Research on preparation and performance tests of the fire retardant coatings for special functionalized wires and cables

Zhipeng Liu[1,4], Bing Li[2,5], Kaimin Huang[1,6], Yuqian Lu[1,7], Shaokui Yu[2,8], Zhengji An[1,9], Zehui Ma[1,10], Junlong Ye[1,11], Yingjie Chen[1,3,12]

[1]Guandong Testing Institute of Product Quality Supervision, Guangzhoiu, Guangdong, China
[2]Guangzhou Siweishi Coating Construction Material Co., Ltd., Guangzhoiu, Guangdong, China
[3]Corresponding author

[4]172074550@qq.com
[5]chnitherm@126.com
[6]295831116@qq.com
[7]sissi.lu823@gmail.com
[8]yushaokui@163.com
[9]869187916@qq.com
[10]775479222@qq.com
[11]33874882@qq.com
[12]120518939@qq.com

Abstract. This study aimed to produce a new potential intumescent flame retardant system through the addition of titanium dioxide and alumina-silica fiber based on optimizing the traditional ammonium polyphosphate (APP) / melamine (MEL) / pentaerythritol (PER) intumescent flame retardant formula. The flame retardant capacity and the physical properties were fully analyzed and discussed. The produced flame retardant coating could resist the rapid rise in 1100℃ of high flame temperature, whereas 40℃ exceeded the national standards. Thus, the produced flame retardant coating in this study could be potentially further applied to the cables and wires that are frequently needed in petroleum, telecommunication, military, tunnel, and electric uses.

Keywords: Intumescent flame retardant system, flame retardant coating, aluminum silica fiber, titanium dioxide, resist high flame temperature.

1. Introduction

With the rapid development in the national economy, energy, construction, and high-tech emerging industries, the issue of production safety takes major importance, especially fire safety. Presently, the most widely used methodology for fire-proofing focused on applying the fire-retardant coatings onto the surface of the materials. For example, the frequently used intumescent fire-retardant coatings on steel structure surfaces applied in large-scale construction processes, and the choice of decorative fire-retardant coatings on top of the constructive substrates, roles as both decoration and fire protection purposes for numerical commercial buildings. However, the appearance of large numbers of cable fires both at home and abroad recently caused huge losses have alerted people to the significance of wire fire protection. Cables and wires are crucial power supply facilities for public buildings, and they are distributed wide and dense like a spider web, thus if a fire occurs, these cables and wires will act as accelerators spreading out the fire quickly and extensively. Results from an actual fire indicated, that the fierce fire could spread as quickly as within 2-3s once a fire appears, and a large quantity of smoke and toxic gases will be generated after the fierce fire spreads beyond 100m, usually limited within 60 seconds. Hence, studies and research in preventing fire disasters caused by wires and cables have become urgent and prior, and by comparison with the existing fire-proof methodologies and previous results, found that the use of fire-retardant coatings will be the most economical and convenient one.

2. Selection of fire-retardant coatings:

Fire retardant coatings manufactured nationally can be divided into two main categories according to different application scenarios: decorative-typed and steel-structure ones. Furthermore, based on the transformative states of the coatings after the fire, it is further categorized into two sub-groups: intumescent and non-intumescent ones.

National production for decorative fire-retardant coatings is mainly intumescent types, while both intumescent and non-intumescent types are manufactured for steel structure fire-retardant coatings. Decorative fire-retardant coatings is a new type of coating that integrates both decoration and fireproof purposes, when it is coated onto the surface of the combustible substrate, it plays a decorative role manually, when fire appears, it protects the basic substrate by preventing the spread of the fire, allow people have sufficient time to escape. For the selection of the fire-retardant coatings used for cables and wires, they usually do not need decoration purposes, thus the steel structure type would be more suitable. In contrast between intumescent and non-intumescent steel structure fire-retardant coatings, previous results mentioned that non-intumescent types cannot satisfy the requirements for cable bending. However, intumescent coatings are thin, and usually made by mixing with non-combustible resin, catalysts, carbonizing agents, and blowing agents, allowing them to absorb a large amount of external heat energy arising from extreme flame and high temperature, followed by forming a much thinker carbonized insulation layer in contrast with the original coatings, which could effectively prevent the external heat source have effect acting on the basic substrates, thus they often selected for cables and wires fire retardant usage [1-2].

