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THERMAL INSULATION

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This invention relates to thermal insulation, particularly powder-in-vacuum insulation, which is less sensitive to pressure changes.

One of the major difficulties involved in the use of a high quality insulating system in which a vacuum space is filled with a low conductive powder, is the sensitivity of the insulating system to changes in pressure. By pressure sensitivity is meant the rate of increase of thermal conductivity with increasing absolute pressure. A high vacuum is difficult to maintain for an extended period of time and should a slight leak occur or should the insulating system undergo a rise in temperature, the absolute pressure of the system will rise and the thermal conductivity of the system tend to increase. This increase is due to the increase in thermal conduction by the residual gas in the insulating space.

The degassing of insulation filler materials at low absolute pressures also contributes to gradual loss of vacuum. Atmospheric gases and water vapor are normally absorbed on the extended surface of the filler and cannot be completely removed even by preheating the insulation before evacuation. Over a period of time, the adsorbed gas molecules will evaporate from the surfaces and cause a gradual rise in the absolute pressure of the insulation space, and as a consequence an increase in the conductive heat transfer across the insulating space.

In some low temperature applications, an adsorbent material such as silica gel is placed in the insulation space to adsorb gas leakage and assist in maintaining low absolute pressures. Adsorbents have higher adsorbing capacities at lower temperatures and are advantageously located at a cold zone within the insulation space, preferably in close contact with the cold inner container. However, when the container is emptied and the adsorbent warms slightly, as frequently occurs in portable containers, the adsorbed gases are released and the pressure rises. As a result, the heat inleak increases, and the entire container warms to an objectionable degree. Even though the container is empty during the period of high heat inleak, low temperature refrigeration must still be expended to recool the container when it is again placed in service.

A similar situation develops when low temperature containers provided with adsorbents are subjected to wide variations in pressure within the liquid container. At low container pressures, the liquid is relatively cold, and the adsorbent adjacent the container in the insulation space adsorbs maximum residual gas to maintain a low absolute pressure in the insulation space. If the pressure in the liquid container increases substantially, as for example by unavoidable heat inleak into a sealed liquid container, the temperature of the liquid will gradually rise, permitting the absorbent to become progressively warmer. A portion of the adsorbed gases is then released, causing the pressure in the insulation space to increase. If the filler material is very pressure sensitive, there will occur an accelerated rate of heat inleak at a time when maximum insulating effectiveness may be most needed.

I have found that the pressure sensitivity of an insulating material is dependent to a large extent upon the particle size of the insulating material. Experimental data shows that the finer the insulating particles, the lower the sensitivity to pressure changes. For fibrous insulating materials, the pressure characeristics are affected by

fiber diameter, the pressure sensitivity decreasing as the fiber diameter is decreased.

A solution to the problem of obtaining favorable pressure characteristics is to employ a low conductive insulating material composed of suitable small size bodies. In the case of fibrous material, "body size" refers to the fiber diameter thereof, and for powders the term refers to the average dimension of the particles. However, presently available insulating materials having these requisites are prohibitively costly for many industrial applications. To illustrate, finely divided silica aerogel with an ultimate particle size of approximately 0.015 micron has approximately one-tenth the pressure sensitivity of coarser particles of perlite (approximately 10 microns ultimate particle size) between selected absolute pressures of about 150 to 200 microns of mercury. But the cost of the silica aerogel is approximately 15 times more than the perlite. The same situation exists for fibrous insulating materials, the cost rapidly increasing as the fiber diameter is decreased. It would be comparably expensive to consider grinding a coarse insulating powder to obtain the fine particle size range required to significantly improve its pressure sensitivity. In fact, a coarse particle insulating material cannot be reduced to particles on the order of 0.015 micron in size by grinding. In addition, many insulating materials are either porous or hollow in structure. Grinding these materials would considerably alter their physical characteristics, making them excessively dense and causing them to exhibit adverse settling characteristics.

It is, therefore, an object of the present invention to provide an improved insulating filler material having a favorable pressure sensitivity behavior and yet relatively inexpensive to manufacture.

