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EXTRUDABLE REFRACTORY FIBROUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

A refractory fibrous product composed of refractory fibers coated with a lubricating layer of aluminum metahydroxide whereby the coated fibers form an injectable and extrudable paste, and process for producing same.

BACKGROUND OF THE INVENTION

This invention relates to a unique refractory fibrous product useful, for example, as insulation, filtering material and filler, and method of forming same, wherein refractory fibers are formed into a semi-fluid injectable and extrudable product having an aluminum metahydroxide coating or binder affixed to the refractory fibers in such a manner that the binder cannot be displaced by pressure. Accordingly, the fibrous mass can be injected under pressure to form a product of required densities without the loss of either fiber or binder, thereby permitting the product to be applied by compressed air or hydraulic guns in pre-selected and formed spaces.

The product of this invention represents a definite and substantial improvement over the present art wherein such refractory fibrous materials cannot be handled in the manner of an extrudable caulking material, because when wetted by heretofore used binders the resultant mass becomes physically compound of wads, pills and lumps of refractory fibers, from which the binder would separate and thereby be lost when the mass was subjected to pressure such as encountered in extrusion. Accordingly, such presently known refractory fibrous materials are limited to applications where expensive and slow ramming and tamping techniques are employable.

SUMMARY OF THE INVENTION

From the foregoing, it will be recognized that it would be desirable to have a refractory fibrous product which it readily extrudable and which can, therefore, be employed in applications where it is either impossible, or impractical to position and secure the fibrous mass by the use of physical restraints or adhesives. For example, a product which due to its putty or paste-like form can be quickly and easily injected into a cavity, such as that formed between the inner and outer walls of an engine exhaust manifold reactor. Thus, this invention permits the use of refractory fibrous materials in conjunction with assembly line techniques. The product of this invention means that refractory fibers are no longer limited to those

applications where expensive and time consuming ramming or tamping applications are employable.

Accordingly, it is the principal object of this invention to provide refractory fibers in the form of an injectable and extrudable paste.

Other objects and advantages of the present invention will become apparent from a further reading of the description and appended claims.

According to the present invention, a unique and desirable extrudable product is provided composed of a ceramic fiber, which makes up the bulk of the product, and a unique ceramic lubricating binder coating affixed to the ceramic fibers. It is the presence of this lubricating binder which is actually physically affixed to the ceramic fiber that makes for the unique product and which represents the significant departure from heretofore known refractory fibrous products. In the product of the present invention, the lubricant binder is affixed to the fibers so that it is not displaced by pressure, thereby providing the extrudability of the product. In contrast, heretofore known refractory fibers were bound together by components such as water or water base cements which were not affixed to the fibers and which, therefore, would separate from the refractory fibers during squeezing or compaction.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The product of this invention comprises an extrudable refractory fibrous cement of refractory fibers coated with a lubricating layer of aluminum metahydroxide. The term "cement" is used to denote a soft putty-like or plastic mass which hardens and forms a firm solid mass. The product of the invention is not an adhesive, however, and the term "cement" is not used to imply adhesive properties.

The fiber component used in this invention is not critical and thus the term "refractory fiber" refers to fibers which are synthetic or natural in origin. Suitable inorganic fibers include all the naturally occurring mineral fibers such as asbestos and related silicate fibers. Suitable synthetic inorganic fibers include glass fibers, aluminoilicate fibers, amorphous siliceous fibers, fibers of potassium titanate, and mineral fibers made from molten rock, as for example, rock wool and asbestos.

In general, any natural or synthetic inorganic fiber containing compounds of silicon, aluminum or titanium, such compounds being present in a particular fiber either singly or in combination with each other, can be used in this invention and such fibers are referred to hereinafter as refractory fibers. Especially preferred fibers for use in this invention are those marketed under the names of J–M Fiberchrome, Fiberfrax, Kaowool and Barikaid, by The Johns-Manville Company, Carborundum Company, Babcock and Wilcox Company and Norton Company, respectively. In this application these materials are referred to as aluminosilicate fibers and the chemical and physical properties of these materials are as follows:

COMPOSITION OF COMMERCIAL FIBERS—(BULK)

	Fiberchrome	Fiberfrax	Kaowool	Barikaid
Al_2O_3	40.5	51.2	45.1	45.1.
SiO_2	55.0	47.4	51.9	51.9.
B_2O_3		0.7	0.08	0.08.
Na_2O	0.15	0.7	0.2	0.2.
Fe_2O_3	0.21		1.3	1.3.
TiO_2			1.7	1.7.
CaO			0.1	0.1.
Cr_2O_3	4.0			
Melting point	>3,200° F.	>3,200° F.	3,200° F.	3,200° F.
Fiber length		To 1½"	To 10"	To 10".
Specific gravity		2.73		2.56.
Bulk density	3 to 6 #/ft.³	4 #/ft.³	3–12 #/ft.³	3–12 #/ft.³.
Use temp	To 2,700° F.	To 2,300° F.	To 2,300° F.	To 2,300° F.
Fiber diam			2.8 microns	2.8 microns.
Specific heat at 1,800° F	0.27 B.t.u./lb./F.			0.255 B.t.u./lb./F.
Hardness				6-MOH's scale.
Tensile strength (fiber)				1.9×10^6 lbs./sq. in.

