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Fire-Retardant Epoxy Composition Modified with Nano-Clays

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ABSTRACT : *Described fire-retardant epoxy composition is an intumescent material. It is used to increase fire resistance of steel elements of civil structures and industrial facilities, mainly those related to nuclear, gas and oil industry. The composition consists of two separate components. Component A comprises epoxy resin (up to 35 %), ammonium polyphosphate (up to 35 %), melamine (up to 10 %), pentaerythritol (up to 11 %), titanium dioxide (up to 5 %), flame retardants and additives (up to 4%). Component B is a polyamidoamine hardener. The main objective of the study was to increase fire-retardant efficiency of epoxy intumescent coating. For this purpose, it is proposed to form an epoxy resin / nano-clay nanocomposite in-situ during the production of intumescent paint. Such pre-modification of the epoxy resin increases the temperature at which the formed intumescent char decomposes during fire exposure. As such, it propagates the formation of a heat-insulating char with increased thermal resistance. The manufacturing process of the fire-retardant composition is technologically facile and waste-free, does not require any separate complex intermediate stages or special equipment. The proposed epoxy intumescent composition is applicable as a basis for mass-manufactured formulations of fire-retardants for steel structural members which can be potentially exposed to hydrocarbon fire.*
KEYWORDS *fire protection of steel, nanocomposite, epoxy resin, intumescent coating, fire-retardant, hydrocarbon fire.*

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I. INTRODUCTION

Epoxy fire-retardant intumescent coatings [1, 2] are indispensable for fire protection of steel structural members that can potentially be exposed to hydrocarbon fire or chemically aggressive environments. Such conditions occur mostly at strategic civil and military facilities – electric power facilities, oil and gas processing facilities, nuclear power plants, military warehouses, etc. [1, 3]. Steel structural elements during fire or explosion at oil and gas processing facilities are subjected to the destructive effects of extreme temperatures and excess pressure, which are comparable to those of hydrocarbon or jet fire, where the temperature reaches 1000 °C or over within the first minutes.

A relatively new trend in fire protection of building structures at strategic facilities is the use of reactive coatings containing epoxy resins as binders. The main features of such coatings are their strong resistance to chemically and corrosion aggressive environments, the low content of volatile substances, service life of at least 25 years, strong adhesion to metal substrates, and good maintainability of the coating during operation [4, 5]. In this regard, the search for effective formulations of epoxy intumescent coatings with improved fire-retardant, ecological and operational characteristics is a relevant direction of research aimed at the development of passive fire protection [6, 7].

A general approach used to increase fire resistance of steel structural members by means of intumescent coatings is based on creating suitable conditions for strengthening intumescent char, as it is crucial for effective heat insulation during fire exposure [7, 8]. This strengthening is usually achieved by applying organic and inorganic fire retardants [9, 10], nano-carbon materials, nanotubes, graphene [11], heat-resistant reinforcing fibers [12] or other modifying additives [13]. One of the effective ways to increase thermal resistance of epoxy resin, and, subsequently, the fire-retardant efficiency of intumescent compositions containing it, is to introduce the resin into the composition in form of epoxy/nanoclay nanocomposite [1, 14, 15]. Generally, this approach to improving intumescent fire protection is practical and effective. However, the studies performed on the individual and joint influence of different classes of flame-retardants, nano-additives, reinforcing additives are hardly systematic and cannot be sufficiently used for any conclusive theoretical generalizations. Given the variety of formulations of intumescent fire-retardant systems (polyphosphate ones, borate ones, heat-resistant ones, etc.), as well as a wide range of flame-retardant additives and their combinations, research on the optimal formulations of epoxy intumescent compositions with nanocomposite components is relevant and of significant scientific and applied interest.

According to market analysis results [16, 17] the size of passive fire protection market in 2022 accounted to approximately $ 5 billion with the expected 4,7 - 6,4 % growth in 2023 to 2030.

Among the main factors contributing to the growth of production and sales of fire-retardant materials worldwide the following should be mentioned:

- increasing rates of construction of permanent buildings;
- development of the oil and gas industry;
- progress in the development of the technology of passive fire protection;
- introduction of new standards with increased requirements for fire safety of buildings and structures;
- capital increase of insurance companies and growing requirements they set for fire safety of insured buildings and facilities.

