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INORGANIC BONDED THERMAL INSULATING BODIES AND METHOD OF MANUFACTURE

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This invention relates to handleable, ceramic-bonded heat insulation shapes which have low thermal conductivity comparable to that of free still air, and methods of manufacturing such insulating bodies.

This application is related to copending U. S. patent applications Serial No. 326,791, filed December 18, 1952, and Serial No. 270,748, filed February 8, 1952, the latter of which is a continuation-in-part of our U. S. patent application Serial No. 226,548, filed May 15, 1951, now abandoned.

A primary object of the invention is to provide a high temperature heat insulation shape which is handleable and is retained in its bonded form by a ceramic bonding material, and which contains a maximum number of minute pore spacings between the finest structural units, such spacings averaging effectively below the approximate mean free path of air.

An additional and more specific object is to provide a high temperature ceramic-bonded, handleable heat insulation shape having a thermal conductivity factor k of approximately 0.4 B. t. u./sq. ft./hour/inch/° F. at 1000° F. mean.

Another object of the invention is to provide a ceramic-bonded, handleable heat insulation shape having a chiefly inorganic composition adapted for insulating service at temperatures ranging as high as 1500° F.

With the above and other objects and features in view, the invention consists in the improved thermal insulation material and method of manufacture which are hereinafter described and more particularly defined by the accompanying claims.

An important novel feature of the herein-disclosed thermal insulating shapes is that, in general, the preferred shapes having densities in the range between approximately 8 and 30 lbs./cu. ft. exhibit thermal insulating characteristics comparable to a correspondingly dimensioned volume of free still air which has a thermal conductivity of 0.404 at 1000° F. mean; that is, have a thermal conductivity factor k of less than 0.55 at 1000° F. mean.

It is additionally of particular note that ceramic-bonded, handleable shapes of this invention in the density range indicated have thermal conductivity factors less than corresponding thermal conductivity factors of unbonded loose mass mixtures of essentially the same composition as the bonded shapes, even after such mixtures have been consolidated by vibration to densities equaling the density of the bonded, handleable shapes. Such a phenomenon is entirely unexpected since, in normal instances of bonding together loose insulating particles, the finally formed body has a higher k than a correspondingly dense mass of loose particles. This is usually due, of course, to an increase of the solids conductivity of the mass.

The handleable insulating shapes made according to this invention exhibit the converse of this general consideration. For example, a ceramic-bonded, handleable rigid block of 9.2 lbs./cu. ft. density formed according

to a hereinafter-disclosed procedure from a mixture comprising 5% by weight of amosite asbestos fibers, 60% by weigh of silica aerogel of approximately 95% voids by volume, 30% by weight of zircon particles, and 5% of a temporary phenolic resin binder, was tested to have a k factor of 0.24 at 350° F. mean. A bulk mixture of the same proportions of the silica aerogel and zircon of the type used in molding the ceramic-bonded shape, was vibrated to a density of 9.2 lbs./cu. ft. and tested to have a k factor of 0.26 at 350° F. mean. The asbestos fiber of the block would also increas the solids conductivity, and would thus be expected to increase the k of the consolidated loose mass. It will be appreciated that a loose mass including fiber could probably not be vibrated to such a density, and retain homogeneity.

While this comparison of the thermal conductivities of a loose mass and a block formed in accordance with this invention clearly indicates better insulating characteristics in the block, it is of particular note that even lower thermal conductivities are obtained when the blocks are fabricated to higher densities than that indicated above. It has been found that blocks in the higher density range as, for example, of approximately 15 lbs./cu. ft., exhibit a lower thermal conductivity than blocks of the same composition molded to a density comparable to that set forth above, that is, approximately 9 or 10 lbs./cu. ft.

In our copending application Serial No. 270,748, there are disclosed and claimed thermal insulating shapes of comparable densities and thermal conductivity factors k to the ceramic-bonded insulating shapes of this invention. The preferred insulating shapes disclosed and claimed in our copending application essentially comprise a reinforcing skeleton or network of fine staple reinforcing fibers which may be either organic or inorganic, a substantial amount of particulate filler material having an ultimate structural unit with a diameter finer than 100 millimicrons, such as aerogel or finely divided channel grade carbon black, and an inorganic or organic binder distributed throughout and holding the body in shape-retaining form. A suitable, disclosed binder for such blocks is a thermosetting phenolic-aldehyde resin. We have now found that insulating bodies having the heretofore-mentioned low densities and very low thermal conductivities may be fabricated without such an added binder, and are paricularly suitable for high temperature insulating service.

