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Study of the Influence of Fillers on Swelling and Water Absorption of Reactive Fire-Retardant Coatings of Metal Structures

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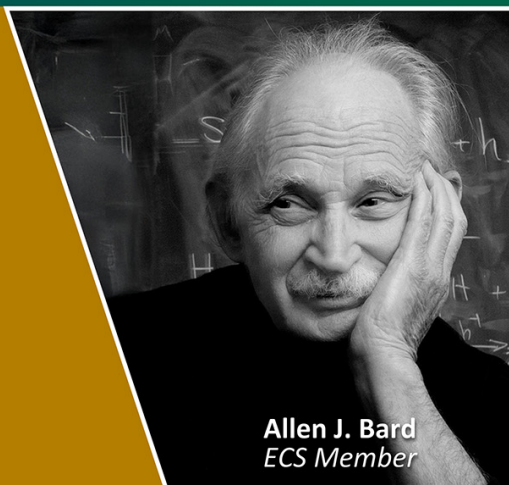


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STUDY OF THE INFLUENCE OF FILLERS ON SWELLING AND WATER ABSORPTION OF REACTIVE FIRE-RETARDANT COATINGS OF METAL STRUCTURES

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Abstract. A study was conducted to determine the linear coefficient of swelling, its strength, the group of fire retardant efficiency and resistance to water sorption of the developed reactive fire retardant coatings of metal structures consisting of ammonium polyphosphate/pentaerythritol/aluminum hydroxide/styrene-acrylic water dispersion. The creation of such polymer fire protection coatings for metal structures has always been and remains one of the priority areas of fire protection of buildings and structures, since the material costs of restoration after a fire many times exceed the costs of preventive fire protection measures. As a result of the conducted experimental studies, it was found that all the experimental coatings belong to the first group of fire-retardant efficiency. The foam coke formed by the experimental components has a porous structure, uniform, dense and small cells, without micro cracks and large cavities, which provides better insulating properties. The obtained results of water absorption of styrene-acrylic coatings can be interpreted from the point of view of increasing the contribution of the barrier effect of aerosil in systems with high viscosity, which preserves the chemical composition of the intumescent coating. The developed coatings can be operated at the water-air interface, low water absorption indicates its high protective characteristics.

1. Introduction

The creation of polymer fire-retardant coatings for metal structures has always been and remains one of the priority areas of fire protection of buildings and structures, since the material costs of restoration after a fire exceed the costs of preventive fire protection measures [1-7].

Fire protection of metal structures by treating them with special fire-retardant materials is a mandatory measure and is regulated by national building standards, in particular, DBN B.1.1-7:2016, DBN B.1.2-7-2008.



One of the main methods of increasing the fire resistance of metal structures is the use of reactive fire protection systems - materials that increase the time of maintaining the load-bearing capacity of building structures in fire conditions.

The most common fire retardants, which are widely used in world practice, are thin-layer intumescent (reactive) coatings. The mechanism of fire-retardant action of the intumescent system is the formation of a carbon expanded layer, which acts as a barrier to heat, oxygen and pyrolysis products. Increasing in volume and decreasing in density, such coatings slow down the process of heating of steel and extend the time until the destruction of the metal structure [8, 9].

The disadvantage of reactive coatings containing a high proportion of hydrophilic components as intumescent additives is the exceptional sensitivity of polymer coating films to water, low mechanical strength and a decrease in the fire-retardant characteristics of the coating film during their operation due to the leaching of hydrophilic components [10-14].

The technical result of this work consists in eliminating or reducing the above-mentioned disadvantages of water-dispersion coatings containing intumescent additives.

This paper reviews the results of experimental studies to determine the fire-retardant properties of the developed coatings consisting of ammonium polyphosphate/pentaerythritol/aluminum hydroxide and their resistance to water sorption, which is a necessary stage in the development of new reactive coating technologies.

Such studies are necessary to predict the service life of the fire protection coating in order to replace it in a timely manner and ensure reliable and effective fire protection of the metal structure.