An important circumstance that stimulates the development of fire protection industry is the increase in oil and gas production, as well as the increase in the number of investment projects related to shale gas production and processing in China and USA, which, subsequently, leads to stricter fire safety requirements for the companies and enterprises involved. This, on the one hand, creates additional favorable conditions for the growth of demand for fire-retardant materials globally, and on the other hand, necessitates certain changes being made to the formulations and characteristics of such materials, which is particularly relevant for thin-layer intumescent coatings. Thus, the demand for coatings capable of providing adequate protection against hydrocarbon fire conditions is expected to increase. According to analysts [17], these factors are responsible for the current increase in the production and sales of epoxy intumescent coatings.

Table 1 presents the expected levels of compound annual growth rate (CAGR) for the consumption of reactive coatings with various polymer binders, and the list of potential end consumers of fire-retardant materials.

Table 1. Segmentation of the passive fire protection market by material type for 2023 to 2030 time period.

Material	Technology	CAGR, %	By polymer type	End consumers
Intumescent coatings	Water-based	6.5-7	Vinyl Acrylic Epoxy Silicone Polyurethane	Civil engineering Oil and gas processing Industrial construction Warehousing and logistics Transport
	Solvent-based	3-3.5		
	Epoxy	5.5-6.5		
	Powder coating	1-2		

The CAGR for epoxy fire-retardant coatings being at solid 5.5-6.5 % level makes this type of passive fire protection an attractive investment field. And in general terms, innovative solutions regarding the improvement of reliability of fire protection, while simultaneously maintaining or reducing its cost, are necessary for the development of a profitable fire protection market.

II. RESULTS AND DISCUSSION

Intumescent fire-retardant coatings are used to increase fire resistance of steel structural members of buildings and constructions. The target reactive components of such systems are: acid source – ammonium phosphates and polyphosphates; carbon source – pentaerythritol and its analogues; blowing agent – melamine, dicyandiamide, urea and derivatives thereof. Fire-retardant compositions usually also include polymer binders, pigments, fillers and rheological additives.

The use of epoxy resins as binders in intumescent coatings is required if the intended use of such coatings would imply the exposure of structural elements to high humidity, aggressive environments, or hydrocarbon fire conditions.

The main indicator of efficiency for any fire-retardant coating for steel is fire resistance rate R. It signifies the amount of time (hours or minutes) from the fire test onset point until a steel member reaches the limit state of its load-bearing capacity. Other things being equal, R depends on the section factor and critical temperature of steel structural member, fire regime and the loads applied to structure.

The main aim of this study is to design an effective reactive fire-retardant composition in a way that it would provide sufficient levels of fire resistance rate at minimal possible coating thickness.

Formulation of epoxy fire-retardant composition.

The key difference of the developed composition is in the binder of the intumescent composition. It is proposed to use a nanocomposite formed by epoxy resin modified with nano-clays instead of a regular resin.

Epoxy resin used in the current formulation is a product of condensation between bisphenol-A or bisphenol-F and epichlorohydrin. The epoxy equivalent weight of it is recommended to be in the range of 160 to 300 g/eq. Intumescent composition described below was prepared using Araldite GY 783 epoxy resin (Huntsman Advanced Materials, Switzerland).

In terms of nano-clays, it is recommended to choose organomodified layered aluminosilicates, preferably bentonites, with the average basal spacing (interlayer distance) $d \geq 2{,}2$ nm. The best results in laboratory tests were obtained with commercially available nano-clays modified with large substituted ammonium or phosphonium cations, such as: Garamite (BYK-Chemie GmbH, Germany), Cloisite (Altana AG, Germany), etc.

The reactive intumescent ingredients of the composition are represented by the most commonly used substances (ammonium polyphosphate, melamine and pentaerythritol) each partaking in the formation of heat-insulating char.

Production of an effective fire-retardant intumescent composition requires the use of ammonium polyphosphate of the $(NH_4PO_3)_n$ general formula, with crystal phase II and n>1000 degree of polymerization. Such polyphosphates due to their cross-linked structure have an increased thermal stability. Thermal decomposition onset temperature for those is close to 300°C.

Aluminum hydroxide was used as an additional flame retardant to increase fire-retardant efficiency of the composition. Titanium dioxide in its rutile crystalline form was used as a pigment.

Aradur 3745 polyamidoamine adduct (Huntsman Advanced Materials, Switzerland) was used as a hardener in the composition.

Defoamer Byk-066 and rheology modifier Byk-410 (both BYK-Chemie GmbH) were applied to improve rheological and operational characteristics of the composition. Mineral spirit, which serves as a solvent for nano-clay, simultaneously acts as a coalescent additive in the described fire-retardant composition.

The studied epoxy fire-retardant composition is manufactured as two separately packaged components: A and B (Table 2).

Table 2. Component A formulation.

