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AQUEOUS COMPOSITIONS OF ALKALI METAL TITANATE FIBERS AND POLYVINYL ALCOHOL

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This invention relates to insulating compositions comprised of alkali metal titanates.

In U.S. Patents 2,833,620 and 2,841,470, it is disclosed that a new class of water-insoluble fibrous alkali metal titanates can be synthesized. These fibrous titanates are asbestos-like in character, and they have proved to be a unique insulation material having exceptional ability to diffuse and reflect infrared radiation.

In many instances, these alkali metal titanate fibers are used for insulating purposes in loose form. On the other hand, it is also desirable to be able to utilize the fibers in sheets or blocks of a desired configuration. The present invention is therefore concerned with a means for forming alkali metal titanates into any desired shape. This means resides in a novel composition comprising a liquid suspension of alkali metal titanate fiber in polyvinyl alcohol and water. By controlling the amount of water in the composition, the consistency of the suspension can be adjusted so that it can be molded, extruded, troweled, brushed, or sprayed. Upon removal of the water by drying, a rigid insulating medium in a desired shape is obtained. Drying may take place in the normal atmosphere or, if desired, temperatures up to 100° C. may be used. Also, if desired, the polyvinyl alcohol and any other organic material present may be removed by heating in air at elevated temperatures, usually within the range of 300° C. to 1100° C., whereupon there remains the alkali metal titanate. The compositions of this invention differ from other compositions comprised of alkali metal titanate and a binder in that the compositions of this invention possess the unique property of having negligible shrinkage upon drying and heating.

The compositions of this invention are formulated on a weight basis, and they comprise alkali metal titanate fibers, polyvinyl alcohol, and water. The weight ratio of polyvinyl alcohol to alkali metal titanate fiber is in the range of about 0.25:1 to about 1.5:1. The amount of water present in the composition is not at all critical and will depend upon the consistency desired in the composition. Usually, the weight ratio of water to alkali metal titanate fibers is in the range of about 0.1:1 to about 25:1.

In a more restricted embodiment of this invention, the compositions comprise alkali metal titanate fibers and polyvinyl alcohol in amounts such that the weight ratio of polyvinyl alcohol to titanate fibers is in the range of about 0.5:1 to about 1:1. The water in such a composition may be adjusted to give whatever consistency is desired. Usually, the amount of water to titanate fibers is in a weight ratio of from about 1:1 to about 10:1.

In a preferred embodiment of this invention, the compositions comprise alkali metal titanate fibers and polyvinyl alcohol in amounts such that the weight ratio of polyvinyl alcohol to titanate fibers is in the range of about 0.5:1 to about 0.6:1. As previously mentioned, the water content may be adjusted to give whatever consistency is desired. Preferably, the weight ratio of water to titanate fibers is from about 3:1 to about 5:1.

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The alkali metal titanate fibers used in this invention are those of the alkali metals having an atomic number of at least 11. These fibers are asbestos-like in character, and the ratio of length to width of such fibers is at least 5:1 and generally in the range of 10:1 to 100:1. Such fibers can also have a length-to-width ratio of up to 1000:1 or higher. These titanates are described in the aforementioned U.S. Patents 2,833,620 and 2,841,470. The titanates of these patents that are suitable for this invention are those having the empirical formula

$$M_2(Ti_nO_{2n+1})$$

where M is an alkali metal having an atomic number of at least 11 and n is in the range of 6 to 7, both limits included. A preferred material is potassium titanate of the formula

$$K_2Ti_6O_{13}$$

Sodium titanate fibers could also be used in this invention as well as other alkali metal fibers, but these are less practical because of their limited availability and high cost.

Alcohols useful in this invention are commercially available products. These products are produced from the hydrolysis of the acetoxy groups in polyvinyl acetate. Such alcohols are classified according to the percentage of hydrolysis which has taken place in the polyvinyl acetate and by their viscosity in a 4% water solution at 20° C. Any reference to viscosity hereinafter means the viscosity of the polyvinyl alcohol in a 4% water solution at 20° C. Alcohols ranging in viscosity from 4–65 centipoises and having a hydrolysis ranging from 87–100% are useful in this invention. A preferred polyvinyl alcohol is one having a viscosity of 21–25 centipoises and a hydrolysis in the range of 87–89%. An alcohol having a viscosity of 55–65 centipoises and a hydrolysis of 99–100% would also be useful. Also, it is contemplated to use an alcohol having a viscosity of 28–32 centipoises and a hydrolysis of 99–100%. Another polyvinyl alcohol that may be used is one having a viscosity of 4–6 centipoises and a hydrolysis of 88–89%.

