

PATENT SPECIFICATION

(11) 1 497 855

1 497 855

- (21) Application No. 19732/76/ (22) Filed 13 May 1976/
 (31) Convention Application No. 50/058'937
 (32) Filed 16 May 1975/
 (31) Convention Application No. 50/115 002
 (32) Filed 22 Sept. 1975 in/
 (33) Japan (JP)
 (44) Complete Specification published 12 Jan. 1978
 (51) INT CL² C09K 3/28
 (52) Index at acceptance
 C3P 2D1A2 7D1B 7D1D E2 PC15 PC20B PC20C PC4A PC7
 PC8B

(19)



(54) FIRE-RETARDANT INTUMESCENT PUTTY /

(71) We, DAINICHI-NIPPON CABLES LTD., a Japanese company of Umeda Building, 7—3 Umeda, Kitaku, Osaka 530, Japan/do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fire-retardant intumescent putties having outstanding fire retardation and air-tightness properties. By "putties" we mean compositions which are permanently of putty-like mouldable consistency.

Known fire-resistant or flame-retardant materials are used as interior finishing materials for buildings, ships and vehicles, and emergency equipment such as an emergency electric source, is protected by fire walls to ensure fire protection. The fire wall is usually provided with a penetrating bore for electrical cables, and it is very important to close the air space in the penetrating bore, because in a fire smoke and flames will permeate through the air space into the opposite side of the fire wall, and consequently burn emergency equipment. To render the penetrating bore of this type fire-proof and smoketight, it has been known to close the air space with non-flammable plates or blocks or to fill the air space with non-flammable fibres. However, these conventional means are not always satisfactory in fireproofness and smoketightness. It is also known to fill the air space with concrete, but this method involves the inconvenience that the concrete must be broken away for the installation of additional cables.

The present invention provides a novel fire-retardant intumescent putty for filling various spaces and joints which has high airtightness under normal and fire exposure conditions, and hence smoketightness, and which bubbles up when heated with flame, producing a foamed carbonaceous layer having outstanding fire retardation properties.

According to the invention we provide a fire retardant intumescent composition having a permanent putty-like mouldable consistency and having a cone penetration value of 2—40 (mm/150 g, 5 sec., at 20°C) determined in accordance with the provision of JIS A5752—1966, which comprises (a) at least 4% by weight of an organic material of non-hardening type in a semi-solid or liquid state at room temperature and having a viscosity of 50—100,000 c.st at 210°F, and (b) at least 13% by weight of a nitrogen-containing phosphate which is a phosphoric acid represented by the general formula,



(wherein

$$0 < \frac{x}{y} \leq 3$$

and n is 1—14), one or all of the hydrogen atoms of which are substituted with a nitrogen containing group of mono-, di-, or tri- valency consisting essentially of nitrogen and either or both of hydrogen and carbon, and containing at least 7% by weight of phosphorus.

The cone penetration value of 2—40 (mm/150 g, 5 sec., at 20°C) is determined in accordance with the provision of JIS A5752—1966.

The organic material serving as the component (a) of the present invention is liquid or semi-solid at room temperature (at about 25°C) and has a viscosity of 50—100,000 c.st. at 210°F. The term "semi-solid" as used herein and in the claims refers to the state of the material having a cone penetration value of at least 50 as determined according to JIS K2560—1969 (Testing Method for Cone Penetration of Lubricating Greases). When the material used as the component (a) has a viscosity outside the above-mentioned range at 210°F for has a cone penetration value smaller than 50 at room temperature, it is difficult to obtain a putty having excellent fire retardation and air-tightness as contemplated by the invention. The material may have a viscosity of 200—50,000 c.st, especially 500—10,000 c.st, at said temperature.