3. Mechanisms for fire-retardant coatings

Fire retardant coatings, also known as flame retardant coatings, especially in two main properties: firstly, the coatings themself are non-combustible or flame retardant, which could prevent being ignited by the flame; secondly, the coatings could foam and expand during the combustion process, results in prolong the diffusion of heat to the protected substrates, saving time for fire suppression.

Combustion is a chemical process that generates light and heat. There are three compulsory conditions for combustion to happen, combustible substances, combustion promoters (air, oxygen, oxidants, etc.), and fire sources (smoke and high temperature) respectively. These three conditions should occur simultaneously and interact with each other for combustion to arise, thus to isolate any one of these three elements would be the key to anti-flaming. Also, there would a lot of heat is released when the substance is burned, generating thermal decomposition and combustion for the surrounding combustible substances, resulting in further expansion and spread of the flame continuously. Hence, finding out the methodology for isolating any form of heat conduction from the protected object would be the major focus for preventing the flame spreading as the propagation of heat energy is the principle of the fire spreading. Existed fire-retardant coatings have the operating principles of having the formation of an expansive insulation layer after being burned, taking advantage of discharging the heat energy based on both high thermal conductivity and high reflection performances of the coating materials themselves. Nonetheless, the available fire-proof coatings formula is having poor effects on wires and cable applications according to the special outer insulating and sheathing materials surrounding [3-5].

The most widely used insulating and sheathing polymer materials for wires and cables and the respective decomposition products are summarized in Table 1, including polyethylene, polystyrene, polyvinyl chloride, epoxy resin, polypropylene butadiene rubber, NBR rubber, and nylon. Although polymers often undergo a thermal decomposition process to release combustible gases, such as CO, CO_2, CH_4, etc., however, if the concentration of those combustible gases can be controlled or reduced to a certain level, the flame or fire will be extinguished afterward. Accordingly, the cables' intumescent fire retardant coatings often rely on the addition of flame retardant resin to achieve flame retardant properties, and also the thick foam layer formed surrounded the wires after reaching the fire, generated from the interactions among the carbonizing agent, dehydrating agent and blowing agent contained inside the coating formula could effectively limit the effect of the external heat sources have on the substrate, and reduce the possibilities for the polymer decomposition reaction to happen, which ultimately protect the functionalities of the wires and cables.

Table 1. Summarized information for Polymers and their respective decomposition products.

Polymers	Decomposed products
Polyethylene	CO, CO_2, CH_4, HCHO, CH_3CHO
Polystyrene	CO, CO_2, CH_4, HCHO, CHO, Styrene, Hydrocarbon
Polyvinyl chloride	CO, CO_2, CH_4, HCHO, CH_3CHO, HCl
Epoxy resin	CO, CO_2, CH_4, HCHO, CH_3CHO
Polypropylene butadiene rubber	CO, CO_2, CH_4, Dipentene, Isoprene
NBR rubber	CO, CO_2, CH_4, NH_3, HCN, Dipentene, Isoprene
Nylon	CO, CO_2, NH_3, Hydroxyl compound

The major mechanism for cable fire retardant coating is mainly related to five directions [5-6]:

The blowing agent will thermal decompose, releasing non-flammable gases, such as melamine decomposed ammonia, NH_3;

The film-forming agent adhered to the cables will soften and melt by the same time the thermal decomposition happens, releasing non-flammable gases;

The molten film-forming agent forms a foam layer composited from the blowing agent expansion and the released gases;

The catalyst will thermally decompose to form powerful water absorbents, which then be esterified and dehydrated with the film-foaming foam layer interior carbonizing agent to form inorganic residues;

The carbonization system will gel, solidify, and dehydrate into an unsaturated main carbon chain after applying catalysts and a high-temperature heat source, then carry out the cyclic bridging reaction to generate the final dense and hard black honeycomb carbonized layer. The thickness of the final carbonized layer is inversely proportional to the heat transfer intensity.

It can be concluded, that the influence factors for the usage of cable fire retardant coatings could be summarized as follows: Initially, the adhesion ability of the film-forming agent, if the adhesion force is large, the coating will be hard to break and form a dense protective surface; Secondly, the matching degree of the chosen catalyst with the film forming agent and the carbon forming agent, if the compatibility is high enough, the carbonization layer will be constructed perfectly, especially in generating high foaming rate, uniform foaming, long foaming duration, thick and hard carbonization layer, and more importantly, results in better flame retardant effect; Thirdly, the selectivity of the plasticizer, which is closely related to the physical properties of wires and cables, such as the flexibility of the wires; Lastly, the mixing ratio of every single component inside the coating formula [7-9]. Hence, this study will concentrate on research in the proportion of the interior materials used for the existing intumescent fire retardant coatings, aimed at developing a new retardant system by increasing the extended ratio and the upper limit of the heat resistance temperature.

