

## The Role of Carbonized Layers for Fire Protection of Polymer Materials

Z.A. Mansurov\*, B.Ya. Kolesnikov, V.L. Efremov

The Institute of Combustion Problems, 050012, Bogenbay batyr str. 172, Almaty, Kazakhstan

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### Abstract

The present work studies the processes occurring in pre-flame zone in the form of «candle-like flame» which is spread over the surface of epoxy polymer. As exemplified by epoxy polymer, it can be seen that the dominating mechanism of heat transfer from flame to pre-flame zone of carbonized polymers is a thermal conductivity by condensed phase (to phase). The mechanism of gasification processes in pre-flame zone is proposed. Gasification of the material in front of the flame edge is a controlling process, and when selecting flame retardants, it is necessary to register their ability to influence on kinetics and mechanism of gasification. The flame leading edge is bordered with the surface of polymer, which largely determines the nature of heat transfer in pre-flame region. Due to investigations of gas-phase composition at «candle-like» combustion of epoxy polymer it has been detected a considerable amount of oxygen (up to 10–12%) near burning surface. Its presence facilitates the thermal oxidation of polymer, moreover the rate of thermal oxidation can significantly exceed the thermal decomposition rate of the polymer. The possibility to form the heat-insulating intumescent layer during decomposition of carbonizable polymers was used at development of flame retardant coatings – complex multicomponent systems. Which in turns forms the intumescent carbonized layer with high porosity and low thermal conductivity, and protects based material or construction from premature heating up to critical temperatures.

### 1. Introduction

Problems related with flammability reduction of polymeric composite materials are actual not only today, but also in the future. This is confirmed by medium and large fires at various buildings (hotels, shopping centers) that accompanied by significant human losses both from burns and poisoning by burning products of surrounding polymer materials [1–6]. In this regard, intensive works are being carried out around the world in order to find the effective flame retardants of polymers. In present paper, there are presented results that carried out at the Institute of Combustion Problems.

The domestic use of organic polymers as well as their use in different productions is widening. In this regard, the requirements to flame-resistance of these materials and to reduction of their fire

hazard in such oxidizing medium as our planet are increasing. Therefore, contractual works related to development of heat shield materials for flying vehicles by means of imparting them the properties of refractoriness, e.g. epoxy materials, required to study the mechanism of burning of polymers. As we have already worked out a number of methodologies for mass-spectral and thermocouple probing of atmospheric hydrocarbon flames, we decided to use them for studying the structure of flames burning over polymers.

What is the difference between burning of polymers and burning of gases, it is possible to independently control the supply of fuel and oxidizer to the flame, while during burning of polymers in the flame, only one parameter – the supply of oxidizer can be changed. Consequently, combustibility of polymers is controlled by the rate of their

\*Corresponding author. E-mail: [zmansurov@kaznu.kz](mailto:zmansurov@kaznu.kz)

gasification process, i.e. destruction with the yield of products in the gaseous phase. It is known that practically all organic polymers at the temperatures higher than 500 °C are thermodynamically unstable and decompose.

Concerning thermal destruction, polymers are divided into two groups. With the growth of temperature, thermoplastic polymers decay or decompose into initial monomers or volatile low molecular compounds, while thermosetting (cross-linked) polymers decompose, as a rule, not only with evolution of volatile substances but also formation of a definite amount of solid residues with a high content of carbon and such polymers are often called carbonizable. It has been studied that epoxy polymers which refer to typical carbonizable polymers though their coke number is not very great.

## 2. Experimental

The most part of studies was carried out using epoxy polymer based on ED-20 resin is cured with m-phenylene diamine. Two types of flame were investigated: the first one is «candle-like» flame – is the burning of rods in cocurrent flow  $O_2+Ar$  (the concentration  $O_2$  was 25%) the second one is a flame propagation over the surface in reversed flotation  $O_2+Ar$  (the concentration  $O_2$  was 80%). Such conditions were chosen in order to obtain a stable flame. For investigation of «candle-like» flame, there were used samples in the form of round rods with a diameter of 20 mm, and a flame propagation over the surface was studied on flat plates with a size  $200 \times 20 \times 3$  mm.

Experimental installations are shown in Figs. 1 and 2. The first installation consists of a quartz tube (1) with a diameter of 60 mm, in center there is a sample (3). Gaseous flow  $O_2+Ar$  was delivered through the bottom of tube, and on the side there were holes for the thermocouple (5) and microprobe (6) for extracting of combustion gases.