Chemically, the component (a) is a non-hardenable material and should be such a material that, when burned in the presence of component (b) explained below, it gives rise to a foamed carbonaceous layer. Preferred are those materials which are somewhat hard to burn. Organic materials to be useful as component (a) satisfying the above requirements are those consisting solely of hydrogen and carbon atoms or those consisting of hydrogen and carbon atoms together with 1 to 6 atoms, preferably 1 to 5 atoms, of an element or elements other than hydrogen such as oxygen, nitrogen, halogen, phosphorus, or sulphur, preferably at least one of oxygen, nitrogen, halogen or phosphorus, per 10 carbon atoms. Exemplary of the component (a) are petroleum hydrocarbon oils; oligomers of butene, propylene, ethylene and like olefins; chlorinated paraffin, chlorinated diphenyl, and like halogenated organic materials; liquid or semi-solid bodies of rubbers such as polychloroprene, polybutadiene, polybutadiene acrylonitrile; oligomers of urethane; and asphalts. These materials are used singly, or at least two of them are usable in mixture. Also useful are mixtures of the above organic materials and natural or synthetic substances in the solid state at room temperature which mixtures fulfil the foregoing requirements. Examples of suitable solid natural or synthetic substances are high-molecular-weight materials such as ethylene-vinyl acetate copolymer; natural rubber, styrene-butadiene rubber, nitrile rubber, chloroprene rubber, polyisobutylene, atactic polypropylene and asphalts; waxes such as paraffin wax, microcrystalline wax, Fischer-Tropsch wax and the like; oil modified alkyd resin; and rosin. Materials free from silicon are more preferable as the component (a).

The nitrogen-containing phosphates useful as the component (b) of the present invention have a structure in which the nitrogen-containing group(s) to be set forth below are substituted for one or all of the hydrogen atoms of phosphoric acid represented by the formula $(xH_2O.yP_2O_5)_n$ wherein

$$0 < \frac{x}{y} \leq 3$$

and n is 1—14, the phosphate containing at least 7% by weight, preferably at least 10% by weight, of phosphorus. When the material used as the component (b) contains phosphorus in an amount less than 7%, it is difficult to form a foamed carbonaceous layer having satisfactory fire retardation. The nitrogen-containing group is an organic group of mono-, di-, or trivalency consisting essentially of nitrogen and either or both of hydrogen and carbon. Exemplary of such groups are NH_2 , NH , NH_3 , and NH_4 . As other examples of such group, those groups may also be included which are formed with a plurality of above groups bonded together cyclically or linearly, such as triamino- β -triazine group and guanyl urea group. Examples of the nitrogen-containing phosphates are monoammonium phosphate, diammonium phosphate, ammonium polyphosphate having an average molecular weight of 200—300,000 and containing 10—25% by weight of nitrogen; melamine monophosphate, melamine diphosphate, melamine triphosphate; guanyl urea phosphate, urea phosphate, polyphosphorylamide, phosphoryl trianilide; etc., among which preferable are melamine monophosphate, and ammonium polyphosphates represented by the formula $H_{(n-m+1)}(NH_2)_mP_nO_{3n+1}$ wherein n/m is 0.7—1.1 and having an average degree of polymerisation of 20—400 or those represented by the formula $(NH_4)_{n+2}P_nO_{3n+1}$ and having an average degree of polymerization of 150—200. These phosphates may be used singly or at least two of them are usable in mixture.

It is required that the putty of the invention comprising the components (a) and (b) contains at least 4% (by weight, same as hereinafter) of the component (a). Smaller amounts of the component (a) than 4% result in poor airtightness. Preferably at least 5%, more preferably at least 6%, of the component (a) is present. On the other hand, at least 13% of the component (b) must be contained in the putty. Below 13% of the component (b), it is difficult for the resulting product to produce a foamed carbonaceous layer even when heated by flame. Preferably the putty contains at least 15%, more preferably at least 20%, of the component (b).

The putty of the present invention must have the chemical composition described above and a cone penetration value of 2 to 40 mm/150 g, 5 sec., at 20°C as determined according to JIS A5752—1966 (Putty for Metal Sash Glazing). If the cone penetration value is below 2, such a putty is not fully amenable to application, whereas above 40, such a putty has poor airtightness and fire retardation. The cone penetration value is preferably 3—20, more preferably 4—15.

According to the present invention, the putty will have greatly improved fire retardation and airtightness when further incorporating at least one of the components (c)—(g) given below, in addition of the foregoing components (a) and (b).

Component (c) polyhydric alcohol or carbohydrate:

The useful alcohols and carbohydrates should have an OH index as defined below of at least 0.2, or preferably at least 0.8, and contain 35—70% by weight of carbon. They may be used singly or two or more of them.

$$\text{OH index} = \frac{100 \times (\text{numbers of OH group contained in one molecule})}{(\text{molecular weight})}$$

Examples of the alcohols are pentaerythritol, dipentaerythritol, tripentaerythritol, triethylene glycol, sorbitol, glycerin, trimethylolmethane, trimethylolpropane, diethylene glycol, propylene glycol, hexamethylene glycol, and inositol. Examples of the carbohydrates are dextrin, starch, glucose, and sucrose. Among these, pentaerythritol, dipentaerythritol, tripentaerythritol and starch are preferable.