4. Experimental materials

Cable fire retardant coatings are generally composed of film-foaming agents, fire retardants, flame retardants, filling materials, and flame retardant plasticizer compositions. The functionalities and the respective materials used for each of the compositions are tabulated in *Table 2*. This study is designed to follow the traditional ternary flame retardant systems, but first offer the addition of double cage formed pentaerythritol phosphate followed by the titanium dioxide and alumina-silica fiber into the formula, each constituent contained inside the formula and its respective roles are also conjugated in Table 2.

Table 2. Summarized information for fire-retardant coatings' components.

Components		Purposes	Materials used
Film-foaming agents		Strong adhesion; Good flexibility; Fire resistant; Foaming quick at high-temperature.	Ethylene vinyl acetate copolymer emulsion, Vinylidene chloride emulsion
Fire retardants	Carbonizing agents	Form the foam carbonization layer rapidly to isolate the heat influence of flame onto the cable under high-temperature / extreme fire conditions.	Pentaerythritol
	Catalysts	Promote the dehydration and carbonization of the hydroxyl organics to form a fire-retardant carbon layer.	Ammonium polyphosphate
	Blowing agents	Guarantee the expansion of the coating to form a sponged-bubbled structure after a large amount of decomposing asphyxiating gas is released when the coating has been heated.	Ammonium polyphosphate, Melamine
Flame retardants		Increase the flammability of the film.	Aluminum silicate fiber
Filling materials		Increase the fire resistance and flame retardant abilities of the coating, mainly made from inorganic substances.	Titanium dioxide, Kaolin powder, Talc powder
Flame retardant plasticizers		Enhance the coating density to prevent cracking and strengthen the flame-retardant abilities.	Phospholipids compounds

5. Experimental setup

Initially, accurately weigh out and mix the formulated ingredients of ammonium polyphosphate, pentaerythritol, melamine, titanium dioxide, aluminum silicate fiber, kaolin, and talc powder, then grind and disperse the mixture with the addition of water to ensure the mixture is evenly dispersed. The rotational speed for the grinding and mixing multipurpose machine applied initially was set at 400 turns/min. The grinding dispersion process functions in mixing the powdered materials uniformly, ensuring the large particles are ground fine for further experimental procedures to take place.

Next, the rotation speed for the machine increases up to 1000 turns/min, lasting for 30 minutes, then a scraper is applied to check the fineness of the mixture, the standard gives as fine as 50 microns to allow progress into the next step. After verifying the fineness of the mixture, the rotation speed will be decreased to 600 turns/min, then pour the ethylene vinyl acetate copolymer emulsion and Vinylidene chloride emulsion into the mixture, continue stirring for 5 minutes to accomplish the entire flame-retardant coating preparation process. The schematic flow for the entire coatings preparation procedure has been drawn in Figure 1.

