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PRODUCTION OF PHOSPHATE BINDER FIRE-PROTECTIVE COATING FOR STEEL BUILDING CONSTRUCTIONS

Brief analysis of means for fire protection of steel building constructions was given, special attention being paid to the advantages of using phosphate binders for protective coatings. The composition of fire-protective coating based on cold-cured phosphate binder was developed, its properties being thoroughly examined.

Introduction. The problem is vital as there is a steady growth of social and economic damages from fire in the Republic of Belarus. Data show [1] the tripled quantity of fires, four-times increase in mortality and the damage of 1% GDP during the past 25 years.

According to the Emergencies Ministry statistics in 2011 there were about 9 thousand fires in the Republic of Belarus that took more than 1.2 thousand lives and destroyed 1.5 thousand buildings.

One of the least protected structural parts is steel supporting structures. For most steels the critical temperature is considered to be 500°C, higher temperatures causing deformation and almost immediate destruction of such structures [2].

To protect steel constructions against fire materials of the 1st flameproof degree are needed, which are capable to ensure their heat insulation under fire attack at temperatures of up to 1,100°C within 150 min [3, 4].

The main components of fire-protecting means determining their properties are binders. These create the coating, determine its main physical, chemical and performance characteristics, i.e. ensure its fire resistance, adhesion to substrate, durability, etc.

To make 1st degree fire-protective coatings special fillers and modifying additives are used that are stable to the action of heat flow and preserve their properties under fire attack.

Fire protective compound [5–7] includes the following ingredients:

– refractory materials capable to preserve their properties at high temperatures;

– swelling or swollen materials capable to provide heat insulation of the construction;

– materials including chemically bound water;

– antipyrines: fusible borates, phosphates and silicates and/or materials decomposing when heated and emitting gases which do not support combustion.

During decomposition of fire-retardants a part of heat is used to suppress endothermic process, thereby raising ignition temperature. Noncombustible gas evolved prevents flame from spreading.

Nowadays various types of fire-protecting materials possessing different flame resistance degree are produced and applied in the CIS. They are prepared on the basis of organic and inorganic binders, fillers and modifying additives.

Swelling coatings based on organic binders [8, 9] are easy to produce and have good architectural, decorative and industrial characteristics. However, they can increase the fire-resistance limit of constructions only within 1 h, and combustion products of such materials are toxic and may lead to mass asphyxia in case of fire. The coatings concerned are insufficiently stable under production air conditions and high humidity, that in case of a long-time service (more than 3 years) leads to emerging and developing corrosion centers on the steel construction and under the coating, to adhesive strength deterioration, coating delamination and cracking resulting in reduced flame resistance time.

Such coatings may be of the following domestic and foreign trademarks: Agnitherm M (Belarus), Agnitherm MP (Belarus), Sinatherm 1 (Belarus), GARD (Belarus), Protherm CE (Russia), Phoenix CTC (Russia), Phoenix CTB (Russia), Unitherm ADR (Germany), Tikra Termostop (Slovenia).

Fire-protective mixtures based on liquid glass are suitable for indoor application at relative humidity of not more than 60%, and, therefore, cannot be used out-of-doors. However, for many constructions outside protection is much more vital. Moreover, such materials cannot be stored for a long time, they are less productive in comparison with dry compounds, fragile, possess low adhesion and insufficient climatic stability and durability. With time passing the materials are covered with spots (whitish layer) and cracks, that deteriorates decorative and service properties of finished surfaces. The reason is carbonizing – chemical interaction of the compounds concerned with carbon dioxide and other reactive gases from the air.

Phosphate-binder-based fire-protective means are used for the protection of steel [10]. Such materials [11] preserve their properties at temperatures up to 1,600°C, have flameproof limit of at least 150 min, they are water-resistant, i.e. suitable for both indoor and outdoor applications. Phosphate-binder-based compounds are widely used in the USA, China, Japan and many other countries, that is confirmed by numerous patents and publications [12–15]. Besides, phosphate compounds are applied industrially as fire-retardants in many fire-protective materials containing organic binders.

All the above mentioned allows to conclude that in the Republic of Belarus there is an acute need to protect metal constructions from fire, but there are no materials of domestic production with flameproof limit of 150 min.

The aim of the present research is to prepare cheap and effective materials of the 1st flameproof degree for protecting steel constructions and to study their properties.