The component (c) is used in an amount of 10—150 parts (by weight, same as hereinafter), preferably 30—100 parts, more preferably 40—60 parts, per 100 parts of the nitrogen-containing phosphate. The use of the component (c) gives a putty having greatly improved fire retardation when foamed. There is rather poor improvement on fire retardation in the case where such an alcohol or carbohydrate is used of which OH index and/or carbon content falls outside of the above regions.

Component (d)—blowing agent:

The blowing agent gives off gases, such as nitrogen, carbon monoxide, carbon dioxide, ammonia when thermally degraded and has a decomposition temperature of 120—400°C. Examples of useful blowing agents are melamine, urea-formaldehyde resin, aminoacetic acid, trimethylolmelamine, hexamethylolmelamine, half to completely cross-linked melamine resin which is solid at room temperature and prepared by the addition condensation reaction of melamine and formaldehyde, guanidine and like organic amines; dicyandiamide, butylurea, casein, azodicarbonamide, nitrososulfonamide and like organic amides; parachlorometaxyleneol, tetrachlorophthalate resin, pentachlorophenyl and like halogenated organic compounds; benzenesulfonhydrazide and like sulfonhydrazides; and aminoguanylurea and like guanyl compounds; among which preferable are melamine, trimethylolmelamine, hexamethylolmelamine, and dicyandiamide. The most desirable example is finely divided melamine at least 95% of which has an average particle diameter smaller than 50 μm . Preferably at least one of these blowing agents is used.

The component (d) is used in an amount of 10—200 parts, preferably 30—150 parts, more preferably 60 to 120 parts, per 100 parts of the nitrogen-containing compound. When used, the component (d) permits the putty to produce a foamed carbonaceous layer having a higher heat-insulating effect and therefore improved fire retardation.

Component (e)—grease:

The greases usable in the invention are those which are in the form of a viscous paste or semi-solid at room temperature and which comprise a thickener

and a natural or synthetic medium. The greases, as component (e), are those generally known as lubricating greases or simply as greases, as distinct from oily lubricants. Exemplary of the medium are natural oils, such as transformer oil, spindle oil, insulating oil for cables and machine oil, rosin oil, castor oil, olive oil, and arachis oil; synthetic lubricating oils such as polybutene oil, chlorinated paraffin and polyethylene glycol. Useful thickeners include, for example, metallic soaps such as higher fatty acid salts of Ba, Sr, Zn, Pb, Cd, K, Na, Ca, Li, Al and like metals, non-soaps such as bentonite, silica gel, and phthalocyanine. Examples of the greases include greases of the soap type such as sodium soap grease, calcium soap grease, lithium soap grease, aluminium complex grease, as, for example, disclosed in U.S. Patent 2768/38, greases of the non-soap type such as bentonite grease, silica gel grease, etc. Also usable are greases disclosed by Hiroshi Horiguchi in "Lubricants and Greases" (pages 402—419, Sankyoshuppan Co. Ltd., Tokyo, February 1970). One or more of them can be employed in the invention. Among these examples, preferable are greases having a cone penetration value of 40—500 as determined according to JIS K2560—1969 (Testing Method for Cone Penetration of Lubricating Greases). Especially preferable are lithium soap grease, aluminium complex grease, bentonite grease and silica gel grease having a cone penetration value of 80—350.

The component (e) is used in an amount of 70—400 parts, preferably 100—300 parts, more preferably 150—250 parts, per 100 parts of the component (a), i.e. the organic material. The use of component (e) improves the non-fluidity of the putty, but in no way impairs the amenability of the putty to application at room temperature. Due to excellent non-fluidity at high temperatures, the putty, even when used in a vertical penetrating bore in a fire wall, remains in the bore without flowing down in the event of fire.

Component (f)—heat-resistant fibre:

One or more of organic or inorganic fibres are used which are free of softening or decomposition at a temperature up to 200°C. Examples of such fibres are asbestos, glass wool, rock wool and carbon fibres; aluminium, iron, copper and like metal fibres; fibres of polyamide, polyimide, polyamideimide, Teflon (Registered Trade Mark), polyphenyl-phenyleneoxide, polysulphone and like heat-resistant organic polymers. The heat-resistant fibres are preferably up to 100 μm , more preferably 0.05—20 μm , in diameter and 0.5—100 mm, more preferably 1—50 mm, in length.