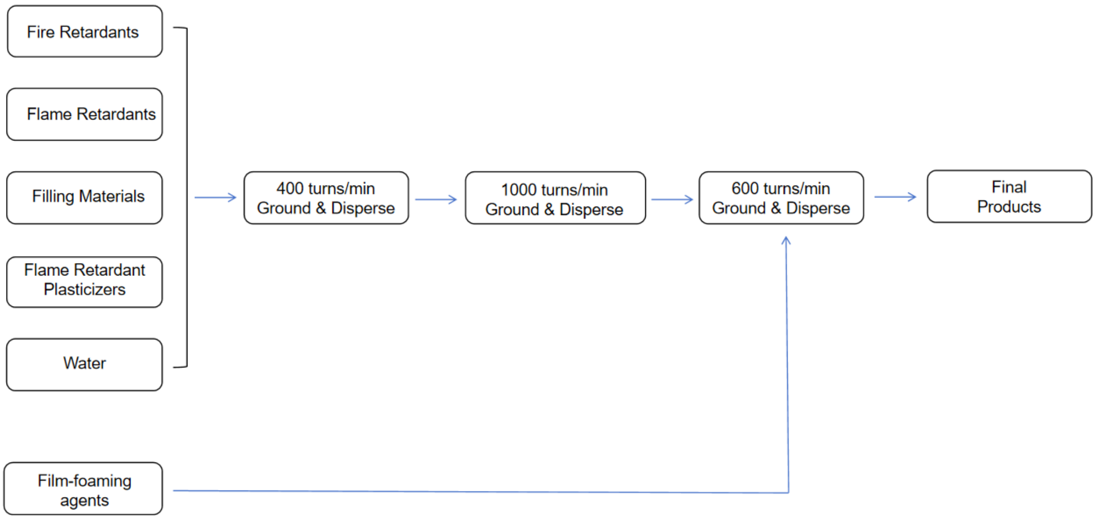

Figure 1. The schematic theme for the coatings preparation procedure.

6. Results

Full fire retardant coatings formula could be separated into two major parts during the fabricating process, one is the production of the standard stock, contained water, ammonium polyphosphate, pentaerythritol, melamine, dispersant, deformer, and preservatives inclusively, other part is the manufacturing of the emulsion, titanium dioxide, and aluminum silicate fiber. The most optimized additive amount for the film-foaming agents, the flame retardant, and the filling materials was determined before the decisive experimental test for the entire formula compositions. The film-foaming agents selected for this study were mixtures between ethylene vinyl acetate copolymer emulsion and vinylidene chloride emulsion. There were 9 experimental trials tested to find the trend between the amount added based on 50 portions of the standard stocks and the corresponding expansion ratio, and the adhesion ability respectively. *Table 3. and Figure 2.* summarize the results which, when increasing the percentage of the emulsion amount added, the expansion ratio declines proportionally, but the adhesion ability becomes better and better, which, in terms of balancing the need for both purposes, it could be concluded that the trail 6 would be the most appropriate amount to be selected, which is approximately 20% addition of the emulsion, results in 35 times in terms of expansion ratio. Next, there could be seen in Table 4., Table 5., Figure 3., and Figure 4., the addition of aluminum silica fiber and titanium dioxide both have an inversely proportional effect on expansion rate, while they both have a directly proportional effect on the strength of the expansion layer. Especially for the addition of the fibers, while aggregates the amount added would enhance the expansion layer strength, but simultaneously restrain the carbonizing layers' expanded ability distinctly. According to the results gained from the expansion ratio tested with the addition of the emulsion, the selective rules for the expansion ratio values for both aluminum silica fiber and titanium dioxide additives would lie between 30-33 times, hence in conjugation with the performance with each corresponding expansion layer strengths, the conformed added percentage for aluminum silica fiber and the titanium dioxide would be roughly 4-5% and 8-9% respectively.

Table 3. Testing 9 trials for the relationship between the emulsion added and the expansion ratio and the adhesion ability.

Number	**Emulsion added**	**Percentage added/%**	**Expansion ratio**	**Adhesion**
1	1.66	3.21	50x	Poor
2	3.33	6.22	50x	Poor
3	4.66	8.50	45x	Weak

Table 3. (continued).

4	8.65	14.70	38x	Good
5	10.65	17.50	35x	Good
6	13.32	20.98	35x	Excellent
7	19.98	28.48	32x	Excellent
8	25.00	33.33	26x	Excellent
9	35.00	38.90	5x	Excellent

