

The Influence of Polymer on Service Life of Intumescent Coating

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Abstract: Service life is the ability of intumescent coating to maintain an appropriate level of fire-retardant efficiency under the influence of environmental conditions, during both construction and further intended use. It is crucial to be able to estimate this parameter with a decent level of accuracy, as premature leaching of components or chemical aging of the coating can partially or completely eliminate its fire-retardant properties, while fire safety requirements for building structures must be met throughout the duration of the life of a building, which according to manufacturers' claims is at least 20–25 years.

The main factors, that can reduce the effectiveness of intumescent coatings applied to steel structures, include but are not limited to: solar radiation, temperature fluctuations, direct contact of water with the coating surface, humidity, presence of corrosive environmental factors such as sea water, gases and vapors at industrial facilities. It should be noted that it is important not only to assess the service life of intumescent coating, but also to find reasonable ways to limit the loss of its fire resistance over time, one of which may be to optimize the formulation of intumescent system. The current review is aimed at distinguishing the influence of the nature of polymer in intumescent coating on its service life, focusing on the two most common types of binders – vinyl acetates and styrene acrylates.

Key Word: Service life; Intumescent; Polymer binder; Accelerated aging; Water resistance.

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I. Introduction

In general case, fire protection of steel building structures is aimed at increasing their load-bearing capacity in the event of fire by using special fire-retardant coatings that prolong the time needed to achieve critical states of structures.^{1,2,3} The most common means of fire protection are intumescent (expandable, reactive) coatings, which consist of phosphates, polyols, amines and polymers.^{4,5} The mechanism of fire-retardant action of such intumescent compositions (IC) implies that under the influence of fire such coating increases in volume with the formation of a sturdy charred layer, which has low thermal conductivity and high resistance to fire. Due to the formation of heat-resistant char on its surface, protected steel structure is temporarily isolated from the influence of flames (Fig. 1).



Fig. 1. The mechanism of protection of steel structures by intumescent coating

The usual criterion of fire-retardant efficiency of intumescent coating for steel structures is fire resistance rating R (min), which indicates the period of time from the start of fire test to the point where load-bearing capacity of structure is lost under the conditions specified by applicable regulations.

The range of possible components for intumescent compositions is limited and mostly preestablished, as their purpose in the IC is regulated by the role they are expected to take in the formation of protective charred layer (Table 1). It should be noted that if the components are randomly selected from the compounds listed in Table 1, they are unlikely to yield a reliable charred layer, and accordingly, to provide the expected fire-retardant efficiency. Therefore, the selection should be aimed at ensuring chemical functionality of an IC (reactivity, sequence of chemical transformations, thermal stability of the formed layer) and physical strength of insulative layer (structure, density, adhesion of the char to the substrate). The acid source, carbon source and blowing agent (Table 1) in their chemical and thermal properties must be compatible with each other, and reactions involving those must happen in a specific temperature regime.^{6,7}

Table 1: The main components of intumescent systems^{7,8,9}

Purpose of the component	Mechanism of action	Examples
Acid source	Release of acid during thermal decomposition, which then takes part in esterification of hydroxyl groups of carbon source	Phosphoric acid, its ammonium salts and esters; melamine and urea phosphates; ammonium polyphosphates. Boric acid and its derivatives - boron, ammonium borates
Carbon source	The source of a significant amount of hydroxyl groups capable of esterification by acids, as well as thermal destruction with the formation of carbon dioxide	Polyhydric alcohols - pentaerythritol, dipentaerythritol, tripentaerythritol, arabitol, sorbitol, saccharides (glucose, maltose, arabinose), polysaccharides (starch, dextrin, cellulose), polyhydric phenols (resorcinol)
Blowing agent	Formation of a large quantity of non-combustible gases during thermal decomposition, yielding a foamed structure of charred layer	Nitrogen or halogen compounds - melamine and its phosphorus salts, urea, dicyandiamide, guanidine and its derivatives, glycine, chlorinated paraffins

Numerous studies performed on IC to determine optimal composition, as well as analysis of patents, formulations of coatings that are mass-produced in various countries around the world, allows us to conclude that the most common trio of acid source, carbon source and blowing agent is ammonium polyphosphate (APP)/melamine (MA)/pentaerythritol (PE)^{7,8,9,10}. Therefore, the study of the mechanisms of intumescence, improving the effectiveness of fire protection, and development of fire protection compositions in literature are all somewhat related to the improvement of the said APP/MA/PE system and to the choice of the optimal binder.

Based on the nature of their binder intumescent compositions for steel structures can be divided into two main groups^{11,12}:

- paints containing aqueous dispersions of polymers – most often copolymers of vinyl acetate (VA): ethylene with vinyl acetate (EVA), vinyl acetate with vinyl versatate (VAVV), vinyl acetate with acrylate (VAA);
- paints based on organosoluble polymers – for example, copolymers of styrene with acrylates (SA), vinyltoluene with acrylates (VTAC).

In addition to the abovementioned polymeric materials, epoxy resins, polyurethanes and silicone polymers are also regularly used in fire protection. However, fire-retardant coatings based on those belong to a higher-price segment and are applied, mostly for protection of building structures against hydrocarbon fire¹¹.

In general, published studies^{4,5,8,10} report on other types of binders being used in IC for research purposes, such as acrylonitrile/vinyl acetate copolymer, polyvinyl acetate, phenolic and amino resins (urea, melamine and dicyandiamide), nitrocellulose polymers, sodium silicate, nitrilophenol latex, etc. However, these polymers have limited use in industrial fire-retardant coatings due to their instability to external factors, primarily moisture^{13,14}.

Patent research and information from other open sources allow us to offer preestablished intumescent formulations of flame-retardant coatings, which are mass-produced globally (Table 2).

Table 2: Compositions (%) of typical fire-retardant coatings

Component	APP	MA	PE	Polymer	TiO ₂
Organo-soluble IC	25-27	8-10	8-10	9-11	7-10
Water-soluble IC	23-25	8-10	8-10	12-14*	9-11

Note.* –recalculated for non-volatile substance parts

The data in table 2 show that the typical fire-retardant coatings have approximately identical composition both in the choice of components and in their ratio. Therefore, researchers generally do not pay much attention to the influence of the polymer (e.g., EVA or SA) on the mechanisms of chemical interactions inside the intumescent coating, and especially on the formation of insulative charred layer and thermal destruction of IC in fire. Usually, the choice between water-soluble or organo-soluble intumescent paints and coatings is based on a comparison of their operational characteristics: it is generally accepted that water-based ICs are more

environmentally friendly, while organo-soluble ICs tend to be more resistant to humidity and other atmospheric and chemical factors.

Most of the fire-retardant intumescent coatings described in recent patents^{15,16,17} contain aqueous dispersions of polymers. When exposed to high temperatures those form, firstly, a polymer-oligomeric structure, which as a result of the carbonization process is transformed into the framework of the charred layer, and secondly, non-combustible gases (mostly ammonia, carbon oxides and water vapor). Coarsely dispersed systems based on vinyl acetate (copolymers with ethylene, butene and esters of acrylic, maleic and other monomers, including vinyl esters of carboxylic acids) are most often used as polymers in regular intumescent coatings^{10,11}. Certain literary sources also contain information on the effective use of aqueous dispersions of acrylates and styrene-acrylates as a binder in intumescent fire-retardant materials¹⁸.