The component (f) is used in an amount of 1—100 parts, preferably 5—60 parts, more preferably 10—30 parts, per 100 parts of the component (a). The component (f) reinforces the putty of the invention and enhances its airtightness.

Component (g)—microballoon:

The microballoon is in the form of fine particles made of an organic or inorganic material and having interior voids. The voids may be closed or open to the atmosphere. One or more kinds of microballoons are used which are 5—1,000 μm , preferably 10—300 μm , in average particle size and 0.01—0.7, preferably 0.1—0.5 in bulk density (g/cc). Examples of microballoons are glass balloons made of borosilicate glass, glass from volcano (shirasu) and like glasses; plastic balloons made of epoxy resin, phenolic resin, chlorinated vinylidene-acrylonitrile copolymer resin such as Saran (Trade Mark) and other synthetic resins; carbon balloons.

The component (g) is used in an amount of 20—700 parts, preferably 100—500 parts, more preferably 200—400 parts, per 100 parts of the component (a). When incorporating the component (g), the putty of the invention produces a foamed carbonaceous layer having an enhanced heat-insulating effect when bubbled up by flame, exhibiting greatly improved fire retardation properties.

According to the present invention, any one of the components (c)—(g), when used conjointly with the components (a) and (b), gives an improved putty. However, use of at least two of the components (c)—(g) is preferable, since the resulting putty will then be rendered more effective in fire retardation, airtightness, and furthermore other properties such as mixing workability, moisture resistance, and thermal ageing resistance as seen from Examples below, due to the synergy of the effects of each component. The preferred combinations of the components are (c and d), (d and e), (d and f), (d and g), (c, d, and e or f or g), (c, d, e, and f), (c, d, e, and g), (e and f), (e and g), (c, d, e, f, and g). In these combinations, the components may be used in the amounts already given for them respectively. However, when the components (c) and (d) are used together, the proportions of the components (b), (c) and (d),

irrespective of whether the components (e)—(g) are used or not, may be within the region represented by the area on the triangular co-ordinates of the Drawing enclosed by the straight lines interconnecting point α (30, 60, 10), point β (10, 60, 30), point γ (10, 30, 60), point δ (30, 10, 60), point ϵ (60, 10, 30) and point ζ (60, 30, 10), more preferably within the region represented by the area enclosed by the straight lines interconnecting point A (20, 50, 30), point B (20, 20, 60) and point C (50, 20, 30), the proportions being such that the total amount of the components (b), (c) and (d) is 200—1400 parts, more preferably 300—1100 parts, per 100 parts of the component (a). With these proportions, the resulting putties exhibit especially outstanding fireproof properties when foamed.

The drawing is a diagram of triangular co-ordinates showing the proportions of components (b), (c) and (d) involved in preferred embodiments of the invention.

Preferred compositions according to the invention fall within the area defined by the points α , β , γ , δ , ϵ , ζ , on the accompanying drawing, these points being defined as:

α : 30, 60, 10

β : 10, 60, 30

γ : 10, 30, 60

δ : 30, 10, 60

ϵ : 60, 10, 30

ζ : 60, 30, 10

The most preferred compositions fall within an area A, B, C defined as:

A: 20, 50, 30

B: 20, 20, 60

C: 50, 20, 30

The putty of the present invention may further contain other additives in an amount of 0.1—15 parts per 100 parts of the putty. The useful additives include pigments, antioxidants, mineral fillers, carbon black, stabilizers and the flame retardants described in "Flame Retardancy of Polymeric Materials," volumes 1—2, edited by W. C. Kuryla and A. J. Papa, Marcel Dekker Inc., New York, 1973.

In a putty in which only components (a) and (b) are present, the 4% by weight minimum of (a) connotes that 96% by weight of (b) will be present. When component (b) is at its 13% minimum, it connotes that 87% of (a) will be present. However, it will seldom be necessary to use as much as 87% of component (a) or as much as 96% of component (b). More commonly, (a) will represent about 4—60% more preferably about 5—35% and most preferably about 6—25% of the total putty, while (b) will generally represent about 13—85% more preferably about 15 to about 60% and most preferably about 20—50%. The above common, more- and most- preferred percentages may be used where the putty contains (a) and (b) alone, but are particularly useful where (a) and (b) are present in admixture with the other components described herein.

The putty of the present invention can be prepared by mixing the desired materials at room temperature or a higher temperature, preferably at a temperature up to about 100°C by a usual mixer such as a kneader, mixtruder, closed-type mixer or two- or three-roll mill.