The exact dimensions of the fibers used in this invention are not critical and may range from a few millimeters to several inches in length and from a few millimicrons to several thousandths of an inch in thickness. The fibers used in any given product will be selected from a consideration of the properties desired in the finished product, and mixtures of fibers can be used.

As set forth above, the product of this invention is unique in that the refractory fiber component has affixed thereto a lubricating layer of aluminum metahydroxide AlO(OH). This material is employed in an aqueous dispersion and, hence, should be of fine physical size to facilitate its dispersion. While either fibrous or granular form is suitable, a fine free flowing powder is preferred. Excellent results have been achieved with the use of Dispal which is marketed by the Continental Oil Company and which has the following analysis: 88 wt. percent aluminum metahydroxide, 10 wt. percent free moisture, 2 wt. percent alcohol. This product is a fine free flowing powder (90%<40 micron) with ultra fine ultimate crystallites (0.01 micron), a high surface area (160 $m.^2/gm.$) and a bulk density of about 45 lbs. per cubic foot.

The product of the present invention is produced by preparing a colloidal sol of aluminum metahydroxide through the slow and careful addition of a quantity of aluminum metahydroxide to water which contains an acid. The amount of aluminum metahydroxide employed should be between about 1 to 50 percent by weight of the water in the colloid. A preferred amount is about 10 percent by weight of water. The type of acid is not critical and literally any acid can be used. The function of the acid is to aid in suspending the aluminum metahydroxide in the water and to insure that the individual aluminum metahydroxide particles agglomerate as little as possible. It has been found that this is accomplished if sufficient acid is present such that the pH of the colloidal sol of aluminum metahydroxide is no greater than about 6.9 and no less than about 2. Again, while the choice of acid is not critical, it is desirable to use an acid which provides some degree of buffering and which would bake out of the product with a minimum of residue. It has been found that a combination of acetic and sulfuric acids gives usually good results in this invention when used in a proportion of acetic to sulfuric of about 10 to 1 by weight.

After the aqueous acidic colloidal suspension of aluminum metahydroxide is prepared, the refractory fiber is added thereto with stirring. The amount of fiber dispersed in the colloidal suspension will, of course, depend upon the application for the product and nature of fiber employed. In general, the amount of fiber added is from about 10 to 45 percent by weight of the water in the aqueous acid colloidal suspension, and an excellent extrudable product has been obtained using about 30 weight percent of fiber.

Experience has shown that the refractory fiber tends to pill or matt and form small clusters and lumps when added to the aqueous acidic colloidal suspension. While such pilling can be controlled through slow addition of the fiber and careful stirring or mixing it has been discovered that pilling may be avoided with greater ease and certainty by providing a small amount of a lubricant in the aqueous acidic colloidal suspension prior to the addition thereto of the refractory fibers. While employment of a lubricant is not essential to this invention, the use of water soluble organic lubricants which will burn out or vaporize at a temperature less than about 500° F. have given good results in preventing pilling when used in an amount in the range of about 0.01 to 1 percent by volume of water in the aqueous acidic colloidal suspension of aluminum metahydroxide. Examples of such a lubricant are gum arabic, gum tragacanth, soaps such as sodium stearate and sodium oleate, and ethylene glycol. A preferred lubricant in this invention is glycerin.

The extrudability of the refractory fibers is realized only when the fibers are well dispersed and are coated uniformly by the aqueous acidic suspension of aluminum metahydroxide. Moreover, the amount of fiber that can be added to the suspension will be controlled by the wettability of the water. Thus, it is advantageous, although not necessary, in the preparation of the product of this invention to employ a surface active agent. By so doing, the amount of water required to make a satisfactory mix can also be cut down which, in turn, reduces the drying shrinkage of the insulation. Again, the type of surface active agent is not critical as long as it does not disturb the colloidal nature of the aluminum metahydroxide. Surface active agents are generally organic compounds and, it is suggested that a compound be selected which will vaporize or burn out with little residue at a temperature less than about 500° F. In this way, the surfactant can be driven off leaving a totally inorganic product. In practice, the surface active agent is added to the aqueous acidic colloidal suspension prior to the fiber addition and in an amount in the range of about 3 to 10 percent by weight of the refractory fiber to be added. Preferred surfactant compounds are the Pluronic materials such as Pluronic L62 which are marketed by the Wyandote Chemical Corporation. Such surfactant compounds are fully disclosed in U.S. Pat. 2,674,619.

After thoroughly blending the refractory fiber and colloidal suspension to completely and uniformly coat the refractory fibers with acidic suspension, the mass is neutralized, that is, brought to a pH of about 7, by the addition thereto of a base. Any base material can be used and good results have been achieved with ammonium hydroxide and sodium hydroxide. The neutralization step is most critical to the invention as it has been found that the neutralization physically transfers the aluminum metahydroxide from suspension to the surface of the refractory fibers where it adheres tightly thereto.