In addition to aqueous dispersions of polymers, intumescent coatings containing organic solutions of polymers are actively used in intumescent fire protection. The most promising is the use of different solutions of acrylates (e.g., methyl methacrylate and butyl methacrylate), copolymer of vinyl acetate with vinyl chloride, styrene-acrylates as organically soluble binders¹⁹.

According to the results of inspections performed on real structures, and based on practical experience, damage to fire-retardant coatings usually occurs due to two basic categories of influences – mechanical damages during intended operation, or prolonged weathering influence^{20,21}. The consequences of mechanical damage are more controllable and manageable, as they can be detected and eliminated by conducting regular inspections of the fire-retardant coating to determine its integrity and thickness. The consequences of damage to the coating as a result of atmospheric influences and the occurrence of internal chemical processes during service life are more difficult to detect, since not all of those manifest themselves externally. The active ingredients of intumescent coatings are most often sensitive to moisture, and UV radiation may affect their molecular structure²².

Aging of coatings is a very complex process that depends on the structure, composition and reactivity of their components, as well as climatic conditions, including extreme and cyclical changes in external temperature, humidity, intensity of solar electromagnetic radiation, nature and amount of precipitation, wind direction and speed. This is particularly complicated by the fact that numerical values of aforementioned factors may sustain significant regional differences even inside the same country²³. Analysis of the aging process of intumescent fire-retardant coatings is further complicated by the variability of the structure of their binders (linear, planar, three-dimensional^{24,25}) and overall composition, which may comprise organic, synthetic, polymeric, oligomeric and/or monomeric binders, as well as inorganic and organic additives to increase fire resistance, and other functional additives such as hardeners, pigments, fillers, etc.²⁶⁻³⁰

Due to the above complications, the exact mechanism of deterioration of fire resistance of intumescent coatings caused by accelerated aging, which involves simultaneous effects of UV radiation, moisture and elevated temperature, is yet to be described. However, it is widely believed that in the process of natural aging, these three aspects may have the greatest impact on coatings.³¹ In general, during the service life of intumescent coating in industrial, civilian and military facilities, it can be a subject to a variety of external factors, which can be divided into³²:

- chemical ones, which in the broadest sense can be describes as the influence of solvent (most often – water, or for industrial facilities – other organic or inorganic acidic or alkaline substances), which has the ability to dissolve and leach components out of the materials;
- physical ones, due to fluctuations in ambient temperature and absorption of moisture by coatings;
- biological ones, caused by direct or indirect action of microorganisms, most often affect intumescent coatings for wood, but can affect any surface if high humidity and lack of adequate ventilation are involved;
- electrochemical ones, manifested mainly in the form of gas or liquid corrosion of fire-protected metal structures, or metal fasteners of fire-protected wooden structures, with the subsequent transition of corrosion processes into fire-retardant coating;
- radiational ones, which most often refer to the action of UV rays, but for some building may also imply IR or gamma rays, which, depending on the chemical composition of the coating, may have different effects and consequences.

All the above factors can directly influence the adequacy of fire-retardant properties of the coating during its use, and thus – its service life. Due to the complexity of the aging process of intumescent coatings, as well as the practical impossibility of taking into account the whole set of external factors for each specific building structure protected by said fire-retardant material, several generalized classifications of conditions for intended use of fire-retardant coatings were adopted.

II. Methods for determining expected service life of intumescent coatings

The complexity and multicomponent formulations of fire-retardant intumescent coatings do not allow to form a detailed universal concept of the mechanism of their action. Only the general mechanisms of the influence of key components on the process of intumescence were identified. A significant amount of previous

research allows us to adequately assess the properties (especially fire resistance) for newly applied coatings only, while their long-term stability in model and actual operational conditions is not taken into account.

To assess the impact of environmental factors and create model operational conditions to determine coating's service life, ISO 12944-2³³ sets out the categories of climatic exposure for protective materials based on temperature and humidity; while EN ISO 9223³⁴ provides a classification of typical environments taking into account indoor or outdoor exposure and the possible effects of aggressive substances. However, both standards apply mainly to protective anti-corrosion coatings, so it should be additionally considered that intumescent fire-retardant coatings have two different types of contact: one – with the environment or with protective top-coatings, and the other – with the substrate, i.e., metal surface, or anti-corrosion primer. Cohesion levels of all coatings which are parts of a fire-protective system change during operation³⁵, so an important condition for reliable assessment of service life is to test a fire-protective system as a whole: certain type of primer, intumescent coating and top-coating if needed.

Research to determine service life of a coating can be accelerated by increasing the intensity of aging factors. Artificial aging is carried out in the laboratory with the help of climate chambers, which simulate natural aging processes. It was established that with simultaneous action of UV radiation and introduction of acids into the chamber environment the effect of both can be enhanced and decomposition process of coatings accelerates^{36,37}.

One of the common classifications of atmospheric exposure types for fire-retardant coatings is provided in EAD 350402-00-1106 European guideline «Reactive coatings for fire protection of steel elements»³⁸. It is much less detailed than those set out in previously mentioned documents^{33,34}, and consists of four general categories:

- Z1 (indoors at temperatures above zero and high humidity);
- Z2 (indoors at temperatures above zero and moderate humidity);
- Y (indoors and semi-exposed outdoors);
- X (all types of exposure).

The guideline also offers a method for assessing the suitability of fire-retardant coatings for use in those categories of exposure. According to it, samples of the fire-retardant system are subjected to accelerated aging with subsequent fire testing and comparing the results with those obtained for unexposed coating.

This method was used for research purposes by Wang et al.³⁹ to estimate service life of the studied fire-retardant coatings. Samples of intumescent coatings were subjected to a different number of accelerated aging cycles under the conditions recommended for Z1 type of exposure. One such cycle requires exposure of the sample to 8 hours at (40 ± 3) °C and relative humidity (98 ± 2) % followed by 16 hours at (23 ± 3) °C and relative humidity (75 ± 2) %. Based on the assumption made in EAD 350402-00-1106³⁸ that the coating, that has not lost its fire-retardant properties after 21 cycles of similar conditions, has a service life of at least 10 years, the authors decided on the following correlation: 4 cycles = 2 years of operation, 11 cycles = 5 years of operation, 21 cycle = 10 years of operation, 42 cycles = 20 years of operation.

Samples of intumescent coatings after aging in a climate chamber were subjected to fire tests according to ISO 834⁴⁰ to assess their fire-retardant effectiveness compared to control samples (0 cycles of accelerated aging).

The possibility of existence of such clear correlation between the number of cycles of accelerated aging and the exact service life of intumescent coating in the form offered by Wang³⁹ is questionable. However, the technique they use is most commonly accepted for coatings designed for indoor use in the absence of aggressive environmental factors.