The putty of the invention is effective when applied to various penetrating bores of walls, joints, etc. and is similarly effective when used for coating the articles or equipment to be protected against fire. Generally penetrating bores for electric cables need to be re-shaped for the replacement of cables or installation of additional cables. The putty of the invention which is of non-hardening type is very convenient to use in such penetrating bores because it is easily removable and reusable, and it is therefore very useful for fireproof works. As seen from the

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Examples, the putty of the present invention has excellent mixing workability, moisture resistance, and ageing resistance as well as excellent fire retardation and airtightness as mentioned above.

Experiments 1—4 were conducted for the comparison of the fire retardation properties of the putty of the invention and those of conventional compositions. The conventional compositions were used for Experiments 1—3, and the putty of the invention for Experiment 4.

Experiment 1.

Ten 600 V insulated cables (cross-linked polyethylene insulated and polyvinyl chloride sheathed), 3×3.5 mm² (outside diameter: about 13.5 mm), were passed through a circular bore, 150 mm in diameter, formed in a 100-mm thick concrete wall, and the bore was closed with a 3 mm thick steel plate secured to each side of the wall by bolts. One side of the penetrating bore for the cables was then maintained at a temperature of 700—800°C by a propane gas burner for one hour. One or two minutes after the initiation of the heating, smoke started to permeate through the another closed side of the bore, and marked permeation of smoke was observed in 30 to 40 minutes. In 50 minutes, flames spread onto the cables on the side away from the burner.

Experiment 2.

The same procedure as in Experiment 1 was repeated except that the air space within the bore was filled with glass wool to a density of 0.4 g/cc instead of closing the bore with the steel plates. As a result, smoke started to permeate through the bore in 1 to 2 minutes, and extremely marked smoke permeation was observed in 20 to 30 minutes.

Experiment 3.

The same procedure as in Experiment 2 was repeated except that a composition of 100 parts of polybutene (viscosity at 210°F: 17 c.st) and 400 parts of ammonium polyphosphate was used in place of the glass wool. In about 20 minutes, marked permeation of smoke took place, with flames noticeably spreading over the cables on the side away from the burner.

Experiment 4.

The same procedure as in Experiment 3 was repeated except that the putty of Example 8 shown in Table 1 below was used in place of the composition. It was 50 minutes after the initiation of heating that slight permeation of smoke was first observed, but on the side away from the burner, the cables were still free of any change at that time.

Examples 1—21.

The putty of each Example given in Table 1 was prepared from the materials listed in the same table by kneading them at room temperature to 80°C for 10 minutes in a kneader having a capacity of one litre and two agitator blades. Each putty was tested by the methods to be described later for mixing workability, fire retardation moisture resistance and ageing resistance to heat. The results are also given in Table 1.

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TABLE 1

Material	Example No.	1	2	3	4	5	6	7
(a)								
Polybutene ¹⁾		100	—	—	—	—	—	100
Polybutene ²⁾		—	100	100	100	—	100	—
Polybutene ³⁾		—	—	—	—	80	—	—
Polyisobutylene ⁴⁾		—	—	—	—	20	—	—
Liquid polybutadiene ⁵⁾		—	—	—	—	—	—	—
(b)								
Melamine phosphate		380	—	—	—	—	—	—
Ammonium polyphosphate		—	350	100	113	135	270	300
(c)								
Pentaerythritol		—	—	160	—	68	270	300
Dipentaerythritol		—	—	—	113	—	—	—
(d)								
Melamine		—	—	140	225	248	360	400
(e)								
Bentonite grease ⁶⁾		—	—	—	—	—	200	—
Aluminium complex grease ⁷⁾		—	—	—	—	—	—	180
(f)								
Asbestos fibre ⁸⁾		—	—	—	—	—	—	—
Glass fibre ⁹⁾		—	—	—	—	—	—	—
(g)								
Shirasu balloon ¹⁰⁾		—	—	—	—	—	—	—
Glass balloon ¹¹⁾		—	—	—	—	—	—	—
Properties								
Mixing workability		A	A	A	A	A	A	A
Fire retardation properties		C	C	B	B	B	A	A
Moisture resistance		B	B	A	A	A	A	A
Ageing resistant against heat		B	B	A	A	A	A	A
Airtightness		A	A	A	A	A	A	A