2. Research Methodology

The basic principles of formulating water-based fire-protective coatings are similar to those of paints and varnishes: film former, fillers, pigments (if necessary), defoamer, rheological ingredients, coalescent. The main difference is the presence of an intumescent system, which is responsible for the process of foam coke formation.

A styrene-acrylic dispersion was used as a film former Acronal 290 D, which is produced by the company BASF (content of non-volatile compounds – 50 wt. %, pH 7.5-9.0, average particle size is approximately 100 μm , viscosity at 23 $^{\circ}\text{C}$ (ISO 3219, DIN 53019) at the shear rate 100 s^{-1} is 7-15 $\text{mPa}\cdot\text{s}$) [15]. Intumescent coatings are typically achieved using three components: a source of inorganic acid, a carbon source, and a gas-emitting agent. Dispersion modifiers used cellulose and acrylic thickeners, antifoam, dispersant, coalescent based on a mixture of ether and alcohol and preservative additive.

The method of preparing fireproof coating involves mixing the components in a single technological cycle, which allows you to produce a single mixture. The components of the intumescent system were mixed in the necessary combinations in a laboratory dissolver with a working bowl volume of 1000 cm^3 during 60 min at a milling speed of 900-1000 rpm. A polymer dispersion was added to the resulting paste and mixed at a milling speed of 500–600 rpm for 30 min. The finished system was stored in a sealed container.

As a source of inorganic acid, one of the most frequently used classes for thermoplastic and thermosetting polymers is currently phosphorus-based flame retardants. Phosphorus-containing flame retardants affect the combustion of the polymer, acting in the condensed and gas phases. When exposed to a flame, phosphorus-containing flame retardants are converted by thermal decomposition into phosphoric acid and, as a result, polyphosphoric acid, which esterifies and dehydrates the polymer with the formation of a carbonized layer having a glassy coating. This

layer protects the polymer from thermal radiation and prevents its decomposition. The most relevant of the phosphorus-containing flame retardants, to date is ammonium polyphosphate with a crystalline phase II ($n > 1000$) [16-19].

Pentaerythritol was used as the raw material for the formation of the carbon skeleton of the expanded layer. It is a finely dispersed white powder that, when exposed to temperatures above 250 °C ensures the formation of a dense carbon layer that has low thermal conductivity and significantly reduces the thermal impact on the material or structure being protected [20, 21].

Aluminum hydroxide was used as a gas-releasing agent - a relatively new mineral additive for the production of fire-retardant materials. Aluminum hydroxide at temperatures of about 200 °C and above releases water vapor with the formation of aluminum hydroxide, cooling and diluting the ignition zone. As a result of the endothermic dehydration of aluminum hydroxide, the dynamics of its decomposition accelerates the carbonization of the polymer and the cross-linking reaction with a reduction in gas exchange during the destruction of the polymer through the intumescent layer formed, which provides additional smoke-reducing and flame-retardant effects [22, 23]. In addition, the stable particle size of aluminum hydroxide and its almost spherical shape increase the resistance of paint and varnish materials to ultraviolet rays due to uniform reflection of light from the surface. It also provides fluidity and thixotropic properties to paint and varnish materials, which is a determining factor in their application technology.

To study the influence of intumescent additives on the fire-retardant performance and sensitivity of polymer coating films to water, the principle of various analogies with a quantitative change in the main components was used. Ammonium polyphosphate was used in an amount of 15, 20, 25, 30, 35, 40 wt. %; pentaerythritol – 15, 20, 25 wt. %; aluminum hydroxide – 20, 30, 40 wt. %.

To reduce the water sorption of highly filled aqueous dispersions, recently, hydrophobicized silicon dioxide has been used as a nanoscale modifier. Silicon dioxide, having strong electric fields, also acts as a stabilizer of aqueous dispersions of polymers, prevents the sedimentation of fillers, and provides sedimentation stability and thixotropic properties to highly filled aqueous dispersion coatings [24, 25].

