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54 **Radiation shielding putty-like composition.**

57 The present invention discloses a radiation shielding putty-like composition comprising a binder having a fluidity in the range from at least 5,000 c.St. in viscosity at 25°C to at least 100 in unworked penetration at 25°C, and 1,200 to 4,000 parts by weight, per 100 parts by weight of the said binder, of an inorganic powder having a density of at least 5 g/cm³ and also having a particle size such that at least 95% by weight thereof passes a 145-mesh sieve, and the said composition being from 1 to 35 mm in consistency and at least 1 g/5sec. in extrudability, and at least 4 g/cm³ in density.

Radiation Shielding Putty-like Composition

Field of the Invention

The present invention relates to a composition suitably used for shielding injurious radiations such as X-rays, γ -rays etc.

Background of the Invention

In order to avoid leakage of injurious radiation through various openings, such as openings provided for electric cables or pipes through room walls or vessel walls in nuclear power stations, cracks and crevices developed at walls etc., it has been ordinary in the art to fill such openings with lead fiber wool or a sealing compound containing a dense metallic powder. However, the method using lead fiber wool is laborious and troublesome and moreover, openings cannot be sealed tightly because only about 50% of the space can be filled. On the other hand, sealing compounds containing a dense metallic powder, if openings being well filled therewith, may exhibit excellent radiation shielding effect. Known or proposed sealing compounds of such type, however, are too hard or too consistent at a room temperature, and therefore in the filling work for small openings those are not only time-consuming, but also in many cases difficult to fill them sufficiently.

Summary of the Invention

Unexpectedly, it was found through experiments

conducted by the inventors of the present invention that a dense and very fine metallic powder can be mixed in great amount thereof with a binder having a specific viscosity or consistency to produce an even putty-like mixture having a high density enough to shield injurious radiations and also having a good fluidity being easy to fill a variety of openings including small one.

An object of the present invention is to provide a novel radiation shielding putty-like composition.

Another object of the present invention is to provide a radiation shielding putty-like composition which is excellent in radiation shielding and has good or temperate fluidity and therefore is easy to fill small openings.

Still another object of the present invention is to provide a radiation shielding putty-like composition which is extrudable by means of a conventional grease gun.

The present invention provide a radiation shielding putty-like composition comprising a binder having a fluidity in the range from at least 5,000 c.St. in viscosity at 25°C to at least 100 in unworked penetration at 25°C, and 1,200 to 4,000 parts by weight, per 100 parts by weight of the said binder, of an inorganic powder having a density of at least 5 g/cm³ and also having a particle size such that at least 95% by

weight thereof passes a 145-mesh sieve, and the said composition being from 1 to 35 mm in consistency and at least 1 g/5sec. in extrudability, and at least 4 g/cm³ in density.

Detailed Explanation of the Invention

The binder to be used in the present invention is the one which is able to produce a stable putty-like composition by mixing with a great amount of an inorganic powder described later. Therefore, liquid or semisolid having a specific fluidity are employed as the binder.

To be concrete, the binder has a fluidity in the range from at least 5,000 c.St. in viscosity at 25°C to at least 100 in unworked penetration (as measured in accordance with JIS K 2220-1980, 5.3.4) at 25°C. With a binder having a viscosity of less than 5,000 c.St. at 25°C, the composition obtained upon incorporation of an inorganic powder is not stable, because the inorganic powder gradually precipitates to make the composition uneven. On the other hand, with a binder having an unworked penetration of less than 100, it is difficult to admix a sufficient amount of inorganic powder to the binder, and furthermore the composition obtained is too hard.

The binder preferably has a viscosity of at least 10⁵ c.St., more preferably at least 2 x 10⁵ c.St., and also has an unworked penetration of at least 150, more

preferably at least 200.

In the present invention there may be used, as the binder, materials of various chemical kinds, such as natural or synthetic organic materials, natural or synthetic inorganic materials, and mixtures thereof.

Greases are a preferable example of the binder. It is generally well known that the grease is defined as a colloidal or micellar dispersion of solid thickener in a natural or synthetic organic liquid. The greases useful as the binder are those defined as above. Examples of useful natural or synthetic liquids are oils from petroleum such as transformer oil, spindle oil, electrical insulating oil, machine oil etc., animal and vegetable oils such as rosin oil, castor oil, olive oil, whale oil etc., synthetic hydrocarbon oils such as polybutene, oligomers or polymers of α -olefin, chlorinated paraffins, liquid rubbers etc., glycols such as polyethylene glycol, polypropylene glycol etc., esters such as dioctylsebacate, dioctyladipate, and other esters which are used as plasticizer of polyvinyl chloride etc., and other synthetic oils such as polydimethylsiloxane, polytrifluorochloroethylene etc. Examples of useful thickeners are metallic soaps such as organic acid salts of Ba, Sr, Zn, Pb, Cd, K, Na, Ca, Li, Al and like metals, metal oxide gels such as aluminum oxide gel, titanium oxide gel, silica gel etc., and others such as urea compounds, N-lauroyl-L-glutamic

acid- α,β -n-butylamide, quaternary ammonium salt of cellulose, fatty acid esters of dextrin, phthalocyanine, powder of organic resins, bentonite etc.