The preferred insulating shapes according to this invention are composed essentially of a reinforcing skeleton or network of fine staple reinforcing fibers which may be either organic or inorganic; a substantial amount, and preferably at least 40% by weight of a particulate filler material having a porous or fibrillate structure, such as aerogels of, for example, silica, chromic oxide, thoria, magnesium hydrate, alumina, and mixtures thereof; and a ceramic binder having a composition comprising the heat reaction product of the ingredients initially present in the aerogel particles. For most kinds of insulation service, it is desirable to include in the composition finely divided opacifier materials.

The aerogel particles utilized to form the ceramic-bonded insulating shapes of this invention are formed by a procedure generally similar to that outlined in the patent to Kistler, No. 2,093,454. The method generally comprises forming a gel, confining the resulting product in a pressure vessel, applying heat thereto until the liquid in the gel has reached a temperature at which the surface dimension of the liquid is so small as to produce no substantial shrinkage of the gel when the liquid is allowed to evaporate, maintaining such a temperature, and then releasing the vapor from the pressure vessel at

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a rate insufficient to injure the gel. Dry, porous, fibrillate aerogel particles are thus obtained. The composition of these aerogels is substantially that of the materials forming the gel. For example, the composition is almost entirely silica when a silica gel is used as the starting material. The particles also evidently contain, however, impurities comparable to those found in the gel. While not limiting ourselves to any particular theory, it is considered that aerogel particles, such as silica aerogel, contain residual impurities in the form of soluble salts such as sodium sulphate and the like formed as reaction products during the formation of the gel. When the molded blocks of this invention formed by the processes as hereinafter disclosed are heated to a sufficient degree, a ceramic bond is formed in the block, probably due to a sintering of the aerogel or an incipient ceramic reaction between the aerogel and the salts present therein, or possibly both. This phenomenon is utilized to obtain the ceramic-bonded low conductivity insulating shapes of this invention.

Staple reinforcing fibers suitable for use in the insulating shapes of this invention may comprise such materials as various types of asbestos fibers of reinforcing grade, cleaned mineral fibers, fine diameter glass fibers, preferably pretreated, as with acid, to roughen the surface or otherwise to improve the surface adhesion characteristics, heat-stable organic fibers such as acrylic fibers which have been treated to render them heat-stable, or mixtures thereof.

The preferred inorganic fiber is a well-opened fine staple amosite asbestos classifying as to length not less than at least 25% longer than ¼". All of such fibers should preferably classify finer than 20 microns diameter and further finer than 10 microns. The amount of fiber present in the bonded insulation shape is usually small but may vary over a considerable range, depending upon the strength requirements for the particular insulation service. The fiber content preferably comprises up to 15% by weight, and normally approximately 5% by weight of the insulating shape is used.

As heretofore indicated, the low conductivity insulating shapes of this invention must contain a substantial amount of a particulate filler material having the structural and chemical characteristics which are necessary to this invention. The particulate filler material is exemplified by aerogels such as those of silica, chromic oxide, thoria, magnesium hydrate, alumina, etc., and mixtures thereof. Such aerogels in particle form have a "straw stack" agglomerate fibril structure, with the fibrils composing the ultimate or finest structural unit of diameter finer than 100 millimicrons. The average aerogel particles should embrace a total void or dead air space of 75–99% by volume, and may be treated to render them hydrophobic in nature.

The amount of particulate filler material of the above-defined nature which must be utilized is dependent upon the nature of the insulating shape formed and its desired use. For many purposes, the insulating bodies may contain from 40–95% by weight of such filler particles. When the shapes are to be utilized for high temperature insulation, the preferred proportion is approximately 40–75% by weight, and a substantial amount of opacifying material is used.

Below 150° F., the opacity of an aerogel, such as silica aerogel, is usually adequate for insulating against heat transfer by radiation. However, above this temperature, the insulating shape should be composed in part of finely divided opacifiers, preferably of inorganic composition. These opacifiers may be of the radiation reflective type, such as metallic aluminum or silicon powder; of the radiation absorbing type, such as powdered metals or finely divided pigments, as for example, chromium oxide; or of the radiation scattering type, such as zircon, titanium dioxide, or other materials of high index of refraction in the infrared. These opacifiers may advantageously be used as an opacifier for the aerogel fillers in amounts up to 125% by weight of the total aerogel particle content of the shape. It will be appreciated that the amount of opacifier required is usually determined by the severity of the radiation problem, which increases with the increase in temperature. Since the blocks of this invention are particularly adapted for high temperature use, the radiation problem will be serious and relatively large amounts of opacifier should be used.

As heretofore indicated, the ceramic binder utilized in the low conductivity insulating shapes of this invention does not require the addition of other than the aforesaid ingredients to the composition; that is, no binder materials are required in the finally fabricated insulating shape which are not present as part of the composition of the aerogel particles.

The ceramic bond of the herein disclosed-insulating shapes may be formed by either of two methods. In both methods the various components used to form the insulating shape are intimately mixed by any suitable mixing procedure to obtain a thorough dispersion and intermixing of all ingredients.

