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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

On the Role and Transformations of Components of Intumescent Fire-Retardant Paint-and-Varnish Formulations in the Course of Thermolysis

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Abstract—Main components of fire-retardant intumescent paint-and-varnish formulations, such as pentaerythritol, melamine, and ammonium phosphate, were considered in detail. A comprehensive thermal study of these components was carried out, including thermogravimetric and differential thermal analyses. A mechanism of transformations of these substances in the course of thermal degradation is described.

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The flammability risk of materials and articles thereof is determined in technology by the following parameters: combustibility, ability of a material to catch fire and maintain and enable propagation of the burning process; smoke emission; toxicity of combustion and pyrolysis products; and fire resistance of a structure, i.e., the ability of an article to retain its physicomechanical (strength, rigidity) and functional properties under the action of flame and high temperatures. There exist a great number of procedures and methods for protection of a diversity of materials from the action of fire, with the so-called intumescent coatings widely used [1].

Intumescent fire-retardant paints constitute a class of materials that are of interest both because of their rather high fire-retardant efficiency and comparative ecological safety and due to the convenience of their use. Formulations forming these coatings are very diverse in nature and include gas-releasing ingredients with decomposition points chosen in accordance with the intended use of a fire-retardant coating (wood, metal, cables with various braids, multilayered plastics, etc.). Intumescent fire-retardant paints are a kind of "state-of-the-art" of the indoor fire protection.

The conditions necessary for foaming processes accompanying transformations of intumescent systems to occur predetermine the choice of their main components. Apparently, the stable foaming of foam-generating coatings requires that gases should evolve within a melted film before a carbonized layer starts to be formed. Therefore, in making a formulation, components with certain melting and composition points are chosen in such a way that they react in a prescribed order and thereby create conditions for purposeful transformations of coatings under the action of flame.

The suggested fire-retardant mechanism of an intumescent coating is mostly based on the behavior of a coke layer as a physical barrier that reduces the heat-and-mass transfer from the gas medium to the condensed phase: first, foamed coke has a heat conductivity close to that of air, and, second, presence of polymer chains in the intumescent layer results in that it absorbs combustible gaseous thermolysis products and thereby hinders penetration of a gaseous fuel into the flame zone [1]. It also hinders supply of atmospheric oxygen to the polymeric layer. In addition, the main physicochemical processes occur in burning of the formulation with a huge endothermic effect and the gases being formed, such as ammonia, carbon dioxide, and water vapor, strongly cool the coke film by passing through its heated layers and thereby remove a considerable part of the thermal energy [1, 3]. Thus,

intumescent materials can diminish the heat transfer toward the protected surface by up to a factor of 100.

Ingredients of fire-retardant intumescent formulations are well known [2]: various kinds of polymeric binders, ammonium phosphates (mostly polyphosphates), polyatomic alcohols, and melamine.

The most important are polyphosphates: it is known that these compounds are ammonium salts of polyphosphoric acid and it is these salts that are responsible for the protective action caused by multiple bloating of the fire-retardant material and good preservation of the carbonized foamed coke layer on the surface of an article being protected.

Ammonium polyphosphate (APP) acts as an inorganic polymer favoring formation of a strong foamed coke and as an effective high-temperature "supplier" of gases, mostly ammonia [2]. The protecting efficiency of APP is due to the high decomposition point of the compound as a whole and of its cation-forming moieties, ammonia and melamine. The role of the latter consists in that it combines a capacity for intense gas evolution after its involvement in the formation of a 3D polymeric structure [2], and functions as a reinforcement matrix of the foamed-coke carbonized layer.

The third main component (after APP and melamine) of fire-retardant intumescent formulations is pentaerythritol (PE), which is actively involved in the formation of foamed coke. Melamine and APP play a double role as gas-releasing agents and ingredients for the synthesis of a foamed coke [1].

In this study, thermal analysis of ingredients of intumescent formulation and their mixtures in various combinations was used to demonstrate their potential in formation of products that can enter into chemical reactions predetermining the formation of protective foamed-coke structures upon carbonization.

EXPERIMENTAL

A comprehensive thermal analysis of components of intumescent fire-retardant paint-and-varnish formulations was made with an MOM Q-1500D derivatograph (Hungary). The comprehensive study included thermogravimetric (TGA) and differential thermal analyses (DTA). Such an analysis is of the phase type, with each substance characterized by a set of individual curves and temperature transitions.