Flame propagation over the surface was investigated using installation shown in Fig. 2. Special transfer mechanism is a main device of this installation (7), with which the sample (3) moved in a direction opposite to flame propagation. Movement rate was equal to flame propagation rate, and a constant distance between leading edge of the flame (4) and fixed probe (6) was maintained. The error during determining the distance was 0.1 mm.

The temperature in gaseous phase was measured by thermocouples Pt–Pt/Rh (10% Rh) and in solid phase by chromel/alumel thermocouple. The diameter of thermocouples was 50–100  $\mu m$ .

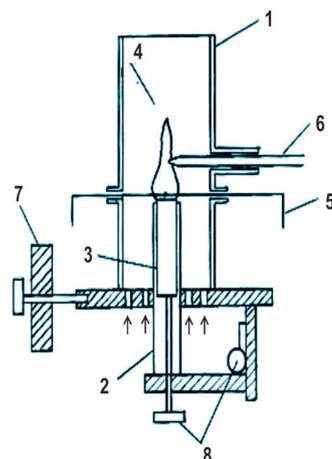


Fig. 1. Installation for investigation of «candle-like» flame: 1 – body frame; 2 – sample holder; 3 – sample; 4 – flame; 5 – thermocouple; 6 – microprobe for selecting of gaseous products; 7, 8 – transfer mechanisms.

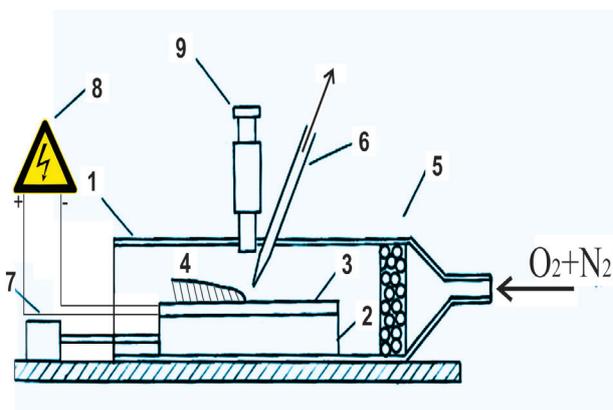


Fig. 2. Installation for investigation of flame propagation over the surface: 1 – body frame; 2 – sample holder; 3 – sample; 4 – flame front; 5 – silica gel bed; 6 – microprobe for selecting of gaseous products; 7 – transfer mechanism; 8 – temperature recorder; 9 – reading microscope, is determining the flame location towards probe.

Qualitative and quantitative composition of gaseous combustion products was determined by mass-spectral method. Microprobe for samples collection from flame was made of quartz glass. The entry-hole diameter was 50–60  $\mu m$ , wall thickness was about 60  $\mu m$ .

In order to study the mass losses of fire-proof coatings during convection heating, a laboratory installation was developed and constructed and shown in Fig. 1. Sample 1 was suspended using the arm of pharmaceutical scales. On the other arm there is a load which is pressed on platform of electronic scales 9, having a weighing limit of 300 g and a sensitivity of 0.01 g. Before experiments begin-

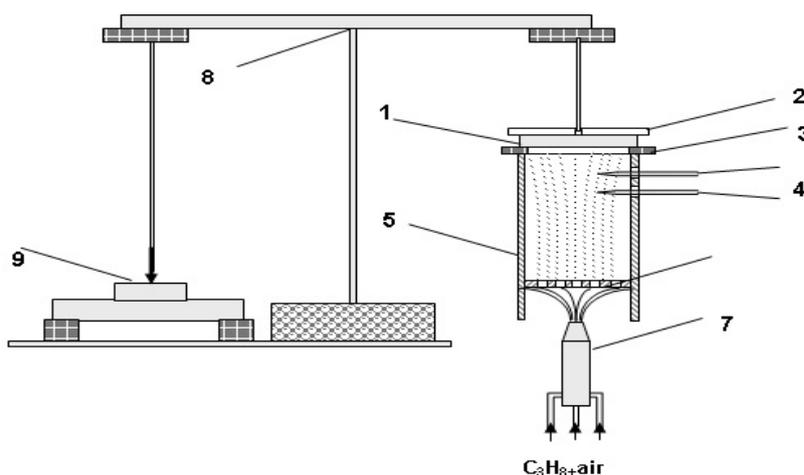


Fig. 3. Installation for determination of mass losses of fire-proof coatings under one-side heating conditions: 1 – test sample; 2 – metal substrate; 3 – heat-insulating plate; 4 – thermocouples; 5 – refractory – lined tube of chamotte; 6 – flame spreader; 7 – gas burner; 8 – rocker with prism; 9 – electronic balance.