Another object of the invention is to provide in a vacuum insulating system an improved low cost insulating filler material having a low pressure sensitivity.

We have discovered that the pressure sensitive qualities of a low, conductive, coarse powder or large diameter fiber insulating material may be enhanced to a substantial degree approaching that of a finely divided insulating power or small diameter insulating fiber material. This is accomplished by filling a vacuum insulating space with a low-conductive insulating material consisting of at least two components, a predominant component being an inexpensive, low heat conductive, coarse particle, such as perlite, or large diameter fiber material, such as glass fiber, having a normally undesirable thermal pressure sensitivity behavoir and a minor component being a very finely divided material, such as silica aerogel, having a low pressure sensitivity. Unlike the pressure sensitive coarse powder insulations, the insulation mixture of the invention behaves substantially like finely divided insulating powder. For illustrative purposes, the invention will be described in terms of a powder insulation, but it is to be understood that the invention is not intended to be limited thereto. The present insulation is particularly suitable for minimizing the atmospheric heat inleak to stored bodies of low boiling liquefied gases, as for example liquid oxygen, nitrogen, hydrogen and the like.

The term "vacuum" as used herein is intended to apply to subatmospheric pressure conditions not substantially greater than 1000 microns of mercury absolute and preferably below 100 microns of mercury.

According to the invention, a vacuum insulated space is provided with a coarse, low conductive insulating filler having interspersed therein in minor amounts a fine-body size low heat conductive insulating powder exhibiting excellent pressure sensitivity qualities. Preferably, the fine powder constitutes between 5% and 40% of the total volume of the coarse material alone.

The coarse insulating filler material to be used in the practice of the invention may comprise a relatively large particle size base filler powder, such as perlite, magnesia, mica, or other similar inexpensive insulating powders exhibiting high pressure sensitivity, whose function is to fill the insulation space with low cost insulating material.

The small-body size insulating material to be used in upgrading the coarse insulating filler material may, for example, be finely divided silica or silica aerogel, calcium silicate, or titanium oxide, whose function is to fill the voids between the coarse material, and thereby produce a composite material or mixture which approaches the pressure characteristics of the fine material alone.

In practicing this invention, the average ultimate body size of the coarse insulating component should be at least 10 times greater than that of the fine component.

The coarse material should have an ultimate body size ranging between three and 1000 microns and preferably have a mean ultimate body size of between 3 and 10 microns. The fine component preferably should be not greater than 0.1 micron in ultimate size in order that it may exhibit exceptionally good pressure characteristics and disperse itself into the voids between the coarse particles.

While we do not wish to be bound by any particular theory, we believe the reason for the improved pressure sensitivity characteristics of the present invention may be explained as follows:

The larger the particle size of the material, the larger will be the voids between the particles. Heat is transferred across the voids by molecules of the residual gas in the insulation space. However, the path of greatest resistance to heat flow is through the individual particles and across the point contacts between the particles. Gas conduction across the voids may, therefore, be viewed as a "short circuit" around the principal resistance. The rate of heat transfer by gaseous conduction is dependent upon the number of molecules present and upon the mean-free-path of molecular motion. Reducing the absolute pressure reduces the number of moles present to transfer heat, and for this reason, a good vacuum is important. However, reducing the absolute pressure will increase the mean-free-path of the molecules and tend to increase gaseous conduction. If the voids are large so that their average dimension exceeds the mean-free-molecular-path, then the adverse effect of increasing the mean-free-path essentially cancels out the beneficial effect of few molecules. For this reason, reducing the absolute pressure will not reduce gaseous conduction until the mean-free-path has lengthened to the point that molecular motion is restricted by the dimensions of the void spaces. This is why extremely low absolute pressures are required in straight vacuum systems or in coarse particle fillers where the dimensions across the void spaces are relatively long. In such systems, a slight increase in absolute pressure not only increases the number of molecules present but also reduces their mean-free-path so that the voids no longer restrict molecular motion. The gas then attains its maximum heat carrying capacity, and the full effect of the "short circuit" by gaseous conduction develops rapidly.

