

The present invention relates to a coating for protecting structures, especially against fire and heat.

The word "coating" is referred-to hereinafter in its strict sense, thus excluding all massive materials
5 such as bricks and hollow blocks which have sufficient strength to form the fabric of the structure.

The term "structures" will mainly designate hereinafter the walls, ceilings, roofs, doors and structural frameworks of residential buildings or
10 industrial or agricultural premises, garages, sheds, constructed of metal joists, beams and posts, full or openwork or latticework frame girders, partition walls, panels of plastic material, expanded materials as well as false ceilings and their suspension sectional members,
15 fire shields, ventilation ducts, smoke ducts and fire ducts, pipelines in particular for conveying petroleum products and like inflammable materials.

The term "structures" will also designate in the following description floating structures such as ships as
20 well as reservoirs for storage of inflammable products such as petroleum and chemical products, frames of hydraulic turbines or nuclear power plant turbines, nuclear reactors and the like.

In order to protect the aforementioned structures against the effects of fire and heat, it has already been a common practice to use products having a base of asbestos, of ceramic fibers, of rock wool or glass wool fibers which may be coated if necessary with an inorganic or organic binder.

Among the binders most commonly used for coating the fibers aforesaid, there can be mentioned in particular the ordinary cements of the "Portland" type, the magnesia cements, plaster, aluminum monophosphate and chlorophosphate and the phosphate binders.

These flameproof products have densities comprised between 0.3 and 1.2. The light products having a density of the order of 0.3 to 0.4 usually have a base of mineral fibers such as rock wool, basalt or blast furnace slag, ordinary cement of the "Portland" type being added thereto in a proportion of 40 to 50 % cement and 50 to 70 % fibers. The temperature resistance of these products is fairly low and their heat-insulating power is rather unreliable. The duration of their fire resistance seldom exceeds one hour to one hour and thirty minutes when they are not sufficiently compacted or compressed in order to increase their density to approximately 0.9, with a thickness of protection greater than or equal to 30 millimeters.

Flameproof products having a higher density

comprised between 0.9 and 1.2 approximately are usually available in the form of projectable mud having a base of plaster or of ordinary or magnesia cement to which are added fibers and refractory particles.

5 These flameproof products have better fire resistance and possess in addition a higher coefficient of heat insulation than the above-mentioned products which have lower density.

 However, none of the known cement-base flame-
10 proof products affords resistance to a temperature above 800-900°C. In fact, these products lose their cohesion at these temperatures by reason of the fact that the cement disintegrates to a powdered state. Thus the flameproof product becomes detached from the surface on which it had
15 been applied, with the result that this surface is then no longer protected against the effects of fire and heat.

 U.S. patent 3,885,980 describes a heat-resistant composition made up of plaster and heptahydrated magnesium sulfate. This composition is subject to the disadvantages
20 attached to plaster. Furthermore, hydrated magnesium sulfate is incompatible with cement.

 French patent Application 2,315,489 describes granular products which contain an inorganic product such as sodium phosphate as well as perlite, vermiculite,
25 plaster and the like. This document does not describe a cement-base coating which, by definition, must adhere to

the surface to be protected. In this document, the inorganic products are employed for the foaming properties which they possess when they are exposed to fire. These properties are useful when the flameproof product is in the form of granules but are unacceptable in the case of a coating which is intended to remain adherent to its support. In fact, foam formation would result in disintegration of the cement and cause it to separate from the support, with the result that this latter would no longer be protected against fire.

The object of the present invention is to provide a coating for protecting structures against fire and heat which have distinctly improved properties with respect to those of known coatings.

In accordance with the invention, the coating for protecting structures against fire and heat, comprising inorganic refractory particles coated with a hydraulic binder is characterized in that it comprises magnesia cement or aluminous cement and/or Portland cement and an alkali-metal or alkaline-earth phosphate which is capable, at the time of setting of the cement and in the presence of water, of providing the coating with a number of molecules of water of crystallization greater than that obtained with the cement alone, the proportion by weight of this alkali-metal or alkaline-earth phosphate being comprised between 1.5 and 20 %.

The above-mentioned cements form molecules of water of crystallization at the time of setting. By virtue of the presence in the coating of the alkali-metal or alkaline-earth phosphate, the number of molecules of water of crystallization in the hardened coating is increased.

Experience has shown this surprising result, that it was thus possible to achieve a considerable increase in the fire protection obtained by the coating.

It has in fact been found that, when a coating of this type was exposed to heat or to fire, its temperature increased at a much lower rate than the known coatings, the mean rate of temperature rise being lower as the number of molecules of water of crystallization contained in this coating was greater.

Although the invention is unrelated to this explanation, the present Applicant believes that this property results from the fact that the liberation of water of crystallization entails the need for a substantial supply of heat, which has the effect of maintaining the temperature of the coating at a low temperature comprised between 100 and 200°C as long as the water of crystallization has not been liberated.

