

INTUMESCENT INORGANIC AND ORGANIC COATINGS

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ABSTRACT

Intumescent inorganic and organic coatings which differ one from the other by the type of gas formers and the mechanisms of foam formation have been obtained and investigated. Inorganic intumescent coatings are the compositions based on water glass and mineral additives with different dispersity. Mineral additives contain adsorbed and absorbed water and carbonates which are destructed with the carbon dioxide and water evolution during the flame action on coating. The decreasing of mineral additives particle sizes under the mechanical milling with the fraction precipitation promotes the foam coke formation with less defects. Here the main structure of comparing compositions does not change. In organic coatings based on epoxy-polymers the polyammonium phosphate additive is used. It is the carbonization catalyst and the foam agent. The polyammonium phosphate of various dispersity employed is uniformly distributed on the polymeric matrix. The decreasing of the particle sizes leads to the increasing of the fire resistant properties of the intumescent coating. The fire resistance analysis of the coating during more than an hour: the coating back side the temperature on plastic or wooden materials does not exceed 423 K, and on metal - 573 K.

INTRODUCTION

Intumescent materials usually contain a carbonization agent (coke former), carbonization

catalysts and gas former (or foaming agent). These materials are transformed into the carbon foam under the action of a fire or heat source.

This paper concerns inorganic and organic polymeric intumescent materials which are differed by the mechanism of gas former decomposition and of foam coke formation.

OBJECTS AND INVESTIGATION METHODS

Objects for investigation. Inorganic intumescent materials are cured compositions based on water glass $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ ($n \sim 5$) and fractions of minerals (with sizes: 6,3; 3,15; $1,4 \cdot 10^{-4}$ m) containing metal carbonates, sulphates, phosphates which are associated with vermiculite ores. The curing process proceeds at the usual conditions and at the heating of compositions to 313 K during 28 days. The compositions of these intumescent coating changes: water glass - from 56 to 77%, accompanied minerals - from 44 to 23%.

Organic polymeric intumescent compositions are obtained by the mixing of the following components: a) 84,4% of epoxy resin and polyethylenepolyamine mixture (ratio of components is 10:1,5) with 14,1% of polyammonium phosphate (PAP) and 1,5% of carbamide formaldehyde resin. Sometimes the melamine formaldehyde resin is used instead of carbamide formaldehyde resin.

PAP particles are separated into fractions with the following sizes: 1, 2, $3 \cdot 10^{-4}$ m.

Samples of materials based on epoxy resins are produced by means of the ultraso- nic dispergation of PAP particles into compositions containing up to 10% of CCl_4 as a solvent which is evolved under the heating and at the subsequent curing. The equal distribution of particles is determined using the optical microscopy. The mid-dle distance between particles equals $7.5 \cdot 10^{-4}$ m.

Investigation methods. Compositions and intumescent materials were investigated by a complex of methods including the determination of a heat layer thickness, thermophysical characteristics, changes of the surface and interface layers chemical structure during the pyrolysis as well as the determination of combustibility of tested materials.

The intumescence degree is determined on the changes of coating thickness (the difference between the final thickness of coatings after the fire temperature action and the initial thickness of coatings, related to the initial thickness and expressed in %).

The mass losses (%) and mass rate of combustion are determined in accordance with National Standards.

The heat layer thickness determined by the temperature distribution throughout the sample thickness is the distance from the combustion surface to the layer temperature natural logarithm of which is $\ln T = \ln T_s - 1$, where T_s - the surface temperature.

The temperature distribution throughout the sample thickness is determined by thermocouples placed inside the sample. The thermoelectromotive force is registered by the lightray oscillograph.

The fire resistance limit (FRL) investigation is carried out according to National Standard.

Standard calorimeters are used for the investigation of the material thermophysical properties. Tested samples are cut out from plates of the material obtained by pasting.

The properties of material subject to different rate of destruction were studied using a step pyrolysis method. The pyrolysis proceeds in a quartz tube furnace. Temperature intervals for the pyrolysis are determined from DTA and DTG curves (initial sample - $2 \cdot 10^{-5}$ kg, heating rate - 0.1 K/s, atmosphere - pure nitrogen or argon).

The changes of surface and interface layers chemical structure during the pyrolysis and combustion are investigated using x-ray photoelectron spectroscopy with MgK_{α} - radiation.

RESULTS AND DISCUSSION

Organic polymeric intumescent coatings. First at the temperature increasing on the boundary "particle-binder" the microcracks and microbubbles appear due to the difference of expansion coefficients of PAP and the binder. During further warming up (up to 463 K) the gases of PAP destruction ($H_2O \sim 3\%$, $NH_3 \sim 1.5\%$) begin to evolve into these bubbles. When the temperature and pressure in bubbles are increased the interaction of ammonia and water vapours is possible with the formation of ammonia hydroxide. In this case the pressure in the bubble decreases a little. At the same time the formed polyphosphoric acid which is appeared along with groups $^+NH_4^- OP(O)O_2=$ on the inner surface of the bubble promotes the dehydration and the carbonization.

