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STUDY ON THE EFFECT OF INORGANIC ADDITIVES ON THE FLAME-RETARDANT PERFORMANCE OF PAINT

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Abstract. Currently, organic flame-retardant coating systems have been widely used due to their effective thermal insulation properties. However, during combustion, these coatings can release toxic gases such as carbon monoxide and phosgene, posing serious risks to human health and the environment. Moreover, to date, no inorganic intumescent coating system on the market utilizes nanographite, a material with significant potential for enhancing thermal resistance and structural stability at elevated temperatures. In this study, nanographite, $Al(OH)_3$, KH_2PO_4, urea, and $CaCO_3$ were used as inorganic additives, investigated, and tested at various ratios to evaluate their flame-retardant properties in paint formulations. The aim was to develop an inorganic flame-retardant paint system that eliminates toxic gas emissions during fires. Experimental results indicate that in a 20 mL inorganic paint system formulation containing 1.0 g of nanographite, 0.5 g of $CaCO_3$, 0.1 g of KH_2PO_4, and 0.3 g of $Al(OH)_3$, the flame-retardant performance of the paint was significantly enhanced, reducing heat transfer and providing better protection for internal structures. Specifically, the fire resistance time exceeded 23 minutes at temperatures approaching 900 °C, offering excellent thermal insulation and material protection.

***Keywords*:** Flame-retardant additives, inorganic flame-retardant paint, gas-generating agents, nanographite.

1. Introduction

In modern construction, steel is widely used to enhance structural strength and load-bearing capacity. However, when exposed to fire, steel rapidly loses its mechanical properties at temperatures above 500 °C, significantly increasing the risk of structural collapse. Most commercially available flame-retardant coatings are based on organic matrices, which, upon combustion, emit toxic gases such as carbon monoxide, carbon

dioxide, and volatile organic compounds (VOCs), posing serious risks to both human health and the environment.

Recent studies have focused on developing inorganic fire-retardant coatings to overcome these limitations. Incorporation of carbon into coating systems has been shown to yield smoother and more uniform surfaces, reducing agglomeration compared to carbon-free formulations [1]. The addition of 5 wt% aluminum hydroxide significantly improves thermal insulation performance, lowering the backside temperature of steel by 98 °C and increasing both the intumescent expansion ratio and the residual char content compared to coatings without additives [2].

Thermal analysis techniques have demonstrated that hybrid fillers consisting of one-dimensional carbon nanotubes (CNTs) and two-dimensional graphene enhance both thermal stability and conductivity of epoxy-based coatings. In particular, the combination of oxidized CNTs and graphene oxide (GO) achieved over 100% improvement compared to individual fillers [3]. Furthermore, incorporating nanoclay and coal ash into coating formulations enhances fire resistance through the formation of barrier layers and synergistic effects [4].

Globally, expanded graphite has proven to be effective in improving the performance of inorganic intumescent coatings. An optimized formulation comprising sodium silicate, metakaolin, ammonium polyphosphate, pentaerythritol, $Al(OH)_3$, and 1 wt% expanded graphite achieved an expansion ratio exceeding 4.7 times that of pure sodium silicate, while maintaining the backside temperature of steel substrates below 510 °C after three hours of fire exposure [5].

The intumescent mechanism typically relies on acid sources, carbon sources, and gas sources. Upon heating, these systems undergo endothermic decomposition, resulting in the formation of a thermally stable, porous char layer with low thermal conductivity. Metal oxides and hydroxides further enhance fire resistance by releasing water and diluting combustible gases [6].

Phosphosilicate and magnesium potassium phosphate cement (MKPC)-based coatings have also shown excellent thermal insulation properties. Coatings formulated with optimized ratios of MgO/KH_2PO_4, wollastonite, vermiculite, $Al(OH)_3$, and $CaCO_3$ kept backside temperatures below 200 °C after one hour of fire exposure, despite surface temperatures exceeding 1000 °C [7].

Expanded graphite, when combined with halogen-free additives such as zinc borate and phosphorus-nitrogen compounds, has been reported to enhance both fire resistance and mechanical properties. However, its large particle size may hinder dispersion and affect coating aesthetics [8]. To address these limitations, the present study uses nano-graphite alongside $Al(OH)_3$, KH_2PO_4, urea, and $CaCO_3$ to develop a fully inorganic flame-retardant coating with high fire resistance and preserved mechanical integrity.