Moreover, the crack formation and disintegration of the coating as indicated earlier are caused precisely by liberation of the water of crystallization formed at the time of setting of the inorganic binder in the

presence of water.

In consequence, any person versed in the art was dissuaded from increasing the quantity of water of crystallization as contemplated by the present invention, for fear of accelerating or amplifying the process of crack formation and disintegration of the coating.

Other particular features and advantages of the invention will further become apparent from the description given hereinafter.

- When the inorganic binder employed is a magnesia cement, the composition by weight of the coating in accordance with the invention is preferably as follows :
- magnesia cement (magnesia chloride or sulfate with added magnesia) : 20 to 80 %
 - perlite and/or vermiculite and/or fillite : 10 to 0 %
 - calcium borate : 0 to 10 %
 - synthetic fibers : 60 to 0 %
 - carbonaceous materials (wood flour) 0 to 4 %
 - iron oxides : 0 to 0.2%
 - fluorspar : 0 to 4 %
 - compound supplying the water of crystallization : alkali-metal or alkaline-earth phosphate : 10 to 1.8%

There is given hereinafter one example of composition of the coating having a magnesia cement base.

Example I

	- magnesia sulfate :	34	%
	- magnesia :	37.5	%
	- perlite :	0	%
5	- synthetic fibers :	0	%
	- calcium borate :	10	%
	- wood flour :	4.5	%
	- fluorspar :	4	%
	- alkali-metal or alkaline-earth phosphate :	10	%

10 When a coating of this type is exposed to heat or to fire, it behaves in the following manner :

 The temperature of this coating as measured within this latter, instead of increasing in accordance with a continuously rising curve as could be expected, 15 remains constant during a period of time which usually attains several hours at a temperature comprised between 100 and 200°C. This result endows the coating in accordance with the invention with fire-resistant and heat-resistant properties which are extremely advantageous.

20 The level-temperature stage mentioned above cannot in any sense be explained by the heat insulation provided by the constituents of the coating. In the opinion of the present Applicant, the explanation for this level-temperature stage lies in the presence within the 25 coating of an appreciable quantity of water of crystallization.

In fact, the liberation of this water of crystallization entails the need for a supply of heat corresponding to the binding energy of the water molecules and 540 kcal. per kg in order to convert this free water to steam. Moreover, the water liberated in the form of steam humidifies the atmosphere, which is helpful in extinguishing the fire.

The level-temperature stage at which this liberation of water takes place remains until the entire quantity of water of crystallization has been vaporized. The duration of this stage is consequently proportional to the proportion of water of crystallization of the coating.

The process of crack formation of the coating as a result of disintegration of the inorganic binder begins before all the water of crystallization has been liberated. At this stage, the inorganic binder which has lost all of its physical properties as a binding agent is no longer capable of ensuring cohesion of the coating. It is at this point that sintering of the refractory particles takes place and ensures a certain cohesion of the coating by preventing this latter from falling into dust.

This sintering process begins by means of the fluxes (calcium borate and fluorspar) at a temperature which is substantially comprised between 850°C and 900°C.

Thus, by virtue of this sintering process, the

coating in accordance with the invention ensures protection against heat and fire up to temperatures which usually exceed 1200°C.

The coating obtained from the composition in accordance with Example I is very hard and exhibits very good adhesion to all supports including glass. However, this coating must not be exposed to bad weather conditions. When these coatings are exposed to fire, their temperature remains constant at approximately 100°C during a period of time comprised between one half-hour and six hours (depending on their thickness) by virtue of the water of crystallization contained in these coatings. Furthermore, sintering of the inorganic particles (perlite or vermiculite) which is achieved by virtue of the fluxes (calcium borate and fluorspar) enables the coating to remain coherent up to temperatures well above 1000°C.

The coating in accordance with Example I is preferably employed for finishing coats applied to already-existing coatings such as mineral or asbestos wools with a view to enhancing their mechanical strength.

Starting from a magnesia cement, it is also possible to obtain a coating which exhibits good sound-insulating power while having an appreciable fire-resisting power by modifying the composition of the constituents as indicated hereinafter :

-10-

	- magnesia chloride or sulfate with added magnesia :	26 to 60	%
	- perlite and/or vermiculite in grains having a diameter comprised between		
5	0 and 5 mm :	15 to 38	%
	- calcium borate and/or calcium carbonate :	3 to 0	%
	- synthetic fibers :	28 to 0	%
	- wood flour :	4 to 0	%
10	- fluorspar :	4 to 0.5	%
	- alkali-metal or alkaline-earth phosphate :	20 to 1.5	%

When the inorganic binder employed is an
aluminous cement of the Portland type (ordinary cement or
15 white cement NF 45 R), the composition by weight of the
coating in accordance with the addition is preferably
as follows :