ning, the system is balanced so that the readings of electronic scales are within 50–100 g. These readings are taken as zero reference point when samples are heated. The samples are heated by a propane-air flame that stabilized inside the tube 5. During the heating, a sample is decomposed, lose its mass, which is recorded by balance reading. Flow temperature is controlled by changing of gas flow rate.

### 3. Results and Discussion

The mass-spectra of volatile products (Fig. 4) showed the predominance of oxygen containing products – CO, CO<sub>2</sub> and H<sub>2</sub>O in them and the presence of light aliphatic hydrocarbons, formaldehyde and acetaldehyde in small amounts, the traces of aromatic hydrocarbons. The main combustible substance in the composition of volatile products is CO; its concentration is so great that it easily forms with oxygen a combustible mixture along which the flame can propagate.

We have also calculated the linear rates of blowing gasification products into the gaseous phase of the pre-flame zone. The values of these rates proved to be quite great to change gravely the fields of flows ahead of the flame and thereby effect the access of oxygen to the gasifying surface of polymer. The totality of the listed facts directly indicate a very important, possibly, a decisive role of thermal oxidation processes in gasification of epoxy resin, i.e. in propagation of the flame along its surface, too. However, it should be noted that in the course of thermal oxidation of polymer in its condensed phase there must evolve a great amount

of heat which apparently, does not have time to dissipate and is consumed for purely thermal decomposition (pyrolysis) of the remaining part of polymer. In the total mass of volatile gasification products, the products of thermal oxidation and pyrolysis, with the exception of carbon dioxide and water, are also able to burning with evolution of heat, and thereby they support flame propagation.

The obtained data facilitated the search for effective flame-retardants for other polymer compositions. However, the mechanism of reducing combustibility of epoxy polymer under the action of a fire-retardant was not fully understood as the mechanism of burning of this polymer itself was not found out. Thermoplastic polymers in the course of candle-like burning gave a stable flame at a distance of 1 mm and more from the decomposing surface and it was easily sounded (Fig. 4).

The structure of such flame was similar to the known structures of gaseous diffusion flames and the researchers supposed that all differences were only in the way of supplying combustible components into the flame – on account of gasification of the polymer base. Oxygen under the flame at the surface of gasifying polymer was not detected, i.e. there proceeded its usual thermal decomposition. In this case, there must be a very simple combustion model: heat from its own flame comes to the surface of polymer, heats and pyrolyzes it and the volatile products of pyrolysis are taken into the flame front and burn in it with evolution of heat. To use such a model, it is quite enough to determine the ways and rates of heat – and mass-transfer. This is not the case with burning of carbonizing polymers.



In the course of experiments on flame propagation for pre- and after-flame zones we studied fields of temperatures in gaseous and condensed zones and fields of concentrations in the gaseous phase (Figs. 6 and 7).

For the after-flame zone and the zone of the flame itself we stated a number of interesting facts which require their interpretation but mainly they corresponded to the results obtained when sounding a candle-like flame. We paid much more attention to the study of the pre-flame zone which would answer not only a practically important question – why the flame propagates along the surface of polymer considerably quicker than into its depth but also the question formulated by a number of researchers 40 years ago – what is the mechanism forcing the flame to propagate along the surface of polymer towards the flow of a gaseous oxidizing mixture? Evidently, a decisive role in this phenomenon is played by the processes taking place in the pre-flame zone in the field of the leading edge of flame. If ahead of the flame in the course of polymer gasification there does not form a gas-phase combustible mixture, the flame can't propagate in this direction.

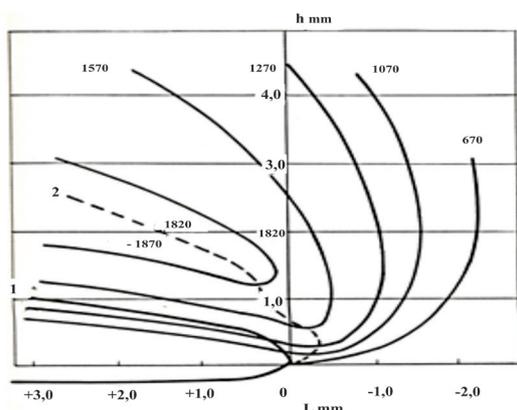


Fig. 6. Temperature field leading edge of the flame, spreading at the surface of epoxy polymer: 1 – flame front boundary; 2 – gaseous preheated layer. Temperature values are shown in Kelvin degree.