When developing new materials to increase the fire resistance of building structures, preliminary tests are necessary to predict the fire-retardant effect of coatings. Therefore, to assess the flammability and coke formation of the developed coatings, the following indicators were used: oxygen index (DSTU EN ISO 4589-2:2018), linear swelling coefficient, mechanical strength of the coating [26-28]. According to GOST 16363-98, the fire protection efficiency group was determined. Water absorption was determined by immersing the samples in distilled water (water temperature 23 ± 2 °C), in percentage by mass according to DSTU B V.2.7-84-99 [29].

3. Results and Discussion

For the initial determination of the flammability of water-dispersion coatings (WD) and the effective content of the inorganic source of acid of ammonium polyphosphate (APP), the oxygen index (OI). This method can only be used as one of the elements of the initial assessment of the fire hazard of coatings.

There is no classification of fire hazard materials based on the oxygen index value in regulatory sources. However, information sources contain classification parameters that can be applied to materials: samples with an oxygen index value of less than 25% are classified as flammable; polymers are considered to be flame retardant materials and are self-extinguishing if

the oxygen index is 25-27%; with an OI value of more than 27% - as flame retardant. Fig. 1 shows the dependence of the oxygen index (OI) and the swelling coefficient (Sc) on the APP content.

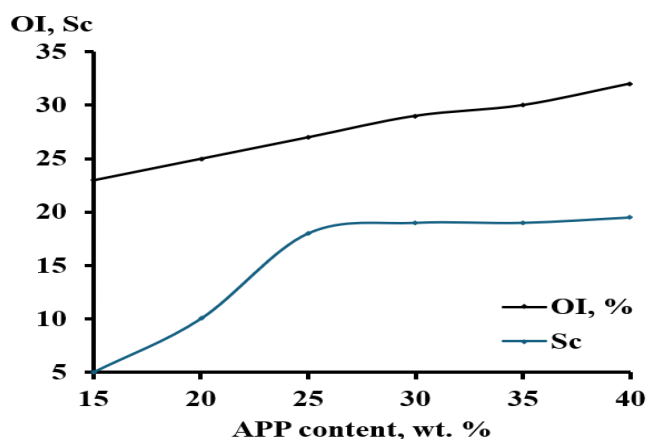


Figure 1. Dependence of oxygen index (OI) and linear swelling coefficient (Sc) on APP content.

As it can be seen from Fig. 1, styrene-acrylic paint and varnish coating passes from the group of flammable materials (OI=16%) to flame retardant self-extinguishing materials at a APP content of 20 wt. % and has OI=25-32%. From the point of view of the influence of APP on the swelling coefficient (Fig. 1), it is clear that its maximum value falls on an APP content of 25 wt. %, a further increase in its content in the composition does not affect the height of the swollen layer, but leads to a decrease in technological properties (increase in viscosity, difficulty in preparing and applying the composition).

It is known that an increase in the swelling coefficient leads to a decrease in the density of foam coke and its mechanical strength. Considering that during swelling, a certain amount of substance in the form of gases and smoke is released from the reaction mass, we can say that with strong swelling, the structure of foam coke is weakened. Also, at high swelling coefficients, according to the law of conservation of mass (even without taking into account gaseous losses), the density of foam coke will be insufficient to withstand the mechanical effects of gas flows in a real fire, therefore the strength of foam coke was determined. The porous structure, which has uniform, dense and small cells, without micro cracks and large cavities, provides better insulating properties.

Fig. 2 shows the structure of the formed expanded layer of coatings filled with the following fillers: ammonium polyphosphate (APP), pentaerythritol (PE), aluminum hydroxide ($\text{Al}(\text{OH})_3$).