Sakumoto et al.⁴¹ offered a method of accelerated aging testing loosely based on DIN4102⁴² and BS8202⁴³, and adapted for coatings that are continuously exposed to high humidity. Characteristics of the referential and adapted methods are listed in table 3. Similar to previously discussed study³⁸, the authors of this one focused on ensuring a guaranteed service life of 10 years when developing an adapted accelerated aging method.

In addition to the methods of accelerated testing, the study⁴¹ also considers and offers the use of natural aging test. It implies exposure of coating samples, applied to the substrate, for a prolonged time (1 year or more) to conditions similar to the expected conditions of intended application. An assessment of fire-retardant properties of the coating should be performed with specified frequency during the exposure time. Several characteristics of the coating can be evaluated during the regular assessments, such as: integrity and appearance, adhesion to the substrate, fire resistance during fire tests, etc. Due to the duration of such tests, they are not frequently used in laboratory studies, but are pretty common in practical research performed mostly by manufacturers of intumescent materials or other corporate parties interested in the results.

Table 3: Comparison of accelerated aging methods

Characteristic	BS 8202	DIN 4102	Suggested method ⁴¹
Accelerated aging tests			
Sample size	I-152×37kg/m×500 mm	300×200×5 mm	300×300×3,2 mm
Number of samples	1	2	3
<i>Intended for outdoor use</i>			
Accelerated aging conditions	2000 h UV irradiation and spraying with water at 20°C for 19 h of every 24 h.	4 cycles Irradiation with a xenon lamp for 5 hours at 55°C	14 cycles (336 h) ¹ UV radiation for 21 h (spraying with water for 12 min every hour) ² 3 h of rest
Freezing/thawing	10 cycles ¹ -20°C for 24 h ² 20°C for 24 h	4 cycles ¹ 40°C and relative humidity of 100% for 32 h ² -25°C for 2 h ³ 70°C and relative humidity of 60% for 2 h	7 cycles (168 h) ¹ -20 ± 2°C for 15 h ² Immersion in water at -20 ± 2°C for 9 h
High humidity	1000 h ≥ 35°C and condensation on coating surface	4 cycles ¹ 40°C and relative humidity of 100% for 32 h ² 40°C and relative humidity of 92% for 8 h 1 cycle 40°C and relative humidity of 100% for 7 h	3 cycles ¹ 40 ± 2°C and relative humidity of 95–100% for 6 days ² 40 ± 2°C and relative humidity of 55–60% for 1 day
SO ₂ exposure	20 cycles ¹ 40 ± 3°C for 8 h ² outside the climate chamber for 16 h	1 cycle (7 h)	1 cycle (8 h)
Salt water spraying	2000 h Artificial sea water at 20°C	1 cycle 20°C for 7 h	14 cycles (336 h) ¹ 5% NaCl at 35±2°C for 18 h ² No spraying for 6 h
<i>Intended for indoor use</i>			
High humidity	250 h ≥ 40°C and condensation on coating	-	1 cycle (48 h) 40 ± 2°C and relative humidity of
Freezing/thawing	5 cycles ¹ -20°C for 24 h ² 20°C for 24 h	21 cycles ¹ -20°C for 4 h ² 20°C and relative humidity of 80% for 4 h ³ 40°C and relative humidity of 50% for 16 h	21 cycles (168 h) ¹ -20±2°C for 4 h ² 20±2°C for 4 h
Natural aging			
Sample size	I-152×37kg/m×500 mm	500×500×5 mm	300×300×3,2–6 mm
Number of samples	1	12	15
- outdoor exposure	1	4	12
- indoor exposure			
Criteria for evaluating the results of accelerated and natural aging			
	Fire tests: - no more than 25% decrease in fire resistance; - the average temperature of the steel plate ≤550°C after 54 minutes of testing	Sample appearance Plate temperature during fire tests Time of char formation Char structure Type of intumescence Char volume Adhesion to substrate	Sample appearance Fire tests: - normal time-temperature curve of the steel plate; - degree of decrease in fire resistance

Such a full-scale assessment of the service life of fire-retardant coatings was performed, for example, in a study by Shell UK⁴⁴ at their marine test site. Fire-retardancy was assessed for eight coatings of different types and manufacturers. The annual evaluation was performed based on the results of visual inspection of coatings to assess corrosion damage, as well as fire tests of samples in standard and jet fire regimes. Samples were prepared in 1987, while the final fire tests for most systems were conducted in 2002. Bilotta et al.⁴⁵ also evaluated fire-retardant effectiveness of intumescent coatings after 30 years long natural aging. For this purpose, the coatings applied to the steel structures of real building were used. Unfortunately, such time lag between the start and the end of research is not a viable option for most research, so accelerated assessment methods are more widely used.

The method of accelerated aging of fire-retardant coatings on wood samples was described and applied by Harada et al.⁴⁶. For this purpose, wood samples with linear dimensions of 100×120×8 mm with different

types of fire-retardant coating were subjected to 2000 hours of accelerated aging according to the Japanese standard JIS K5600-7-7⁴⁷. The accelerated aging included continuous irradiation of the samples with xenon arc ultraviolet radiation (0.5 W/m² at 340 nm and 550 W/m² at 290–800 nm), and spraying with deionized water for 18 min every 2 hours at 40±2 °C. After exposure of the samples in climate chamber, their weight loss, degree of ingredients leaching, color change and water-repellent properties were evaluated. The weight of the sample was measured before and after 250, 500, 750, 1500 and 2000 hours of aging. Color change and water repellency index were measured before and after 500, 1000, 1500 and 2000 hours of artificial aging. A colorimeter (Nihon Denshoku Kogyo NF333) was used to measure the color change on the surface of samples after exposure. Fire resistance of the samples was evaluated by cone-calorimetry (Toyo Seiki Cone3a) with a heat flux of 50 kW/m².

EN 16623:2015 standard⁴⁸ can also be used to roughly estimate service life of intumescent coatings. According to it, coatings can be divided into 6 categories according to their resistance to external factors (Table 4).

Table 4: Resistance of intumescent coatings to external factors⁴⁸

Category	Description of the exposure type of the coating
X	Intended for operation in any exposure type (indoors, partially or fully outdoors)
W/Y	Intended for operation in the conditions of temporary full outdoors exposure for no more than 6 months with subsequent partial exposure
Y	Intended for operation indoors, and partially exposed outdoors. Partial exposure to outdoor conditions includes sub-zero temperatures, but no rain exposure and limited exposure to UV radiation. (The effect of UV radiation is not evaluated)
W/Z1	Intended for operation in the conditions of temporary full outdoors exposure for no more than 6 months with subsequent indoors exposure with high humidity
W/Z2	Intended for operation in the conditions of temporary full outdoors exposure for no more than 6 months with subsequent indoors exposure
Z1	Intended for operation indoors (no sub-zero temperatures) with high humidity
Z2	Intended for operation indoors (no sub-zero temperatures) with humidity levels other than for category Z1

The tests are performed on steel plates in a climate chamber for a certain number of cycles of artificial aging (Table 5), and then subjected to fire tests.

