

# The Chemical Mechanism of Thermolytic Synthesis in Charring Intumescent Coatings for Passive Fire Protection

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## ABSTRACT

Fireproofing properties of charring intumescent materials are determined by the formation of the carbonaceous porous layer, which is generated as a result of thermolytic synthesis. The layer has low thermal conductivity, and it shields the construction from the external heat flux. Char-forming coatings have been used for passive fire protection for more than 50 years. However, the existing technologies of creating new intumescent compositions are still fully empirical, and the problem of ensuring optimal combination of material properties has not been resolved yet. This implies the need in an in-depth understanding of the thermolysis mechanism that controls the performance of the coating in fire conditions.

The primary objective of this work is to identify the main chemical reactions occurring in the thermolytic synthesis of the intumescent carbonaceous layer. The intumescent coatings were exposed to annealing in a furnace and thereby produced carbonaceous samples were studied by chromatography-mass spectrometry and IR spectroscopy. TGA-DSC thermal analysis of the virgin samples of the intumescent coatings has also been undertaken. It has been established that in the thermolytic synthesis the melamine forms three-dimensional polymer-oligomeric structures with aldehydes. In its turn, the aldehydes are produced by the pentaerythritol decomposition catalyzed by ammonium polyphosphate and titanium dioxide. It is also shown that the role of the ammonium polyphosphate is two-fold. First, it generates ammonia gas, which facilitates swelling. Second, it serves as a blocking catalyst in hardening of the ammonia-aldehyde porous char produced by the resin. As a result, the heat-resistant layer of graphite-like carbon nitride ( $g\text{-C}_3\text{N}_4$ ) forms. It consists of condensed nitrogenous fragments incorporated into a graphene  $\pi$ -linking system inlaid with refractory inorganic compounds such as titanium pyrophosphate. The above mechanism is expected to be useful to enhance the efficiency of porous char formation by new intumescent coatings.

**KEYWORDS:** fireproofing, intumescent coatings, thermolysis, chromatography, mass spectrometry, IR spectroscopy.

## INTRODUCTION

The paper overviews a sequence of physico-chemical transformations of swelling multi-component systems in the process of their annealing and the way how those systems act as fireproofing materials. Experimental data made it possible to establish the concept of thermolytic synthesis of polymer-oligomeric structure of a charred layer and roles of ingredients in an intumescent process.

An intumescent composition must be prepared according to strict recipes in order to maintain its fireproofing efficiency. Intumescent components which perform in the best way have been already established [1-3] and thus intumescent compounds have proven themselves as an effective method of ensuring fire protection. However, there are several studies in which traditional intumescent

components are replaced by their functional analogs [4-6]. We have conducted the experiment to replace one of the intumescent components by its analog. Coatings formed by such compositions were exposed to annealing (at 600 °C) in a furnace and after that the volumes of the charred layers were compared. Results represented in Table 1 show that pentaerythritol is an indispensable component of intumescent systems since the coating formed from the composition without pentaerythritol loses its fireproofing properties. Also, replacing melamine and ammonium polyphosphate with their «functional analogs» leads to degradation of swelling ability and deterioration of fireproofing properties of the intumescent materials [7].

**Table 1. Results of basic intumescent component replacement**

№ of sample	The replaced component	The substitutional component	Swelling coefficient
Initial	–	–	47
1	Pentaerythritol	Galactose	–
2	Pentaerythritol	D-Fructose	–
3	Melamine	Urea	13
4	Ammonium polyphosphate	Potassium phosphate	15

According to the theory, an intumescent composition forms ester resins as a result of heating, and these resins get swelled by the gaseous products [8-12]. However, this becomes incorrect at the technology level. That is why we aim to reconsider and clarify the char-forming process.

## METHODS

To understand the interactions between the basic components of intumescent compositions during heating, the thermal analysis was conducted of the basic components and the melamine-pentaerythritol binary mixture using Derivatograph Q-1500D (J. Paulik, P. Paulik, I. Erdey, MOM, Hungary). The measurements were performed in air, at the constant heating rate of 20 °C/min. The sample mass was 50 mg. Aluminium oxide was used as the reference substance. The thermal analysis included differential thermal analysis (DTA) and thermogravimetric analysis (TG).