The water used to form the compositions of this invention should be free of ions, i.e., one should use deionized or distilled water. As previously pointed out, the amount of water used may vary over a wide range depending upon whether the composition is to be molded, extruded, troweled, brushed, or sprayed. For such uses, water is added to give a consistency ranging from a thick paste to a slurry having the characteristics of a thin liquid. When the composition is to be sprayed, the water content is high and the weight ratio of water to titanate fibers may be as high as 25:1. In a brushing formulation, the ratio of water to titanate fibers is usually in the general area of 10:1, and in a material which is to be extruded, it would be common to use a water-to-titanate ratio of 1:1. In troweling pastes, the water-to-fiber ratio is usually in the general area of about 3:1 to 5:1. It is also contemplated to prepare a solution suitable for spraying and to spray dry such a material at temperatures up to 100° C. so that the water content of the composition is very low, e.g., a weight ratio of water to titanate of as low as 0.1:1. This procedure causes the individual fibers to be coated with the polyvinyl alcohol, and such a composition is a very suitable one for storage and shipping purposes. Water necessary to give a desired consistency can be added when the material is ready for use.

In a preferred embodiment of this invention, it is contemplated to replace up to 10% (by weight) of the alkali metal titanate fibers with another inorganic fibrous insulating material. Fibrous aluminum silicate is a preferred material for this purpose. However, it would also be possible to use asbestos, rock wool, fibrous SiO_2, and the like. It has been found that the compositions of this invention containing up to 10% fibrous aluminum silicate have improved strength at elevated temperatures, while still retaining good insulating characteristics. When these other inorganic fibrous insulating materials are used, the weight ratio of polyvinyl alcohol to fiber and the weight ratio of water to fiber are calculated on the basis that the substituted insulating material is alkali metal titanate. A particularly preferred composition according to this invention is comprised of a fibrous mixture composed of at least 90% potassium titanate fibers and up to 10% of fibrous aluminum silicate. The polyvinyl alcohol used in such a mixture is such as to give a weight ratio of alcohol to total fiber weight of about 0.5:1 to about 0.6:1, and the ratio of water weight to total fiber weight is in the range of about 3:1 to about 5:1.

In preparing the compositions of this invention, it is preferable to first make a mastermix composition by dissolving polyvinyl alcohol in hot water, preferably of low mineral content, to prepare a stock solution containing about 12.5 to 14% polyvinyl alcohol. To this is added a compatible fungicide for mold prevention while the paste is being stored. Titanate fibers are admixed in a kneading mill with the alcohol solution and additional water depending upon the concentration of the alcohol solution. Various consistency pastes are obtained by regulating the pressure in the mill. By evacuating to a range of from 1 to 55 mm. of Hg in the mixer, a dense paste is formed which contains no entrapped air bubbles. If the paste is to be used as a cement, the absence of air bubbles is desirable since a dense mat of fibers between titanate blocks has greater strength. Better insulation properties are found when pastes are kneaded at atmospheric pressure in the presence of air so that entrapment of air takes place in the paste. However, lower strength is a result of voids in the fiber mat.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not in limitation thereof.

Example I

The composition prepared according to the procedure outlined below is a troweling paste in which the weight ratio of polyvinyl alcohol to potassium titanate fibers is 0.6:1 and the weight ratio of water to potassium titanate fibers is 4:1.

Into a three-liter steam-jacketed vessel was placed 1720 grams of deionized water and heated to 95° C. to 100° C. To this was added slowly 280 grams of commercial polyvinyl alcohol which was produced by the hydrolysis of polyvinyl acetate to an extent of 87–89% to the alcohol and having a viscosity of 21–25 centipoises in a 4% water solution at 20° C. The alcohol was added to the hot water with gentle stirring so that the solid was completely wetted and did not float on the surface. As the solution became viscous, a high-speed propeller-type agitator was used for 10 minutes after the addition was completed. This solution was then heated at 95–100° C. in the covered vessel for two hours, after which it was cooled rapidly by running cold water through the jacket of the vessel.