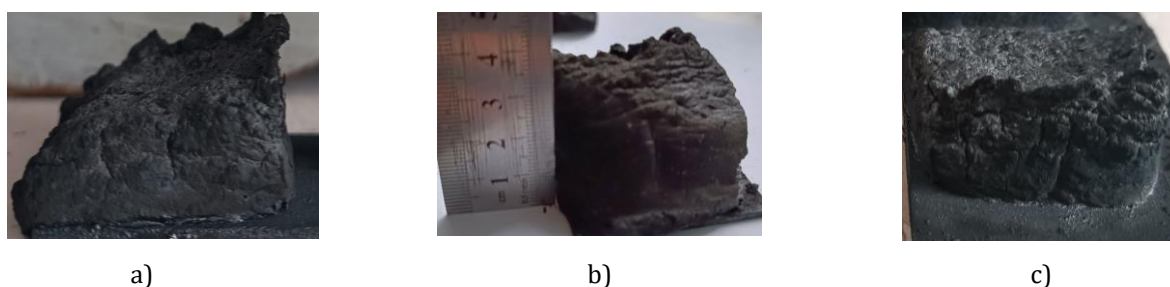


Figure 2. Structure of foam coke with different content fillers: APP:PE: $\text{Al}(\text{OH})_3$ = 15:20:35 wt. % (a), APP:PE: $\text{Al}(\text{OH})_3$ = 15:20:40 wt. %, (b), APP:PE: $\text{Al}(\text{OH})_3$ = 25:15:40 wt. % (c).

The results of the combined use of APP (25 wt. %), PE (15, 20, 25 wt. %) and $\text{Al}(\text{OH})_3$ (20, 30, 40 wt. %) on the flame retardant characteristics of styrene-acrylic dispersion, namely: swelling coefficient (Sc), strength of foam coke (F , g/cm^2), loss of mass after the test to determine the fire protection efficiency (Δm , %) are shown in Fig. 3 in the form of response surfaces.