Table 5: Regimes of artificial aging for different exposure types⁴⁸

Full or partial outdoor exposure				
Days	Cycles (time, temperature, relative humidity)			
1+2	6 h (20 ± 3) °C; (95 ± 5) %	6 h (70 ± 3) °C; (20 ± 5) %	6 h (20 ± 3) °C; (95 ± 5) %	6 h (70 ± 3) °C; (20 ± 5) %
3 + 4	6 h (20 ± 3) °C; (95 ± 5) %	6 h (30 ± 3) °C; (40 ± 5) %	6 h (40 ± 3) °C; (95 ± 5) %	6 h (30 ± 3) °C; (40 ± 5) %
5 + 6 + 7	6 h (-20 ± 3) °C	6 h (40 ± 3) °C; (95 ± 5) %	6 h (-20 ± 3) °C	6 h (40 ± 3) °C; (95 ± 5) %
8 + 9	6 h (20 ± 3) °C; (95 ± 5) %	6 h (70 ± 3) °C; (20 ± 5) %	6 h (20 ± 3) °C; (95 ± 5) %	6 h (70 ± 3) °C; (20 ± 5) %
10 + 11	6 h (20 ± 3) °C; (95 ± 5) %	6 h (30 ± 3) °C; (40 ± 5) %	6 h (40 ± 3) °C; (95 ± 5) %	6 h (30 ± 3) °C; (40 ± 5) %
12 + 13 + 14	6 h (-20 ± 3) °C	6 h (40 ± 3) °C; (95 ± 5) %	6 h (-20 ± 3) °C	6 h (40 ± 3) °C; (95 ± 5) %
Indoors exposure with high humidity				
Number of cycles	Cycles (time, temperature, relative humidity)			
21	8 h (40 ± 3) °C; (98 ± 2) %		16 h (23 ± 3) °C outside of climate chamber	
Indoors exposure with regulated climate parameters				
Number of cycles	Cycles (time, temperature, relative humidity)			
21	4 h (23 ± 3) °C; (80 ± 5) %		16 h (40 ± 3) °C; (50 ± 5) %	
			4 h (5 ± 3) °C; (50 ± 5) %	

This method does not allow to accurately determine service life of coatings, but if all the requirements of the standard are met, the average service life of intumescent coating is guaranteed to be from 10 to 25 years. Therefore, each of the above methods involves testing the possibility of at least 10 years of operation of intumescent coatings in the given conditions of atmospheric influence. In addition, a number of authors considered the possibility of a direct correlation between the number of cycles of artificial aging and the service life of coatings, thus determining the possibility of using them for 1, 2, 5, 10 and 20 years.

III. Performance of coatings with different types of binders

In most studies the aging process of fire-retardant coatings is usually associated with two types of processes: leaching of target components of the coating under the influence of atmospheric water, and structural changes in the polymer affecting the appearance and mechanical properties of the film.⁴⁹

Leaching of the components from the coating happens due to⁵⁰⁻⁵⁴:

- penetration of water molecules into the coating;
- solvation followed by migration of sensitive compounds to the surface of the coating.

In this case, the penetration of water molecules through the polymeric binder is usually explained by free volume theory^{55,56}, according to which the volume of the polymer consists of:

- the volume occupied by polymer chains;
- volume, formed due to the vibrational energy of atomic bonds in the polymer, which is usually considered inaccessible;
- free volume resulting from the relaxation of the plasticized polymer during thermal cycling.

This free volume is the place where water molecules diffuse to, which in turn causes the film/coating to swell. This indicates that the glass transition temperature (T_g) of polymers plays a crucial role in determining the kinetics of aging process of the coating caused by humidity or direct contact with water. At temperatures below and even slightly above the T_g of the polymer, the amount of free volume is usually too small, and the probability of local fluctuations in density producing a hole large enough to allow the solvent molecule to penetrate is low. Thus, according to this model, the polymer selected as a binder must have higher T_g in order to reduce the aging rates of fire-retardant coating.

It should be noted that this applies to the idealized polymer; while the degradation of the real ones due to other environmental parameters, such as UV radiation, can lead to coating defects such as cracking, which will accelerate the diffusion of water molecules into the coating. In addition, higher T_g means that the elasticity of the coatings will be lower than preferred, which may affect short- and long-time performance of the fire-retardant coating.

Although interactions of polymeric materials with a combination of environmental factors form a rather complex process, it is well known that actinic solar radiation (wavelength in the range of 280–390 nm), combined with oxygen and humidity, is crucial for the onset of coating degradation⁵⁷⁻⁶⁰. Table 6 contains information on the sensitivity of some polymers to UV radiation, which is determined by the dissociation energy of the bond⁵⁷.

Photooxidation or photodegradation processes involve the absorption of light, excitation of molecules and their relaxation by radiative or non-radiative energy transitions, or by the transfer of energy to acceptors. Ultimately, this leads to the polymer surface becoming fragile (due to local crosslinking of chains), increase in surface roughness, yellowing, chalking, etc.⁶¹

Table 6: The wavelength of UV radiation (photon energy), which causes maximum degradation of polymers, or to which polymers have maximum sensitivity⁴⁹

Polymer	Wavelength, nm	Energy, kcal/mol
Styrene acrylonitrile	290, 325	99, 88
Polyvinyl chloride	320	89
Polyethylene	300	96
Polypropylene	370	77
Polystyrene	318	90
Polycarbonate	295, 345	97, 83
Acrylonitrile-butadiene-styrene	330, 360	86, 80
Polyamide 6	390	72

The influence of aging, accelerated by exposure to water, UV radiation and other external factors, on the operational parameters of intumescent coatings with different types of binders was researched by the authors of several studies. Table 7 contains information on the effect of accelerated aging on the intumescence factor and fire resistance of metal samples protected by intumescent coatings.

Table 7: Influence of accelerated aging on relative values of fire-retardant characteristics of coatings with different types of polymers

Intumescent system composition	Thickness, mm		Accelerated aging model	Reduction of expansion factor	Reduction in fire resistance
	Steel plate	Coating			
APP-MA-TiO ₂ epoxy-based ⁶²	1,5	1,5	Immersion in distilled water for a month	30%	17%
APP-MA-PE acrylic-based ⁶³	5	1	500 hours of water spraying and drying cycles with additional UV radiation	70%	60%

APP-MA-PE-fillersacrylic-based ⁵⁰	10	1	Immersion in distilled water for 500 h at 25°C	45%	35%
APP-MA-PE-acrylic-based ⁶⁴	5	1	500 h of salt water (3.5% NaCl) spraying and drying cycles	5–50% (depending on the silicate content)	30–43% (depending on the silicate content)

For the most part, researches focused on epoxy coatings only consider their use in harsher operational conditions (outdoor exposure, influence of sea water, etc.), while intumescent coatings based on acrylates or vinyl copolymers are recommended for milder conditions. However, a difference in behavior under accelerated aging conditions can also be spotted for coatings based on acrylates and vinyl polymers based on the type of solvent used in formulation.