When the solution had cooled to 30–40° C., one milliliter of 37% formaldehyde was admixed into the alcohol solution with gentle stirring. At no time was the agitation so vigorous that entrapment of air bubbles took place.

The alcohol-water mixture was then transferred to a 3-quart "sigma" bladed kneading mill which could be operated at low pressure. The mixer used was a 3-quart

Baker-Perkins type vacuum mill. Fibrous potassium titanate (468 grams) having the following characteristics was placed in the mill along with 214 grams of water.

Av. diameter, microns	1
Length after dispersion, mm.	0.2 to 0.5
Melting point, ° F.	2500
Surface area, sq. m./g.	11
Theoretical density:	
G./cc.	3.6
Lbs./cu. ft.	225
Calc'd specific heat, B.t.u./° F./lb.	0.22
Hardness, Mohs	4.0
Moisture pickup:	
47% R.H.	0.34
90% R.H.	1.7
Chemical composition	$K_2Ti_6O_{13}$

The mixer was covered, evacuated to 1 mm. of Hg pressure, then run for a period of four (4) minutes. Mixing was performed for an additional 30 seconds with the blades rotating in the reverse direction, then again in the original direction for another minute. This procedure for mixing was repeated again after the mixer was opened to scrape the blades clear of unmixed fibers. A tacky troweling paste resulted from this formulation.

Example II

The procedure followed in this example was identical with that of Example I except that 500 grams of potassium titanate fibers were used instead of 468 grams, as used in Example I. This gave a weight ratio of polyvinyl alcohol to titanate fiber of 0.56:1 and a weight ratio of water to titanate fibers of 3.9:1. A tacky troweling paste was obtained, and a thin layer of this paste was spread uniformly over the surface of a one-inch thick block of felted potassium titanate fibers, and an identical black of felted potassium titanate fibers was pressed into this thin layer of troweling paste. After the cemented blocks were air dried, a tightly bonded structure resulted. These blocks were then fired at 1000° C. for one-half hour, during which time the polyvinyl alcohol was burned out of the troweling paste layer. The bonded structure maintained its integrity with no evidence of shrinkage.

A portion of the troweling paste prepared as described above was also spread in a layer one-sixteenth of an inch thick and twelve inches square on a smooth surface and was air dried to a tough, pliable sheet. The surface of the sheet was wetted with deionized water, and the sheet was then spindled so that adjacent layers of the sheet were in close contact. The spindled structure, which retained its shape without restraint, was again dried and was subsequently fired at 1000° C. for 15 minutes. The resulting structure was a strong cylinder of felted potassium titanate fibers.

Example III

This example illustrates the preparation of a troweling paste wherein 10% of the potassium titanate fiber is replaced by fibrous aluminum silicate. The weight ratio of polyvinyl alcohol to total fiber weight is 0.5:1 and the weight ratio of water to total fiber weight is 3.5:1.

The contents of a beaker containing 5 liters of cold deionized water, 450 grams of the potassium titanate fibers described in Example I, and 50 grams of commercially prepared fibrous aluminum silicate were agitated with a high-shear-type stirring paddle for 20 minutes until fibers of the two materials were intermixed.

The aqueous mixture was permitted to stand overnight to allow the titanate-silicate fiber mixture to settle out. Excess water was decanted off before the fibers were dried in an oven at 100° C.

The dry fibrous pulp was then transferred to a kneading mill and mixed under 55 mm. of Hg pressure with 2000 grams of 12.5% polyvinyl alcohol-water (deionized) solution according to the procedure outlined in Example I. A tacky paste resulted from this formulation.

Example IV

The composition prepared according to the procedure outlined below is a brush or spray formulation in which the weight ratio of polyvinyl alcohol to potassium titanate fibers is 0.5:1 and the weight ratio of water to potassium titanate fibers is 10:1.

Into a two-liter vessel equipped with an agitator was charged 650 grams of deionized water. While the water was vigorously agitated, 500 grams of the troweling paste described in Example II was added to it and the mixture was stirred until it was smooth and homogeneous.

The brush formulation prepared as described above was applied with a brush to blocks of commercial insulation material. The thin coat of the brush formulation was allowed to air dry to a tough film. The insulation block was installed in a commercial furnace as back-up insulation. The polyvinyl alcohol was burned out of the film during operation of the furnace, leaving an integral film composed of infrared-reflective potassium titanate fibers.