Main part. Having examined the main types of binders and fire-protection means it can be concluded that the basic requirements to fire-protective compounds of the 1st flameproof degree are:

– ability to preserve their properties under temperatures of up to 1,100°C within at least 150 min;

– ability to insulate fire heat flow, to prevent protected materials from destruction;

– durability;

– water resistance;

– adhesion to steel constructions;

– ability to inhibit corrosion of steel constructions;

– no toxic materials evolved under fire impact.

And it is phosphate-binder-based fire-protective compositions that mostly comply with these requirements. Such types of binders provide the highest fire-resistance limits as they are mainly refractory materials that are stable to heat flow and preserve their structure and properties under heat impact.

Monomeric phosphates are the most suitable ones for fire-protective compounds. The reason is that the original monomeric anion being a constituent part of the acid salt (orthophosphate) is capable to polycondensate, with temperature increasing. It leads to the formation of chemically bound water at 150–170°C and, consequently, of the dimer (pyrophosphate). The dehydration process is endothermic and decreases the temperature of the fire. Water vapor formed blocks the way of heat flow to the construction, and of oxygen to fire site. Chemically bound water formation stops only at 450°C when metaphosphates (polyphosphates) are formed. Besides, another advantage of monomeric anion is the fact that monomer in the acid salt will show adhesive properties, the adhesion being determined by chemical interaction of acid salt with surface iron-oxide film of the steel building constructions face.

Metals (Na, Ca, Mg, Al) can be used as a cation in phosphate binders, as it is metal cations that when interacting with phosphates reveal somewhat similar characteristics. Ammonium salt may also be used for this purpose. It is preferable, however, to use ammonium phosphates, as at high temperatures the ammonium cation may self-decompose evolving nonflammable gaseous products (ammonia) and, therefore, contribute to blocking combustion zones. Moreover, at further temperature impact ammonia decomposes into nitrogen and hydrogen with energy losses, which decreases the temperature of the fire.

Summarizing the above mentioned and taking into account the economic factor it may be concluded that the raw material component can be ammophos consisting mainly of ammonium dehydrophosphate with a small portion of ammonium hydrophospate.

However, ammophos is not widely used for fire protection of steel constructions as ammonium phosphates are not stable on exposure to the weather, not waterproof and require heat treatment for hardening.

To make fire-protective materials capable to harden in cold-weather conditions a magnesium-containing compound was added to the basic composition. But for magnesium-phosphate binders the setting time is 1–2 min even with retarder (5–10% of weight). Adding more retarder is technically and economically not expedient.

Considering all this the fire-protective material was developed on the basis of magnesium-chrome-phosphate binder, it possessing longer setting time and, moreover, better anticorrosion properties when used for steel constructions. When producing such binders a secondary refractory material (periclase-chromite, chromite-periclase, etc.) can be used as a neutralizing agent for phosphoric acid [16]. It should be noted that the $NH_4H_2PO_4 – (NH_4)_2HPO_4 – MgO – Cr_2O_3 – H_2O$ system has not been studied yet, and no data concerning the crystallization processes on which hardening of the composition involved is based have been found in recent publications. The study of the phase formation process in such a system in non-equilibrium conditions is of scientific interest. The results obtained will al-low to control the binder formation process and will thereby contribute to the study of the chemistry and technology of phosphate materials.

Hence, the fire-protective material was developed on the basis of used periclase-chromite refractory, ammophos and vermiculite.

For better adhesion of the coating to steel constructions and more "productive" application process polymeric additives were used – redispersible polymeric powder and cellulose ester. Boric acid was added to the compound in order to control the performance time, i. e. that of setting and hardening.

The composition of the fire-protective coating was optimized by varying the quantity of the components mentioned in the following range: binder – 50–60 wt %, binder hardener – 40–50 wt %, the content of vermiculite being 5–30 wt %, of boric acid – 3–7 wt %, of polymeric additives – 0.2–4.0 wt % that of the binder. The research results are presented in Fig. 1–4.

The investigation revealed that at temperatures of 300 and 900°C adhesion and compression strength were lower because of structural and phase transformations in the composition.

According to some authors [17], $MgNH_4(PO_4)_3$ and MgO form at the temperature of approximately 300°C, and at 900°C the formation of orthophosphate β-$Mg_3(PO_4)_2$ is X-rayed, this explaining the results obtained.

The present research has revealed that with the developed material layer thickness of 5 cm and its 5–15 kg/m^2 use a steel construction fireproof limit is at least 150 min. Therefore the coating can be recommended for outside applications.

The results of further investigations on phosphate binder fire-protective coatings for steel constructions will be presented in future publications.