To identify the products formed in material decomposition, the charring samples were studied by chromatography-mass spectrometry. The study included two steps, manufacturing and annealing the samples with the compositions shown in Table 2, followed by the chromatography-mass spectrometry of the samples extracted from the carbonaceous residue.

**Table 2. Recipe of the intumescent composition**

Components	Quantity, mass. particles
Aqueous dispersion of vinyl acetate with ethanol	23
Ammonium polyphosphate	27
Melamine	9
Pentaerythritol	11
Dicyandiamide	2
Titanium dioxide	5
Water	23

Results are represented by chromatograms of mixtures separated from hexane, benzene, methyl chloride, acetone, ethanol and acetic acid fractions of carbonaceous samples formed from intumescent compositions which were exposed to annealing in a furnace for 10 min at 200, 300, 400, and 500 °C.

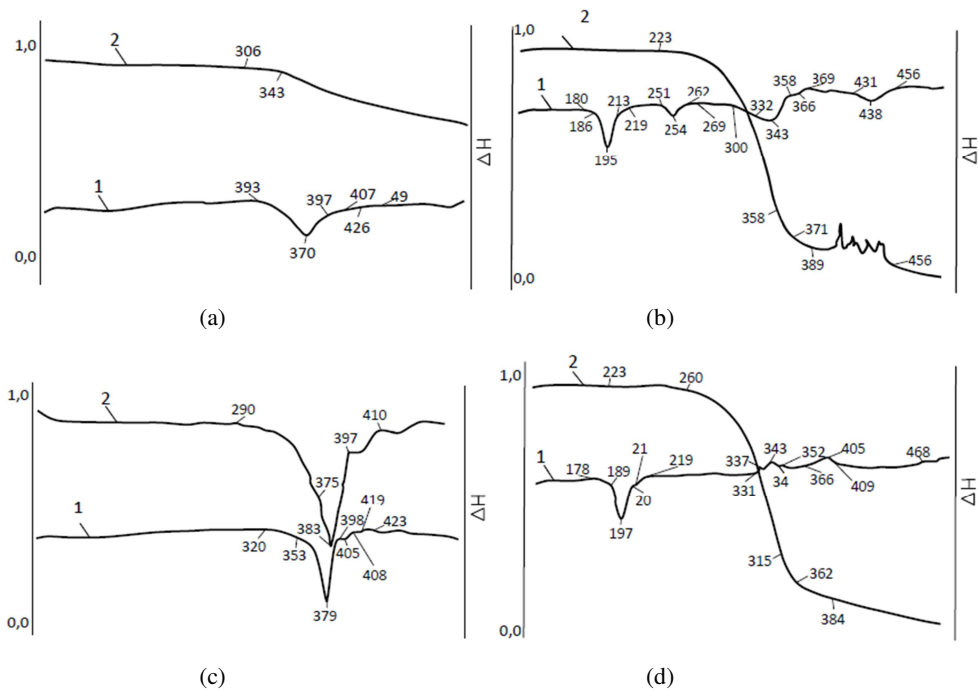
Chromatography-mass spectrometry was conducted using the gas chromatograph Agilent 6890 and the interface with the high-molecular mass-selective detector Agilent 5973N. Chromatograph included quartz capillary (30 m length, 0.25 mm diameter) column modified by HP-5MS phase. Helium was used as the carrier gas flow at the flow rate of 1 ml/min. The evaporator temperature was 320 °C. The sample temperature increased from 100 to 300 °C at the rate of 6 °C/min. The voltage of the ionizing source was 70 eV. A full ionic current regime was used. The individual substances were identified using the NIST library.

The carbonaceous sample made by annealing the intumescent coating in the furnace at 500 °C was also investigated by IR spectroscopy.

Thermolytic synthesis of swollen resin was conducted using the mixture of melamine and pentaerythritol located at the molten ammonium polyphosphate surface. The melamine and pentaerythritol (in 1:1 proportion) were mixed and adjusted to the mass of ammonium polyphosphate. This mixture was then annealed in the furnace at 350 °C.