The novelty of this study lies in the development of a fully inorganic coating system, incorporating nano-graphite with optimally dosed additives determined through experimental analysis, to enhance the fire-retardant performance of the coating.

2. Content

2.1. Experiment

2.1.1. Materials

The materials used in this work are listed in Table 1.

Table 1. Composition of the paint system

No.	Materials and chemicals	Technical specifications	Origin
1	Graphite	Specific surface area: 50 - 800 m^2/g Size: 10 - 500 nm Carbon Content: ≥ 98%	Tianjin Dengke Chemical Reagent, China
2	Urea	Purity: ≥ 95%	Xilong scientific, China
3	$CaCO_3$	Size: 1 - 100 µm Purity: ≥ 95%	Xilong scientific, China
4	$Al(OH)_3$	Size: 1 - 10 µm Purity: ≥ 95%	Xilong scientific, China
5	KH_2PO_4	Purity: ≥ 99.5%	Xilong scientific, China
6	Kaolin	Purity: ≥ 99.5%	Xilong scientific, China
7	Na_2SiO_3	Purity: ≥ 40%	Xilong scientific, China

2.1.2. Process for fabricating paint

Step 1: Synthesis of nanographite.

- Principle: Graphite is expanded by treating it with 98% H_2SO_4 and $(NH_4)_2S_2O_8$. Upon decomposition, ammonium persulfate releases SO_4^{2-} radicals, which oxidize the graphite and increase interlayer spacing. This oxidation introduces functional groups, disrupting the π-π bonds and separating the graphite layers. The modified graphite exhibits enhanced absorption, improved adsorption capacity, and stronger interactions with its surroundings. Nanographite is synthesized via an ultrasonic method.

- Procedure:

+ Prepare a mixture in a ratio of 1 : 23 : 25 as follows: Accurately weigh 25.0 g of $(NH_4)_2S_2O_8$, place it into a 250 mL heat-resistant glass beaker. Add 12.5 mL of concentrated H_2SO_4 and stir well. Gradually add 5 g of graphite to the beaker, continuously stirring for 120 minutes at room temperature. The product is thoroughly rinsed with distilled water and then dried at 90 °C for 24 hours to obtain expanded graphite.

+ Disperse the expanded graphite in water and place it in a digital ultrasonic argo lab machine with a 100 W power capacity. Apply ultrasonic treatment for 120 minutes at room temperature to produce nanographite.

Step 2: Fabrication of inorganic fire-resistant paint system.

- Accurate measurement of materials: Precisely weigh the required amounts of nanographite, urea or $CaCO_3$, $Al(OH)_3$, KH_2PO_4, kaolin, liquid glass, and water for each experimental sample according to the specified parameters under investigation.

Figure 1. Filtering porous graphite

Figure 2. Synthesis of nanographite

Figure 3. Preparation of the coating system

Figure 4. Coating on steel material

Table 2. Sample codes and coating components for the study

No.	Evaluation criteria	Code		No.	Evaluation criteria	Code	
		Symbol	***Content (%)***			***Symbol***	***Content (%)***
1	*Liquid glass*	*All specimens*		3	$Al(OH)_3$	**M9**	0.77
	Nanographite	**M1**	0.99			**M10**	1.15
		M2	1.96			**M11**	1.53
		M3	2.91	4	KH_2PO_4	**M12**	0.19
		M4	3.85			**M13**	0.38
		M5	4.76			**M14**	0.58
2	Urea	**M6**	1.15	5	$CaCO_3$	**M15**	1.32
		M7	2.28			**M16**	2.18
		M8	3.38			**M17**	3.03

- Mixing process: Sequentially, the materials were added into a mortar and manually stirred the mixture thoroughly for 30 minutes to form the paint system.

Liquid glass was functioned as both a solvent and binder to unify the system components, while KH_2PO_4 was added to bind to the steel substrate and form a water-insoluble amorphous glassy phase with kaolin through the K–Al–Si–P–O bonding mechanism [8]. The effect of KH_2PO_4 dosage is examined in Section 2.2.4.

2.1.3. Characterization of paint coatings

The properties of paint coatings are analyzed using the following methods:

- Structural Morphology Analysis: Nanographite particles were analyzed using a Nikon electron microscope and a Zetasizer particle size analyzer. Their sizes were observed and measured at progressively higher magnifications with specialized equipment.

- Measurement of film thickness: The paint film thickness was measured using the Sauter TC 1250-0.1F thickness gauge.

