds of cationic starch (Cato 8, National Starch and Chemical Corporation) in 40 gallons of cold water, heating the mixture to 190° F., agitating for fifteen minutes, and thereafter diluting with water to a total volume of 60 gallons.

The glass fiber-aluminum flake-colloidal silica slurry was further diluted to a consistency of 0.25 percent by weight solids and fed into the headbox of a papermaking machine using an inclined Foudrinier wire. At the same time, the cationic agent solution was fed into the headbox at a rate providing approximately 1.2 percent by weight starch based upon the solids in the slurry. Simultaneously, hydrochloric acid was metered into the headbox to maintain the pH at approximately 3.4.

The glass fibers, aluminum flakes, and colloidal silica deposited almost immediately upon the wire along with a portion of the cationic agent to form a paper which was removed from the Foudrinier wire and dried in accordance with conventional practice.

The base sheet thus formed contained about 30% by weight aluminum at a thickness of 3.2 mils. The tensile strength was 856 grams in the machine direction and 325 grams in the cross direction. The density was 0.315 gram per cubic centimeter and the porosity was 5.7 cu. ft. per minute on a 0.4 inch diameter circle using the Frazier Pernometer. The wet tensile strength was 250 grams in the machine direction and 90 grams in the cross direction.

EXAMPLE TWO

The sheet in this instance utilized ceramic fibers and 45% by weight copper flakes.

To the heater were added 25 pounds of 2.5 micron diameter ceramic fibers and 1200 gallons of water, this mixture being defibered for ten minutes. Twenty-five additional pounds of the same ceramic fibers were added to the beater, followed by a defibering operation for five minutes. Next 60 pounds of colloidal silica sol and 50 pounds of clean (grease-free) copper flakes having major dimensions less than 50 microns, were added to the beater.

The resultant slurry was admixed and fed into the headbox at a consistency of about 0.25 percent. The cationic starch solution was added at the same rate as in Example One and hydrochloric acid was metered in to maintain the pH at about 4.5–5.0.

The dried 45 percent copper flake-containing paper had a thickness of 12.4 mils. The tensile strength was 1775 grams in the machine direction and 1069 grams in the cross direction. The density was 0.359 gram per cubic centimeter, and the porosity 19.3 cu. ft. per minute on the Frazier Pernometer. The wet strength was 494 grams in the machine direction and 319 grams in the cross direction.

Referring now to the drawings and FIG. 1 in particular, the composite insulation includes low-conductive fibrous sheet material layers **2** of permanently precompacted material containing finely-divided radiant heat reflecting bodies **3** having metallic surfaces uniformly dispersed through the fibers **4** comprising the composite layers. An inorganic or organic binder (not shown) cements the heat reflecting bodies **3** to the fibers **4**.

FIG. 2 illustrates a double-walled liquefied gas container **10** comprising inner vessel **11** and outer casing **12** arranged and constructed with evacuable space **13** therebetween. Space **13** is filled with the composite insulation **14** of FIG. 1, for example, spirally or concentrically wrapped around inner vessel **11** to provide the desired number of layers. The ends of the composite insulation **14** may, for example, be folded over the ends of inner vessel **11**. Conduit **15** extends laterally through insulation **14** and the inner end terminates within inner vessel **11** while the outer end terminates in liquid filling-discharge valve **16**. Sleeve **17** forming a wall portion of the inner vessel **11** is concentrically positioned around conduit **15** so that an annular space **18** exists therebetween. Annular space **18** communicates with and forms part of the evacuated insulating space **13**, and is filled with composite insulation **14**. The latter is preferably wrapped around sleeve **17** so that the layers are parallel to the length of conduit **15**.

With respect to any point along the insulated length of conduit **15**, temperature differences exist to drive heat in two directions: (a) radially outward toward the cold contents of inner vessel **11** and (b) longitudinally inward from the warm contact with the outer casing **12**. If the conventional alternate layered aluminum foil-glass fiber composite were used to insulate conduit **15**, it would effectively obstruct the radial heat leak (a), but its continuous foils will augment the longitudinal heat leak (b). The present insulation is ideal for conduit **15** because of its thermal homogeneity; it obstructs both radial heat leak and longitudinal heat leak.