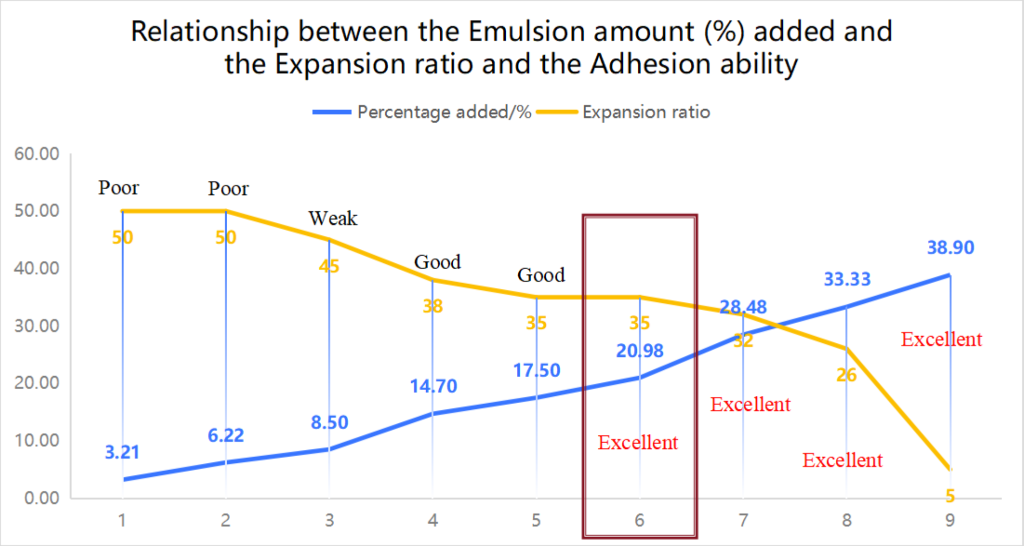

Figure 2. Trends for the relationship between the emulsion amount added and the expansion ratio and the adhesion ability.

Table 4. Testing 9 trials for the relationship between the aluminum silicate fiber added and the expansion ratio and the strength of the expansion layer.

Number	**Aluminum silicate fiber added**	**Percentage added/%**	**Expansion ratio**	**Expansion layer strength**
1	0.00	0.00	35x	Soft
2	1.20	2.00	35x	Normal
3	1.50	2.50	33x	Normal
4	1.80	3.00	33x	Excellent
5	2.40	4.00	30x	Excellent
6	3.00	5.00	25x	Excellent
7	3.60	6.00	25x	Excellent
8	4.20	7.00	20x	Excellent
9	4.80	8.00	18x	Excellent

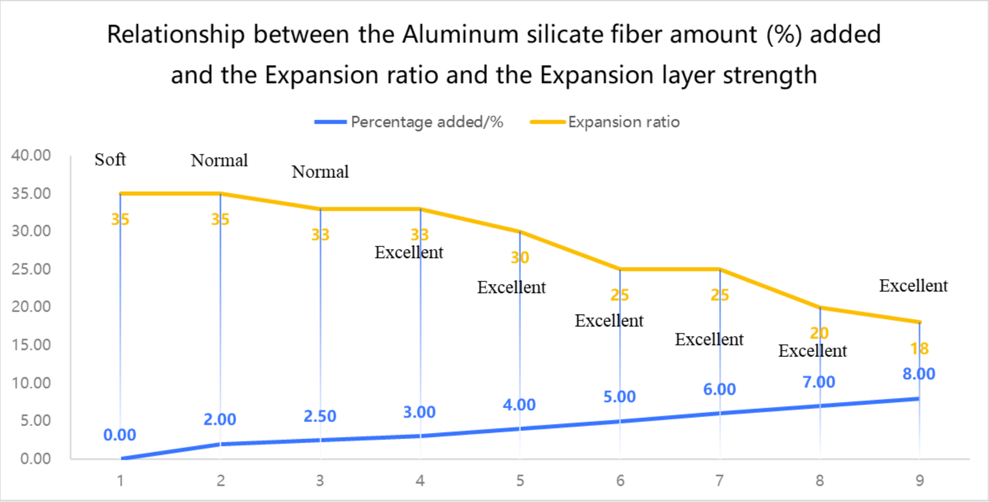

Figure 3. Trends for the relationship between the aluminum silicate fiber added and the expansion ratio and the strength of the expansion layer.

Table 5. Testing 9 trials for the relationship between the titanium dioxide added and the expansion ratio and the strength of the expansion layer.

Number	**Titanium dioxide added**	**Percentage added/%**	**Expansion ratio**	**Expansion layer strength**
1	0.00	0.00	32x	Normal
2	2.00	3.20	31x	Normal
3	2.50	4.00	32x	Normal
4	3.00	4.80	31x	Normal
5	3.50	5.60	31x	Normal
6	4.00	6.40	31x	Normal
7	5.00	8.00	32x	Good
8	6.00	9.60	32x	Excellent
9	7.00	11.20	31x	Good