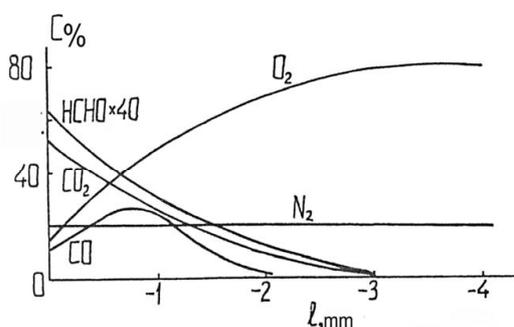


Fig. 7. Concentration distribution of stable in pre-flame zone at high  $h = 0.5$  mm above the surface.

The temperature rise on the surface of the polymer part which is not inflamed yet is observed [9] already at a distance of 2.5 mm ahead of the leading edge of flame and in the same gaseous phase one can observe the beginning of formation of  $\text{CO}_2$  and consumption of oxygen. It could be supposed that oxygen in this area is consumed for oxidation of the surface itself. However, the surface temperatures at which noticeable rates of gasification of our polymer are observed are only realized at distances not exceeding 1 mm from the leading edge of flame.

Using a rich experience on the study of carbonization of different mineral and plant materials gained in the works of our researchers, perhaps it is worth returning to the study on the actions of flame-retardants on the behavior of polymers under the conditions of their burning paying special attention to the kinetics of formation of a carbon framework, the form of carbon structures and general morphology of the carbonized layer. As a result, we could expect creation of effective flame-retarding compositions not only satisfying fire protection requirements but also providing many other properties of modern polymer composition materials.

Investigation of flame structure of carbonizing polymers opens the applying possibility of this phenomenon (carbonization) in flame retardant intumescent coatings.

Fire-proof coating under the fire conditions prevent the heating of metal up to critical temperature, which is  $500^\circ\text{C}$ . At this temperature, the metal durability is decreased sharply, and building can collapse under its own weight.

Protection is achieved due to the fact that under heating or open flame conditions, the coating is foaming and forms a highly porous carbonized layer with low thermal conductivity, which thickness is several tens greater than the thickness of the original layer.

Investigation of carbonization processes of polymers during their pyrolysis and combustion has an important value in order to reduce the combustibility of polymers, obtaining of effective heat-shielding materials, understanding the combustion mechanism, because the carbonized layer is formed at the surface of polymers upon their destruction and determine the heat and mass transfer characteristics between the gas phase and decomposing material. At pyrolysis of such polymers, the reactions of structure formation as well as the formation of thermodynamically stable systems

are predominating over the destruction reactions, breaking of bonds of the main chain [13]. From the literature it is known that, for non-charring polymers, the pyrolysis has endothermic nature [14], because it is associated only with breaking bonds. The formation of carbonized condensed products in char-forming polymer, during pyrolysis and combustion is occurred through the formation of various polyene structures, the cyclization of destructive macromolecule fragments, intermolecular cross-linking. etc., so the thermal effect of pyrolysis reactions should be determined from the energies ratio of tearing and formed bonds. As a rule, the total process is exothermic.

The transformation process of polymers into carbonized products is multiple-stage. At moderate temperatures – 500–600 °K, the tearing of less strong bonds of main chain or heterocycle-sis occurred usually and accompanied by the release of significant amount of volatile products, but non-volatile residue is enriched by carbon. At higher temperatures, the non-volatile residue undergoes profound structural changes - as a result of recombination reactions of macroradicals and dehydrocondensation there is formed condensed aromatic systems. Coke is the final product – which entirely consists of carbon, mostly from amorphous structure.