## RESULTS

Results of thermal analysis of basic intumescent components and of melamine-pentaerythritol binary mixture are presented in Fig. 1.



**Fig. 1.** Results of thermal analysis: (a) DTA (1) and TG (2) curves of ammonium polyphosphate; (b) DTA (1) and TG (2) curves of pentaerythritol; (c) DTA (1) and TG (2) curves of melamine; (d) DTA (1) and TG (2) curves of melamine-pentaerythritol binary mixture. Horizontal axis is  $t$  [mp]tur[°C], vertical axis is  $\Delta H$  (kJ)

It is known that intensive pentaerythritol decomposition begins at 190–220 °C and stops at 265 °C [13]. According to DTA, ammonium polyphosphate reacts with pentaerythritol at 300 °C. However, at that instant pentaerythritol is already decomposed and, at the same time, there is melamine which can «accept» aldehydes formed from pentaerythritol. DTA of binary mixture including melamine and pentaerythritol shows that the mass loss starts at about 240 °C and nearly stops at 360 °C. It should be mentioned that, according to the theory, melamine serves as the gas-forming agent and therefore the mass loss should significantly increase at a temperature above 350 °C [14–16]. However, it does not happen because melamine binds aldehydes thereby forming the polymer-oligomeric resins [17, 18]. At 300 °C, melamine-pentaerythritol mixture mass loss is almost 100%. At that temperature, amino-aldehyde resin and the intumescent material are produced.











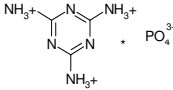

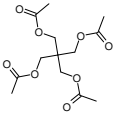
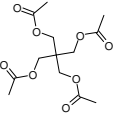
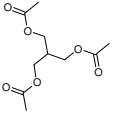


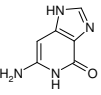
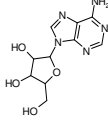
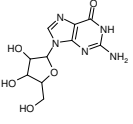
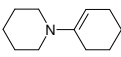
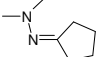
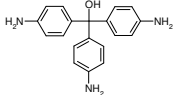
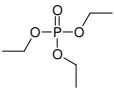
Activation energies shown in Table 3 indicate the possible interaction between pentaerythritol and melamine. During the intumescent process, ammonium polyphosphate is expected to preferably react with melamine, rather than with pentaerythritol. Products of these reactions were detected in the intumescent samples as shown below. Results of chromatography-mass spectrometry are presented in Table 4.

**Table 3. The results of thermal analysis of intumescent components and their mixtures**

Sample	$T_{5\%}^*$ , °C	$T_{10\%}$ , °C	$T_{20\%}$ , °C	$E_a$ , kJ/mol
Melamine	320	342	355	129
Ammonium polyphosphate	306	343	416	128
Pentaerythritol	265	285	303	96
Melamine – pentaerythritol	281	296	302	98

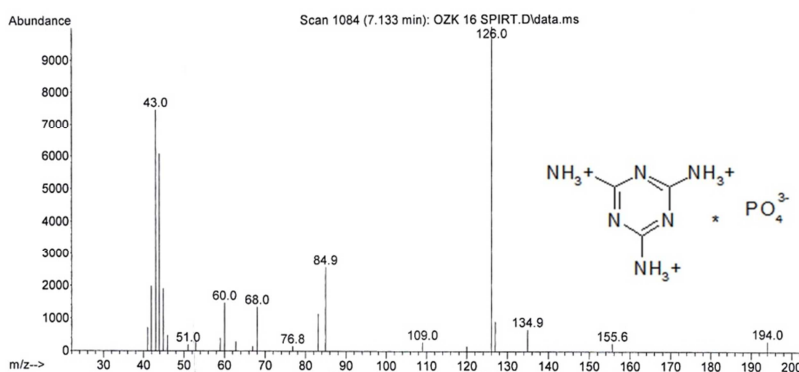
\* $T_{5\%}$  – value of temperature related to the percent of weight loss according to TG

