The research of influence polymeric compounds on the effectiveness of intumescent coatings for the fire-protection of construction structures

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Abstract. This article focuses on the devoted to the investigation of the influence polymeric binders on the flame retardant characteristics of intumescent species. It has been found that polymeric binders are the most preferable in the intumescent type of fire retardant compositions, with the thermal destruction of which graphite-like crystalline structures are formed. The chloroparaffin to improves the swelling of intumescent coatings based on acrylic binders by lowering the temperature of their thermal degradation, which occurs under the influence of the dehydrating agent - chlorohydrogen, which catalyzes the processes of carbonization and graphitization into the compounds.

1. Introduction

The range of polymeric binders in the compositions of intumescent (intumescent) compounds designed for the fire protection of building structures is rather narrow, despite the huge variety of film formers present in the world market. The most preferred are [1,2]: the homopolymers of vinyl acetate; the copolymers of vinyl acetate, ethylene and vinyl chloride; the copolymers of vinyl acetate and vinyl ether of one or more long chain or branched chain carboxylic acids; the copolymers of vinyl acetate and dibutyl maleic acid; the copolymers of vinyl acetate and acrylic acid ester; the copolymers of styrene and acrylic acid ester; the copolymers of acrylic acid ester; the copolymers of vinyltoluene and acrylic acid ester. The groups of film-forming agents have been selected experimentally. In publications, there are individual studies on the effect of certain binders on the flame retardant characteristics of the intumescent composition. For example, R. McNair and T. Stapler [3] came to the conclusion that, as applied to flame retardant paints, the binder plays an important role in the development of the foaming process. Polymer binders can inhibit foaming, so their content should be maintained at a minimum level.

In addition to the aqueous dispersions of polymers and synthetic latexes, a great interest is shown to film formers on the organic solutions of polymers. Coatings formed on their basis have the number of important features: high adhesion to the substrate, resistance to UV rays, the weak solutions of alkalis and acids, greater operational capacity compared to coatings prepared on the aqueous solutions of polymers, high moisture and weather resistance, less drying time and the possibility of coating at low temperatures. The most promising is the use of various solutions of acrylic copolymer solutions (for example, methyl methacrylate and butyl methacrylate) as film formers, which allow obtaining coatings with high strength characteristics, good adhesion to the surface to be protected, and weather resistance.

We investigated the influence of film formers on the flame retardant characteristics of intumescent
coatings, in particular, the swelling coefficient and the time of reaching the limiting state of the samples under temperature conditions corresponding to cellulose fire were determined [4].

2. Results The Determination of the flame retardant effectiveness of paints for metal structures is carried out with the help of standardized complex thermophysical tests that are as close as possible to real fire conditions [5], these methods are labor intensive and expensive. Their use is advisable at the stage of material certification, so researchers in the chemical laboratory use semi-quantitative comparative methods for assessing the characteristics of intumescent compositions, which they themselves develop and substantiate in accordance with the scientific and practical tasks being solved. The most common when assessing the characteristics of intumescent coatings, judging by the publications, is the determination of the expansion coefficient and adhesion-strength parameters of foam coke [6]. The coefficient of swelling of intumescent coatings can be considered a function of flame retardant efficiency, our studies [7] to show that it correlates with the decomposition temperature of pentaerythritol during the thermolytic synthesis of foam coke. This indicator should be considered in conjunction with other methods for assessing the fire-retardant properties of intumescent coatings, since there is no data on the thickness of the foam layer, other things being equal, contributing to the necessary time of resistance to unfavorable fire factors. It is well known that epoxy intumescent coatings have poorer viscosities than, for example, compositions based on vinyl acetate copolymers, due to which they are applied in thicker layers - about 4 mm, and even thus they "do not catch up" with water-dispersion compositions in terms of the number of foam boxes but in inefficiency they are not to be blamed. They are most widely used in the protection of oil and gas facilities, and they are recommended for protection against hydrocarbon fire. Although, of course, there is a search for increasing the degree of swelling of epoxy compositions, for example, there are descriptions of hybrid epoxy-vinyl materials, where the epoxy part is responsible for good climatic stability, and vinyl for reducing the destruction temperature and, as a consequence, increasing the multiplicity of coke.

The expansion ratio was determined as the ratio of the thickness of the intumescent carbonized layer to the thickness of the original coating layer. To determine the time of resistance to heating (the time of the onset of the limiting state), the specialists of FNPP GEFEST LLC collected a laboratory installation on the basis of a test site, shown in Figure 1. The essence of the method consists in the thermal action on the prototype and the determination of the time from the onset of the thermal action to the onset the limiting state of the sample.

![Figure 1](image)

Figure 1. A laboratory installation for the thermophysical tests of flame retardant coatings; types: a) general; b) in a section from above; c) in a side view

The tests of the samples were carried out in the "standard fire" mode, in which the average temperature of the furnace, measured by the installed thermocouples, was controlled and regulated according to the dependence [9]:

\[
T_{\text{furnace}} = T_o + 345 \log_{10} (8t + 1),
\]

(1)

where \(T_o\) — initial furnace temperature; \(t\) — time, min.

Steel plates measuring 200 × 200 × 4 mm, with a flame retardant composition, were used as the samples. Fire-retardant compounds were applied to a clean, degreased, primed GF-021 surface. The thickness of the dry layer was 1 mm, without taking into account the primer layer (0.3 mm). Before the tests, control measurements were made of the actual coating thicknesses at no less than nine points. The
average of all measurements was taken as the result. The temperature on the surface of the test plates was measured with the help of thermoelectric converters (TEC), which were installed by the method of cobbling onto the unheated surface of the samples in an amount of three pieces. The unheated surface of the prototype was isolated with a Rockwool mineral wool board 100 mm thick. The temperature of the metal of the test sample was determined as the arithmetic average of the TIC readings located at the specified locations. The tests were carried out before the onset of the limiting state of the prototype. The limiting state was taken to reach the temperature of 500 °C of the steel of the test samples (the average temperature for the three TICs).