- Fire resistance evaluation: Fire resistance refers to the paint's ability to withstand exposure to a gas flame, including measurement flame spread, retardation time, swelling behavior, and thermal insulation performance on different materials.

The research procedure for assessing the influence of inorganic additives on the intumescent and fire-resistant properties of the coating system was carried out as follows:

Step 1: Fabricate a fire-retardant coating system incorporating inorganic additives such as nanographite, $Al(OH)_3$, KH_2PO_4, urea, or $CaCO_3$.

Step 2: Investigate the effect of each additive component and the thermal durability of the coating system, including:

Nanographite: 5 painting samples from **M1** to **M5**;

Urea: 3 painting samples from **M6** to **M8**;

$CaCO_3$: 3 painting samples from **M9** to **M11**;

$Al(OH)_3$: 3 painting samples from **M12** to **M14**;

KH_2PO_4: 3 painting samples from **M15** to **M17**.

Their thermal durability (intumescence time) and insulation performance were evaluated. Temperatures on the front and back surfaces of the coated material were measured carefully. Each sample was coated with 3 or 5 uniform layers. Moreover, some selected coatings were analyzed for thickness and intumescence degree. Additionally, the temperature measurements and burn duration were recorded to assess the fire-retardant effectiveness.

2.1.4. Methods

- The fire-resistant paint was tested following the TCVN 9311-1:2012 standard method.

- Fire resistance/thermal insulation test was assessed by measuring the temperature difference between the front and rear surfaces when exposed to a gas flame. The temperatures were recorded using an Ennologic eT650D infrared thermometer, with measurements taken at 5 points on each side to obtain the average value.

- Intumescence was measured by the expansion ratio, defined as the ratio of coating thickness after and before heat exposure. Thickness was determined using a mechanical caliper.

- Post-fire surface morphology was analyzed using a Nikon optical microscope.

- The coating's adhesion to the substrate was measured using the cross-hatch cutting method.

- Film thickness was measured using sauter TC 1250-0.1F coating thickness gauge with measurements taken at 5 different locations to obtain the average value.

2.2. Results and discussion

2.2.1. The influence of nanographite on the fire-retardant properties of paint

In order to evaluate the influence of nanographite on the fire-retardant properties, we investigated five coating samples (**M1** to **M5**) and obtained the following results.

Table 3. Influence of nanographite on the fire-retardant properties

Sample	Nanographite (g)/20 mL paint	Front surface temperature (°C)	Back surface temperature (°C)	Intumescence time (minutes)
M1	0.25	765.00 ± 0.78	388.89 ± 4.06	5.16 ±0.25
M2	0.50	831.11 ± 3.89	376.39 ± 3.61	6.16±0.29
M3	0.75	839.78 ± 4.11	395.78 ± 3.72	6.45±0.45
M4	1.00	878.50 ± 3.17	399.61 ± 1.39	8.90 ± 1.70
M5	1.25	866.67 ± 4.33	471.39 ± 5.28	6.40 ± 0.20

The results indicate that sample **M4**, containing 1.0 g of nanographite, exhibited the longest thermal durability (8.9 ± 1.7 minutes) and the highest temperature differential between the front and back surfaces (478.90°C), along with the formation of large, uniformly distributed intumescent bubbles. In contrast, samples **M1** to **M3** demonstrated lower thermal durability, irregularity, and a smaller temperature difference. Sample **M5**, with an excessive nanographite content, showed limited intumescence.

Thus, nanographite exhibits high thermal stability without decomposition. When exposed to fire, it forms a protective ash layer that acts as a thermal barrier, shielding the underlying material from heat and flame, inhibiting fire propagation, and preserving the structural integrity of the coated substrate. The optimal fire-retardant performance is achieved with a nanographite content of 1.0 g per 20 mL of paint.

*Sample **M1*** *Sample **M2*** *Sample **M3*** *Sample **M4*** *Sample **M5***

Figure 5. Samples with nanographite

2.2.2. Influence of urea on the intumescence properties of the coating

The experiment measuring the influence of Urea was conducted using three samples: **M6**, **M7**, and **M8**.