There is considerable evidence that the precompaction of a fiber-reflective flake composite paper produces a surface effect which further enhances the ability of the material to block radiation. Thermal conductivity tests were conducted using two precompacted composites, both consisting of glass fibers of 0.5–0.75 micron diameter with 30 wt.-percent aluminum flakes and 14 wt.-percent colloidal silica binder. One composite weighed 6.4 gm./sq. ft. while the other weighed 2.48 gm./sq. ft. In both tests, the sheets were wrapped to a density of about 12 lb./cu. ft.

In other similar tests with 30% aluminum-glass fiber permanently precompacted composite, 2.48 gm./sq. ft. and 1.1 gm./sq. ft. composites were compared at about 4.5 lb./cu. ft. density.

From the above tests, it was found that equal quantities of identically composed material but with different degrees of precompaction can produce widely different results. Many layers of thin composite are far more effective insulators than a few layers of thicker material. This is believed due to the previously mentioned surface effect produced by precompaction, and which results in a more effective radiation barrier.

The inclusion of reflecting bodies in the fiber structure must be accomplished without significantly affecting the solid conductance of the composite. We have found that relatively large amounts of metal may be precompacted with the fiber without noticeably increasing the solid conductance. Electrical resistance measurements were made on glass permanently precompacted composites containing 30% by weight aluminum and 14% by weight colloidal silica, in order to show the degree of metal flake isolation, i.e., to indicate the extent to which flake-to-flake bridging through the composite was prevented by the fibers. The electrical measurements showed infinite resistance through the layer thickness and also across its surface, indicating that the fibers did in fact prevent metal bridging.

While the approximate electrical measurements on the reflective body-containing composite showed uniformly zero conductance both through and along the sheet, more sensitive thermal conductivity measurements showed the heat conductance parallel to the sheet to be appreciably greater than through the sheet thickness. This is to be expected, in view of the lateral orientation of the fibers whose length is much greater than their diameters. The glass fibers exhibit virtually zero electrical conductance, but exhibit measurable thermal conductance. Thus, precise thermal conductivity measurement on a tightly wrapped 30 wt.-percent aluminum composite gave a value of 38×10^{-3} B.t.u./hr. sq. ft. ° F./ft. parallel to the sheet and a value of 0.085×10^{-3} B.t.u./hr. sq. ft. ° F./ft. through the thickness normal to the sheet. While the parallel conductivity appears large compared to the normal conductivity, it is manyfold less than would result if aluminum foils were present and between the layers. The conductivity of aluminum is 3,000 times greater than the observed parallel conductivity of wrapped aluminum flake composite. It is this low parallel conductivity relative to aluminum foil-containing insulation that renders the metal flake-containing composite essentially thermally homogeneous.

A series of tests were performed using permanently precompacted sheets 2–3 mils thick containing 20%, 30%, and 40% by weight aluminum flakes (less than 50 microns size) and 14% by weight colloidal silica with 0.5 to 0.75 micron diameter glass fibers. In a first test the electrical conductivity of the sheet was determined under various compressive loads. Each of the sheets was compressed between two metal electrodes with an electrical voltage imposed thereacross. The samples containing 20% and 30% by weight aluminum showed infinite electrical resistance under compressive loads estimated to be as high as 40 to 50 lb. per sq. in. However, the sample containing 40% aluminum exhibited measurable electrical conductivity under a compressive load estimated to be 25 p.s.i. Since it appears that appreciable cross-bridging of the aluminum-flakes occurs at this composition, the range of 10% to 40% by weight aluminum flakes represents a preferred embodiment.

The thermal performance of 20% by weight aluminum flakes in glass fiber sheets was compared in two thermal conductivity tests, over a temperature range of ambient to −196° C., and a vacuum pressure below 1 micron Hg. The results are shown in Table I, along with plain glass fiber sheeting of the same size.