In the first method, aerogel particles, the fiber, and opacifier, if used, are intimately mixed to develop a particle-filled fibrous mass. This mass is then moisturized by treatment in a humidifying chamber. In the chamber, the mass is exposed to a gas with a relatively high humidity and an elevated temperature, for example, air with a relative humidity of 90–95% and a temperature of 100° F. The mass is exposed to the humidified gas for a sufficient time to enable it to adsorb some moisture, and preferably approximately 2–35% by weight of said particles. It will be appreciated that the amount of moisture required to be adsorbed is dependent upon that required to give the shape its "green" strength, that is, to enable the formation of an initial handleable "green" body upon molding, which in turn is dependent upon the density of the molded body. For example, "green" bodies having densities of approximately 13 lbs./cu ft., have been fabricated employing only approximately two percent moisture. The maximum amount of moisture which may be employed is dependent upon the consideration that the insulating characteristics of the final product must be obtained, and thus the aerogel structure may not be destroyed.

The resultant humidified or "wetted" mixture may then be pressed, with or without heat, to the desired shape and to a density sufficient to form a handleable, self-sustaining "green" body. The final ceramic-bonded, handleable low conductivity insulating shape is then obtained by heating the thus formed shape for a time and at an elevated temperature sufficient to develop the ceramic bond, apparently by a partial sintering and/or a reaction between the impurities present in the aerogel, as, for example, between the sodium sulphate and the silica itself, in a silica aerogel. This temperature should preferably be approximately 1000° F., and temperatures from approximately 600 to 1600° F. have been utilized successfully with silica aerogel compositions.

The second method for forming the ceramic-bonded insulating shapes of this invention is generally similar to the foregoing. In this procedure a mixture of aerogel particles, fiber, opacifier, and a thermally decomposable temporary binder is intimately mixed to obtain a particle-loaded, fibrous network mass.

Any suitable temporary binder may be utilized which has the characteristics of rendering to the mass a handleable shape upon the intial forming and the capability of being burned out of the shape at the sintering temperature. Most organic binders, such as common thermosetting resins, as, for example, phenol- or urea-formaldehyde, and common thermoplastic resins such as vinyl chloride, vinyl chloride-acetate copolymers, or silicons, have these de-

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sired characteristics. The temporary binder is utilized in an amount sufficient to render the initially formed shape handleable for all future manufacturing procedures, and should be capable of obtaining its shape-retaining form under the conditions utilized to obtain the initially formed shape.

When the temporary binder is utilized a light, fluffy mass is formed by intimately mixing the aerogel particles, fiber, and binder, preferably in dry particulate form. The mass is then subjected to sufficient heat and pressure to obtain the desired density and to set or cure the binder to its shape-retaining form. The thus formed temporarily bonded, handleable shape is then heated to a sufficiently high temperature to burn out the temporary binder and develop the ceramic bond as heretofore disclosed. It is of particular note that a substantially lower thermal conductivity is obtained in a burned out body formed in accordance with this procedure and containing a relatively large amount of thermally conductive opacifier particles than that found for the temporarily bonded body use in its formation. This is apparently due to the destruction of thermally conductive bridges of temporary binder between opacifier particles.

In either or both of the aforementioned procedures, the intimately mixed light and bulky mass can be molded and set to a shape of any desired conformation and density. Suitable "green" bodies may be obtained by molding the mass in a conventional press mold, utilizing suitable pressures and/or temperatures to either activate and develop a set for the temporary binder, or to develop a set in the moisturized shape. Such bodies may also be obtained by uniformly distributing, i. e. felting, and consolidating the fluffy mass in known manner and then heating the thus consolidated mass to obtain a handleable shape.

Excellent thermal insulating shapes have been produced according to this invention having densities in the range of 8 to 30 lbs./cu. ft. with thermal conductivities, or k factors, approximating 0.35 to 0.55 at 1000° F. mean. As heretofore indicated, the preferred insulating shapes have a thermal conductivity factor k of approximately 0.4 at 1000° F. mean; that is, the preferred shapes formed according to this invention have insulating characteristics comparable to free still air. Opacified shapes having the essentially inorganic compositions which are set forth above are adapted for insulating service for temperatures up to 1500° F. The ceramic-bonded insulating shapes have ample strength characteristics and handleability for subsequent insulating service. For example, a ceramic-bonded insulating shape formed from a composition approximately comprising 5% by weight of amosite fibers, 75% by weight of silica aerogel, 15% by weight of zircon, and 5% by weight of thermosetting resin temporary binder, and having a density of 13 lbs./cu. ft. was found on test to develop a transverse modulus of rupture of approximately 25 lbs./sq. in.