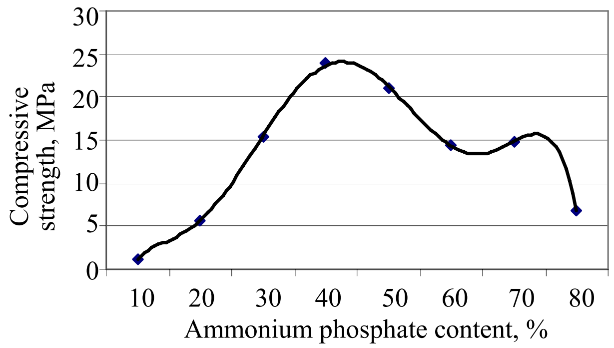

Fig. 1. The dependence of the compressive strength of the fire-protective composition of the content ammophos

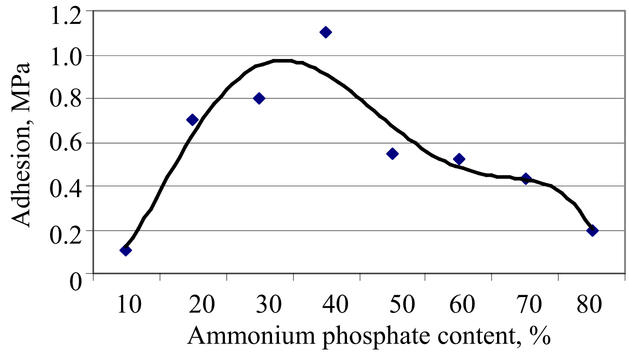

Fig. 2. The influence of ammonium phosphate flame retardant composition for adhesion

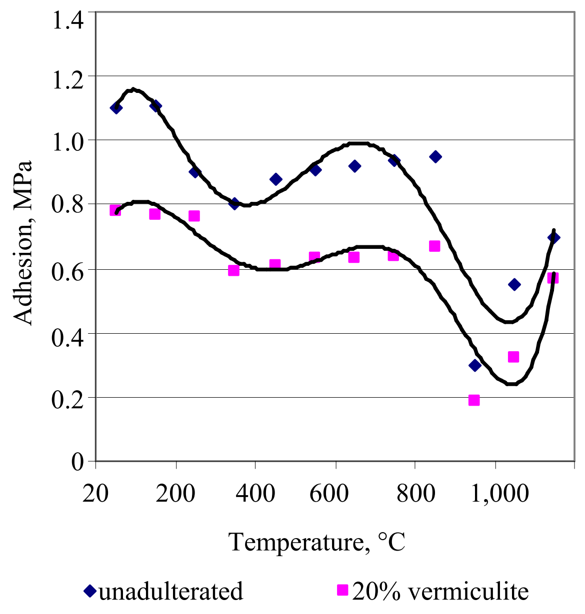

Fig. 3. The dependence of the flame-retardant adhesive composition on the temperature

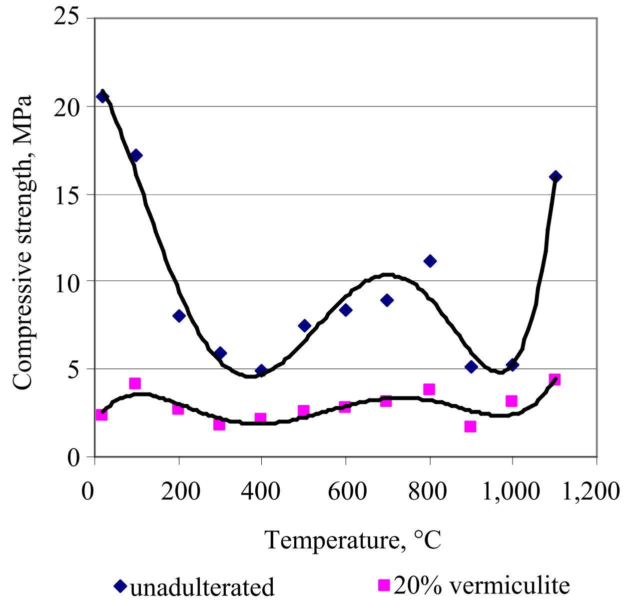

Fig. 4. Effect of temperature on the compressive strength of the flame-retardant composition

Conclusion. The composition of fire-protective coating including ground periclaso-chromite refractory, ammophos, boric acid, redispersive polymeric powder and cellulose ester has been developed. Its performance parameters have been determined. Preliminary cost calculations of phosphate- binder -based coatings have shown that they are 5–10 times cheaper in comparison with liquid-glass-based ones, and 30 times – in comparison with swelling organic fire-protective compounds. Materials developed are effective and accessible and can be widely applied in building complexes.

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