Table 4. Influence of urea on the fire-retardant properties

Sample	Ure (g/20 mL painting)	Front surface temperature (°C)	Back surface temperature (°C)	Intumescence Time (minutes)
M6	0.3	861.4±0.3	417.0±0.8	6.87±0.07
M7	0.6	873.1±1.4	424.7±4.2	7.99±0.06
M8	0.9	874.4±2.2	427.2±4.1	6.35±0.07

The experimental results indicate that sample **M7**, containing 0.6 g of urea, produced the most uniform intumescent coating and exhibited the highest thermal durability, with an intumescence time of (7.99 ± 0.06) minutes. It also achieved the largest temperature differential between the front and back surfaces, reaching 448.4 °C. Although sample **M8** exhibited the most significant degree of intumescence, its thermal durability was the lowest at (6.35 ± 0.07) minutes.

Thus, when urea was used as the gas-generating agent, it thermally decomposed at high temperatures, releasing gases that promoted coating intumescence and enhanced the thermal insulation. A urea content of 0.6 g was optimal for this coating system.

*Sample **M6*** *Sample **M7*** *Sample **M8***

Figure 6. Samples with urea

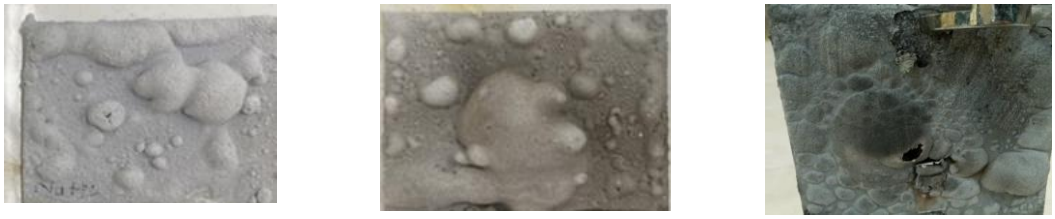
2.2.3. Influence of $Al(OH)_3$ on the intumescence properties of the coating

The influence of $Al(OH)_3$ was investigated using three coating samples, and the experimental results are presented in Table 5.

Table 5. Influence of $Al(OH)_3$ on the fire-retardant properties

Sample	$Al(OH)_3$ (gram)/20 mL painting	Front surface temperature (^{0}C)	Back surface temperature (^{0}C)	Intumescence time (minutes)
M9	0.2	861.4±4.7	419.8±4.4	6.58±0.49
M10	0.3	834.7±0.8	361.1±3.3	7.86±0.34
M11	0.4	847.5±5.3	409.7±4.7	6.52±0.20

The results indicate that varying the amount of $Al(OH)_3$ significantly affects the thermal durability of the coating system. Sample **M10**, with 0.3 g of $Al(OH)_3$, showed the best performance, with a maximum temperature differential of 473.60 °C between the two surfaces and the longest intumescence time of 7.86 minutes. This can be explained by the decomposition of $Al(OH)_3$ into Al_2O_3, a thermally stable oxide at high temperatures, while the released H_2O acts as an insulating barrier, slowing liquid evaporation due to the Leidenfrost effect. Therefore, a content of 0.3 g of $Al(OH)_3$ per 20 mL of paint is optimal for achieving the best intumescence performance for this system.



*Sample **M9*** *Sample **M10*** *Sample **M11***

Figure 7. Samples with $Al(OH)_3$

2.2.4. Influence of KH_2PO_4 on the intumescence properties of the painting

The influence of KH_2PO_4 was investigated using three coating samples, and the experimental results are presented in Table 6.

Table 6. Influence of KH_2PO_4 on the fire-retardant properties

Sample	KH_2PO_4 (gram)/ 20 mL painting	Front surface temperature (^{0}C)	Back surface temperature (^{0}C)	Intumescence time (minutes)
M12	0.05	896.4±9.7	663.1±10.3	6.83±0.03
M13	0.10	895.3±6.4	396.9±3.6	8.13±0.03
M14	0.15	893.9±3.9	427.8±4.4	7.62±0.05

The experimental results indicate that sample **M13**, containing 0.10 g of KH_2PO_4, performed the longest intumescence time, averaging 8.13 minutes, and the highest temperature differential, 498.5°C, between the front and back surfaces. In contrast, sample **M14** experienced rapid drying of the coating, while sample **M12** resulted in a more diluted coating with reduced thermal durability. KH_2PO_4 enhances thermal insulation, improves substrate protection, and reduces the risk of fire propagation. However, KH_2PO_4 can also make the coating more brittle and reduce adhesion, leading to suboptimal intumescence. Therefore, an optimal KH_2PO_4 content for the coating system is determined to be 0.10 g.