The function of the fine particles in the insulation fillers of this invention is to fill the large voids between the coarse particles which usually comprise about 35% of the total volume occupied by the coarse material. This breaks up the long molecular paths of the gas molecules and eliminates the "short circuit."

Since the fine particles tend to fill the voids between the coarse particles, the addition of the fine material theoretically should not appreciably increase the total volume of the insulation over that occupied by the coarse material alone. However, a slight increase in volume does occur when the fine particles are added, due to at least part of the coarse particles being separated by the fine particles. The number of point contact resistances to heat flow by solid conduction is thereby increased. This results secondarily in a reduction in heat transfer by solid conduction, and thus contributes to the improved performance of these mixtures.

In the mixtures of this invention, the number of point contacts between the coarse bodies is preferably about the same after mixing as before, meaning that there should be minimum "dilution" of the coarse material with the expensive fine material. The extent of such dilution should normally be at least on the order of 5%. Since the voids usually comprise about 35% of the volume occupied by the coarse material, it should not be necessary to add a volume of fine material greater than about 40% of the coarse material alone.

To indicate still more fully the nature of the present invention, the following test results are set forth:

Example I

A double walled vessel was well insulated using a powder-vacuum insulating system. The powder filling material consisted of perlite having an ultimate particle size of approximately 10 microns. The increase in conductivity that occurred during a pressure rise from 150 microns of mercury absolute to 200 microns was $.027 \times 10^{-3}$ B.t.u./hr. ft.^{2} ° F./ft. In a similar test using a powder filling of the invention consisting of a mixture of 85% by weight perlite and 15% silica aerogel (.015 micron ultimate particle size), the change in conductivity was only 0.16×10^{-3} B.t.u./hr. ft.^{2} ° F./ft.

Example II

In a test conducted according to the procedure described in Example I, a powder filling of perlite exhibited a 160% increase in conductivity during a pressure rise from .01 micron absolute to 100 microns, amounting to 1.3×10^{-3} B.t.u./hr. ft.^{2} ° F./ft. In a similar test, a powder filling of 85% by weight perlite and 15% silica (.015 micron) indicated an increase in thermal conductivity of only 60%.

From the results shown, it will be seen that optimum reduction in pressure sensitivity depends on the selection and proportion of the components used in the insulation mixture. The addition of a minor amount of finely divided insulating powder to a coarse base produces a significantly large reduction in gaseous conduction.

Although the invention has been described in terms of a mixture of coarse and finely divided low conductive particles, it is to be understood that the invention is also applicable to a mixture of coarse diameter and fine diameter fiber bodies as well as a mixture of coarse diameter fiber bodies having interspersed therein finely divided low conductive powder. The fibrous bodies may, for example, be formed of glass.

It will be understood that modifications and variations may be effected without departing from the spirit and scope of the novel concepts of the present invention.

This is a continuation-in-part application of copending application, S.N. 683,454, filed September 12, 1957, in the name of L. C. Matsch.

What is claimed is:

1. In a solid-in-vacuum insulation system consisting essentially of a low conductive coarse thermal insulating material selected from the group consisting of perlite, magnesia, glass and mica having ultimate body sizes between about 3 and 1000 microns and being thermally sensitive to changes in pressure, the combination therewith for substantially decreasing its sensitivity to such changes in pressure, of an additive low conductive insulating material selected from the group consisting of silica, calcium silicate and titanium oxide and composed of relatively small bodies disposed in minor amounts in the interstices of said coarse material, said additive insulating material having an average ultimate body size not greater than 1/10 the average ultimate body size of said coarse material, and constituting between about 5 and 40% of the total volume of said coarse insulating material alone.

2. In a solid-in-vacuum insulation system wherein the insulation space is filled with a low conductive thermal

insulating material in coarse form of ultimate body sizes between about 3 and 1000 microns, and selected from the group consisting of perlite, magnesia, glass and mica, and being thermally sensitive to changes in pressure, the combination therewith for decreasing its thermal sensitivity to changes in pressure of a finely divided low conductive silica aerogel insulating material in the interstices of said coarse material in an amount between about 5 and 40% of the volume of the coarse material alone, said finely divided insulating material having an average ultimate particle size not greater than 1/10 the average particle size of said coarse particle material.