Examples of greases to be suitably used in the present invention are metallic soap greases such as sodium soap grease, potassium soap grease, lithium soap grease, aluminum soap grease, barium soap grease etc., non-soap greases such as silica gel grease, urea grease, bentonite grease etc. Among them, most preferable are lithium soap grease, aluminum soap grease, silica gel grease, and bentonite grease.

Other useful greases are disclosed by Hiroshi Horiguchi in " Lubricants and Greases ", pages 402-419, Sankyoshuppan Co., Ltd., Tokyo, February 1970.

Other preferable examples of the binder are hydrocarbon oils from petroleum, oligomers or polymers of olefin such as polybutene, α -olefin oligomer, polyalkylene glycol oils such as polypropylene glycol, halogenated hydrocarbon oils such as chlorinated paraffin, liquid rubbers such as liquid chloroprene rubber, liquid butadiene rubber, liquid acrylonitrile rubber, silicone oils, water glass etc. A mixture of polybutene and a grease is one of the most preferable examples as the binder.

The inorganic powder to be used in the present invention functions as the radiation shielding material, and as mentioned previously, is employed in great amount,

that is 1,200 to 4,000 parts by weight thereof per 100 parts by weight of the binder. The inorganic powder has a density of at least 5 g/cm^3 and also has a particle size such that at least 95% by weight thereof passes a 145-mesh sieve of the JIS Z 8801 Standard Sieve series. With an inorganic powder having a density of less than 5 g/cm^3 , such a low density powder needs to be used in too large amount exceeding the above-mentioned upper limit, that is 4,000 parts, in order to produce a composition at least 4 g/cm^3 in density, and therefore has difficulty in being integrated with a binder as putty-like material. On the other hand, when an inorganic powder which does not satisfy the above particle size requirement is used in an amount of 1,200 parts or more per 100 parts of a binder, the powder is also hardly integrated with the binder because of its too large particle size. Therefore, preferable inorganic powders have a density as large as possible and have a particle size as small as possible in the standpoint of producing a composition being putty-like, stable and excellent in radiation shielding effect. Preferable inorganic powders are those having a density of at least 9 g/cm^3 , and/or having a particle size such that at least 95% by weight thereof passes a 200-mesh sieve, moreover at least 99% by weight thereof passes a 200-mesh sieve. The most preferable inorganic powders are those having a density

of at least 10 g/cm^3 and also having a particle size such that at least 99% by weight thereof passes a 280-mesh sieve, furthermore at least 90% by weight thereof passes a 350-mesh sieve.

Besides, the use of a mixture of a coarser powder, for example those at least 95% by weight of which passes a 145-mesh sieve and does not pass a 200-mesh sieve, and a finer powder, for example those at least 95% by weight of which passes a 200-mesh sieve, makes it possible to incorporate the inorganic powder in the composition in larger amounts, since such inorganic powder mixture is dispersed in the composition in a manner such that the finer powder particles are packed among the coarser powder particles.

In the present invention, when the amount of the inorganic powder is lower than 1,200 parts per 100 parts of the binder, the radiation shielding effect is insufficient. Conversely, when the amount is higher than 4,000 parts per 100 parts of the binder, the resulting composition will not have putty-like properties, or is too hard. Therefore, the amount of the inorganic powder is preferably 1,300-3,000 parts by weight, more preferably 1,500-2,000 parts by weight per 100 parts by weight of the binder.

As such inorganic powder, there may be used any of inorganic powders which are compatible with the above-

mentioned binder. Examples of the inorganic powders are powders of metals or metal oxides, more specifically, lead, zinc, iron, zirconium, and copper, oxides of these and other various compounds. Preferred are lead powder and lead oxide powder since they have a high density of not less than 9. Moreover, most preferred are powders of a pure lead at least 99.5% by weight in purity. Examples of the pure lead are six kinds of pig lead defined in JIS H 2105-1955. Preferable purity of the pig lead is not less than 99.8% by weight, particularly not less than 99.9% by weight.

The putty-like composition of the present invention comprises above-mentioned components, and also has a consistency (as measured in accordance with JIS A 5752-1975) of 1 to 35 mm at 25°C, an extrudability (as measured by the method described below) of at least 1 g/5sec., and a density of at least 4 g/cm³.