*Sample **M12*** *Sample **M13*** *Sample **M14***

Figure 8. Samples with KH_2PO_4

**** Results of evaluating the parameters with the painting system using urea as the gas-generating agent***

The formulation of the 20 mL selected intumescent coating system is as follows: 1 g nanographite, 0.6 g Urea, 0.1 g KH_2PO_4, 0.3 g $Al(OH)_3$.

The intumescence performance of the selected coating system was evaluated through two experiments: Experiment 1 with three coating layers and Experiment 2 with 5 coating layers. The objective was to examine the effect of coating layers on intumescence performance. The results are summarized in Table 7.

Table 7. Effect of the number of coating layers on the intumescence performance of the coating

Experiment	Average front surface temperature (°C)	Average back surface temperature (°C)	Intumescence time (minutes)
Exp. 1	859.89 ± 14.43	412.67 ± 8.88	8.023 ± 0.682
Exp. 2	803.61 ± 8.84	40.50 ± 5.54	15.03± 0.83

Thus, in the coating system, heat resistance is significantly high, with front surface temperatures reaching between 800 °C and 900 °C. In Experiment 2, insulation performance is excellent, achieving a temperature differential of 763 °C while the intumescence time exceeds 15 minutes under direct flame exposure.

2.2.5. Influence of $CaCO_3$ on the intumescence performance of the coating

The gas-generating additive in the coating system was replaced from urea to $CaCO_3$, applied 5 coating layers, and evaluated three coating samples. The results are shown in Table 8.

Table 8. Influence of $CaCO_3$ on the fire-retardant properties

Experiment	$CaCO_3$ (gram)	Average front surface temperature (°C)	Average back surface temperature (°C)	Intumescence time (minutes)
M15	0.3	726.94 ± 6.94	60.00 ± 6.11	16.05±6.05
M16	0.5	860.00 ± 4.44	102.50 ± 1.94	23.39±1.39
M17	0.7	803.06 ± 4.17	88.89 ± 6.11	22.49±1.68

The results show that sample **M16**, containing 0.5 g of $CaCO_3$, achieved the longest intumescence time (23.39 ± 1.39 minutes) and the largest temperature differential between the front and back surfaces, reaching approximately 758°C.

Average coating thickness and intumescence height were also measured:

Coating Thickness:

M15: 820.2 ± 9.7 µm; **M16**: 829.8 ± 12.3 µm; **M17**: 876.6 ± 11.3 µm

Intumescence Height:

M15: 2.7 ± 12.5 cm; **M16**: 2.75 ± 0.5 cm; **M17**: 2.65 ± 0.1 cm

Thus, sample **M16** demonstrated the highest degree of intumescence and the best insulation performance on both surfaces.

In conclusion, the coating system using $CaCO_3$ as the gas-generating additive outperforms the system using urea. This is attributed to the fact that $CaCO_3$ decomposes at higher temperatures (approximately 600 - 800 °C) compared to urea, producing CO_2 and CaO. This decomposition helps maintain protective performance at elevated temperatures and extends the fire-resistant duration. Moreover, $CaCO_3$ does not participate in side chemical reactions upon decomposition, thereby stabilizing the coating, and the resulting CaO contributes to increased hardness and mechanical durability of the protective layer.