**Table 4. Substances detected in a carbonaceous sample by chromatography-mass spectrometry**

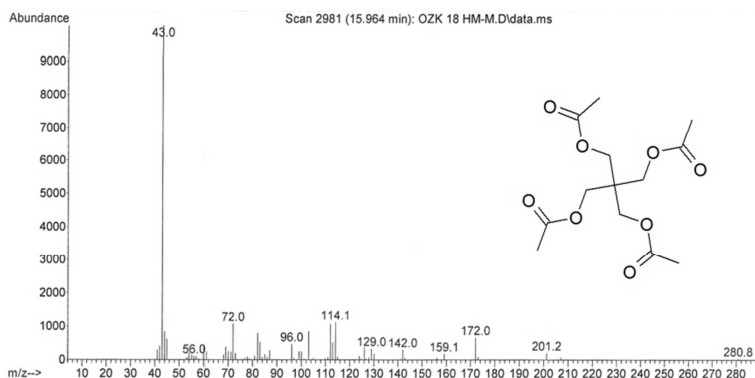
Temperature of coating thermolysis, °C	200	300	400	500
				
				
				
Products of thermolysis				
				
				

At the annealing temperatures listed above, the acetic acid was detected in hexane. Initially, it forms as a result of binding polymer destructive saponification to 250 °C, and at higher temperatures – when pentaerythritol decays wherein it's an oxidized acetaldehyde. Also another acetaldehyde's form was detected at all temperatures; in particular it's an acetic acid's ammonolysis product – N,N-dimethylacetamide which subsequently can take part in cyclization reactions as a reagent or as a catalyst.

Melamine phosphate (Fig. 2) which was detected in acetic acid extract of a carbonaceous sample made at 400 °C serves as a proof for our hypothesis about the role of melamine: it does not act as a porophore in intumescent process and does not decay with releasing of NH<sub>3</sub>, H<sub>2</sub>O and CO; instead its structure does not change and it can react and release gases mentioned above as by-products. As soon as phosphoric acids form, as a result of ammonium polyphosphate decay (at 350 °C), they get an ability to react with free melamine's NH<sub>2</sub>-groups and form salts.



**Fig. 2.** Mass-fragmentogram of melamine' solid form in acetic acid extract of a sample made at 400°C; y-line is abundance (mV), x-line is m/z.

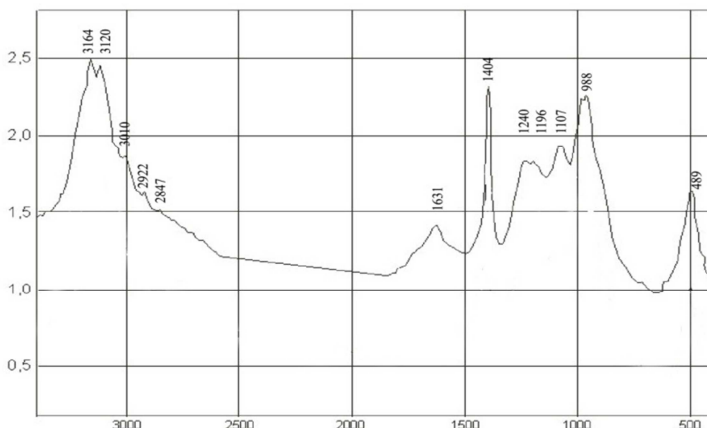


**Fig. 3.** Mass-fragmentogram of pentaerythritol in acetic acid extract of a sample made at 300 °C; y-line is abundance (mV), x-line is m/z.

Spectrograms (Fig. 3) show that there is pentaerythritol in its initial form in acetic acid extracts of carbonaceous samples made at 300 °C. It was not detected in samples at higher temperatures, which means that pentaerythritol decayed. Efforts which were made to prove pentaerythritol's ability to form ethers at temperatures below its melting point (215 °C) are inefficient, if a reaction does not occur in a liquid phase. As pentaerythritol is produced by the method of aldol condensation of formaldehyde with acetaldehyde and alkali as a catalyst, in appropriate topochemical conditions

(catalyst and high temperature) there will occur an opposite process – decay with releasing water, initial aldehydes and/or products of their condensation.