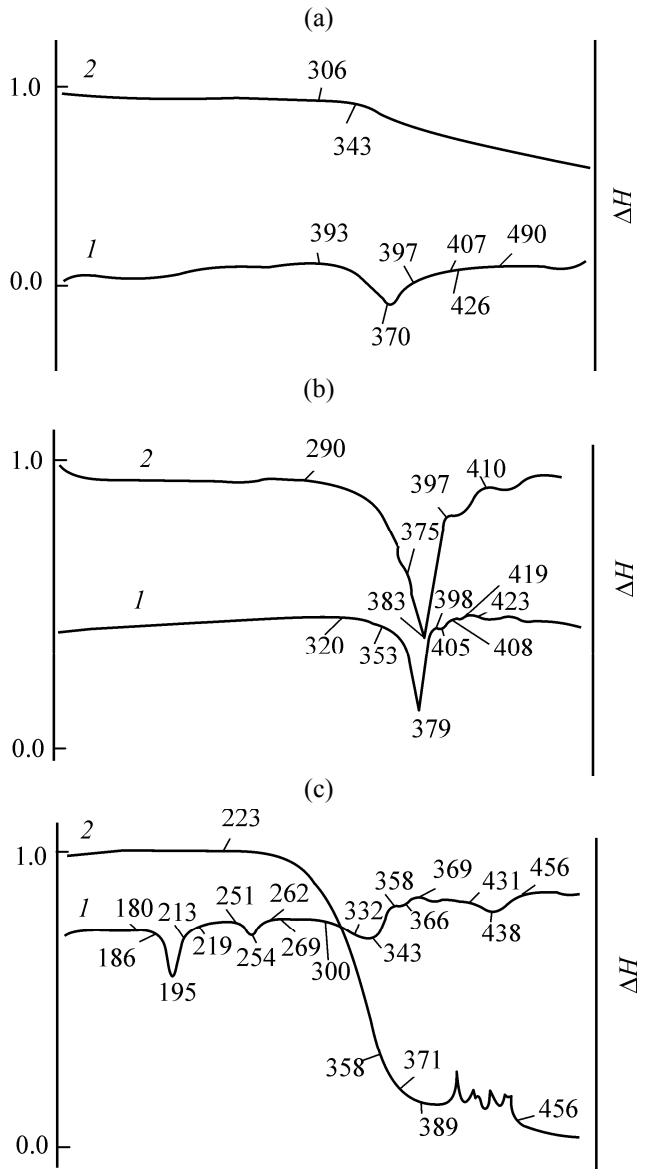

Fig. 1. Thermolysis curves for (a) ammonium polyphosphate, (b) melamine, and (c) pentaerythritol. (*1*) DTA and (*2*) TGA; the same for Fig. 2.

The study was performed in the temperature range 20–500°C at a constant sample heating rate of 5 deg min^{-1}. The weighed portion of a sample was 50 mg. Platinum crucibles and aluminum oxide as reference substance were used. The sensitivity of self-recorder channels was 0.5 mV for TGA and 0.25 mV for DTA. The motion velocity of the chart paper was 2.5 mm min^{-1}.

As starting substances were used micronized PE (white crystalline powder, ≥98% mass fraction of the main substance, mp 250°C), APP (pure white powder; P_2O_5 content 72%; solubility in water, 0.8 g/100 cm^3; decomposition point 300°C), and melamine (white