Table I

Material	Sheet Weight, gr./sq. ft.	Layers-in. Thickness	Density of Insulation, lb./cu. ft.	Conductivity $K\times10^{-3}$, B.t.u./hr. sq. ft. ° F./ft.
Glass fiber	1.6	105	4.44	0.319
20% aluminum-glass fiber	1.9	142.6	7.16	0.104
30% aluminum-glass fiber	2.48	185	12.12	0.085

Thermal conductivity tests at various wrapped densities have been conducted using a 30% aluminum-glass fiber composite approximately 2–3 mils thick composed of glass fibers ranging from 0.5 to 0.75 micron in diameter. Conductivity was measured under the same conditions as for the Table I tests, and the results are shown in Table II.

Table II

Layers/in.	Pounds/cu. ft.	Thermal Conductivity $K\times10^{-3}$, B.t.u./hr. ° F./ft.
62	4.25	0.162
118	7.73	0.096
185	12.12	0.084

Reference to the above values shows that the thermal conductivity is considerably lower than can be obtained with opacified powder insulation of the same metal content. For example, 28.6% aluminum flakes in silica aerogel under the same temperature and vacuum conditions exhibits a conductivity of 0.187×10^{-3} B.t.u./hr. sq. ft. ° F./ft. which is more than twice the best value reported for the present insulation.

The mechanical advantages of the new insulation are quite impressive. Settling tendencies do not exist, and the installed insulation is as readily evacuated as alternate-layer forms of insulation. Oxidation of the reflecting bodies has not proved to be a problem in fiber sheets as long as the material is not subjected to oxidizing atmospheres while at high temperature. In addition to offsetting the disadvantages of opacified powders, the new material provides a substantial improvement in thermal conductivity in the direction normal to the sheet.

There is a marked difference in thermal performance and appearance between the present insulation in which the radiant heat reflecting bodies are uniformly dispersed in all directions through a permanently precompacted sheet, and an insulation in which the reflecting bodies are merely distributed on the surface of the sheet. This was vividly illustrated by a test in which the previously described fine aluminum flakes were dusted into the same 0.5–0.75 micron glass fiber sheet. The resulting sheet weight was 2.82 gm./sq. ft. and when wrapped 125 layers/in. (9.33 lb./cu. ft.) exhibited a thermal conductivity of 0.11×10^{-3}. This material is inferior to the Table II insulations when compared on a weight basis. Also, it was extremely difficult to handle, and a considerable quantity of the aluminum flake was lost in the normal wrapping procedure.

In additional to the previously described experiments with aluminum flake-glass fiber composite, we have also prepared and tested copper flake-glass fiber composite, and copper flake-ceramic fiber composite. (See Example Two.) The copper flakes were less than 50 microns in major dimension, the glass fibers were 0.5–0.75 micron diameter, and the ceramic fibers about 2.5 microns diameter.

The results of these tests are shown in Table III, below. The data for aluminum flake-glass fiber permanently precompacted composite is repeated for comparison.

Table III

Paper[1] Material	Sheet Weight, gr./sq. ft.	Layers/in.	Total Density, lb./cu. ft	$K_a\times10^{-3}$
20% by weight aluminum in glass fibers	1.9	142.6	7.16	0.104
30% by weight aluminum in glass fibers	2.48	185	12.12	0.085
30% by weight copper in glass fibers	2.58	52.6	3.6	0.15
30% by weight copper in glass fibers	2.58	133	9.1	0.14
45% by weight copper in ceramic fibers	10.35	58.1	15.9	5.83

[1] The binder for the glass fiber and ceramic fiber papers was 14% and 18.5% by weight colloidal silica, respectively.