The inhibition evidence by carbonized layer of heat and mass transfer between the flame (or high-temperature gas flow) and decomposing polymer during combustion indicates the fact that the combustibility of polymers must influence not only on coke formation, but also on morphological structure of the forming coke layer (density, poros-

ity, availability of cellular closed structure, etc.). The structure of carbonized layer is determined by the chemical nature of the polymer and its decomposition conditions. High porosity of coke should correspond to its good insulating properties. However, the electron microscopic studies of coke structure that formed during combustion and pyrolysis of polymers have shown that less combustible polymers such as (polycarbonate, polyphenylene dioxide) forms dense, nonporous cokes [14]. So, in this case, the main effect of carbonized layer is the inhibition of mass transfer.

A detailed study of carbonization processes and foaming in the ammonium polyphosphate system with pentaerythritol, which are the part of many known flame retardant coatings, was performed in works [15, 20]. Investigation of microstructural transformations in this system with heating up to 560 °C is prove convincingly the formation of phosphorus-carbon structures - large polyaromatic molecules that connected by phosphate bridges.

It is reported that the additions of metallic zinc powder with a dispersion of 4–5 μm (up to 8% by weight) for fire-protective foaming compositions based on ammonium polyphosphate, pentaerythritol and flake graphite promotes the hardening of carbonized layer at high temperatures due to formation of polymer-oligomeric cross-linking reagents [16].

In works [17–19], by summarizing the known literature data since the early 1950s concerning chemical reactions of components and physical transformations during formation of foaming coke, the basic concepts of material science of foaming fireproof coatings based on ammonium polyphosphate are formulated.

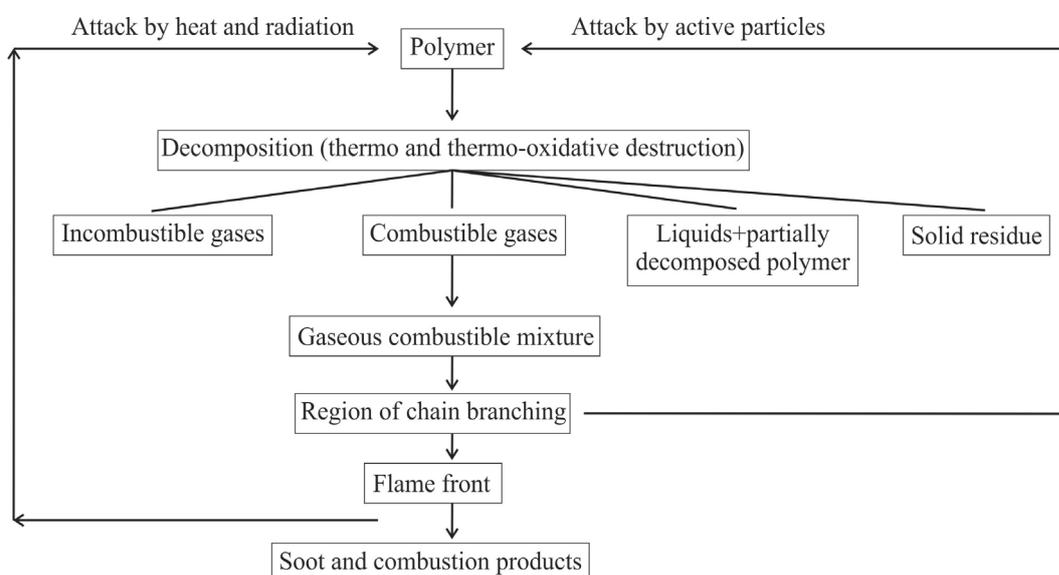


Fig. 8. Stationary process of diffusion combustion of polymers.

Despite numerous studies of foaming and carbonization processes, the microstructures of foam coke, performed mainly using model systems, an empirical approach predominates in the practical development of effective foaming compositions. The basic principles formulated more than 20 years ago in work [21] are relevant at the present time. Fire protection material should consist of four functional components.

a) inorganic acid or the material that released an acid at a temperature of 100–250 °C (acids, ammonium polyphosphate in various forms);

b) hydrocarbon compounds enriched by carbon (sorbitol, pentaerythritol, resorcinol, phenols, triethylene glycol, urethanes, methylol melamine);

c) organic amine or amide (urea, butyl urea, dicyandiamide, benzenesulfanylhydrazide, melamine, aminoacetate acid, casein);

d) halogenated compound (chloroparaffin, chlorinated resins, para-chloromethoxylyene, tetrachlorophthalate resins, pentachlorophenylglycidyl ether). Unfortunately, there is not enough attention to processes occurring at final stage of protective carbonized layer formation, although these processes, associated with structuring and oxidative decomposition (burning out) of coke, take a lot of time on fireproof coating at temperatures above 800 °C. At the same time, the oxidation resistance of formed carbonized layer along with its physico-mechanical and thermo-physical characteristics may prove to be important, but in many cases the decisive criterion for evaluation of coating effectiveness.