3. In a solid-in-vacuum insulation system, wherein the insulation space is filled with a low conductive thermal insulating material in glass fiber form of ultimate fiber diameters between about 3 and 1000 microns, and which is thermally sensitive to changes in pressure, the combination therewith for substantially reducing the thermal sensitivity of said system to changes in pressure of a finely divided low conductive calcium silicate powder in the interstices of said fiber material in an amount between about 5 and 40% of the volume of the fiber material alone, said finely divided calcium silicate powder having an average ultimate particle size not greater than 1/10 the average diameter of said fibers.

4. In a solid-in-vacuum insulating system, the combination of an insulation mixture consisting essentially of a filling of coarse thermally pressure-sensitive material selected from the group consisting of perlite, magnesia, glass and mica and having ultimate body sizes between about 3 and 1000 microns; and a second low conductive thermal insulating material selected from the group consisting of silica, calcium silicate and titanium oxide and composed of relatively small bodies disposed in minor amounts in the interstices of the coarse material, said second insulating material having an average ultimate body size not greater than 1/10 the average ultimate body size of said coarse material and constituting between about 5 and 40% of the total volume of said coarse insulating material alone.

5. In a solid-in-vacuum insulating system, the combination of an insulation mixture consisting essentially of a filling of coarse thermally pressure-sensitive perlite having ultimate body sizes between about 3 and 1000 microns; and finely divided silica aerogel having ultimate body sizes not greater than 1/10 the average ultimate body size of said coarse thermally pressure-sensitive perlite and characterized by relatively constant heat transmittance under varying pressure disposed primarily in the interstices of said perlite, said silica aerogel constituting between about 5 and 40% of the total volume of the perlite alone.

6. A solid-in-vacuum insulating system according to claim 5 in which the mean ultimate boxy size of the perlite particles is between about 3 and 10 microns.

7. In a solid-in-vacuum insulating system, the combination of an insulating mixture consisting essentially of a filling of coarse thermally pressure-sensitive perlite having ultimate body sizes between about 3 and 1000 microns; and finely divided calcium silicate having ultimate body sizes not greater than 1/10 the average ultimate body size of said coarse thermally pressure-sensitive perlite and characterized of relatively constant heat transmittance under varying pressure disposed primarily in the interstices of said perlite, said calcium silicate constituting between about 5 and 40% of the total volume of the perlite alone.

8. A powder-in-fiber insulating mixture consisting essentially of a coarse, low heat conductive, glass fiber material having fiber diameters between about 3 and 1000 microns and having a thermal conductivity sensitive to increases in absolute pressure; and a substantially pressure insensitive, fine, low conductive, silica aerogel insulating powder having body sizes not greater than 1/10 the average ultimate fiber diameter of said coarse glass fiber material and being disposed primarily in the voids of said fiber material, said silica aerogel constituting between about 5 and 40% of the total volume of the fiber material alone.

9. A fiber-in-fiber insulating mixture consisting essentially of a coarse, low heat conductive, glass fiber material having a thermal conductivity sensitive to increases in absolute pressure and fiber diameters between about 3 and 1000 microns; and a substantially thermally pressure insensitive fine low conductive glass fiber material interspersed in said coarse fiber material, and having fiber diameters not greater than 1/10 the average ultimate fiber diameter of said coarse glass fiber material, the fine fibers constituting between about 5 and 40% of the coarse fibers alone.

10. In a solid-in-vacuum insulating system, the combination of an insulating mixture consisting essentially of a filling of a coarse insulating material selected from the group consisting of perlite, magnesia, glass, and mica, having a mean ultimate body size between 3 and 10 microns; and a finely-divided insulating material selected from the group consisting of silica, calcium silicate and titanium oxide, having mean ultimate body sizes not greater than 1/10 the mean ultimate body size of said coarse insulating material and characterized of relatively constant heat transmittance under varying pressure, disposed primarily in the interstices of said coarse insulating material, said finely-divided insulating material constituting between about 5 and 40% of the total volume of the coarse insulating material alone.

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