Synergism of Physical and Chemical Processes in Intumescent Fire-Retardant Paints

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Abstract. The aim of the research presented is to investigate influence of main components of fireproof paints, their physical and chemical properties on fire retardant properties of the coating. The influence of chemical nature of binder on fire-protective properties of intumescent paints is studied. Thermal studies of fire protection properties of water-dispersion fire-protective paint formulation by PFA samples of different manufacturers are given. The work presents quantitative and qualitative estimation parameters which characterize influence of physical and chemical processes on fire retardant properties of the paint. The conclusions about the synergy of physical and chemical processes and its influence on the fire protection properties are made. The research results allow estimating the importance of developed compositions for fire proof paints, for which each component is chosen in order to heighten an effect of the others.

1. Introduction

Steel metal structures are the main supporting framework of buildings, their strength and fire resistance play a key role in fire conditions. Various methods and means of protection are used to increase the fire resistance limits of structures. It is known that one of the effective ways to protect steel structures in case of fire are thin-layer polymer coatings that can increase many times when heated. The intumescent fireproof paints are multi-component formulas. The basis of intumescent fire protection paints is a polymeric binder and fillers, stabilizers of the foamed coal layer. In case of fire the coating structure bloats, fine-meshed layer of coating with low thermal conductivity is formed, as a result of which the heating of metal structures is slowed down dramatically and the limit state is achieved before the loss of strength at 500°C [1-7].

However, despite the popularity of such formulations, the effect of the main components of the intumescent paints on the fire protection properties and the creation of the synergic effect has not been studied much. In accordance with theoretical and experimental studies of the structure of foam coke of fire-retardant inflammable coatings it is possible to distinguish the synergy effect due to
the work of all ingredients and the functional contribution of each of them in the process of thermolytic synthesis of inflammable fire-retardant coatings.

As mentioned above, an important part of the formulation of the intumescent fire-retardant coatings is the binder (resin). Binders are solid or liquid polymers that dissolve or disperse in solvent or water. As the binder dries, a paint film is formed. The drying process may be physical or chemical. Typically, the binder is dried and polymerised in a mixed process. The physical process means drying the binder without a chemical reaction, e.g. as a result of evaporation of solvents. In the case of chemical drying, hardening is achieved by a chemical reaction. The coating can be formed, for example, by oxygen in the air or by a reaction with a hardener [8-10].

The effect of fire protection of thin-layer intumescent paints not only depends on heating conditions (temperature, its rate of rise), but also on physical and chemical properties of the components of the formulation and their possible synergy.

2. Experimental part
Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described. This section also may include theory, background, calculations which represent practical development from a theoretical basis. Etc.

To determine the influence of the chemical nature of the binder on fire protection characteristics, a number of studies were carried out on the example of intumescent water-dispersion paint.

The time of reaching the limit temperature of 500°C and the intumescence coefficient were recorded as determining parameters (Table 1). The time of reaching the limit state by this criterion of fire resistance is considered to be the time (in minutes) that has passed from the beginning of the test to the first sign of the limit state by this criterion. Tests of paint with different types of binders have shown that film-formers based on acrylates are inferior to vinyl acetate copolymers and their modifications according to the fire protection properties criteria.

Table 1. Results of influence of binder nature on coating properties

| №  | Chemical nature of binder                          | Intumescence coefficient, k | Time to reach limit state, min. |
|----|---------------------------------------------------|-----------------------------|--------------------------------|
| 1  | Polyvinyl acetate-based dispersion                 | 54                          | 65                             |
| 2  | WD vinyl acetate copolymer with ethylene and vinyl chloride | 44                          | 61                             |
| 3  | WD vinyl acetate copolymer ethylene               | 41                          | 56                             |
| 4  | WD vinyl acetate copolymer with vinylversatatate  | 54                          | 69                             |
| 5  | Styrene acrylate dispersion                       | 19                          | 41                             |
| 6  | Acrylic dispersion                                | 36                          | 49                             |

The main antipyrenes of the fire-protective intumescent compositions are ammonium polyphosphate, melamine, pentaerythritol and their compounds. They have a complex of properties that create a synergetic effect due to the energy stability of triazine nuclei and the ability to form multifunctional reactive chemical compounds. Melamine melting point is clearly indicated by the endothermic peak at 340°C. After melting in the temperature range of 350-430°C melamine transforms into melem, and at 430-500°C melem transforms into melon. Melon is resistant to heating to 740°C. Thus, melamine and products of its transformation are durable enough and, therefore, can react with aldehydes, forming melaminoaldehyde oligomers. High temperature of synthesis should,
naturally, favour the formation of spatially cross-linked structures - melaminoaldehyde resins with complex composition. Similar processes take place in intumescent systems, where instead of melamine urea or dicyandiamide is used. Ammonium polyphosphate is the main fire retardant in a fire protection paint. When PFA is heated to temperatures around 250-280°C (depending on the degree of polymerization) there occurs endothermic decomposition with the formation of polyphosphoric acid and the release of ammonia [11-13].