	- aluminous cement and/or Portland cement :	30 to 62	%
	- inorganic particles (perlite and/or		
20	vermiculite, for example) :	25 to 10	%
	- carbonaceous materials :	0 to 2	%
	- cement-setting retardants or accelerators :	0 to 2	%
	- fluxes :	0 to 3.5	%
25	- mineral and/or organic fibers :	40 to 0.5	%

- compounds supplying or forming water of crystallization : alkali-metal or alkaline-earth phosphate : 5 to 20 %

There are given hereinafter a few examples of
5 compositions of coatings having a base of aluminous cement or Portland cement :

Example II

- Portland cement : 29 %
- aluminous cement : 16 %
- 10 - fluorspar : 5 %
- silica : 20 %
- hydrated alumina : 20 %
- alkali-metal or alkaline-earth phosphate 10 %

Example III

Example IV

- | | | | |
|----|--|-------|--------|
| 15 | - aluminous cement : | 62 % | 50 % |
| | - perlite : | 10 % | 15 % |
| | - vermiculite : | 0 % | 10 % |
| | - synthetic fibers : | 0.5 % | 0.5 % |
| | - wood flour : | 4 % | 4 % |
| 20 | - fluorspar : | 3.5 % | 2.5 % |
| | - alkali-metal or alkaline-earth phosphate : | 20 % | 17.5 % |

Example V

- aluminous cement : 16 %
- 25 - Portland cement : 29 %
- quicklime : 14 %

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	- perlite :	18	%
	- fluorspar :	2	%
	- wood flour :	3	%
	- alkali-metal or alkaline-earth phosphate :	18	%
5		<u>Example VI</u>	
	- aluminous cement :	0	%
	- Portland cement :	58	%
	- quicklime/or slaked lime :	0	%
	- perlite :	5	%
10	- vermiculite :	10	%
	- synthetic fibers :	0.5	%
	- fluorspar :	3.5	%
	- cement-setting retardant or accelerator :	1	%
	- wood flour :	2	%
15	- calcium carbonate :	0	%
	- alkali-metal or alkaline-earth phosphate :	20	%

The coatings obtained from the compositions in accordance with Examples II to IV are a little less hard than the coating obtained from Example I. They possess good adhesion to plaster, cement and iron. After exposure to fire, they adhere a little less strongly than the coatings having a base of magnesia cement but they have higher fire resistance than these latter by virtue of the excellent sintering which is obtained between the inorganic particles.

In addition, the coatings in accordance with

Examples II to VI can be exposed to bad weather conditions.

Moreover, the coatings in accordance with Examples II to VI retard the temperature rise in the event of fire to the greatest extent since, at the time of setting, they retain a maximum quantity of water of crystallization.

In the case of ordinary cements of the Portland type, slag cements, monocalcium aluminate cement, artificial cements of tricalcium silicate and calcium borosilicate and refractory cements having a high alumina content, it is found that the addition of the compound which produces the water of crystallization accelerates the setting of these cements to an appreciable extent, which constitutes a disadvantage for the application of the coating.

The present Applicant has discovered that this drawback could be removed by adding to the coating composition a setting retardant consisting of borax (sodium tetraborate) or boric acid.

In the case of magnesia cements, the setting time depends on the loss by burning of the magnesia employed in cements of this type. The setting time is of optimum value when the magnesia has a loss by burning of approximately 12-13 %. Should this not be the case, setting is often slow.

The present Applicant has discovered that this disadvantage could be overcome by adding quicklime and/or slaked lime as a setting accelerator to the composition of a magnesia cement containing any type of magnesia.

CLAIMS :

1. Coating for protecting structures against fire and heat, comprising inorganic refractory particles coated with a hydraulic binder, characterized in that it
5 comprises magnesia cement or aluminous cement and/or Portland cement and an alkali-metal or alkaline-earth phosphate which is capable, at the time of setting of the cement and in the presence of water, of providing the coating with a number of molecules of water of crystalliz-
10 ation larger than that obtained with the cement alone, the proportion by weight of this alkali-metal or alkaline-earth phosphate being comprised between 1.5 and 20 %.

2. Coating in accordance with claim 1, characterized in that its weight composition is as follows :

15	- magnesia cement (magnesia chloride and/or sulfate with added magnesia)	:	26 to 60	%
	- perlite and/or vermiculite in the form of grains having a diameter comprised between 0 and 5 mm	:	15 to 38	%
20	- calcium borate and/or calcium carbonate	:	3 to 0	%
	- synthetic fibers	:	28 to 0	%
	- wood flour	:	4 to 0	%
	- fluorspar	:	4 to 0.5	%
	- alkali-metal or alkaline-earth phosphate which is capable, at the time 25 of setting of the cement and in the			



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