These processes proceed within the temperature interval 533 - 573 K. At the temperature equals to 573 K ~ 12 at.% of Carbon (in account to overall Carbon in the surface layer investigated), which corresponds to Carbon into graphite according to the binding energy ($E_b C1s = 283.7 \pm 0.2$ eV) are found in the x-ray photoelectron spectra (XPE spectra) of the split surface. This Carbon was not found on the outer surface of the sample under above conditions of sample preparing. Therefore we can suppose that the above Carbon refers to the inner surface of bubbles.

Overall amount of carbon determined from XPE spectra of the split surface equals to 60.2 at. % ; and analogous amounts of nitrogen and of phosphorus equal to 7.2 and 8.1 at.% , relatively. Below the amounts of Carbon, Nitrogen, Phosphorus determined from XPE spectra of the surface and of the split surface after the warming up of samples to 553 and to 573 K are shown:

Elements		C	N	P
Amounts of	Surface	56.1	8.3	9.2
Elements at	Surface of			
553 K	split	78.3	4.8	2.5
Amounts of	Surface	73.5	5.7	5.0
Elements at	Surface of			
573 K	split	60.2	7.2	8.1

It is noted the polyphosphoric acid is formed on the inner surface of bubbles (the split surface) at 553 K, and then at 573 K the carbon substances are formed.

Data of XPE spectra testify to step mechanism of thermal transformation process and to breaking of surface integrity in the result of which the ammonium phosphate, ammonia and phosphorus oxide systems on the surface of sample appeared. However the appearance of carbon substances is registered in the split surface at 573 K only.

The heat capacity of the intumescent material within the temperature interval 373-573 K is changed. These changes are characterized by the curve with two maximums. In this case overall heat capacity corresponds to the sum of heat capacity changes for water and ammonia at the increasing of temperature and pressure.

The formation of carbon walls of bubbles increases the possibility of the formation of canals between the bubbles. At the temperature above 573 K the heat capacity decrease is explained by the decrease of the pressure as well as in partial pressures of ammonia and water vapours.

The thermal conductivity of growing foam coke is a sum of thermal conductivities of carbon walls and gas components of bubbles. In this case the thermal conductivity of carbon walls is increased, and that of the intumescent materials is changed differently. The investigation of foam coke cuts

shows that the bubbles which have the form of polyhedron (from dodecahedron to truncated icosahedron) are connected between themselves by canals or micropores.

According to the results of fire resistance limit determination intumescent materials obtained can be recommended for the fire protection of plastics and metals as well as for the protection of those materials from high temperature streams (Fig. 1).

Comparing intumescent materials with a different dispersity degree of PAP one can conclude that the material obtained from the composition containing the PAP particles with size equal to $\sim 10^{-4}$ m is better in thermophysical properties and in fire resistance than the other investigated materials. This fact is explained by a more proportional structure of foam coke and also by a small amount of connected pores between bubbles. Under the action of fire temperature the materials investigated resist fire for more than 1.5 hours.

Inorganic intumescent coatings. In inorganic intumescent materials the minerals mixed with the water glass are used. These minerals contain the following oxides:

Oxides:	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO
Content, % :	37.0	6.0	12.5	26.0	2.0

which refer to different alumosilicate ores (46-67%), apatite (15-18%), calcite (10-12%), magnetite (2%) and are associated with vermiculite ores.

Comparing the DTA and DTG curves of mineral fractions and their compositions with water glass the character of changes of mass losses and heat effects is shown (Fig. 2). Here it is noted that the composition mass losses are considerably greater than analogous losses of fractions. This is possible on account of the evolution of water vapour both from water glass and from minerals.

In accordance with the component content in minerals mass losses during thermo-gravimetry should be 14-15% chemically linked water. However overall mass losses on TG curves exceed the values calculated for fractions 1, 2, 3 on 17, 7 and 14%, respectively (numbers of fractions and compositions are written according to the increasing of the particles sizes).

We supposed that the efficiency of compositions containing the finely ground mineral fractions should be higher for the decreasing of flammability in the comparison with the usual analogous additives because with particle size decreasing the number of active centres of additives is usually increased. In this case the increasing of adsorbed water on the finely ground powders of minerals

used is possible. From the investigated compositions the composition 3 contains the relative finely ground fraction (the size of particles equals $1.4 \cdot 10^{-4}$ m). Therefore we compared the properties of this composition with two others which contain the mineral particles with the most size.

Exothermal effects corresponding to the changes of DTG curves of the first two compositions are considerably higher than these effects during the thermal transformations of composition 3. Therefore during the intumescence of compositions 1 and 2 the local growth of temperature which leads to the breaking of coating integrity is possible. Here it is noted that after the removing of the intumescent material layer the carbonized wood layer is detected if the inorganic intumescent coating was placed on the wood products. At the same time the material formed from composition 3 containing mineral fraction with the size of particles equal to $1.4 \cdot 10^{-4}$ m has pores characterized by a small expansion. This coating is warmed up to a lower temperature, and there is no the carbonization of wood under the intumescent layer.

