Influence of carbon additives on operational properties of the intumescent coatings for the fire protection of building constructions

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Abstract. In work ability of the intercalated graphite entered into the fireproof intumescent compositions to act as catalytically active additive raising operational characteristics of the classical distending coverings intended for fire protection of building constructions. It is established that thermal expanded graphite, as well as nano-additives, increase frequency rate, durability, elasticity, density and uniformity of a coke layer of a fireproof covering for increase of fire resistance of a building construction.

1. Introduction

Carbon nano-products (fullerenes and nanotubes) are of essential interest to creation of the intumescent materials with the improved properties, the building constructions of various types intended for fire protection of building constructions. They catalyze reactions of thermolytic synthesis of the protective heat-insulating layer - a coked cellular material with the increased thermal stability [1 - 5]. However the high cost of carbon frame structures (for single-layer nanotubes it makes several tens and even hundreds of dollars for gram) dictates the choice of such additives which along with ability to provide the set operational indicators of fireproof coverings are available to industrial producers of materials both from the point of view of outputs, and in respect of commercial prospects of realization of a product [6 - 8]. The alternative to expensive hydrocarbonic frame structures is made today by the intercalate graphite (IG) and its derivative – thermal expanded graphite (TEG) which cost on several orders is lower [9, 10], and effects of introduction to fireproof composition as it will be shown further, are commensurable with effects of introduction of fullerenes and nanotubes. Intercalated graphite of various brands (various extent of introduction) are widely applied in fireproof materials as an independent intumescent component [1 - 5]. They can be received by effect of sulfuric or nitric acid on crystal graphite, in the presence of an additional oxidizer, for example, of hydrogen peroxide. Similar graphite receive by also electrochemical method. Intercalated graphite is rather inexpensive and available in the range of various temperatures of expansion. It keeps characteristics of thermal stability of solid graphite and extends sufficiently to use in fireproof structures of the distending type. A lack of IG is its amorphy and easeness that does not allow remaining to the intumescent layer formed by it on a surface of the protected material. In intumescent compositions the graphite beginning a distend in rather low interval of temperatures - about 160-180 °C are, as a rule,
used. In classical option of IG contains in a compounding in number of 6-30% on weight. The more as a part of IG composition, it is more difficult to provide sufficient strength properties of a foam coke. The source [1] including only intercalated graphite and polymeric binding are known, however structures of this sort are effective only in the closed volumes (wall openings, cases of couplings, etc.) since the extended graphite after burning out binding is showered from the protected surface. The sources [3, 4] in which IG is kept from a collapse by an intumescent triad are known: polyphosphate of ammonium (PPA) - melamine (MM) - pentaerythritol (PET) at which the pitch connecting the extended intercalated graphite is formed. However, in the specified materials in the classical understanding characteristic of the PPA-MM-PET systems as the cellular carbonized structure is not formed - IG imposes "fibrous" structure to an intumescent layer [6], however such materials are adequately effective.

2. Results and Discussion

Authors found an additional method of application of intercalated graphite, which can be added to the fireproof intumescent compositions in small amounts as the component raising operational characteristics of an intumescent covering - frequency rate of a foam coke, its mechanical durability, thermal stability, adhesion to the protected substratum. Similarity of superficial electronic structure of graphene layers of IG to that at carbon nanoparticles allows make the assumption of close nature of catalytic influence of these objects on process of thermolytic synthesis of the heat-insulating foam coke layers of intumescent material. Let's consider nature of influence of UKS and thermal expended graphite on indicators of the distending fireproof covering. IG in an initial look did not use to exclude its intumescent contribution to the process of formation of a foam coke which is absent at nanoparticles. Carbon structures (Table 1 - 2) entered into composition of the certified water and dispersive fireproof paint for a metalwork.