The coked cellular material is forming at the surface, possesses a high porosity and low thermal conductivity, reduces the heat transfer from the flame, prevents the oxygen diffusion to the surface of protected material and prevents the gaseous-phase combustion. All these factors preventing the temperature increase of protected materials and increase the limit of their fire resistance.

At the same time, it should be noted that insufficient attention is paid to the processes occurring at the final stage of the protective carbonized layer formation, although these processes related to the structuralization and oxidative decomposition (burning out) of coke, is occupying most of the time of fire-proof coating. Only oxidation resistance of the formed carbonized layer, along with its physico-mechanical and thermo-physical characteristics may prove to be important, and in many cases a decisive criterion for coating efficiency, because an increase of oxidation resistance leads to an increase in fire resistance limit.

Essential role in burning of coke plays the processes that occurred not only at the surface, but also in depth of carbonized layer. In view of this an explanation of factors leading to degradation of burning speed of carbonized layer as well as the effect of various additives on its structure and oxidative stability has great scientific and practical importance.

The studies were carried out using flame retardant coating «X-Flame», which was developed at the Institute of Combustion Problems and is widely used in Kazakhstan. This coating includes various flame retardants like micronised components, such as melamine, ammonium polyphosphate, melamine cinurate, pentaerythritol, melamine, melamine polyphosphate, etc. The varnish XB-784 or other chemically resistant varnishes are bindung agents.

The effect of cobalt salts, nickel and iron on mass decomposition rates of intumescent coatings and their erosion resistance was studied.

Studies of mass losses of intumescent coatings in one-sided heating regime by high-temperature gaseous flow have showed that about 80% of total mass losses occurred during initial heating period – in the first 10 min. Only in this time interval there is occurred a foaming of coating and the formation of coke structure. The results of metal salts effect of variable valency on mass losses of flame retardant coatings are given in Figs. 9–10.

Studies of metal salts of variable valency towards mass losses rate of flame retardant coating «X-Flame» (Figs. 9 and 10) have showed that additions of chloride and nickel acetate in an amount of up to 1% leads to an increase in mass losses of coating. At the same time, the cobalt salts, reduce the losses of coating mass during the heating. In comparison with higher heating temperatures (Fig. 4), this effect is more pronounced.

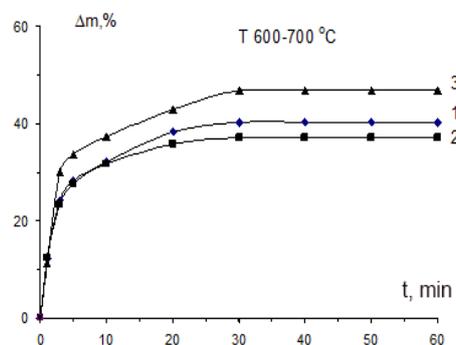


Fig. 9. Mass losses of flame retardant coatings «X-Flame» with various additives when heated by one-way gas flow: 1 – The coating «X-Flame»; 2 – «X-Flame» + 1% AcCo; 3 – «X-Flame» + 1% AcNi. The stream temperature is 600–700 °C.

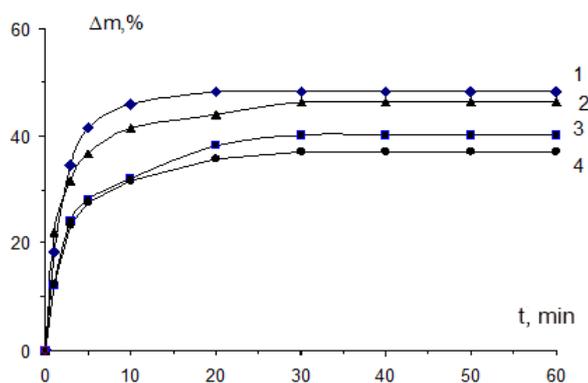


Fig. 10. Mass losses of fire-proof coatings «X-Flame» at heating of fire-proof coating by one-sided gaseous flow of various temperature: 1, 2 – Stream temperature is 750–800 °C: 1 – coating «X-Flame»; 2 – «X-Flame» + 1% AcCo; 3, 4 – stream temperature is 650–700 °C: 3 – coating «X-Flame»; 4 – «X-Flame» + 1% AcCo.