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TABLE 1

Material \ Example No.	8	9	10	11	12	13	14
(a)							
Polybutene ¹⁾	—	—	100	—	—	100	100
Polybutene ²⁾	100	—	—	100	100	—	—
Polybutene ³⁾	—	—	—	—	—	—	—
Polyisobutylene ⁴⁾	—	—	—	—	—	—	—
Liquid polybutadiene ⁵⁾	—	100	—	—	—	—	—
(b)							
Melamine phosphate	—	—	—	—	900	900	350
Ammonium polyphosphate	270	270	105	120	—	—	—
(c)							
Pentaerythritol	270	270	105	120	—	—	—
Dipentaerythritol	—	—	—	—	—	—	—
(d)							
Melamine	360	360	140	160	—	—	—
(e)							
Bentonite grease ⁶⁾	200	200	—	—	200	200	—
Aluminium complex grease ⁷⁾	—	—	—	—	—	—	—
(f)							
Asbestos fibre ⁸⁾	20	—	—	20	—	20	—
Glass fibre ⁹⁾	—	30	—	—	—	—	—
(g)							
Shirasu balloon ¹⁰⁾	—	—	250	—	—	—	—
Glass balloon ¹¹⁾	—	—	—	—	—	—	250
Properties							
Mixing workability	A	A	B	A	A	A	B
Fire retardation properties	A	A	B	A	C	C	C
Moisture resistance	A	A	A	A	B	B	B
Ageing resistant against heat	A	A	A	A	B	B	B
Airtightness	A	A	A	A	A	A	A

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TABLE 1

Material	Example No.	15	16	17	18	19	20	21
(a)								
Polybutene ¹⁾		—	—	100	—	100	100	—
Polybutene		100	100	—	100	—	—	100
Polybutene		—	—	—	—	—	—	—
Polyisobutylene ⁴⁾		—	—	—	—	—	—	—
(b)								
Melamine phosphate		280	400	—	—	—	210	—
Ammonium polyphosphate		—	—	200	650	170	—	240
(c)								
Monopentaerythritol		—	—	—	—	—	—	240
Dipentaerythritol		140	—	—	—	—	—	—
(d)								
Melamine		—	—	180	—	160	190	320
(e)								
Bentonite grease ⁶⁾		—	—	—	200	—	—	200
Aluminium complex grease ⁷⁾		—	—	—	—	—	—	—
(f)								
Asbestos fibre ⁸⁾		—	20	—	20	20	—	20
Glass fibre ⁹⁾		—	—	—	—	—	—	—
(g)								
Shirasu balloon ¹⁰⁾		—	—	100	—	100	—	80
Glass fibre ¹¹⁾		—	—	—	300	—	—	—
Properties								
Mixing workability		A	A	B	B	B	A	B
Fireproof properties		C	C	B	B	B	C	A
Moisture resistance		B	B	A	A	A	B	A
Ageing resistant against heat		B	B	A	A	A	B	A
Airtightness		A	A	A	A	A		

Notes:

- 1) Viscosity at 210°F: 2,150 c.st.
- 2) Viscosity at 210°F: 4,050 c.st.
- 3) Viscosity at 210°F: 90 c.st.
- 4) Viscosity at 210°F: 100,000 c.st.
- 5) Viscosity at 210°F: 1,600 c.st.
- 6) Cone penetration value: 230 (JIS K2560);
drop point: at least 200°C (JIS K2561).
- 7) Cone penetration value: 125 (JIS K2560);
drop point: at least 200°C (JIS K2561).
- 8) Diameter: 0.07 μ m; length: about 3 mm.
- 9) Diameter: 13 μ m; length: 13 mm.
- 10) Particle size: 20–300 μ m; apparent density: 0.24 (g/cc).
- 11) Particle size: 20–80 μ m; apparent density: 0.21 (g/cc).

Mixing Workability.

The specified amounts of the materials are placed into a 1-liter test kneader equipped with two agitator blades and are kneaded at room temperature to 80°C for ten minutes. The resulting mixture is checked for the appearance and feel to evaluate the homogeneity thereof according to the three criteria of excellent, good and poor, which are represented by "A, B and C" respectively.

Fire retardation.

About 30-cm long 600 V insulated cables (cross-linked polyethylene insulated and polyvinyl chloride sheathed), 3 $\times$ 3.5 mm² (outside diameter: 13.5 mm), is coated with putty by a trowel to a thickness of about 3 mm to prepare a specimen. To measure the temperature beneath the polyvinyl chloride sheath during the fire retardation test, a thermocouple is placed between the core and sheath at the portion of the cable to be exposed to flame.