Substance	Recommended amount, wt.%
Epoxy resin, modified with nano-clay	30-35
Ammonium polyphosphate	33-35
Melamine	9-10
Pentaerythritol	9-11
Aluminum hydroxide	1-2
Titanium dioxide	4-5
Flame-retardants, additives	up to 4

Component B consists solely of a polyamidoamine hardener described above.

Preparation of the fire-retardant epoxy composition includes several main technological stages presented below.

Formation of the epoxy/aluminosilicate nanocomposite

In the first stage, modified epoxy resin is obtained «in situ» by mixing nano-clay/mineral spirit gel with epoxy resin. Preliminary to that, the gel is prepared by mixing nano-clay with mineral spirit in 2:8 weight ratio for 30 minutes at 1000 rpm. This gel can be stored for at least 3 months before being used in the production of nanocomposite.

Subsequently, when mixed with epoxy resin, the nano-clay gel takes part in the formation of nanocomposite – a two-component material where the epoxy polymer acts as a plastic base with the organomodified layered aluminosilicate distributed within. Such epoxy/aluminosilicate nanocomposites are characterized by improved thermal characteristics compared to those of the original epoxy resin. TGA results shown in table 3, confirm that the presence of Garamite nano-clay in Araldite GY 783 epoxy resin (№ 2, table 3) causes the shift of thermal decomposition to higher temperatures. At the same time, the residual mass (m, %) for the composite at 700 °C is almost double that of the original polymer (Araldite GY 783, № 1, table 3).

The temperature regime of the main stages of intumescent process is changed in the presence of nanocomposite. First and foremost, it increases the temperature of char decomposition stages, thus resulting in the formation of more durable heat-insulating char with increased thermal resistance.

Table 3. TGA results for developed compositions

№	Sample	T_o, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	$T_{80\%}$, °C	m, %, 700 °C
1	Araldite GY 783	194	296	390	551	9
2	Araldite GY 783/ aluminosilicate nanocomposite	206	312	418	578	17

T_o – thermal destruction onset temperature for either polymer or nanocomposite sample, and $T_{20\%}$, $T_{50\%}$, $T_{80\%}$ correspond to 20, 50 and 80% mass loss of samples.

Preparation of Component A.

Epoxy resin and the nano-clay mineral spirit gel, at an approximate ratio of 6:1, are placed in a high-speed dissolver equipped with a dispersing disc. The mixture is continuously stirred for 3 hours at (35 ± 5) °C and 1000 rpm until a transparent liquid is formed. After that step is completed, titanium dioxide, aluminum hydroxide, pentaerythritol, ammonium polyphosphate and melamine are sequentially loaded into the tank of the stirrer. After the last component from the sequence is loaded, the mixture is then stirred for 60 minutes at 1000 rpm.This results in the formation of Component A; its main physico-chemical characteristics are listed in table 4.

Table 4. Component A characteristics

Property	Value
Density, g/cm^3	1,62±0,09
Non-volatile substances content, %, no less than	80%
Dynamic viscosity, Pa•s, no less than (spindle N7 at 30 rpm)	26
Shelf life, months, no less than	6

Component A can be stored for 6 months with no loss in properties. It should be done in a sealed container in warehousing conditions, that do not permit its exposure to temperatures above 30 °C.

Preparation of the fire-retardant paint before application.

Component B (polyamidoamine hardener) is slowly added through a funnel into a container with Component A, continuously stirred with a mixing drill. The required amount of Component B is calculated as approximately 25-30 % of the mass of Component A. After that, the mixture is stirred for another 2-3 minutes, which results in the formation of the epoxy intumescent paint EP, which can be immediately applied to prepared steel surfaces. Application can be done by hand or using manual or automatic coating equipment. After the two components are mixed together, EP is suitable for application for at least the next 60 minutes, until it starts actively displaying signs of hardening.

Evaluation of the fire-retardant efficiency.

Fire-retardant efficiency of commercially available intumescent coatings is evaluated by large scale fire tests conducted according to the requirements of local or international standards, with the results of those tests being eligible for material certification purposes. However, the use of industrial furnaces required for such tests, as well as steel I-beam samples subjected to the tests, are not economically feasible for research laboratories at the R&D stage. One of the simpler and readily available ways to obtain preliminary comparative data on the fire-retardant characteristics of coatings is to subject smaller steel plates with coating samples to fire tests in a mini-sized furnace capable of maintaining the required time-temperature conditions (Fig.1). The results obtained in these preliminary tests using mini-furnace display satisfactory correlation with those obtained in the full-scale fire tests.