For example, in one of our previous studies⁶⁵ the difference in water resistance between intumescent coatings based on two types of polymers was studied: organo-soluble coating based on styrene-acrylic polymer (SA), and water-soluble coating comprising ethylene vinyl acetate. Basic formulations for both coatings were modified by using a variety of nano-clays (each added at 1w.%) to test their ability to stabilize the coatings under the influence of high humidity. In all, ten samples of coatings were produced and a dry film 30×30×1 mm was made of each coating. Film samples were then subjected to immersion in distilled water for a specified amounts of time with their operational properties being determined regularly throughout the experiment duration. First and foremost, the change in mass of the films was monitored daily for the first 10 days of the experiment and then on the final 15th day (Fig.2).

All tested samples, regardless of the nature of binder, display the same type of behavior when immersed in water. First, the mass of a sample increases due to water sorption, followed by a decrease in mass due to the components being washed out the coatings. Similar as they may be, the results obtained for EVA-based samples display a much more rapid and significant mass loss then that for SA-based samples.

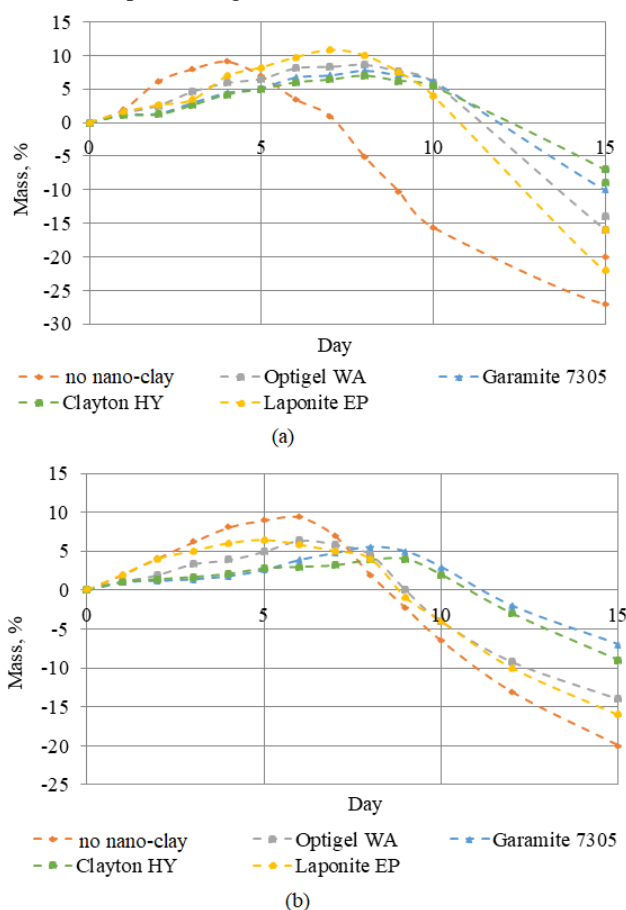


Fig. 2. Change in mass for coating samples registered during 15 days of static water immersion (a – EVA-based coating series, b – SA-based coating series)⁶⁵

Fire-retardant properties were also measured for samples at various stages of the experiment (Table 8). However, the data obtained in those studies does not depict any significant differences in expansion factor (K) of water-soluble versus organo-soluble coating.

Table 8: Fire resistance of coatings after water-immersion tests

Coating	$K, \text{cm}^3/\text{g}$			
	0 days	2 days	6 days	15 days
EVA-based	51	48	32	3
SA-based	55	53	34	5

Daus et al.¹⁷ studied the effect of accelerated aging on the performance of intumescent coatings of different composition based on polyvinyl acetate copolymers. The following were used as binders: vinyl acetate terpolymer with ethylene and vinyl ether, vinyl acetate copolymer with ethylene and vinyl ether, vinyl acetate copolymer with vinyl ether. Studied coatings contained either the triple APP/MA/PE intumescent system, or some variations of their derivatives, as well as titanium dioxide, and rheological additives. All intumescent coatings were applied to metal plates measuring 75×75×5 mm with 1 mm dry layer thickness of the fire-retardant coating. After drying, the samples were subjected to accelerated aging cycles according to the scheme described in EAD 350402-00-1106.

The authors note that all coatings displayed cracking during aging, with the number of cracks for each coating in the range of 3–355 and their size mostly < 2 mm. The thickness of the coating layer after aging increased for most samples by 15–21%, which may indicate either absorption of water by coatings, physical changes in the polymer, or both. The mass of coatings for each of the samples decreased during the tests by 10–25%, which may indicate leaching of solid components from the coating. This could be the reason for the loss of fire-retardant properties of the samples. Fig. 3 shows time-temperature curve obtained during fire tests for the sample containing vinyl acetate terpolymer with ethylene and vinyl ether, which contained unmodified APP, PE and MA. As one can see, the coating after artificial aging has lost its fire-retardant properties providing the level of fire resistance similar to that of unprotected metal. The nature of these changes in fire-retardant properties is well explained by the quality of the formed charred layer (Fig. 4) registered for coatings before and after their artificial aging.

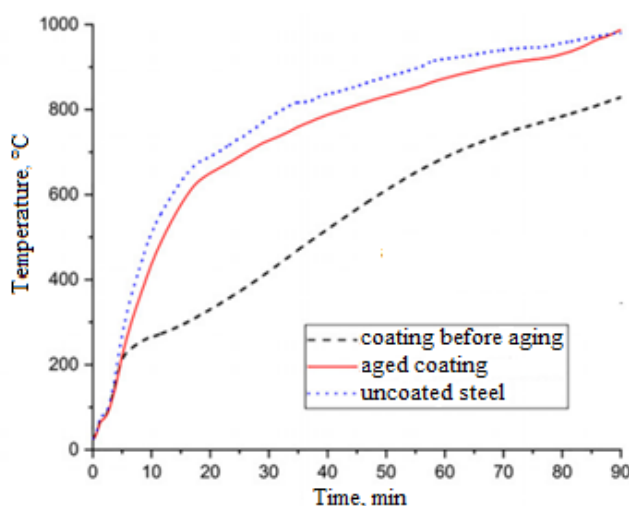


Fig.3.Results of fire tests for coating samples before and after accelerated aging¹⁷

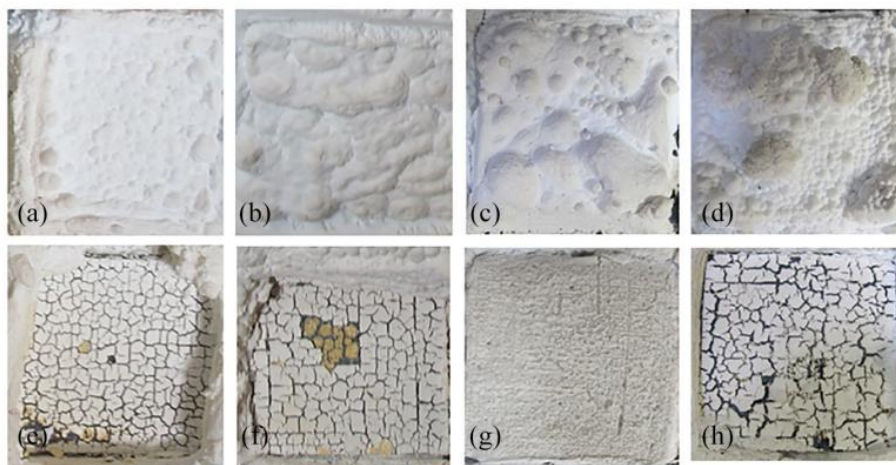


Fig. 4. Charred layer samples obtained after fire tests for coatings before (a, b, c, d) and after (e, f, g, h) artificial aging¹⁷