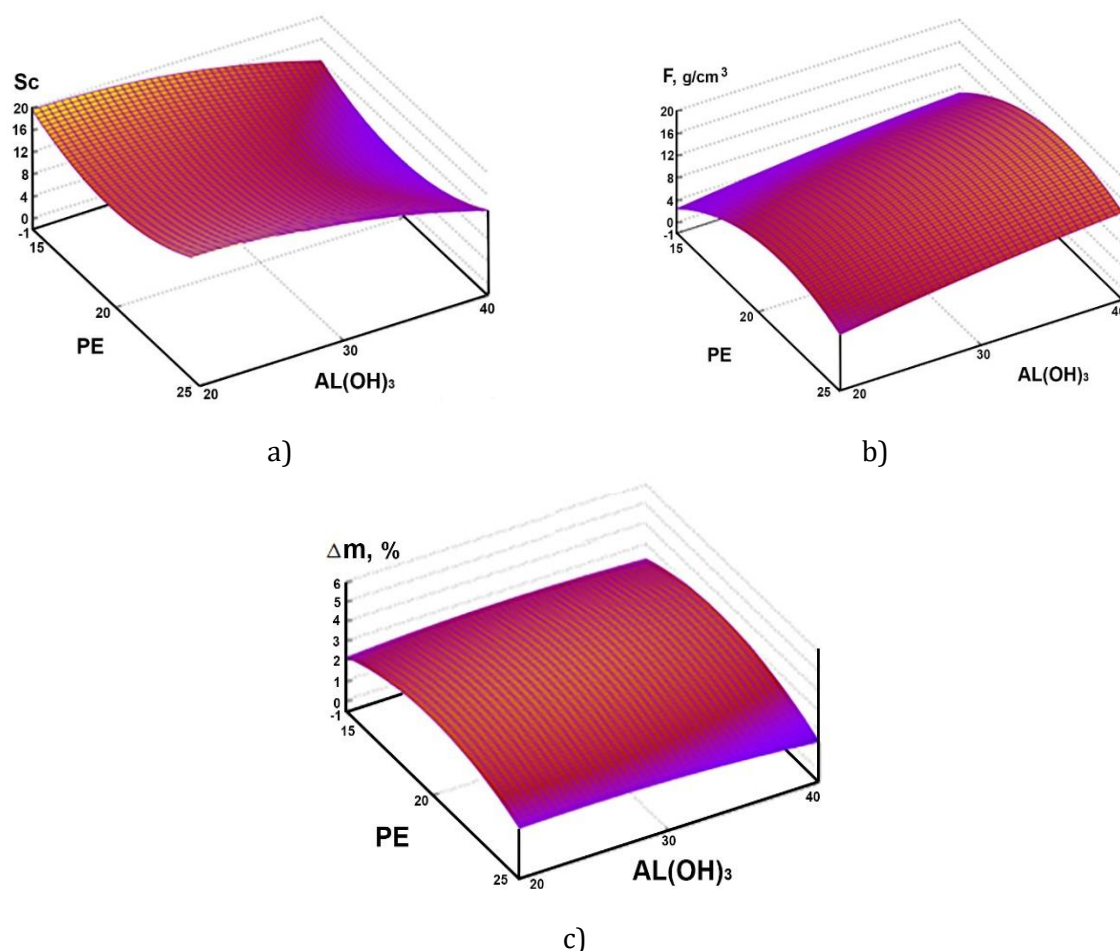


Figure 3. The results of the combined use of APP, PE and $\text{Al}(\text{OH})_3$ on the swelling coefficient (a), strength of foam coke (b), loss of mass after the test to determine the fire protection efficiency (c).

It should be noted that the absolute value of the swelling coefficient is not a measure of fire protection efficiency, i.e., the larger the parameter Sc , the greater the probability of high values of the fire resistance limit. First of all, the thermal insulation efficiency of the coke frame, all other things being equal, depends on its strength and stability. Thus, fine-pored foam, which best provides the greatest strength of the carbon layer and thermal insulation properties is observed for the developed thin-layer water-dispersion coatings filled with the following components: APP 25 wt. %, PE 15-25 wt. % and at $\text{Al}(\text{OH})_3$ 40 wt. %.

Despite the fact that all tested coatings have the first group of fire-retardant efficiency at a coating thickness of $2 \text{ mm} \pm 0,2$, foam coke formed by APP components 25 wt. %, PE 15-25 wt. % and at $\text{Al}(\text{OH})_3$ 40 wt. % has a porous structure, uniform, dense and small cells, without micro cracks and large cavities, which provides better insulating properties.

On these Fig. 4 it is possible to see dependence of water absorption index on time of samples exposure in water. In the first 24 hours of exposure in water the greatest water absorption effect is shown by phosphorus-containing flame retardant APP (from 3.17 to 5.4 times). The coating

filled with aluminum hydroxide in the amount of 20 wt.% has less water absorption (by 2 %) in comparison with WD. Water absorption increases rather slowly and balances out, which indicates maximum swelling of the polymer film.

For coatings filled with PE, the mass of the sample initially increases due to water sorption by the coating, then there is a decrease in mass due to dissolution of the coating and leaching of PE and as a result, it can lead to a loss of fire resistance of the coating.

From the graphs of the dependence of the water absorption rate on time, it can be concluded that the water absorption rate of the styrene-acrylic dispersion has a high value when the sample is kept in water for a day, after which the water absorption rate decreases.

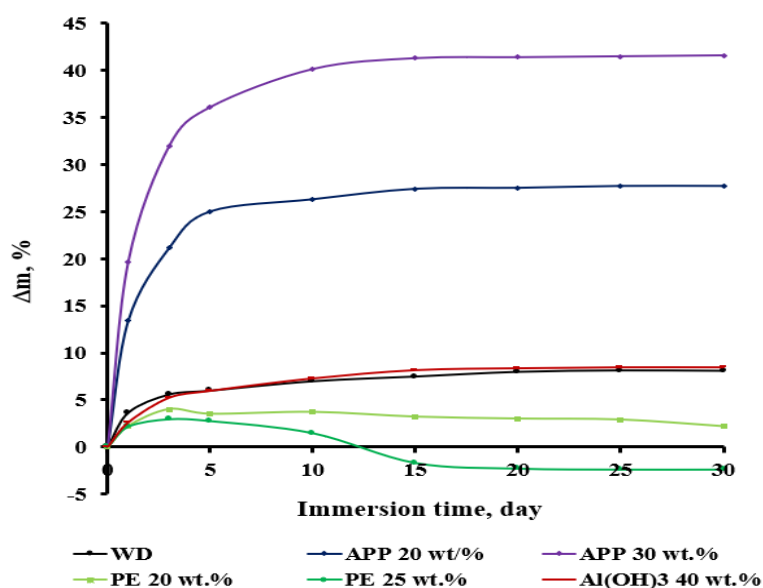


Figure 4. Dependence of the influence of the quantitative content of intumescent fillers (APP=20, 30 wt.%; PE=20, 25 wt.%; Al(OH)₃=40 wt.%) for 30 days on water absorption of the studied WD.