All the tests reported in Table III above were conducted between boundary temperatures of ambient and liquid nitrogen and under a vacuum of below 1 micron

Hg except for the 45% copper flakes in ceramic precompressed composite. The ceramic composite is intended specifically for high-temperature service above the melting point of glass and for this test, the boundary temperatures were about 120° and 1255° F. The high temperature accounts in part for the higher value of Ka. The thermal conductivity value for the copper flake-ceramic fiber composite is to be compared with the best high-temperature materials available to the prior art, for example, a blend of ceramic and ceramic potassium titanate fibers which in vacuum would exhibit a thermal conductivity of about 11×10^{-3}. This figure is about twice as high as the thermal conductivity of the copper flake-ceramic fiber permanently precompacted composite of the present invention.

The particular ceramic sheet employed in the Table III tests is approximately 5 mils thick. This ceramic fiber is reported by the manufacturer to have a melting point of 3,200° F. and to possess a thermal conductivity in air of 0.058 B.t.u./hr. sq. ft. ° F./ft. at a mean temperature of 1,000° F One type of suitable ceramic material has the following chemical analysis: Al_2O_3—51.3%, SiO_2—45.3%, and ZrO_2—3.4%. Another satisfactory ceramic fiber has the following chemical analysis: Al_2O_3—51.2%, SiO_2—47.4%, B_2O_3—0.7%, and Na_2O—0.7%. These materials are sold by the Carborundum Company, Niagara Falls, New York under the name of "Fiberfrax."

It has been previously indicated that a range of 10% to 40% by weight aluminum flakes is preferred as the radiant heat reflecting body. The preferred amount of reflector is related to its specific gravity; that is, copper is considerably heavier than aluminum so that more copper is necessary to provide the same amount of reflective surface. For this reason, a range of 30% to 60% by weight of the composite is preferred with copper flakes.

Although preferred embodiments of the invention have been described in detail, it is to be understood that modifications and variations may be effected without departing from the spirit and scope of the invention.

What is claimed is:

1. A composite multi-layered insulation for use in a space between warm and cold boundaries comprising permanently precompacted low-conductive layers of (1) fibers having diameters less than about 20 microns for reducing heat transfer by conduction, being oriented substantially perpendicular to the direction of heat inleak across the space; (2) finely-divided radiant heat reflecting bodies of sizes less than about 500 microns being incorporated in and uniformly dispersed through the layers in an amount between about 10% and 60% by weight of the layers; and (3) a binder for cementing the heat reflecting bodies to said fibers.

2. An insulation according to claim **1** in which the fibers are formed of a member selected from the group consisting of glass, quartz, potassium titanate, ceramic, rayon, nylon, a condensation product of dimethyl terephthalate and ethylene glycol, Dynel and cotton.

3. An insulation according to claim **1** in which the fibers are formed of glass.

4. An insulation according to claim **1** in which the fibers are formed of a ceramic material.

5. An insulation according to claim **1** in which the fibers are formed of glass having diameters of about 0.02 to 3.8 microns.

6. An insulation according to claim **1** in which said heat reflecting body is a member selected from the group consisting of aluminum, copper, molybdenum and nickel.

7. An insulation according to claim **1** in which said heat reflecting body is aluminum flakes of less than about 50 microns size.

8. An insulation according to claim **1** in which the fibers are formed of glass with diameters of about 0.2 to 3.8 microns, and said heat reflecting body is aluminum flakes of less than about 50 microns size in an amount between about 10% and 40% by weight of the layers.

9. An insulation according to claim **1** in which said heat reflecting body is copper flakes of less than about 50 microns size.

10. An insulation according to claim **1** in which the fibers are formed of glass with diameters of about 0.2 to 3.8 microns, and said heat reflecting body is copper flakes of less than about 50 microns size in an amount between about 30% and 60% by weight of the layers.

11. An insulation according to claim **1** in which the fibers are formed of glass and the binder is colloidal silica.

12. An insulation according to claim **1** in which the fibers are formed of glass, said radiant heat reflecting bodies are metal flakes of less than about 50 microns size, and the binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of said insulation.

13. An insulation according to claim **1** in which the fibers are formed of glass, said radiant heat reflecting bodies are aluminum flakes of less than about 50 microns size and the binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of said insulation.