Results of IR spectroscopy of carbonaceous sample made at 500 °C are presented on Fig. 4. A group of bands represented on a spectra at the interval 2882–3000  $\text{cm}^{-1}$  is caused by C-H bond vibrations in carbonaceous structure; doublet 3164–3120 is caused by  $-\text{NH}_2$  vibrations. The spectroscopy band at 1631  $\text{cm}^{-1}$  is related to C=N bond vibrations which are possibly an azomethine bond typical for products of amines and aldehydes interactions. There are evidences of amide groups existing at 1404  $\text{cm}^{-1}$ . Groups  $-\text{C}-\text{N}-\text{H}$  are presented by bands at 988  $\text{cm}^{-1}$ . A band at 1007  $\text{cm}^{-1}$  represents a phosphate ion. An intensive wide band at 1240  $\text{cm}^{-1}$  represents P-O bond vibrations; P=O bond is possibly shielded. Also the group O-P-O is detected at 489  $\text{cm}^{-1}$ . Thus IR spectroscopy allowed to detect functional groups and molecules of substances which were detected by chromatography-mass spectrometry before.



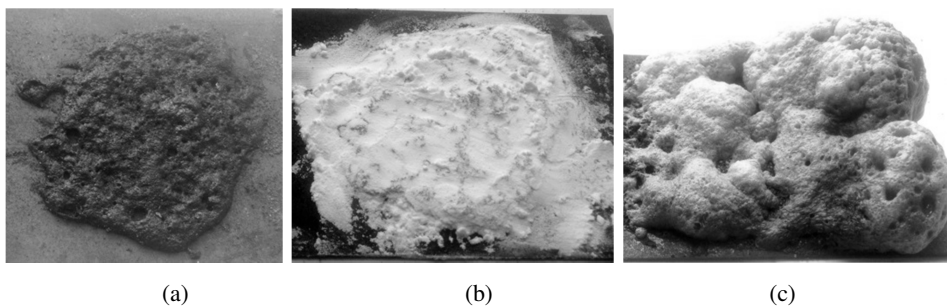
**Fig. 4.** IR spectra of the carbonaceous sample; y-line is absorption, x-line is wavenumber ( $\text{cm}^{-1}$ ).

In conclusion, there are results of thermolytic synthesis of swollen resin. As the system was exposed to annealing in a furnace at  $>350$  °C, the forming and swelling of sand-colored resin were detected (Fig. 5, Fig. 6b). A sensitive test of releasing gases by resorcinol dissolved in water has shown the presence of aldehydes in those gases. A swelling coefficient of resin is close to such of a charred layer made from melamine - pentaerythritol - ammonium polyphosphate (3:1:1) mixture whereas a mixture of pentaerythritol and ammonium polyphosphate did not form a resin (Fig. 6a).

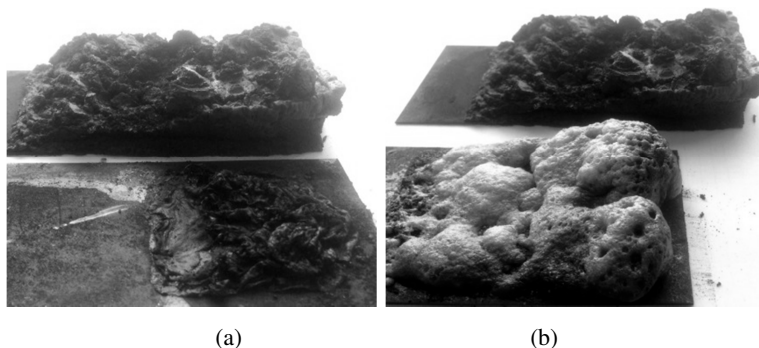
## DISCUSSION

Previous studies show that melamine resins start decaying at above 350 °C [19, 20]. Melamine phosphate in its turn has higher thermostability and remains the same until 386 °C which was proven above by chromatography-mass spectrometry.