Investigated intumescent inorganic materials (compositions 1, 2 and 3) differ from one another very little on the mass losses and on the intumescence degree:

Numbers of compositions	1	2	3
Sizes of particles, $\cdot 10^{-4}$ m	6.3	3.15	1.4
Mass losses, %	10.6	13.0	10.9
Intumescence degree, %	42	59	50

However the essential difference is registered in the fire resistance limit. From the comparison of fire resistance limits the best intumescent material is the material based on the composition 3 containing the mineral fraction with the particle size equal to $1.4 \cdot 10^{-4}$ m. The warming up of $3 \cdot 10^{-3}$ m coating obtained from composition 3 does not exceed 443 K within a fire temperature range for a period more than one hour (Fig. 3). At the same time for the best intumescent coating containing the finely ground mineral powders, the physico-mechanical characteristics (the breaking stress at the bending and at the shrinkage) are better in comparison with others. Especially the most increasing of the breaking stress at the bending is observed for the coating 3 in comparison with the coating 1 (in

2 times). This is explained by the density increasing of surface layer with the decreasing of particles size.

CONCLUSION

Thus the increasing of gas former particles sizes or a particle sizes of additives initiating the gas formation leads to the increasing of flammability of material samples. This fact is explained by the increasing of closed pores sizes, and then by the formation of cracks, caverns and open pores which increase the combustion area. On the contrary the above mentioned for the composition containing the finely ground mineral additives the considerable increasing of coating fire resistance and of breaking stress at the bending is note.

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FIGURES

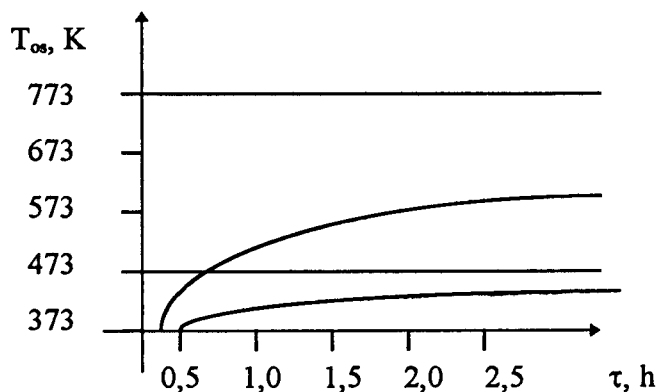


Fig.1. Changes of temperature on the opposite side of sample (T_{os} , K) (the determination of fire resistance limit) containing PAP particles during the heat source action (τ , h)
 a - the temperature limit for the coating on glass reinforced plastics,
 b - the temperature limit for the coating on metal.

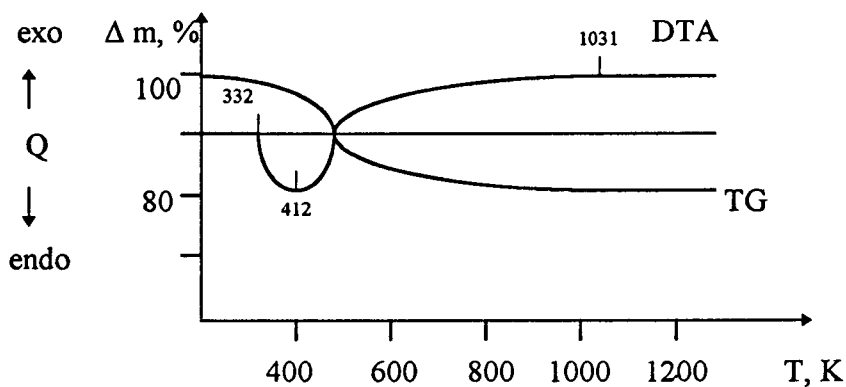


Fig.2. TG and DTA curves of the composition 3 (size of particles - $1,4 \cdot 10^{-4}$ m).

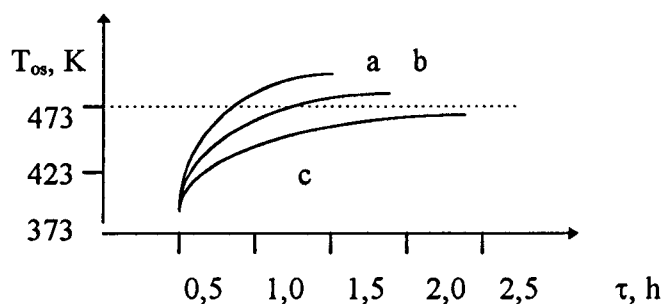


Fig.3. Changes of temperature on the opposite side of sample (T_{os} , K) (method of determination of the fire resistance limit) containing fractions of minerals 1(a), 2(b), 3(c).