Example V

The composition prepared according to the procedure outlined below is a molding formulation in which the weight ratio of polyvinyl alcohol to potassium titanate fibers is 0.54:1 and the weight ratio of water to potassium titanate fibers is 1.9:1.

By the identical procedure outlined in Example I, 504 grams of a 22.1% solution of polyvinyl alcohol in deionized water was mixed with 207 grams of the potassium titanate fibers described in the first example. A stiff, slightly tacky, plastic mass suitable as a molding composition was obtained.

A portion of this molding formulation was placed in a mold and subjected to pressure. Upon removal from the mold, a six-inch square sheet three-eighths of an inch thick was obtained which was oven dried at 80° C., and there was obtained a strong, tough sheet of the same size as the mold.

A portion of this molding formulation was also pressed in a mold to yield a cap which fitted a standard threaded two-inch pipe. The structure was dried on the male portion of the die. After drying, the cap was readily unscrewed from the die and was subsequently fired at 1000° C. for 15 minutes. The resulting product was a dense felt of potassium titanate fibers in the form of a standard two-inch pipe cap.

The above examples are representative of the non-shrinkable insulating compositions which can be prepared according to this invention. It should be pointed out that the claimed compositions will tolerate small amounts of other materials without adversely affecting the insulating properties of the finished product. For example, colloidal silica, alumina, or clay could be incorporated into the claimed compositions in amounts up to 25% by weight of the fibers. Bentonite, a colloidal aluminum silicate clay, would be useful for this purpose. It is also contemplated that small amounts of coloring materials, metallic fibers, etc., can be added to the compositions of this invention to achieve modified physical properties, such as strength, without adversely affecting thermal conductivity.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition consisting essentially of alkali metal titanate fibers, polyvinyl alcohol having a viscosity, in a 4% solution in water at 20° C., of 4 to 65 centipoises and a hydrolysis of 87 to 100%, and deionized water, the weight ratio of polyvinyl alcohol to alkali metal titanate fibers being about 0.25:1 to about 1.5:1, the weight ratio of water to alkali metal titanate fibers being about 0.1:1 to about 25:1.

2. A composition consisting essentially of alkali metal titanate fibers and polyvinyl alcohol having a viscosity, in a 4% solution in water at 20° C., of 4 to 65 centipoises and a hydrolysis of 87 to 100% in a weight ratio of said polyvinyl alcohol to alkali metal titanate fibers of about 0.25:1 to about 1.5:1, and deionized water, the weight ratio of water to alkali metal titanate fibers being from 3:1 to 25:1.

3. The composition of claim 1 in which the alkali metal titanate fibers are potassium titanate fibers.

4. The composition of claim 2 in which the alkali metal titanate fibers are potassium titanate fibers.

5. A composition consisting essentially of potassium titanate fibers, polyvinyl alcohol having a viscosity, in a 4% solution in water at 20° C., of 4 to 65 centipoises and a hydrolysis of 87 to 100%, and deionized water, the weight ratio of polyvinyl alcohol to potassium titanate fibers being about 0.5:1 to about 0.6:1, the weight ratio of water to potassium titanate fibers being about 3:1 to about 5:1.

6. A composition consisting essentially of a fibrous mixture of at least 90% by weight of potassium titanate fibers, the balance being a fibrous material selected from the group consisting of aluminum silicate, asbestos, rock wool, and silica, with polyvinyl alcohol having a viscosity, in a 4% solution in water at 20° C., of 4 to 65 centipoises and a hydrolysis of 87 to 100%, and deionized water, the weight ratio of polyvinyl alcohol to total fiber weight being about 0.5:1 to about 0.6:1, and the weight ratio of water to total fiber weight being about 3:1 to 5:1.

7. A composition consisting essentially of a fibrous mixture of at least 90% by weight of potassium titanate fibers, the balance being fibrous aluminum silicate, with polyvinyl alcohol having a viscosity, in a 4% solution in water at 20° C., of 4 to 65 centipoises and a hydrolysis of 87 to 100% and deionized water, the weight ratio of polyvinyl alcohol to total fiber weight being about 0.5:1 to about 0.6:1, and the weight ratio of water to total fiber weight being about 3:1 to about 5:1.

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