Melamine and its different forms can react with acetic acid and dimethylacetamide forming nitrogenous polycyclic substances. The latter can also be formed in the following way. Acetonitrile and aminoacetonitrile are formed as a result of dehydration of acetamide under the influence of phosphorus oxide and as a result of acetic ammonolysis of acid in excess of ammonia. Acetonitrile and aminoacetonitrile can then react with formamide (at 250 °C) and form 4,5-diaminopyrimidine. The latter cyclizates and forms purine and similar substances such as glycosylamines, adenosine and guanosine which are detected in char samples starting from 300 °C. Its molecules include residue of purine basis tied with residue of ribose by a nitrogen atom. Ribose forms as a result of pentaerythritol restructuring into aldehydes and their self-condensation [21-26].



**Fig. 5.** Synthesis of swollen resin from melamine and pentaerythritol located on molten ammonium polyphosphate surface: (a) ammonium polyphosphate melting; (b) adjusting the mixture of melamine and pentaerythritol to molten solid ammonium polyphosphate; (c) a swollen resin formed as a result of heating.



**Fig. 6.** Presentation of binary mixtures exposed to annealing in comparison with the primal sample (on the background): (a) pentaerythritol + ammonium polyphosphate (no swelling); (b) pentaerythritol + melamine (thermolytic synthesis of a resin).

Dicyandiamide and urea are known to be the typical ingredients for melamine synthesis [27, 28]. By-products in melamine synthesis are  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and carbon oxides, just like in intumescent process. For the intumescent compositions, which include dicyandiamide and urea, and do not include melamine, it is possible that formation of char will still follow the synthesis of melamine or another nitrogen-containing heterocyclic substances and their reaction with aldehydes which will result in formation of spatially cross-linked resins.

Our experimental data show that, during an intumescent process, the melamine forms the three-dimensional polymer-oligomeric structures with aldehydes, which, in its turn, form as the pentaerythritol decays. If these structures are not clearly three-dimensional (with  $\text{NH}_2$ -groups incorporated into melamine-aldehyde resins), then the free amino-groups form the compounds jointly with the ammonium phosphates, thereby completing formation of the spatial structures. On the contrary, previous studies [7, 29] have shown that the ether is formed as a result of heating the intumescent composition, followed by partial thermal decay of the ammonium polyphosphate.

The mechanism of synthesis of carbonaceous layers in thermolysis of intumescent composition including melamine, pentaerythritol and ammonium polyphosphate can now be generalized. The initial stage of heating includes restructuring of pentaerythritol with titanium dioxide and ammonium polyphosphate acting as catalysts. Pentaerythritol decays releasing aldehydes (mainly formaldehyde and acetaldehyde); by that time a polymer binder must be decayed. As aldehydes join the system, the synthesis of polymer-oligomeric resins (mainly melamine-aldehyde resins) starts. A spatial regularity of those resins is maintained by ammonium polyphosphate. Ammonium phosphates play another important role: they catalyze dehydration of the polymer binder and capture

generated water. Thus, thermo-oxidative decay of the binder decelerates, whereas both carbonization and graphitization accelerate, and the original material structure remains unchanged. Since the ammonium phosphates act in thermolysis as a source of phosphorous acids, they not only tie the melamine-aldehyde structures, but also increase its chemisorption the substrate surface. This is essential in fireproofing of metals. Lots of by-products (including ammonia, carbon oxides and water) evolve as the resin forms. Gaseous products expand and get the resin swollen and harden. Finally, the heat-resistant graphite-like carbon nitride ( $g-C_3N_4$ ) forms. It consists of condensed nitrogenous fragments incorporated into the graphene  $\pi$ -linking system inlaid with refractory inorganic compounds such as titanium pyrophosphate [30, 31].

## CONCLUSIONS

The experiments conducted in this work enable reconsidering and clarifying the role of basic intumescent compositions ingredients such as melamine, pentaerythritol, and ammonium polyphosphate. A concept of thermolytic synthesis of intumescent coatings is suggested. It is shown that pentaerythritol decays and generates aldehydes. This process is catalyzed by ammonium polyphosphate and titanium dioxide. Melamine and urea react with the aldehydes and form resins wherein the by-product gases induce swelling of the resin. Ammonium polyphosphate acts as a dehydrating agent and as a catalyst of hardening the structure of the charred layer.

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