The same authors⁶⁶ continued their study on the mechanism of aging of coatings based on vinyl acetate polymers using thermogravimetric and spectroscopic methods, the main hypothesis being that the loss of fire-retardant properties of the coating during aging is mainly due to major changes in three components – ammonium polyphosphate, melamine and polymer. The influence of accelerated aging cycles on two intumescent coatings, as well as on individual components (APP, PE, MA, TiO₂, polymer) and their various combinations (APP+MA, APP+PE, APP+TiO₂, TiO₂+MA, TiO₂+PE, TiO₂+APP+MA, TiO₂+APP+PE) was investigated.

All samples of coatings, individual components and their combinations were subjected to accelerated aging (weathering per authors) in a climate chamber according to the following scheme: 6 hours at 40°C and relative humidity 95%, followed by 6 hours at 70°C and relative humidity 20%, repeatedly. In addition, the samples were exposed to UV radiation of 35 W/m² with a wavelength of 290 nm to 400 nm. After 9 weeks of artificial aging, deposits were observed on the surface of both intumescent coatings, which indicate the migration of APP, PE and MA to the surface. This theory is partially confirmed by the data of thermogravimetric studies conducted by the authors (Fig. 5).

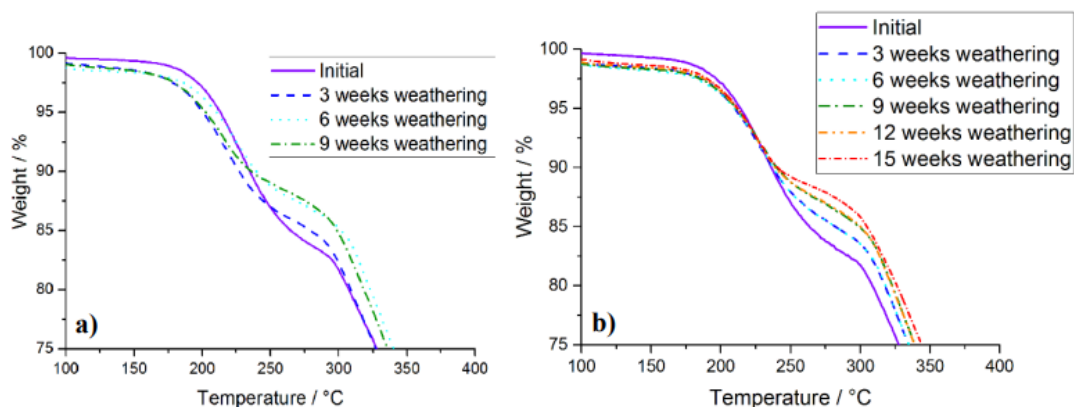


Fig. 5. Thermograms of two studied intumescent coatings at different stages of artificial aging⁶⁶

The appearance of weight loss areas at 100 °C on the thermograms of aged coatings, which were previously absent for samples before artificial aging, indicates the absorption of water by coatings, as it coincides with the temperature range of active water evaporation. Another difference in the weight loss of samples at different stages of aging is observed at temperatures between 200 and 300 °C. According to the research of Kunze⁶⁷, in which the coating based on vinyl acetate polymer was analyzed thermogravimetrically, it is in this temperature range that water and ammonia are actively released and the coating starts to expand. Both substances are released during the thermal decomposition of APP and MA. Reduction of weight loss levels in the temperature range where the expansion occurs, indicates a deterioration in the performance of fire-retardant coating after aging. The fact that fewer gaseous compounds are released gives reason to believe that expansion factor of the coating will be insufficient to ensure required levels of fire resistance. This can be explained by two reasons: firstly, during artificial aging the ingredients required for intumescence migrated to the surface of the

coating and became inaccessible for the normal course of reactions, and secondly, chemical reactions occurred between APP and MA in the climate chamber conditions and changed their ability to participate in intumescent process.

The hypothesis about reactions occurring between APP and MA in atmospheric conditions of climate chamber was confirmed by the data obtained by FTIR (Fig. 6) and thermogravimetric studies (Fig. 7) of a mixture of these two substances before and after artificial aging.

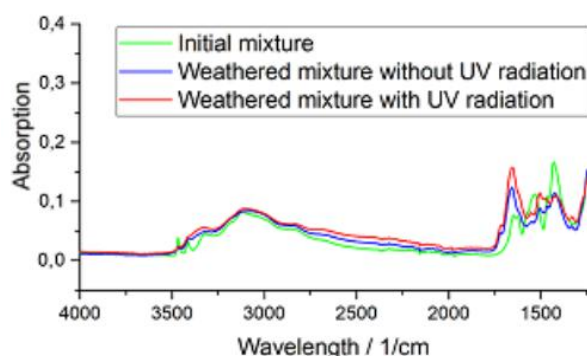


Fig. 6. FTIR spectra of APP-MA mixture at different stages of artificial aging⁶⁷

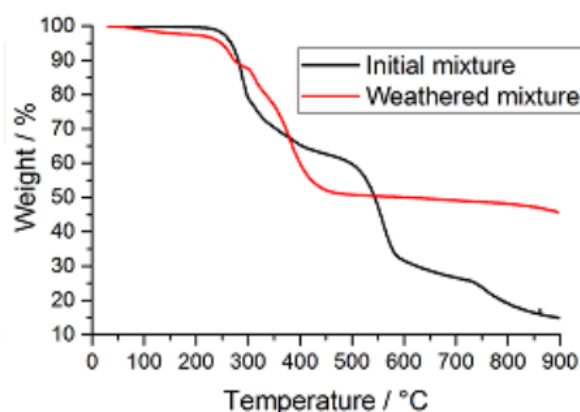


Fig. 7. Thermograms of APP-MA mixture before and after artificial aging⁶⁷

Differences are obvious both in the FTIR spectra and in the mechanism of thermal degradation measured thermogravimetrically. After its artificial aging the mixture demonstrates a much sharper weight loss in the temperature range of 350–550 °C, and at the same time, is significantly less affected by temperatures above 550 °C, which may indicate the yield of stable reaction products under the influence of moisture, temperature and UV radiation.

Vinyl acetates may also undergo chemical transformations under the influence of these environmental factors. For example, large-scale studies of the service life and atmospheric stability of ethylene vinyl acetate copolymer (EVA) under the influence of different scenarios of accelerated aging were conducted by Gagliardi et al.⁶⁸ The authors claim that when EVA decomposes (1.1–1.2), it forms smaller-sized molecules (H₂O, H₂, CH₃CHO and CH₃COOH), which diffuse throughout the polymer, and other macromolecular compounds, which do not do so due to their size.