The following example illustrates a preferred method of preparing the extrudable refractory fiber product of this invention.

EXAMPLE

One hundred cubic centimeters of glycerin (100 cc.), 75 grams of acetic acid and 6 grams of sulfuric acid were added to ten thousand cubic centimeters (10,000 cc.) of distilled water. Nine hundred grams (900 grams) of Dispal (aluminum metahydroxide) were then slowly added to the aqueous glycerin solution which was continuously stirred by hand. After all the Dispal had been added, the mixture was machine stirred for three minutes at low speed and then stirred at medium machine speed for an additional one-half minute to yield an aqueous acidic suspension of aluminum metahydroxide. The suspension was continuously stirred and one hundred ten cubic centimeters (110 cc.) of Pluronic L62[1] was added followed by fifteen hundred grams (1500 gms.) of aluminosilicate (Kaowool). After stirring for about four minutes, a second fifteen hundred gram batch (1500 gms.) of Kaowool was added and stirred for another four minutes. Lastly, one hundred cubic centimeters (100 cc.) of distilled water and one hundred cubic centimeters (100 cc.) of concentrated ammonium hydroxide were mixed and added to the suspension coated Kaowool thereby neutralizing the fibrous mass and producing a remarkable extrudable product.

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[1] Pluronic L62 has the polyether molecular structure

$$HO(CH_2-CH_2-O)_b\left(\begin{matrix}CH-CH_2-O\\ |\\ CH_3\end{matrix}\right)_a(CH_2-CH_2-O)_b$$

It is a liquid material having a total molecular weight of 2500 of which the ethylene oxide comprises 20%, a specific gravity 25/25° C. of 1.03 and a Brookfield viscosity at 25° C. of 400 cps.

If desired, a small amount of organic binder such as polyvinyl alcohol can be added to the semi-fluid, paste like extrudable mass. Such an addition will provide rigidity to the product upon its being dried and the product will not be detrimentally affected by such addition.

The semi-fluid, extrudable paste refractory product of this invention has found wide application as insulation in turbine engines as, for example, in the burner cap component. Moreover, the product of this invention has been successfully extruded through a one-quarter inch orifice, as well as at pressures ranging from about 15 to 100 pounds per square inch through a one-half inch orifice.

In summary, it can be seen that a unique and desirable product has been provided, namely a fibrous mass, comprised of refractory fibers coated with aluminum metahydroxide which can be injected into place with a device such as a compressed air caulking gun at pressures up to about 100 pounds per square inch. The product of this invention may also be laid up by hand, by knife or by vacuum. Once applied, it is treated in the manner normal to the refractory fiber insulation art, i.e., it is baked dry and then fired to dehydrate the aluminum metahydroxide. Its final performance is superior because the known and pre-selected amount of aluminum metahydroxide has been fully retained and not diminished or rendered un-workable by the process of application.

We claim:

1. An extrudable refractory fibrous paste of refractory fibers coated witha lubricating layer of aluminum metahydroxide produced in the absence of heating by adding said refractory fibers to an aqueous acidic colloidal suspension of aluminum metahydroxide, said suspension having a pH in the range of about 2 to 6.9 and containing from about one to fifty percent by weight of water in said suspension of aluminum metahydroxide, dispersing said refractory fibers in said aqueous suspension and then transferring through neutralization said aluminum metahydroxide from said colloidal suspension to the surface of said fibers by adding a pH adjusting agent to the dispersible fibers to neutralize the wetted refractory fibers. ~~fractory fibers.~~

2. An extrudable fibrous aluminosilicate paste of aluminosilicate fibers coated with aluminum metahydroxide produced by adding said aluminosilicate fibers to an aqueous acidic colloidal suspension of aluminum metahydroide, said suspension having a pH in the range of about 2 to 6.9 and containing from 1 to 50 percent by weight of water in said suspension of aluminum metahydroxide and from about 0.01 to 1 percent by volume of water in said suspension of an organic lubricant, dispersing said aluminosilicate fibers in said aqueous suspension and then transferring the aluminum metahydroxide to the surface of the fibers by adding a pH adjusting agent to the dispersed fibers to neutralize the wetted aluminosilicate fibers.

3. An extrudable cement product according to claim 2 wherein organic lubricant in said aqueous acidic colloidal suspension is glycerin.

4. An extrudable cement product according to claim 2 wherein the aluminosilicate fibers are added to said aqueous acidic colloidal suspension in an amount of about 10 to 45 percent by weight of water in said suspension.

References Cited

UNITED STATES PATENTS

2,593,818	4/1952	Waggoner	117—126 GI
2,917,426	12/1959	Bugosh	117—126 GI
3,013,903	12/1961	Bugosh	117—126 GI
3,150,034	9/1964	Vukasovich et al	117—126 I
3,346,186	10/1967	Fulton et al.	117—126 GI

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