The specimen is burned with a Bunsen burner which is adjusted to a flame temperature of 1,000–1,200°C.

Immediately after the specimen has been contacted with the flame, a line voltage of A.C. 600 V is applied to the cable, and the time taken for short-circuiting is measured.

On the other hand, the temperature beneath the sheath at the centre of the portion held in contact with the flame is continuously measured by the thermocouple inserted into the cable.

The fire retardation is rated according to the following five criteria: excellent when the short-circuiting time at A.C. 600 V is at least 40 minutes and the time taken for the above-mentioned temperature to rise to 400°C is at least 30 minutes; good when the short-circuiting time is at least 30 minutes and the rise of the temperature takes at least 30 minutes; fair when the short-circuiting time is at least 10 minutes and the elevation of the temperature takes at least 10 minutes; acceptable when the short-circuiting time is at least 4 minutes and the rise of the temperature takes at least 4 minutes; and unacceptable when the short-circuiting time is less than 4 minutes and the rise of the temperature takes less than 3 minutes. In Table 1, the terms excellent, good and fair are represented by A, B and C respectively.

Moisture resistance.

About 30-cm long cable specimen prepared in the same manner as for the fire retardation test is sealed at its both ends and then allowed to stand for 7 days in a constant-temperature and constant-humidity chamber adjusted to 40°C and

relative humidity of 90%. The specimen is thereafter withdrawn from the chamber, dried and then tested for fire retardation in the same manner as in the fire retardation test described above. The moisture resistance is rated according to the following criteria, based on the foregoing criteria for fire retardation:

- A: Excellent to good in fire retardation.
B: Fair to acceptable in fire retardation.
C: Unacceptable in fire retardation.

Ageing resistance against heat.

About 30-cm long cable specimen prepared in the same manner as for the fire retardation test is allowed to stand for 30 days within a Gear oven adjusted to 70°C and is then tested for fire retardation in the same manner as in the fire retardation test. The heat resistance is rated according to the same criteria as the moisture resistance.

Airtightness.

An iron pipe, 300 mm in inside diameter and 600 mm in length, is filled at its one end with each putty to a thickness of 100 mm. While exposing the putty to the atmosphere at room temperature, air pressure of 0.8 kg/cm² gauge is applied to the other end of the pipe for five minutes. When the flow rate of air through the layer of putty during the pressure application is up to 5 litres/minute, the putty is evaluated as acceptable, which is represented by A in Table 1.

WHAT WE CLAIM IS:—

1. A fire retardant intumescent composition having a permanent putty-like mouldable consistency and having a cone penetration value of 2—40 (mm/150 g, 5 sec., at 20°C) determined in accordance with the provision of JIS A5752—1966, which comprises (a) at least 4% by weight of an organic material of non-hardening type in a semi-solid or liquid state at room temperature and having a viscosity of 50—100,000 c.st. at 210°F, and (b) at least 13% by weight of a nitrogen-containing phosphate which is a phosphoric acid represented by the general formula,



(wherein

$$0 < \frac{x}{y} \leq 3$$

and n is 1—14), one or all of the hydrogen atoms of which are substituted with a nitrogen containing group of mono-, di-, or tri- valency consisting essentially of nitrogen and either or both of hydrogen and carbon, and containing at least 7% by weight of phosphorus.

2. A fire retardant intumescent composition according to claim 1 wherein said organic material is polybutene having a viscosity of 500—10,000 c.st at 210°F and said nitrogen-containing phosphate is melamine monophosphate or ammonium polyphosphate of which average molecular weight and nitrogen content are 200—300,000 and 10—25% by weight, respectively.

3. A fire retardant intumescent composition according to claim 1, which contains at least one further component selected from (c) polyhydric alcohols and carbohydrates, (d) blowing agents, (e) greases, (f) heat resistant fibres, and (g) micro balloons.

4. A fire retardant intumescent composition according to claim 3, which contains (c) a polyhydric alcohol or a carbohydrate and (d) a blowing agent, the proportion of said components (b), (c), and (d) being within the region represented by the area on the triangular co-ordinates of the drawing enclosed by the straight lines interconnecting point α (30, 60, 10), point β (10, 60, 30), point γ (10, 30, 60), point δ (30, 10, 60), point ϵ (60, 10, 30), and point ζ (60, 30, 10), and the total amount of said components (b), (c) and (d) being 200—1400 parts by weight per 100 parts by weight of said (a) organic material.