In addition, it was noted that during exposure to environmental factors, EVA coating tends to absorb oxygen and water from the air.

Wang³¹ conducted similar studies to ones described above⁶⁷ for intumescent coating based on acrylic copolymer. The main components of the coating were: acrylic emulsion, APP, MA, PE (mass ratio 15%, 21%, 9%, 8%, respectively). The coating was applied to 80×40×1.2 mm steel plates with a dry coating thickness of 0.7 mm. The samples were exposed to accelerated aging cycles in the climate chamber. One cycle of accelerated aging lasted 12 hours and included an 8-hour period of exposure to UV radiation at 60±3 °C and relative humidity of 15%, and a 4-hour period of exposure to moisture condensation at 50±3 °C and relative humidity of 100%. Irradiation of UV lamps was fixed at 0.65 W/m²·nm. The samples were kept in climate chamber for 0, 120, 240, 360, 480 and 600 hours, and after the required number of aging cycles were subjected to fire tests. Additionally, spectroscopic and thermogravimetric studies were performed for aged samples, and the appearance of the coating surface was evaluated. Table 9 shows the results of fire tests for coating samples.

Table9: Fire-retardant characteristics of samples during artificial aging³¹

Exposure time, h	Fire resistance, min	Char thickness, mm	Linear expansion factor
0	39,42	29,2	39,6
120	35,20	27,5	38,3
240	30,53	21,9	30,1
360	25,73	16,4	22,4
480	23,73	14,8	20,1
600	20,20	13,1	17,7

As can be seen from the results of fire tests of acrylic intumescent coating samples, its fire resistance decreases with increasing the exposure time to the accelerated aging conditions. When the aging time reaches 600 h, the coating loses 48.8% of fire resistance, i.e., half of its fire-retardant characteristics. The expansion factor also decreases sharply from 39.6 (for coating before exposure) to 17.7 (after 600 hours of aging).

The authors attribute this loss of fire-retardant properties to the occurrence of a number of chemical reactions in the coating during the course of artificial aging. It is noted that the polymer could have suffered the biggest impact, as UV radiation with a wavelength of less than 300 nm could cause homolysis in the polymer, which leads to a decrease in its relative molecular weight.

In general, during UV aging, acrylic resin can form an internal ester; depending on the chemical structure of the functional groups of the material, bonds in side chain groups can break with the formation of free radicals that enter into crosslinking reactions. The ether group present in the polymer of the intumescent coating studied by Wang³¹, can decompose by three mechanisms under the influence of accelerated aging conditions (1.3–1.5).



Under the influence of atmospheric oxygen, all the above variants of the final products (reactions 1.3–1.5) are possible. Hydrogen peroxide can also be formed as the result of interaction between radicals and oxygen, and further react with the formation of carbonyl and hydroxyl groups under the influence of UV radiation or heat. Large free radicals produced in reactions 1.4 and 1.5 can be oxidized with the formation of carboxylic acid, which will arise from the main chain, or can also react with the release of gas (1.6, 1.7).

1.6

1.7

After that, the products formed as a result of reactions 1.6 and 1.7 can themselves enter into reaction 1.3. Thus, during its aging, acrylic resin can form carboxylic acid, aldehydes, alcohols and other monomeric and polymeric substances as results of decomposition, crosslinking and chain breakage reactions.

To investigate changes in other major coating ingredients during accelerated aging, MA, PE, and APP were kept under the same climatic conditions as the ones described for coating samples for 240 hours, after which FTIR spectra were recorded for ingredient samples (Fig.8, a–c).

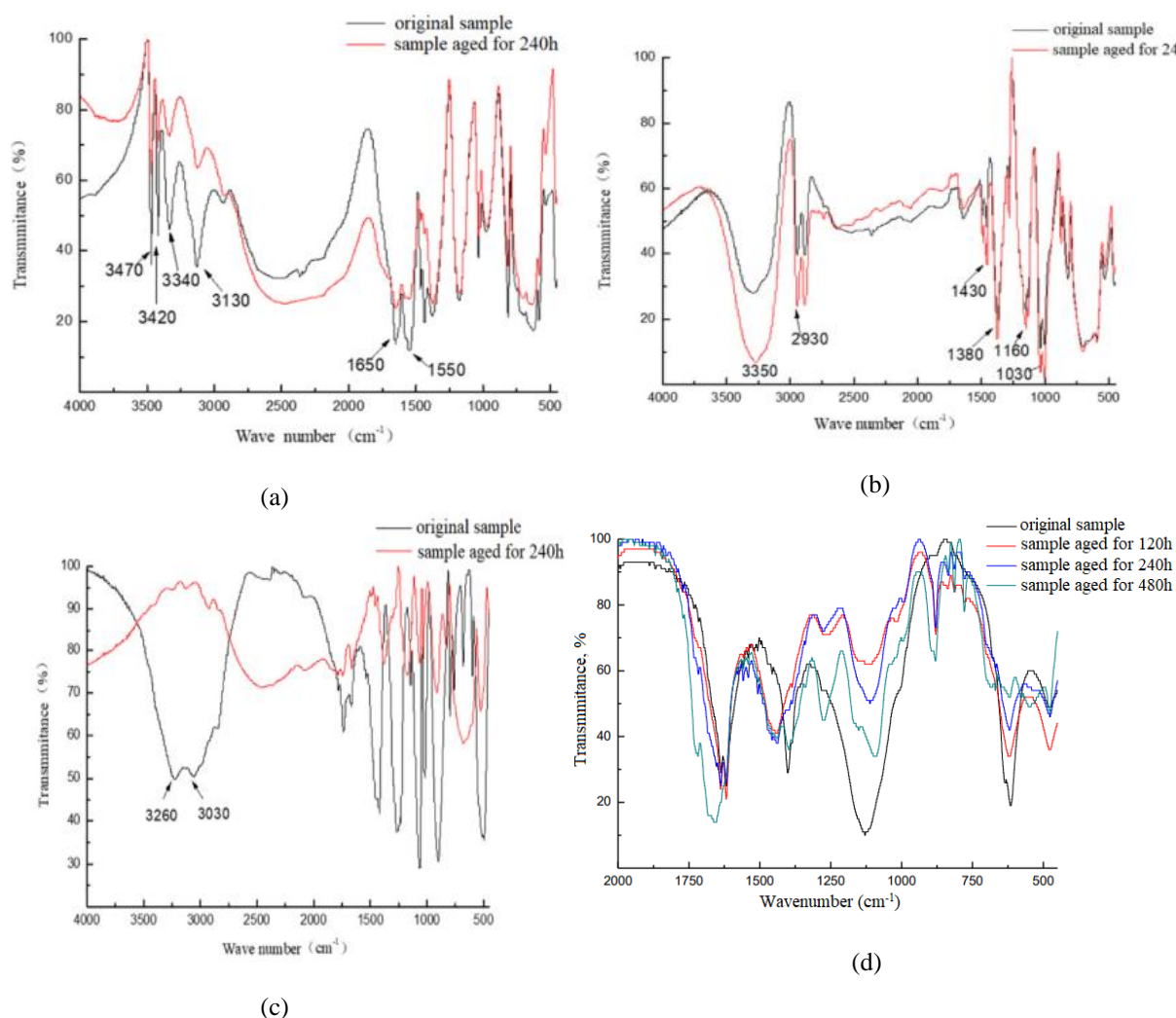


Fig. 8. FTIR spectra for melamine (a), pentaerythritol (b), ammonium polyphosphate (c) and intumescent coating (d) before and after artificial aging (adapted from Wang³¹)