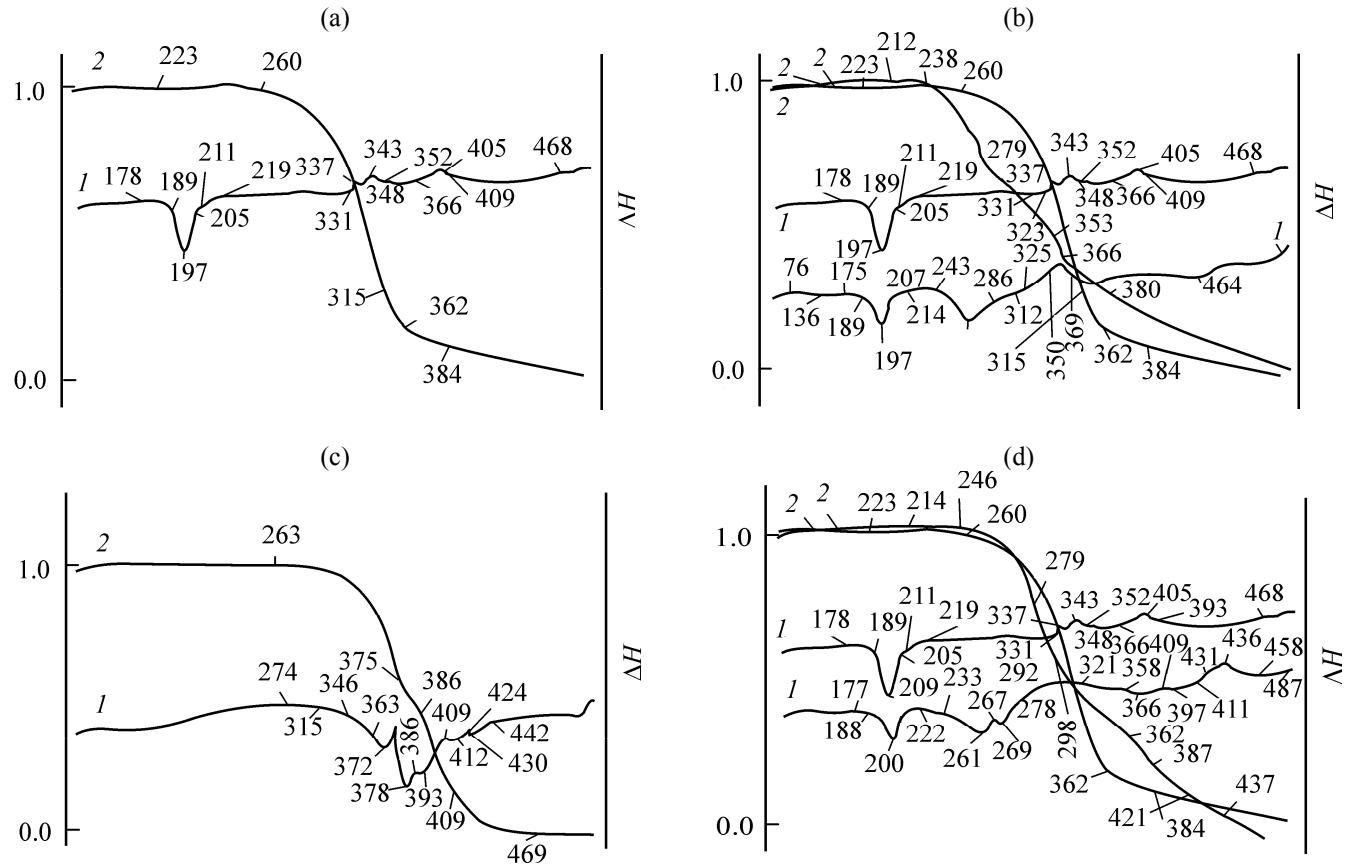

Fig. 2. Thermolysis curves for mixtures of (a) melamine and pentaerythritol, (b) ammonium polyphosphate and pentaerythritol, (c) melamine and ammonium polyphosphate, and (d) melamine, pentaerythritol, and ammonium polyphosphate.

crystalline powder, ≥99.8% mass fraction of the main substance).

In the first stage of the study, individual substances were analyzed. It can be seen from the results of APP analysis (Fig. 1) that the endothermic peak associated with melting of the crystalline phase lies beyond the range 340–350°C and corresponds to the onset of decomposition. Further thermolysis occurs rather slowly. Thus, APP functions at high temperatures [4, 5].

The curves obtained in analysis of melamine (Fig. 1) indicate that the thermolysis of melamine occurs in a temperature range 350–400°C comparable with that of APP. It is noteworthy that melem can be formed in thermolysis of melamine under these conditions [6].

It follows from the DTA curves for PE (Fig. 1c) that its melting occurs in two stages (two endothermic peaks): the first (195°C) is identified with a transition of the tetragonal lattice to a cubic one [5, 6], and the second (254°C), with melting of the cubic lattice and its simultaneous decomposition, possibly involving release of acetaldehyde and formaldehyde [5, 6].

Analysis of a mixture of melamine and PE (Fig. 2a) shows that the second endothermic peak of PE is shifted to lower temperatures; the cubic lattice being formed has structural defects. This is due to the reaction of melamine with thermolysis products of pentaerythritol, formaldehyde and acetaldehyde, and to synthesis of melamine-aldehyde resins. The synthesis must proceed comparatively rapidly [7].

At high temperatures, presence of APP stabilizes the cubic lattice of PE (Fig. 2b); the melting point of PE somewhat increases and the decomposition of PE becomes faster because of the binding of the aldehydes being released. The strong endothermic effect may be due to APP-initiated reactions of polymerization of PE decomposition products, formaldehyde and acetaldehyde, by the cationic polymerization mechanism.