To study the effect of PFA on the physical and chemical processes in the fire protection paint, thermal analysis was performed on the Derivatograph Q-1500D device. PFA samples from various manufacturers were chosen for the study. Thermograms are presented in Figures 1,2,3. On the basis of the presented graphical data it is possible to see, that the PFA trade marks presented on the raw material market can differ in quality and physical and chemical characteristics, which will influence fire retardant properties of the paint as such.

![Figure 1. Thermogram of various PFA samples (thermal gravimetric analysis).](image1)

![Figure 2. Differential thermal analysis thermogram of various PFA samples](image2)
Further, the intumescence coefficient of coating samples was determined using different PFA brands of water-dispersion intumescent paints. Thermal testing of coating samples to determine the intumescence coefficient [14] showed that the use of different brands of PFA with the same composition has a different effect on the intumescence coefficient and quality of the formed foamcoke, the results are presented in Table 2.

**Table 2. Influence of Different Brands of PFA on the Intumescence Coefficient**

| Sample number | Intumescence coefficient | Visual characteristics of foamcoke       |
|---------------|--------------------------|----------------------------------------|
| 1             | 58                       | Homogeneous, dense                      |
| 2             | 58                       | Homogeneous, dense                      |
| 3             | 56                       | Large pores up to 5 mm                  |
| 4             | 52                       | Large pores up to 3 mm                  |
| 5             | 58                       | Large pores up to 3 mm                  |
| 6             | 55                       | Homogeneous, dense                      |
| 7             | 52                       | Homogeneous, dense                      |
| 8             | 56                       | Large pores up to 5 mm                  |
| 9             | 42                       | Homogeneous, dense                      |
| 10            | 65                       | Homogeneous, dense                      |

In the course of the tests, samples Nos. 3, 4, 5, 7 and 9 of PFA brands showed no synergistic effect of the composition components within the given formulation and were not suitable for use according to quality parameters.

3. Conclusions
The investigation of main components of fireproof paints allows concluding that accurate assortment of components at the stage of development and modernization is the key point to achieve optimal fire retardant properties. Research of physical and chemical processes of formulations of intumescent fire protection paints clearly demonstrated the results of synergism and its influence on fire protection
properties. Continual improvement and research of component interaction and their influence on fire retardant properties mean reliability guaranty for fire safety concept.

References
[1] E. D. Wail, “Fire-Protective and Flame-Retardant Coating”, Journal of Fire Sciences, Vol. 29, pp. 259-296, 2011.
[2] R. B. R. S. Olivera, A. L. Moreno Jr., L. C. M. Vieira, “Intumescent paint as fire protection coating”, Structures and Materials Journal, vol. 10, № 1, pp. 220-231, 2007.
[3] A. R. Horrocks, D. Price, “Fire retardant materials”, Cambridge: Woodhead Publishing Limited, 442 c., 2001.
[4] D. Korolchenko, T. Eremina, D. Minailov, “New Method for Quality Control of Fire Protective Coatings”, IAPE ’19 Conference, Oxford, United Kingdom, 2019.
[5] J. Q. Wang, W. K. Chow, “A brief review on fire retardants for polymeric foams”, Journal of Applied Polymer Science, №97, pp. 366-376, 2005.
[6] N. Khalturinsky, V. Krupkin, “On the mechanism of action of fire retardant intumescent coatings”, Fire and Explosion Safety, № 10, pp. 33-41, 2011.
[7] L. Ruban, G. Zaikov. “Importance of intumescence in polymers fire retardancy”, International Journal of Polymeric Materials, №48, pp. 295-310, 2001.
[8] T. Eremina, “Modeling and evaluation of fire retardant efficiency of intumescent flame retardants”, Fire and Explosion Safety, V. 12, № 5, p. 22, 2003.
[9] T. Eremina, D. Korolchenko, I. Kuznetsova, “Features of Properties of the Fireproof Paint during the Operation”, World Multidisciplinary Civil Engineering Architecture Urban Planning Symposium, 2019, https://www.wmcaus.org/archive.html
[10] T. Eremina, E. Yushko, E. Nikolaeva, “The influence of phosphoric acid on the reduction of crater formation of water-borne fire retardant intumescent paint”, Paints and Varnishes and Their Use, № 3, pp. 40-42, 2015.
[11] T. Eremina, M. Gravit, Y. Dmitrieva, “Aspects and principles of formulation development for flame retardant intumescent compositions based on epoxy resins”, Fire and Explosion Safety, № 7, pp. 52-56, 2012.
[12] O. Zybina, O. Babkin, “On the formulation of effective fire retardant paints and varnishes for building structures”, Paints and Varnishes and Their Application, № 3, pp. 44-47, 2018.
[13] D.E. Zav’yalov, O.A. Zybina, N.S. Chernova, A.V. Varlamov, S.S. Mnatsakanov, “Fire Intumescent Compositions Based on the Intercalated Graphite”, Russian Journal of Applied Chemistry, V.83, № 9, pp. 1679-1682, 2010.
[14] GOST R 53293-2009 "Fire Hazard of Substances and Materials. Materials, Substances and Means".