14. An insulation according to claim **1** in which the fibers are formed of glass, said radiant heat reflecting bodies are copper flakes of less than about 50 microns size and the binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of said insulation.

15. An insulation according to claim **1** in which said heat reflecting body is copper-coated mica.

16. A composite multi-layered insulation for use in a vacuum space between warm and cold boundaries comprising permanently precompacted low-conductive layers of (1) fibers having diameters less than about 20 microns for reducing heat transfer by conduction, being oriented substantially perpendicular to the direction of heat inleak across the vacuum space; (2) finely divided radiant heat reflecting bodies of sizes less than about 500 microns having metallic surfaces, being incorporated in and uniformly dispersed through the layers in an amount between about 10% and 60% by weight of the layers; and (3) a binder for cementing the heat reflecting bodies to said fibers.

17. A double-walled liquefied gas container comprising an inner vessel; an outer casing surrounding said inner vessel so as to provide an evacuable space therebetween; a composite multi-layered insulation in said space comprising permanently precompacted low-conductive layers of (1) fibers having diameters less than about 20 microns for reducing heat transfer by conduction, being oriented substantially perpendicular to the direction of heat inleak across the vacuum space; (2) finely-divided radiant heat reflecting bodies of sizes less than about 500 microns having metallic surfaces, being incorporated in and uniformly dispersed through the layers in an amount between about 10% and 60% by weight of the layers; and (3) a binder for cementing the heat reflecting bodies to said fibers.

18. A double-walled container according to claim **17** in which the fibers are formed of glass having diameters of about 0.2 to 3.8 microns.

19. A double-walled container according to claim **17** in which the fibers are formed of glass having diameters of about 0.2 to 3.8 microns, and said heat reflecting body is aluminum flakes of less than about 50 microns size.

20. A double-walled container according to claim **17** in which the fibers are formed of a member selected from the group consisting of glass, quartz, potassium titanate, ceramic, rayon, nylon, a condensation product of dimethyl terephthalate and ethylene glycol, Dynel and cotton, and said heat reflecting body is a member selected from the group consisting of aluminum, copper, molybdenum, and nickel.

21. A double-walled container according to claim **17** in which the fibers are formed of glass having diameters of about 0.2 to 3.8 microns, said heat reflecting body is metal flakes, and said binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of said insulation.

22. A double-walled container according to claim **17** in which the fibers are formed of a member selected from the group consisting of glass, quartz, potassium titanate, ceramic, rayon, nylon, a condensation product of dimethyl terephthalate and ethylene glycol, Dynel and cotton, and said heat reflecting body is copper-coated mica.

23. A composite permanently precompacted multilayered thermal insulation for use in an evacuable space between warm and cold boundaries prepared by the steps of providing an aqueous solution containing fibers having diameters less than about 20 microns, finely divided radiant heat reflecting bodies of sizes less than about 500 microns, and a binder for cementing the heat reflecting bodies to the fibers being present in quantity of about 2 to 20% by weight of the fiber-reflecting body-binder mixture, said heat reflecting bodies constituting between about 10% and 60% by weight of said mixture; mixing the aqueous solution sufficiently to form a defibered, substantially homogeneous aqueous dispersion; depositing the dispersion on the wire of a paper-making machine to form a sheet having said heat reflecting bodies uniformly dispersed therethrough; thereafter compacting and drying said sheet as the composite layer; and assembling a multiplicity of such composite layers in overlying and contiguous relationship in said evacuable space.

24. An insulation according to claim **23** in which the fibers are formed of glass having diameters of about 0.02 to 3.8 microns, said radiant heat reflecting bodies are aluminum flakes of less than about 50 microns size in an amount between about 10% and 40% by weight of the insulation and the binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of the insulation.

25. An insulation according to claim **23** in which the fibers are formed of glass having diameters of about 0.02 to 3.8 microns, said radiant heat reflecting bodies are copper flakes of less than about 50 microns size in an amount between about 30% and 60% by weight of the insulation, and the binder is colloidal silica in sufficient quantity to constitute between about 10% and 20% by weight of the insulation.

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