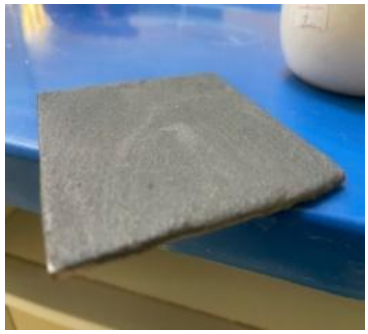


Figure 9. Sample M16 before burning

Figure 10. Sample M15 after burning

Figure 11. Sample M16 after burning

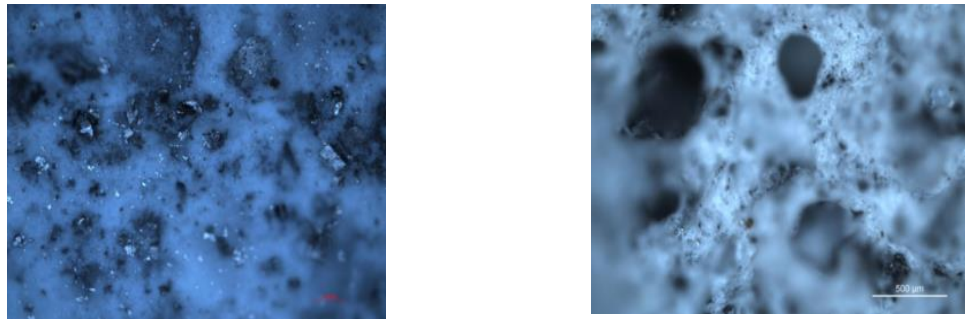


Figure 12. Sample M16 under Nikon microscope

**** Analysis and evaluation of the selected coating system***

The influence of inorganic additives on the intumescence properties of the coating was investigated. It found that the inorganic fire-retardant coating system containing 1.0 g of nanographite, 0.5 g of $CaCO_3$, 0.1 g of KH_2PO_4, and 0.3 g of $Al(OH)_3$ per 20 mL of coating performed the best in intumescence performance.

Test results for coating sample **M16** (performed in accordance with BS EN 13381-8:2013 at the Fire Prevention and Fighting University): The sample temperatures were monitored based on BS EN 13381-8, and the result was recorded according to standard TCVN 9311-1. The test results are presented in the following Table 9.

Table 9. Sample M16 with Standard BS EN 13381-8:2013

Time (minutes)	Average sample temperature (°C)	Furnace temperature (°C)	Time (minutes)	Average sample temperature (°C)	Furnace temperature (°C)
0	57.8	45.5	5	327.6	612.8
1	81.8	126.0	6	381.2	610.3
2	145.6	354.2	7	438.4	663.3
3	215.6	530.4	8	481.7	669.0
4	277.6	615.1			

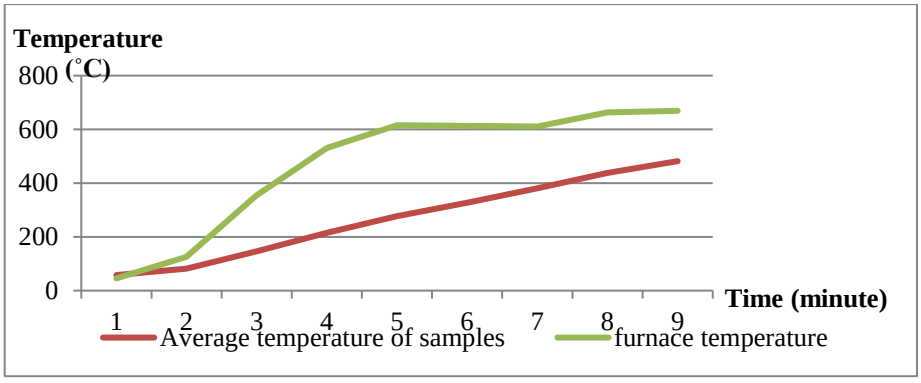


Figure 13. M16 monitoring chart

**** Analysis result***

Temperature variation over time (according to ISO 834 or TCVN 9311-1): The data show that the furnace temperature increases steadily, in accordance with the standard curve. The average temperature of the sample gradually increases but always remains lower than the furnace temperature, indicating effective thermal insulation and protection of the sample. The temperature difference between the furnace and the sample decreases over time, which is attributed to a reduction in protective performance as the furnace temperature rises.

Temperature differential as an indicator of coating protection: In the initial period (0-3 minutes), a large temperature differential is observed (due to the sample's initially excellent insulation). After 6-8 minutes, the differential decreases significantly, indicating that the insulation effectiveness diminishes as the temperature increases.

Assessment of protective performance: Thermal insulation: The sample temperature remains significantly lower than the furnace temperature. Fire Resistance Duration: No clear signs of temperature instability or material failure were observed during the first 8 minutes. The fire resistance of the coating or protective material may extend beyond this period

Overall, the fire protection performance of the **M16** coating system is acceptable, with good insulation and flame retardancy during the 8-minute test.

3. Conclusions

It found that inorganic additives - including nanographite, $Al(OH)_3$, KH_2PO_4, urea, and $CaCO_3$ - significantly affect the intumescence properties of the coating. The inorganic coating system using $CaCO_3$ as the gas-generating agent demonstrates better flame retardancy than the system using urea. Experimental results show that in a 20 mL inorganic coating system containing 1.0 g nanographite, 0.5 g $CaCO_3$, 0.1 g KH_2PO_4, and 0.3 g $Al(OH)_3$, the flame-retardant performance is optimal.

Further experiments with additional inorganic additives to develop a new coating system overcoming the limitations of the initial system to achieve the highest possible flame retardancy and fire resistance have been being investigated.

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