In work [22] it is noted that carbon metal-containing nanostructures, the formation of which is occurred with the participation of Co, Cu, Ni chlorides, which may be act as formation stimulants in nanophases material, which stimulates the growth of nucleus of coked surface with rise in temperature. This should lead to the formation of graphite-like structures in carbonized layer.

X-ray patterns of cokes that obtained during high-temperature heating of flame retardant coating «X-Flame», both as original and with addition of nickel chloride, are shown in Figs. 11–12. For salts such as Co, Fe, Mn, Cu, Sn, the X-ray diffraction patterns are similar.

The results of X-ray phase analysis have shown that the addition of metal salts has an effect on the coke structure for flame retardant coating «X-Flame». Although the X-ray patterns do not show any noticeable graphitization, there is

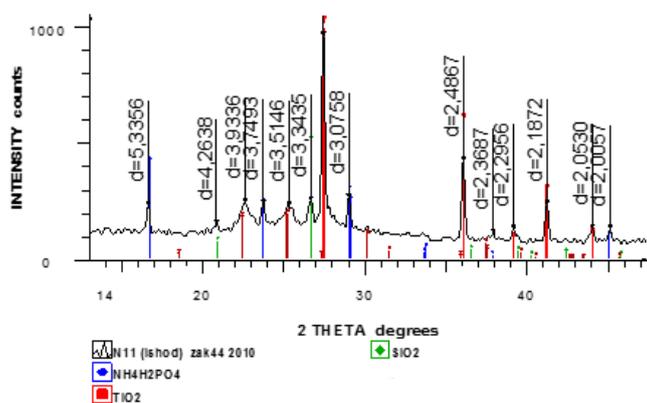


Fig. 11. X-ray patterns of coke, is formed as a result of high-temperature heating of fire-proof coating «X-Flame».

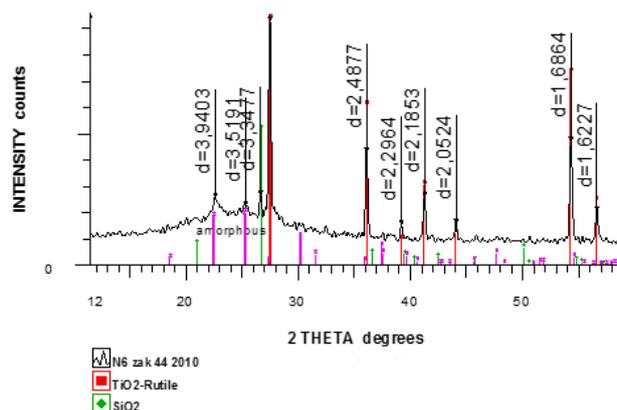


Fig. 12. X-ray patterns of coke, is formed as a result of high-temperature heating of fire-proof coating «X-Flame» + NiCl<sub>2</sub>.

appeared only a small blurred peak in the range of 21–29 THETA degrees is corresponding to amorphous form of carbon, and as a consequence a very interesting conclusion can be drawn from these data. In foamed coke layer that formed by heating of coatings do not contain additives, there are presented free phosphate groups in the form of mono- and polyammonium phosphate. At the same time, when introducing the metal salts into composition of these fire-proof coatings, free phosphate groups are not detected. This can be explained based on studies of model system polypropylene/ ammonium polyphosphate/pentaerythritol [20, 21], where it is shown that during decomposition of this system, its foaming and carbonization is occurred. At the same, there is formed «phosphorus-carbon» cellulose coke, in which the elements of graphite-like structure are connected by phosphate bridges (Fig. 13). In composition of our fire retardant coatings, there are also presented ammonium polyphosphate and pentaerythritol, so it should be expected that the high-temperature transformation schemes should be similar.

It can be assumed that metal chlorides of variable valence in these systems are original "catalysts" that promote a more complete transition of phosphorus compounds into coke structure, thereby increasing the degree of its cross-linking. This influence is common to all salts studied and it is not allowed to speak about any predominant effect of individual metal. Studies of metal salts of variable valency towards mass losses rate of flame retardant coating «X-Flame» have showed that additions of chloride and nickel acetate in an amount of up to 1% leads to an increase in mass losses of coating. At the same time, the cobalt salts, reduce the losses of coating mass during the heating.