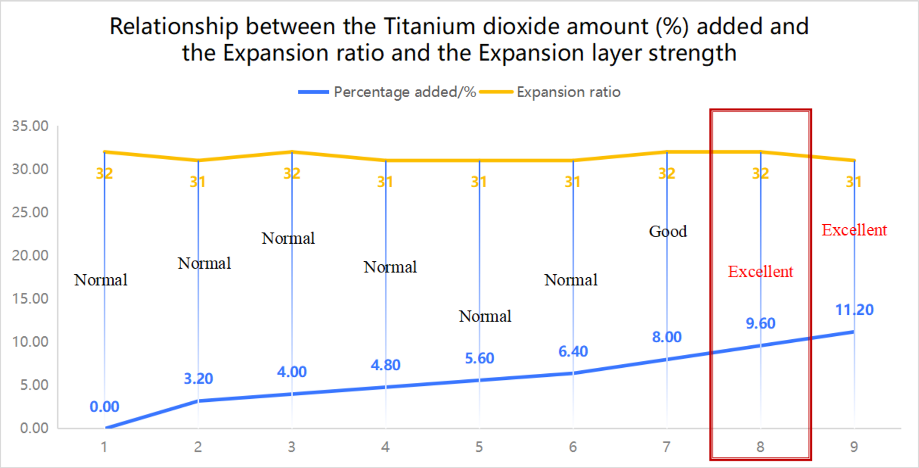

Figure 4. Trends for the relationship between the titanium dioxide added and the expansion ratio and the strength of the expansion layer.

DOI: 10.54254/2755-2721/65/20240533

Based on the previous results of the percentage added for the emulsion, aluminum silica fiber, and titanium dioxide, this study further attempts multiple tests to apply these data to the standard stocks to explore the suitable usage amount for the ammonium polyphosphate (APP), melamine (MEL), and pentaerythritol (PER) into the final flame retardant formula. *Table 6.*, *Table 7.* and *Figure 5.* combined represent the most optimum formula compositions would be formula Number 10 and Number 11, which, conclude that based on the APP-MEL-PER expanded system, further adding titanium dioxide, aluminum silica fiber and our selected mixture of the emulsion can further optimize the traditional flame retardant expanded system.

Table 6. Tabulated 12 testified formula compositions.

Number	**Water**	**Ammonium polyphosphate**	**Pentaerythritol**	**Melamine**	**Emulsion**	**Titanium dioxide**	**Aluminum silicate fiber**	**Dispersant**	**Deformer**	**Preservatives**	**Total percentage**	**Total mass**
1	23.48	32.05	12.02	12.02	16.03	0.00	3.85	0.32	0.16	0.08	100	62.4
2	22.75	31.06	11.65	11.65	15.53	3.11	3.73	0.31	0.16	0.08	100	64.4
3	22.57	30.82	11.56	11.56	15.41	3.85	3.70	0.31	0.15	0.08	100	64.9
4	22.40	30.58	11.47	11.47	15.29	4.59	3.67	0.31	0.15	0.08	100	65.4
5	22.23	30.35	11.38	11.38	15.17	5.31	3.64	0.30	0.15	0.08	100	65.9
6	22.06	30.12	11.30	11.30	15.06	6.02	3.61	0.30	0.15	0.08	100	66.4
7	21.90	29.90	11.21	11.21	14.95	6.73	3.59	0.30	0.15	0.07	100	66.9
8	21.74	29.67	11.13	11.13	14.84	7.42	3.56	0.30	0.15	0.07	100	67.4
9	21.58	29.46	11.05	11.05	14.73	8.10	3.53	0.29	0.15	0.07	100	67.9
10	20.93	28.57	10.71	10.71	15.41	8.40	4.76	0.29	0.14	0.07	100	71.4
11	20.34	27.77	10.41	10.41	16.02	8.68	5.87	0.28	0.14	0.07	100	74.9
12	19.81	27.04	10.14	10.14	16.58	8.93	6.89	0.27	0.14	0.07	100	78.4

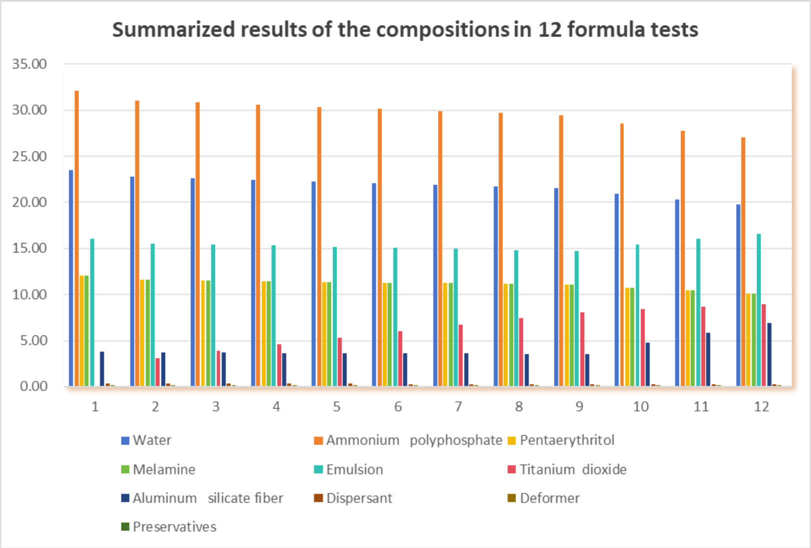

Figure 5. Summarized results for 12 testified formula compositions.