The following are examples of various ceramic-bonded insulating shapes of low thermal conductivity, and their general method of preparation. It is understood, of course, that the compostion of, and methods for producing, these blocks are exemplary and are not to be considered to limit the invention to the particular compositions and operating conditions outlined. In all examples the indicated proportions of ingredients are in parts by weight.

Example I

A strong, ceramic-bonded thermal insulating shape was formed by molding with sufficient heat and pressure to set the resin, an intimately dispersed mixture of:

Silica aerogel	55
Zircon	40
Amosite asbestos fiber	5
Phenol-formaldehyde resin	5

The thus formed "green" shape was then heated for approximately one hour at 1200° F. to completely burn out the resin and to develop the desired ceramic bond. The ceramic-bonded shape obtained had a density of approximately 16 lbs./cu. ft. and a thermo conductivity factor k of 0.37 at 1000° F. mean, and 0.29 at 700° F. mean.

Example II

A strong, ceramic-bonded thermal insulation shape was formed by humidifying, with air at 90° F. and 95% relative humidity, to a 10% moisture content an intimately dispersed mixture of:

Silica aerogel	55
Zircon	40
Amosite asbestos fiber	5

and then molding a "green" body of this composition with sufficient pressure to obtain a handleable shape. The thus formed "green" shape was heated for approximately one hour at 1200° F. to develop the desired ceramic bond. The ceramic-bonded shape obtained had a density of approximately 17 lbs./cu. ft. and a thermal conductivity factor k of 0.22 at 350° F. mean, and 0.4 at 1000° F. mean.

In order to determine the characteristics of the bonding medium utilized in accordance with this invention, a series of insulating bodies having a density of approximately 20 lbs./cu. ft. were molded from a humidified mixture containing 85 parts of silica aerogel and 10 parts of zircon opacifier. Half of the blocks fabricated were fired at 1400 F. as herein disclosed, while the remainder were tested in an unfired condition. Standard test conditions indicated a modulus of rupture of approximately 13.4 lbs./cu. ft. for the unfired blocks, while the fired blocks were found to have a modulus of rupture of 24.0 lbs./cu. ft. A comparison of these moduli of rupture immediately indicates substantially greater strength in the fired blocks fabricated in accordance with this invention, which must be due to the bonding medium formed during the firing procedure.

It will be understood that the details given herein are for the purpose of illustration, not restriction, and that variations within the spirit of the invention are intended to be included in the scope of the appended claims.

What we claim is:

1. A ceramic-bonded, handleable insulating body having a density of less than approximately 30 lbs./cu. ft. and a thermal conductivity factor k of less than approximately 0.55 at 1000° F. mean, comprising heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of inorganic aerogel particles containing a total void space of approximately 75 to 99% by volume, finely divided opacifier particles, and a ceramic binder distributed throughout said body essentially comprising the heat reaction product of the ingredients initially present in said aerogel particles.

2. A ceramic-bonded, light weight, handleable insulating body having a low thermal conductivity, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of inorganic aerogel particles, and a ceramic binder distributed throughout said body essentially comprising the heat reaction product of the ingredients initially present in said aerogel particles.

3. A ceramic-bonded, light weight, handleable insulating body having a low thermal conductivity, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of inorganic aerogel particles, finely divided opacifier particles in amount up to approximately 125% by weight of said aerogel particles, and a ceramic binder distributed throughout said body essentially comprising

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the heat reaction product of the ingredients initially present in said aerogel particles.

4. A ceramic-bonded, handleable insulating body having a density of less than approximately 30 lbs./cu. ft. and a thermal conductivity factor k of less than approximately 0.55 at 1000° F. mean, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of inorganic aerogel particles, and a ceramic binder distributed throughout said body essentially comprising the heat reaction product of the ingredients initially present in said aerogel particles.

5. A ceramic-bonded, handleable insulating body having a density of less than approximately 30 lbs./cu. ft. and a thermal conductivity factor k of less than approximately 0.55 at 1000° F. mean, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of inorganic aerogel particles, finely divided opacifier particles in amount up to approximately 125% by weight of said aerogel particles, and a ceramic binder distributed throughout said body and essentially comprising the heat reaction product of the ingredients initially present in said aerogel particles.

6. A ceramic-bonded, light weight, handleable insulating body having a low thermal conductivity, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of silica aerogel particles, and a ceramic binder distributed throughout said body essentially comprising the heat reaction product of the ingredients initially present in said silica aerogel particles.

7. A ceramic-bonded, light weight, handleable insulating body having a low thermal conductivity, which comprises heat-stable, staple reinforcing fibers in amount sufficient to form a reinforcing skeleton up to approximately 15% by weight, approximately 40 to 95% by weight of silica aerogel particles, finely divided opacifier particles in amount up to approximately 125% by weight of said aerogel particles, and a ceramic binder distributed throughout said body essentially comprising the heat reaction product of the ingredients initially present in said silica aerogel particles.

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