FTIR spectrum for MA (Fig. 8, a) before and after accelerated aging demonstrates that the positions of bands for both samples are approximately the same, and only the intensity of some signals varies. For example, bands at 3470 cm^{-1} , 3420 cm^{-1} , 3340 cm^{-1} and 3130 cm^{-1} weaken with aging of the sample. All of those bands

are attributed to NH_2 vibrations: the first three – to asymmetric, the last one – to symmetric. This indicates a decrease in the amount of NH_2 . At the same time, the band at 2250 cm^{-1} , which is usually attributed to stretching vibrations of $\text{C}\equiv\text{N}$, increases. This indicates that reaction 1.8 occurs in the process of artificial aging of melamine.

1.8

The absorption spectrum for PE (Fig.8, b) does not undergo significant changes after aging, except for a slight increase in the intensity of individual peaks: 3350 cm^{-1} (O–H), 1380 cm^{-1} , 1160 cm^{-1} and 1030 cm^{-1} (C–O–H). These changes indicate that during its aging PE produces substances with larger amount of hydroxyl groups. The increase in the intensity of band at 1430 cm^{-1} , which corresponds to the COH group of carboxylic acid, may be the result of the formation of a small amount of acidic products during the oxidation of PE. In general, chemical transformations of pentaerythritol during aging can be described by scheme 1.9.

1.9

The spectrum for APP (Fig.8, c) has undergone the most obvious changes after aging compared to those for other studied components of the intumescent system. It is known that in the presence of moisture and UV radiation APP can suffer degradation and hydrolysis. This is confirmed by spectroscopy data. The signals at 3260 cm^{-1} and 3030 cm^{-1} , which belong to NH_4 , disappeared after the cycles of accelerated aging. At the same time a new peak can be spotted at 3030 cm^{-1} (indicating stretching vibrations of P–H). To sum this information up, P–O bond in PFA can be broken during aging, with the simultaneous loss of NH_4 (1.10), after which a focal phosphate and a substance containing the P–H group are formed (1.11).

1.10

1.11

The existence of mentioned reactions is also confirmed by the spectra registered for the surface layer of the intumescent coating at different stages of aging (Fig.8, d). Band intensity at 1640 cm^{-1} , attributed to C=O vibrations, increased with the increase of aging time. This can be due to the formation of acids and aldehydes during the photooxidation of polymer and PE. Band at 1400 cm^{-1} , which can correspond to the vibrations of C–H in CH_2 and asymmetric bending vibrations of NH_4 , weakens due to chain scission and oxidation reactions in polymer and APP, which leads to a decrease in the content of CH_2 and NH_4 groups. Compared to the spectra taken for the coating before exposure, after the accelerated aging peaks appear at 1430 cm^{-1} and 1270 cm^{-1} , which can be attributed to C–OH groups of carboxylic acids, formed during the oxidation of polymer and PE. The signal at 1128 cm^{-1} , which corresponds to the vibrations of PO_4 groups and C–O bond in alcohols, significantly weakens with increasing the number of aging cycles, indicating the degradation of PE and APP. At the same time, the appearance of a band at 885 cm^{-1} (attributed to P–O–P vibrations) on the spectra of the aged coating confirms the formation of pyrophosphates in the coating as a result of APP hydrolysis.

Analyzing the information on the mechanism of aging of vinyl-acetate-based and acrylic-based intumescent coatings, a somewhat generalized scheme of this process can be established (Fig. 9).

Obviously, the factors that may affect intumescent coating during its service life are not limited to those shown on the scheme. In addition, each of the mentioned chemical transformations contributes to changes in

both operational and fire-retardant parameters. Therefore, Fig. 9 does not reflect a complete detailed picture of changes during the aging of fire-retardant coatings, only summarizes the described in the literature and empirically identified relationships between chemical processes and their external manifestations in coatings.

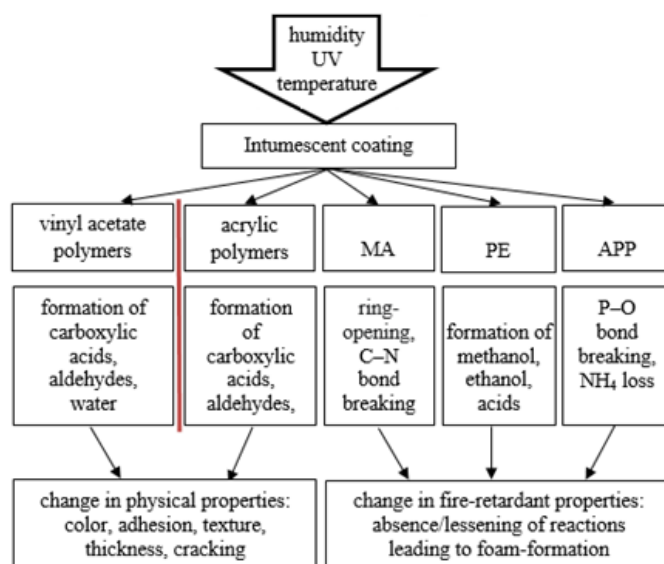


Fig. 9. Physical and chemical processes that occur to the components of intumescent coating during aging

In view of the above, there are two obvious and most often suggested methods which can be used to reduce the impact of environmental factors on the level of aging of fire-retardant coatings: opting for more stable polymers, and replacing APP/PE/MA with less water-soluble and more stable analogues.

IV. Conclusion

There are two aspects to deterioration of intumescent coatings during their service life. The first one is the loss of mechanical properties of the coating due to physical changes in its surface or loss of adhesion to the surface of fire-protected building structure. The second one is diminishing of fire-retardant properties due to leaching or degradation of target ingredients of the coating. Both aspects are affected by a number of external and environmental factors, which may differ according to the atmospheric conditions in which the coating is operated. Because the two phenomena are not necessarily related, the functionality of intumescent coatings cannot be visually assessed during their service life.

As a result of the analysis of literature sources available on the topic, it is possible to determine two successful approaches to maintain fire resistance of waterborne intumescent coatings during prolonged exposure to atmospheric influences, and as a consequence, increase their service life. The first and most important option is to choose a binder that will provide sufficient water resistance. It is important to use binders that harden with forming covalent bonds. The second approach is to replace the most vulnerable target components of intumescent coating with more stable analogues. In this case, PE is the substance most affected by leaching. In general case, the leaching of the target components is further facilitated by the use of a weak polymer as binder.

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