Table 7. Painted coating thickness with fire-resistance time under 1100°C test results.

Number	Painted Coating Thickness / mm	Flame Retardant Time / mins
1	0.50	3
2	1.00	5
3	1.50	12
4	2.00	24
5	2.50	37
6	3.00	44
7	3.50	48
8	4.00	52
9	4.50	56
10	5.00	58
11	5.50	60

Table 8. Tabulated 12 tests with their corresponding performance test results.

Number	**Expansion ratio**	**Expansion layer strength**	**High temperature / Flame resistance**
1	32	Normal	Weak
2	31	Normal	Weak
3	32	Normal	Weak
4	31	Normal	Weak
5	31	Normal	Weak
6	31	Normal	Weak
7	32	Normal	Good
8	32	Good	Good
9	31	Good	Good
10	32	Excellent	Excellent
11	32	Excellent	Excellent
12	31	Good	Excellent

After confirming the portions required for every ingredient contained inside the formula content, there were various fire-proofing experiments were tested to ensure the fire-retardant ability. *Figure 6.* demonstrates the relationship between the painted coating thickness and the fire retardant time. There was presumed to be a linear relationship between the painted thickness and the flame-proofing time initially, but surprisingly, the results show there was a huge rise in the flame retardant time when the painted coating thickness increased up to 2.00mm, then steadily leveled off when the thickness measurement accelerated to 5.50mm, and the following fire-proofing time reached 60 minutes at this maximum point. The statistical results trend could extrapolate the data which, when increasing the painted coating thickness over 5.50mm, the flame-proofing time will rise over 60 minutes accordingly. However, considering both economic and environmental factors, taking 5.50mm of the painted coating thickness would be appropriate.

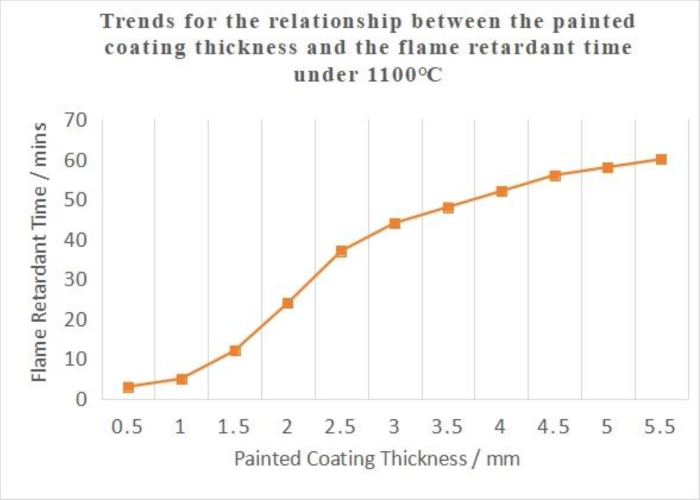

Figure 6. Trends for the relationship between the painted coating thickness and the flame retardant time under 1100 ^{o}C

7. Conclusions and Discussion

In this work, an optimized intumescent fire-retardant coating formula was successfully prepared under a traditional flame-retardant expanding system adding aluminum silica fiber and titanium dioxide. The experimental results confirm that the addition of 4% aluminum silica fiber and 8% titanium dioxide was an effective flame retardant capacity condition compared to others. Furthermore, the produced flame retardant coating could resist the rapid rise in 1100°C of high flame temperature, whereas 40°Cexceeded the national standards, confirming its flame retardant property. Overall, although this formula still requires large quantities of other extreme conditions tests to confirm its feasibility, its ability to continue the coatings' heat insulation effect when reaching extreme fire could be confirmed, as the addition of titanium dioxide and aluminum silicate will be sintered at high temperature in the presence of phosphoric acid to form a fluff-like structure network titanium aluminum silico-phosphates, which confirmed its potential value, making it an attractive matrix for various industries.

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