Extrudability : One kilogram of a putty-like composition to be tested is charged into a grease gun comprising a cylinder portion 47 mm in inner diameter, a cylindrical nozzle 16 mm in inner diameter and 19 mm in length, and a tapered portion 12 mm in length joining the cylinder portion and the cylindrical nozzle, and each inner surface finish of the above three portions being corresponding to one triangular mark defined in JIS B 0601-1976. Pressing the composition by means of

a piston with a force of 5 kg, the amount of the composition extruded through the cylindrical nozzle during 5 seconds is measured, and is expressed as extrudability.

A composition having a consistency of less than 1 mm, or having an extrudability of less than 1 g/5sec. is so hard that it requires time-consuming work for filling small openings. On the other hand, in a composition having a consistency of more than 35 mm precipitation of the inorganic powder included therein tends to occur gradually and makes the distribution of the inorganic powder in the composition uneven. Furthermore, a composition having a density of less than 4 g/cm³ is poor in shielding effect for radiations, especially x-rays and γ -rays. Therefore, the preferable putty-like composition of the present invention has a consistency of from 3 mm to 30 mm at a room temperature, an extrudability of at least 5 g/5sec., more preferably 10 g/5sec., and a density of at least 6 g/cm³. Those can be conveniently applied by hand working for filling large openings, and also applied by using an usual grease gun for filling small openings.

In addition to the above-mentioned binder and the inorganic powder, the putty-like composition of the present invention may, as necessary, contain an appropriate amount of a flame retardant such as aluminum hydroxide, magnesium hydroxide, antimony trioxide, a colorant, a plasticizer such as dioctyl phthalate, a coupling agent,

and other additives ordinarily used in rubber or plastics, provided that the physical characteristic requirements above-mentioned are satisfied.

In general, the higher the content of an inorganic powder is in the composition, the lower the extrudability of the composition is. However, the low extrudability of a composition due to higher content of an inorganic powder can, if necessary, be improved by using a coupling agent. The composition of the invention may furthermore contain a small amount of a fiber, such as asbestos, rock wool, glass wool, carbon fiber, a metallic fiber, and like inorganic fibers and polyamide fiber, fluororesin fiber, phenol-based polymer fiber and like organic fibers. In general, the incorporation of fiber improves the dimensional stability of the present putty-like composition after application at an opening requiring radiation shielding, while tends to make the extrudability of the composition poor. However, the extrudability problem can also be improved by using a coupling agent.

Examples of the coupling agent are silane coupling agents, such as γ -methacryloxypropyl trimethoxy silane, γ -glycidoxypropyl trimethoxy silane, methyl trimethoxy silane, vinyl trimethoxy silane, γ -anilinopropyl trimethoxy silane, titanium coupling agents, such as isopropyl triisostearoyl titanate, isopropyl distearoyl titanate, isopropyl dimethacryl isostearoyl titanate, isopropyl

tri-n-stearoyl titanate, isopropyl tricumylphenyl titanate and like monoalkoxy types, tetraisopropyl di-dilaurylphosphite titanate, tetraoctyl di-ditridecylphosphite titanate and like coordinate types, diisostearoyl oxyacetate titanate, diisostearoyl ethylene titanate and like chelate types.

Preferable amount of the coupling agent to be used for improving extrudability is from 0.1 to 20 parts, more preferably from 0.5 to 10 parts by weight per 100 parts by weight of the binder mentioned above.

The method of producing the radiation shielding putty-like composition of the present invention is not critical. Thus, for instance, the composition can be obtained by uniformly kneading the required components in the conventional manner, for example, a kneader or roll.

The composition of the present invention, which contains such high density inorganic powder at such high addition level, has an excellent radiation shielding effect and, in spite of its high density, has good fluidity, and most of the preferable embodiments of the present invention can in practice be extruded by means of a conventional grease gun. Therefore, it can easily be applied to a variety of openings where there is a danger of radiation leakage. Furthermore, since the composition, when not including a curing agent, is noncuring, any after-treatment following application is not required.

In addition, once applied, the composition can be removed easily as necessary.

The following examples, which by no means limit the present invention, will illustrate the invention in more detail. Since it is known that the radiation shielding effect of a composition is generally proportional to the surface density thereof, the radiation shielding effect of the examples were evaluated by the density thereof.

Examples 1-9, Comparative Examples 1-5

The composition given in Table 1 were kneaded together on a roll to produce radiation shielding putty-like compositions. The compositions of the invention each contains a lead or leadoxide powder in a large amount. As shown in Table 2, although it has a high density, each composition has a good extrudability and therefore is excellent in applicability and workability. Furthermore, it is nonhardening and can be easily removed after application.

The nonhardening property was regarded as good if the composition showed a change in consistency of not more than 3.0 mm after standing at room temperature for 1 month. The initial consistency was measured 24 hours after preparation of the composition by kneading.