5. A fire retardant intumescent composition according to claim 4, which

(19)

relative humidity of 90%. The specimen is thereafter withdrawn from the chamber, dried and then tested for fire retardation in the same manner as in the fire retardation test described above. The moisture resistance is rated according to the following criteria, based on the foregoing criteria for fire retardation:

- A: Excellent to good in fire retardation.
- B: Fair to acceptable in fire retardation.
- C: Unacceptable in fire retardation.

Ageing resistance against heat.

About 30-cm long cable specimen prepared in the same manner as for the fire retardation test is allowed to stand for 30 days within a Gear oven adjusted to 70°C and is then tested for fire retardation in the same manner as in the fire retardation test. The heat resistance is rated according to the same criteria as the moisture resistance.

Airtightness.

An iron pipe, 300 mm in inside diameter and 600 mm in length, is filled at its one end with each putty to a thickness of 100 mm. While exposing the putty to the atmosphere at room temperature, air pressure of 0.8 kg/cm² gauge is applied to the other end of the pipe for five minutes. When the flow rate of air through the layer of putty during the pressure application is up to 5 litres/minute, the putty is evaluated as acceptable, which is represented by A in Table I.

WHAT WE CLAIM IS:—

1. A fire retardant intumescent composition having a permanent putty-like mouldable consistency and having a cone penetration value of 2—40 (mm/150 g, 5 sec., at 20°C) determined in accordance with the provision of JIS A5752—1966, which comprises (a) at least 4% by weight of an organic material of non-hardening type in a semi-solid or liquid state at room temperature and having a viscosity of 50—100,000 c.st. at 210°F, and (b) at least 13% by weight of a nitrogen-containing phosphate which is a phosphoric acid represented by the general formula,



(wherein

$$0 < \frac{x}{y} \leq 3$$

and n is 1—14), one or all of the hydrogen atoms of which are substituted with a nitrogen containing group of mono-, di-, or tri- valency consisting essentially of nitrogen and either or both of hydrogen and carbon, and containing at least 7% by weight of phosphorus.

2. A fire retardant intumescent composition according to claim 1 wherein said organic material is polybutene having a viscosity of 500—10,000 c.st at 210°F and said nitrogen-containing phosphate is melamine monophosphate or ammonium polyphosphate of which average molecular weight and nitrogen content are 200—300,000 and 10—25% by weight, respectively.

3. A fire retardant intumescent composition according to claim 1, which contains at least one further component selected from (c) polyhydric alcohols and carbohydrates, (d) blowing agents, (e) greases, (f) heat resistant fibres, and (g) micro balloons.

4. A fire retardant intumescent composition according to claim 3, which contains (c) a polyhydric alcohol or a carbohydrate and (d) a blowing agent, the proportion of said components (b), (c), and (d) being within the region represented by the area on the triangular co-ordinates of the drawing enclosed by the straight lines interconnecting point α (30, 60, 10), point β (10, 60, 30), point γ (10, 30, 60), point δ (30, 10, 60), point ϵ (60, 10, 30), and point ζ (60, 30, 10), and the total amount of said components (b), (c) and (d) being 200—1400 parts by weight per 100 parts by weight of said (a) organic material.

5. A fire retardant intumescent composition according to claim 4, which



* C L M S *

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contains at least one component selected from (e) greases, (f) heat resistant fibres, and (g) microballoons.

5 6. A fire retardant intumescent composition according to claim 5, wherein
10 said (a) organic material has a viscosity of 500—10,000 c.st. at 210°F and said (b) nitrogen-containing phosphate is at least one member selected from melamine monophosphate, melamine diphosphate and melamine polyphosphate, and said (c) polyhydric alcohol is at least one member selected from pentaerythritol, dipentaerythritol and tripentaerythritol, and said (d) blowing agent is at least one member selected from the group consisting of melamine, trimethylol melamine, hexamethylol melamine, dicyandiamide, said (e) grease is at least one member selected from lithium soap grease, aluminium complex grease, bentonite grease and silica gel grease, the grease having a cone penetration value of 40—500, and said (f) heat resistant fibre is asbestos and glass wool, and said (g) microballoons are glass balloons.

15 7. A fire retardant intumescent composition substantially as hereinbefore described, with reference to any one of the Examples.

8. A fire retardant composition as claimed in claim 1, substantially as herein described.

For the Applicants:
MATTHEWS, HADDAN & CO.,
Chartered Patent Agents,
33 Elmfield Road,
Bromley, Kent.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