The estimation of fire-retardant efficiency of epoxy intumescent coating described in the current invention, as well as its industrially produced analogue Nullifire SC902, was carried out using a mini-furnace capable of maintaining a time-temperature curve characteristical for a hydrocarbon fire. Nullifire SC902 fire-retardant paint was chosen as a reference material as it is well-known worldwide among epoxy fire-retardant coatings.

Steel plates measuring 300×200×5 mm with thermocouples attached to one side were prepared for tests. A primer coating with an average thickness of 80±10 μm was applied to the surface of the plate subjected to fire test. After the primer coating was dried for 3 days, an intumescent composition (either EP or Nullifire SC902) with an average thickness of 5,00±0,30 mm was applied to the plates. Intumescent compositions were obtained by thoroughly mixing Component A (220 g) and B (26 g) for EP, or part A (223 g) and part B (27 g) for Nullifire SC902. Plates were conditioned at 20±3 °C for at least 10 days. The average thickness of dry coatings was measured using a Qnix1500 magnetic thickness gauge. In order to carry out the preliminary fire tests, steel plates were placed in the openings of the furnace. Time-temperature curve in the oven and on the outer surface of test samples was recorded using K-type thermocouples and «TEST-1» temperature recorder.

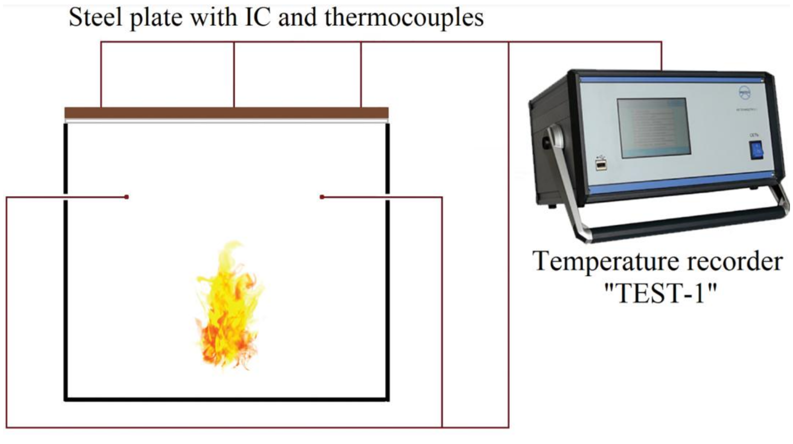

Fig.1. Setting of mini-furnace used in fire tests

The time it took to reach an average temperature of 500 °C on the outer surface of steel plates was recorded as fire resistance rate R (min).

Physical strength of intumescent chars was studied using an electronic dynamometer AFG 100 (Mecmesin). In order to compare the strength of intumescent chars after fire tests, the force (N) required to achieve 80% compression of the char sample, was estimated at a penetration speed of 0.25 mm/s.

The results obtained in the described experiments are provided in table 5.

Table 5. Comparison of physicochemical characteristics of intumescent composition described in the invention to those of Nullifire SC902

№	Parameter	EP epoxy composition	Nullifire SC902 epoxy composition
1	Fire resistance, R, min	54	49
2	Load, N	32	28

A comparison of fire resistance R determined for the EP composition described in the current study with that for its analogue, Nullifire SC902, shows that at the same coating thickness of 5 mm, the described composition demonstrates higher fire-retardant efficiency. Studies of the intumescent char hardness levels (№2, table 5) show that the heat-insulating char obtained from EP is on par with and even somewhat stronger compared to that obtained from Nullifire SC902 composition.

Comparative studies also prove that the studied fire-retardant epoxy composition can be used as a basis for developing commercial formulations of fire-retardant materials for structural steel, capable of providing suitable levels of fire resistance in hydrocarbon fire conditions.

III. CONCLUSION

The results obtained in this study are useful and important, as they concern a crucial aspect of civil engineering – ensuring safety of civilians, personnel and first responders during fire which emerged as a result of spontaneous combustion or arson. The problem of fire protection becomes especially relevant due to recently increased worldwide threats of terrorism and military conflicts with the use of explosive weapons.

The described process for the production of epoxy fire-retardant composition can be useful to technologists and manufacturers of intumescent paints. It is a simple and effective method for increasing fire-retardant efficiency of epoxy coatings. The process of manufacturing described in this study is technologically facile and waste-free. It does not require any additional intermediate stages or special equipment.

The invention can be used as a basis for formulating new epoxy fire-retardant compositions for steel, intended for use at strategic facilities with possible threat of hydrocarbon fire.

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