While we did not establish any direct correlation between standardized full-scale tests and those used by us, in our opinion, the comparative laboratory methods for determining the given indices of fire-retardant coating, nevertheless, can characterize the change in the fire-protective properties of the intumescent material. Although it is obvious that in a compact electrical laboratory installation there are, for example, such important factors characteristic for a fire as impact impacts of turbulent flows of hot gases. And, consequently, the time of the onset of the limiting state of the samples in full-scale tests will be less than the results obtained by us. We tested identical composition compositions based on a triple intumescent mixture consisting of ammonium polyphosphate, melamine and pentaerythritol. Only the type of film former has changed. The content of 15% solutions of various binder polymers in the composition (see table 1) was 20% by weight with respect to the rest of the ingredients. The results of our study of fire retardant characteristics of intumescent compositions based on various types of binders are presented in the table 1. The tests showed (see table 1) that unplasticized acrylic film-forming agents are inferior to the copolymer of vinyl acetate with vinyl chloride. Presumably, acrylates, due to higher temperatures of thermal destruction, suppress the intumescent process.

### Table 1. The fire retardants of intumescent compositions based on the various solvent solutions of binding polymers

| Brand binder   | Type of binder                                      | Coefficient of intumescent, k | Time to reach the limit state, min |
|----------------|-----------------------------------------------------|-------------------------------|-----------------------------------|
| Degalan LP 64\12 | The copolymer of butyl methacrylate with methyl methacrylate | 26.5                          | 50                                |
| Degalan LP 64\12 c XI-470 | The copolymer of butyl methacrylate with methyl methacrylate | 45.5                          | 71                                |
| Degalan P 675  | The homopolymer isobutyl methacrylate               | 24.4                          | 51                                |
| VINNOL H15/42 | The copolymer of vinyl acetate with vinyl chloride   | 43.2                          | 62                                |

The situation changes with the introduction of chloroparaffins (CP-470) in the amount of 10% (by weight) into the composition. The multiplicity of coke during thermolysis of the material containing HP-470 increases, which, it seems to us, gives rise to some researchers to attribute chloroparaffins to porophors. Although, in fact, it only lowers the destruction temperature of the acrylic binder due to the dehydrating effect of the hydrogen chloride formed and directs the process toward the formation of graphite-like crystalline phases, which, according to X-ray diffraction analysis of the foam, we observe (in Figure 2) as a diffraction peak in area 22°, located approximately in the angular position in place of the corresponding three-dimensional reflection of graphite. The peak obtained does not have a clear maximum, which indicates the absence of three-dimensional ordering in carbonizate samples. One of the explanations for the asymmetry of the line profile is the presence of amorphous carbon in the analyzed samples.

The x-ray diffraction analysis of the carbonized residue of an intumescent composition consisting of ammonium polyphosphate, melamine, pentaerythritol and a solution (in xylene) of unplasticized acrylic resin Degalan 64/12 showed that the crystalline phase is not detected (Figure 3). In addition, the chloroparaffin has a stabilizing effect on ammonium phosphates, preventing their premature (before the formation of resin) decomposition with the release of foaming gases [9].
Figure 2. Diffractogram of the carbonized residue of the intumescent composition on a solution of Degalan 64/12 acrylic copolymer, plasticized HP-470

Figure 3. Diffractogram of the carbonized residue of the intumescent composition on a solution of acrylic copolymer Degalan 64/12

3. Conclusion
Satisfactory results in the tests of fire retardant efficiency (table 1) showed the copolymer of vinyl acetate with vinyl chloride.

Let us consider the possible contribution of vinyl chloride monomer to the thermolysis of a copolymer with vinyl acetate. At temperatures around 150 °C, the polymer begins to decompose with the liberation of hydrogen chloride which being a Lewis acid shifts the flow of thermolysis towards carbonization. In the process of carbonization an increase in the conjugated systems is observed. By the Diels-Alder reaction, structuring takes place with the formation of aromatic planes which contribute to an increase in the thermal stability of the fireproof material.

References
[1] Zybina O Varlamov A Mnaacakon S 2010 Problemy tekhnnologii koksoobrazuyushchih ognezashchitnyh kompozicij 34 pp 50
[2] Shatalin S Varlamov A Mnaacakon S and Zybina O 2014 Dizajn Materialy Tekhnologiya 4 pp 37-40
[3] MacNairR N and Stepler J 1970 American Duestuff Rep pp 27-36
[4] Russian State Standard GOST 30247.0-94.
[5] Russian State Standard GOST R 53295-2009
[6] Borboni A, Mor M, Faglia R 2016 *Journal of Dynamic Systems, Measurement and Control, Transactions of the ASME, 138 (11)*, art. no. 111003. DOI: 10.1115/1.4033831
[7] Aggogeri F, Borboni A, Merlo A, Pellegrini N, Ricatto R 2017 *Materials 10 (3)*, art. no. 297 DOI: 10.3390/ma10030297
[8] A. Reinheimer Pat. № 7820736 USA. 2010 *Intumescing, multi-component epoxide resin-coating composition for fire protection and its use*
[9] SHumilov S Varlamov A Zybina O Babkin O and Mnacakanov S 2016 *Lakokrasochnye materialy i ih primenenie 1-2* pp 54-57