Table 1

Example or Comparative Example	Putty Composition (parts by weight)								
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
	Light grease	Poly-butene	Poly-butene	Liquid chloro-prene rubber	Liquid chloro-prene rubber	Vinyl-phenyl-methoxy silane	Lead powder	Lead oxide powder	Aromatic polyamide fiber
Ex. 1	100	-	-	-	-	-	1,300	-	-
Ex. 2	-	-	-	30	70	-	1,350	-	-
Ex. 3	-	-	100	-	-	-	1,360	-	-
Ex. 4	65	35	-	-	-	-	1,700	-	-
Ex. 5	65	35	-	-	-	2.5	1,700	-	1.5
Ex. 6	65	35	-	-	-	1	1,700	-	3
Ex. 7	65	35	-	-	-	4	1,000	500	-
Ex. 8	-	100	-	-	-	-	1,700	-	-
Ex. 9	-	20	80	-	-	6	3,600	-	-
Co.Ex. 1	65	35	-	-	-	-	400	-	-
Co.Ex. 2	-	-	100	-	-	-	1,110	-	-
Co.Ex. 3	65	35	-	-	-	-	1,700	-	7
Co.Ex. 4	-	-	100	-	-	-	1,700	-	7
Co.Ex. 5	65	35	-	-	-	-	4,200	-	-

Note:

- (1) Unworked penetration as measured in accordance with JIS K 2220-1980, 5.3.4: 240-280 (0.1 mm)
- (2) Viscosity at 25°C: about 2×10^6 c.St.
- (3) Viscosity at 25°C: about 1×10^4 c.St.
- (4) Viscosity at 25°C: about 4.5×10^4 c.St.
- (5) Viscosity at 25°C: about 1×10^5 c.St.
- (6) Average particle size: 96.5% passing a 350-mesh sieve, Purity of lead: more than 99.0% by weight
- (7) Average particle size: 100% passing a 350-mesh sieve, Pb: 38.2% by weight, PbO: 61.8% by weight
- (8) KEVLAR[®] dry pulp (Du pont): 0.01 mm in average diameter, 4.0 mm in average length

Table 2

Example or Comparative Example	Characteristics of Putty- like Composition				Nonhardening property
	Density (g/cm ³)	Consistency (mm)	Extrudability (g/5sec.)		
Ex. 1	6.1	17.7	98		Good
Ex. 2	6.8	15.1	70		Good
Ex. 3	6.0	27.1	96		Good
Ex. 4	6.8	14.0	96		Good
Ex. 5	6.6	10.5	51		Good
Ex. 6	6.7	7.5	30		Good
Ex. 7	6.6	12.6	77		Good
Ex. 8	6.5	7.9	40		Good
Ex. 9	7.0	3.5	4		Good
Co.Ex. 1	3.5	>40	60		Good
Co.Ex. 2	5.7	39.4	92		Good
Co.Ex. 3	6.5	5.8	0		Good
Co.Ex. 4	6.5	7.1	0		Good
Co.Ex. 5	-	-	0		-

What is claimed is :

1. A radiation shielding putty-like composition comprising a binder having a fluidity in the range from at least 5,000 c.St. in viscosity at 25°C to at least 100 in unworked penetration at 25°C, and 1,200 to 4,000 parts by weight , per 100 parts by weight of the said binder, of an inorganic powder having a density of at least 5 g/cm³ and also having a particle size such that at least 95% by weight thereof passes a 145-mesh sieve, and the said composition being from 1 to 35 mm in consistency and at least 1 g/5sec. in extrudability, and at least 4 g/cm³ in density.

2. A radiation shielding putty-like composition of claim 1, wherein the said binder has a viscosity of at least 10⁵ c.St. at 25°C.

3. A radiation shielding putty-like composition of claim 1, wherein the said inorganic powder is lead powder or lead oxide powder.

4. A radiation shielding putty-like composition of claim 3, wherein the said inorganic powder is powder of a pure lead at least 99.5% by weight in purity.

5. A radiation shielding putty-like composition of claim 3, wherein the said inorganic powder is powder of a pure lead at least 99.8% by weight in purity.

6. A radiation shielding putty-like composition of claims 1 to 5, wherein the said inorganic powder has

a particle size such that at least 99% by weight thereof passes a 280-mesh sieve.

7. A radiation shielding putty-like composition of claims 1 to 5, wherein the said inorganic powder has a particle size such that at least 90% by weight thereof passes a 350-mesh sieve.

8. A radiation shielding putty-like composition of claims 1 to 5, which comprises from 1,300 to 3,000 parts by weight of the said inorganic powder per 100 parts by weight of the said binder.

9. A radiation shielding putty-like composition of claim 1, which is at least 5 g/5sec. in extrudability, from 3 to 30 mm in consistency, and at least 6 g/cm³ in density.