### Table 1 Characteristic of mixed soot of fullerene of C_{60-70}

| Diameter of particles, nanometer | 0.72 - 0.75 |
|---------------------------------|------------|
| Density, g/cm³                  | 1.65       |

### Table 2. Characteristic of UNT of production "Nano Tech Centre"

| External diameter, nanometer  | 8 - 15     |
| Internal diameter, nanometer  | 4 - 8      |
| Length, micron                | 2 and more |
| Heat stability, °C             | 600        |
| Active surface, m²/h          | 300 - 320  |
| Density, g/cm³                | 0.03 - 0.05|

As TRG used the intercalated graphite of the ADT 351 brand subjected to expansion in the muffle furnace at a temperature of 600 °C. Value of expend coefficient increased at addition in structure of composition of carbon additives. The best indicators showed compositions with UNT. More available TEG showed the maximum expend indicators at contents it in composition in number of 0.7% (masses.). Further tested compositions with such maintenance of UKS. Results of comparative tests of intumescent compositions with UKS are given in tables 3-4 and in Figure 1.
Figure 1 Change of frequency rate of height of foam coke (the relation of thickness of the made foam layer, initial to thickness) from contents in intumescent composition of TEG and UNT

Table 3. Results of research of characteristics of an initial covering: adhesions by method of a normal separation and microhardness on Buchholz

| №  | UKS type  | Contents, % | Adhesion, MPa; character of a separation | Value of microhardness |
|----|-----------|-------------|------------------------------------------|------------------------|
| 1  | -         | 0           | 1.5 adhesive                              | 73                     |
| 2  | C_{60-70} | 0.7         | 2.5 cohesive                              | 81                     |
| 3  | UNT       | 0.7         | 3.0 cohesive                              | 86                     |
| 4  | TEG       | 0.7         | 1.8 mixed                                | 80                     |

Adhesion of coverings measured according to ISO 2815 "Paints and varnishes - Buchholz indentation test". This standard is describes a method for carrying out an indentation test on a single coating or multicoat system of paint, varnish or related product, using a Buchholz indenter. The length of the indentation produced is indicative of the residual deformation of the coating. Lack of the adhesive or mixed nature of destruction (table 3) at a separation of a covering demonstrates that the adhesive durability of coupling of a covering with a substrate is more than specific effort of a separation. Such phenomenon observed in a case with the samples containing UNT and fullerene of C_{60-70}. At introduction of TEG values of adhesion also increase, though to a lesser extent. The same dependence observed also for indicators of adhesion of foam coke to a metal plate (table 4) which was determined by method of the return blow. The mass fraction of the showered coke characterized coupling of the last with a substrate.

Table 4. A share of the remained height of foam coke on a substratum surface after mechanical influence by method of the return blow

| №  | UKS type  | Contents, % | Share of the remained coke, % |
|----|-----------|-------------|-------------------------------|
| 1  | -         | 0           | 45                            |
| 2  | C_{60-70} | 0.7         | 87                            |
| 3  | UNT       | 0.7         | 93                            |
| 4  | TEG       | 0.7         | 64                            |
All obtained data illustrate increase of operational characteristics of the intumescent coatings in the presence of UKS including TEG. Smaller efficiency of the thermos extended graphite in comparison with UKS is explained by lack of a steric regularity of monolayers unlike highly organized nanobodies.

3. Conclusion
Carbon frame structures - the most perspective structuring and reinforcing agents whose introduction to structure of composition promotes increase of efficiency of fireproof intumescent materials in the conditions of the thermophysical characteristic of the fire. Carbon frame structures to which with certain assumptions it is possible to carry and thermally expanded intercalated graphite show catalytic activity concerning the chemical reactions proceeding during thermolytic synthesis of foam coke layer. Catalytic activity can be caused by a complex of the properties characteristic of carbon frame structures are dimensional and superficial, and also, allegedly, emission and concentration effects. Besides, UKS increase strength and adhesive properties of intumescent material as a result of its reinforcing.

By authors it is established that thermos expanded graphite, as well as nano-additives, (in large numbers, than UKS) increase frequency rate, durability, elasticity, density and uniformity of a coke layer of the intumescent coatings thanks to a structure of their surface made by six-sided cycles with alternating δ-and π- orbitals.

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