An analysis of published data [9] demonstrated that a higher thermal stability, compared with homo-polymers, is observed for a copolymer of formaldehyde with acetaldehyde, whose melting begins at temperatures higher than 300°C. In this context, it can be suggested that the enhanced exothermic effect at

>310°C is due to the formation of a copolymer of formaldehyde (acetaldehyde) with melamine; the copolymer, in turn, undergoes thermooxidative degradation at 350–360°C, which is confirmed by the coincidence of peaks in the TGA and DTA curves and by the mass loss by a sample in this temperature range. The maximum thermooxidative degradation rate is observed at 360°C. Similar thermal effects were also observed in the ternary mixture (Fig. 2d), with the exothermic effect masked by the decomposition of melamine. It can be stated that the magnitude of the exothermic effect of secondary reactions exceeds that of the endothermic effect of melamine decomposition, because no endothermic effect is recorded in the thermogram of the ternary mixture in the temperature range 360–380°C (compare with Fig. 2d).

Thus, it can be stated that addition of melamine to pentaerythritol affects the phase transitions and promotes the reaction of melamine hydroxymethylation by a product of PE thermolysis. It will be recalled that the PE thermolysis yields a molecule of formaldehyde and two molecules of acetaldehyde and water [9, 10]. The reaction of melamine hydroxymethylation, which occurs at a high rate with heat release [5, 7], accounts for the absence of an endothermic effect at 330–370°C. It can be readily suggested that thermolysis of a mixture of melamine and pentaerythritol, accompanied primarily by formation of methylol derivatives of melamine and then by their predominantly spatial polycondensation, strongly blocks the endothermic reaction of melem formation [6].

The thermolysis of a mixture of melamine and ammonium polyphosphate (Fig. 2c) involves only combination of the effects noted for each of these components.

The study revealed inaccuracies and even errors in a number of conclusions concerning the role played by ingredients of fire-retardant formulations.

For example, pentaerythritol is designated as a polyatomic alcohol by numerous authors (the term "polyol" is frequently used). Therefore, it is suggested to replace PE with starch or cellulose derivatives (see, e.g., [2]),which fails to produce effective results. So far, pentaerythritol is an irreplaceable ingredient if ecological safety regulations are to be satisfied and no aldehydes are used in formulations; PE is of interest because it forms aldehydes under "necessary" topochemical conditions.

An ambiguity also exists in how the role of polyphosphates is understood. Conclusions about their catalytic nature [1] are erroneous. Actually, polyphosphates (of ammonium or melamine, with mixed cations) are completely insoluble and favor spatial ordering of growth directions of melamine-aldehyde resins further forming the skeleton of foamed coke.

Monoammoium phosphate is "inoperative" in aqueous systems, aqueous-dispersion formulations. It originally enters into a reaction with melamine and thickens systems via structuring by salts formed in interaction of two free acid groups and melamine molecules. Therefore, melamine becomes less active in the formation of melamine-aldehyde resins and the bound monoammonium phosphate does not promote formation of melamine-aldehyde resin regularly spatially arranged with respect to the surface.

On the whole, the fire-retardant mechanism or, more precisely, the effect of high temperatures consists in the following. In the initial stage of formation of intumescent materials, formaldehyde and acetaldehyde are released in PE decomposition and synthesis of melamine-aldehyde resins begins. The spatial regularity of formation of these resins is maintained by ammonium polyphosphate "fixed" on the metal surface by chemical bonds. When deposited onto a metallic surface, APP forms ionic bonds with the metal via its unsubstituted acid groups. Other part of these same groups add melamine, and just this compound begins spatial synthesis of resins. The process of resin synthesis is followed by decomposition of the ingredients, which release ammonia and water. Gaseous products move toward the surface and bloat the resin mass whose temperature exceeds the flow point. Then follows the carbonization of the bloated mass, which yields the protective foamed coke layer that diminishes the heat conductivity and hinders the heating or the onset of combustion of the surface being protected.

CONCLUSIONS

(1) Exclusively carbonized 3D structures formed by melamine-aldehyde resins are possible products of a thermolytic destruction of coatings constituted by fire-retardant intumescent polymeric formulations based on ammonium polyphosphate, melamine, and pentaerythritol.

(2) Ammonium polyphosphate serves as an agent of a spatially regular "assembly" of melamine-aldehyde resins and their attachment to the substrate.

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