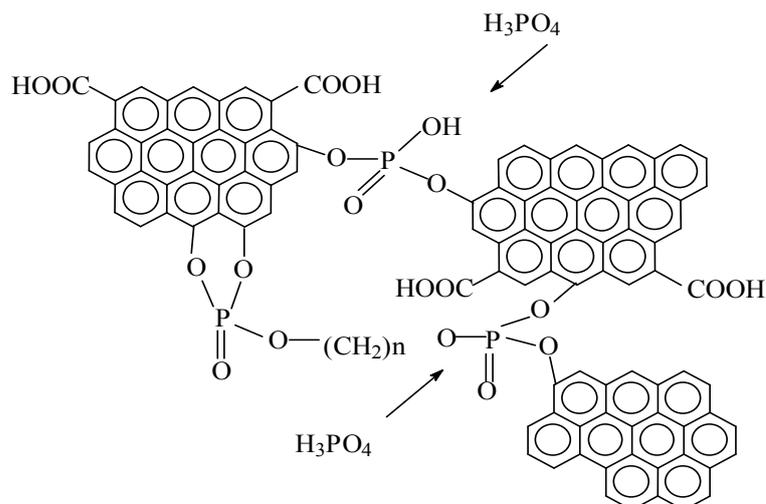


Fig. 13. Formation of phosphate and polyphosphate bonds in carbonized structure.

A definite influence of metal salts of variable valence on structuring degree of carbonized layer during heating of foaming coatings is observed. The introduction of metal chlorides such as Co, Fe, Mn, Cu, Sn into the flame retardant coating «X-Flame» promotes a more complete transition of phosphorus compounds into the coke structure, thereby increasing the degree of its crosslinking.

Modern production of domestic fire-proof coatings for metal and wood constructions

The developer: The Republican State Enterprise «The Institute of Combustion Problems».

Novelty: Modern fire-proof compositions such as «X-FLAME» and «POKROZAN-M» were developed at the Institute of Combustion Problems and they are very competitive with world analogues and with respect to quality-price are superior

The result: Every year the Institute of Combustion Problems has produced and realized about 40–50 t of compositions for metal and wood constructions. Fire-proof coatings were used during construction of «SCKA» sport complex in 2011, Almaty city, shopping and recreation centers such as «MEGA» «Ritz-Palace» in 2005, trading house «ABDI-company» in 2006, as well as biofuel plant «Biohim» (Petropavlovsk region) in 2006 and many other industrial enterprises of the Republic of Kazakhstan

At present time, in Kazakhstan there are applied fire-proof coatings of domestic and foreign production.

The Institute of Combustion Problems is one of the domestic producers of fire fireproofing compositions, where in the laboratory of structural and functional materials (headed by the Candidate of

Chemical Sciences Efremov V.L.) were developed and produced flame retardant coatings for metal «Birlik-2M», and «X-FLAME» fire-proof coatings on wood «Pokrozan», impregnating fire-proof composition «POC-BIO».

Test results showed that the coating «X-Flame» has much higher fire-proof characteristics, compared to the coating «Birlik-2M» and according these indicators is highly competitive with best world analogues. Its fire-proof efficiency for plates with effective thickness of 6–10 mm is about 120 min. Currently, this coating has been registered with a trademark and commenced its serial production. This coating was used in the construction of the CSKA sports complex in Almaty in 2011 and at many other industrial facilities in Kazakhstan.

#### 4. Conclusions

Investigations results of flame structure of carbonized polymers, using cured epoxy resin, shows that thermo-oxidation processes play an important role at gasification of initial polymer and generation of combustible products into the gas phase. In combustion of carbonized polymers, the resulting coke layer is a particular barrier-regulator, but its composition, morphological structure determining the intensity of heat and gas transfer processes between condensed (decomposing polymer) and gaseous (flame) phases.

This approach may become a basis in order to solve a number of applied problems – the creation of effective flame retardants, which can accelerate the formation of carbon structures and the direction of polymer destruction processes towards the

release of relatively more non-combustible products. Also, at the formation of coke bed with a high foaming, it has found an application in the development of effective flame retardant coatings, where the resulting carbonized layer preserve the protected structure from premature heating. There were developed flame-retardant coatings for wood and metal constructions, which has found a wide practical application. Further researches in this field should be aimed primarily at improvement of oxidation resistance of carbonized layer at high temperatures, which is an important criterion for effectiveness of flame retardant coatings.

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