To regulate water absorption, a filler, hydrophobic aerosil was used, which also acts as a stabilizer for aqueous dispersions, prevents pigment sedimentation, and imparts thixotropic properties. Hydrophobized aerosil is a highly dispersed amorphous silicon dioxide with a hydrophobic particle surface obtained by treating the particle surface with finishing agents that replace the hydrophilic silanol groups contained on the particle surface with nonpolar organic groups such as methyl, with a specific surface area of 300 m²/g and medium density 0,051-0,059 g/cm³.

Results of the combined use of intumescent fillers on water absorption of styrene-acrylic dispersion (immersion time 30 day), filled with APP in quantity 25 wt.% and aerosil in quantity 1,0 wt.% and joint combination PE and Al(OH)₃ in the form of response surfaces are shown in Fig. 5.

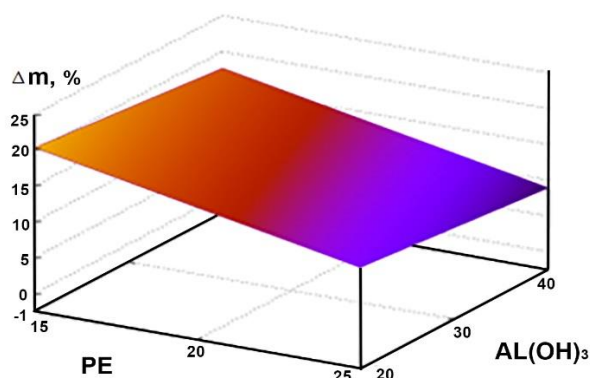


Figure 5. Response surfaces of the dependence of water absorption value of WD on the content of intumescent agents.

Loss of fire resistance of reactive coatings occurs due to leaching of PE, APP. Introduction to the studied system of hydrophobized aerosil with high specific surface area ($300 \text{ m}^2/\text{g}$) forms a more densely packed structure, which leads to a decrease in the surface defects of the styrene-acrylic coating. The localization of hydrophobic aerosil particles on the surface of the defective structures also causes a decrease in the wetting of these structures by water, as a result of which the wetting of the surface of the styrene-acrylic coating deteriorates and the defects of such a structure decrease.

The proposed approach to using a hydrophobic filler with a high specific surface area to maintain fire protection during the operation of intumescent coatings can be used as a promising approach in the development of durable fire-retardant coatings.

4. Conclusions

As a result of experimental studies to determine the swelling coefficient, its strength and the group of fire-retardant efficiency of the developed fire-retardant coatings based on styrene-acrylic aqueous dispersion depending on the content of fire-retardant components it was established that all experimental coatings have the first group of fire-retardant efficiency. Foam coke formed by APP components of 25 wt.%, PE 15-25 wt.%, $\text{Al}(\text{OH})_3$ 40 wt.% has a porous structure, uniform, dense and small cells, without micro cracks and large cavities, which provides better insulating properties.

The obtained results of water absorption of styrene-acrylic coatings can be interpreted from the point of view of increasing the contribution of the barrier effect of aerosil in systems with high viscosity, which preserves the chemical composition of the intumescent coating. The developed coatings can be operated at the water-air interface, low water absorption indicates its high protective characteristics.

Therefore, the obtained results can be used in the development of waterproof fire-retardant coatings for metal structures based on the system of ammonium polyphosphate/pentaerythritol/aluminum hydroxide/styrene-acrylic dispersion.

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