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Effect of Curing Agent Dosage on Fire Resistance of Waterborne Epoxy Coating

Jingying Wang[1], Rongrong Zheng[1, *], Xingwei Li[2], Hongjing Liu[1], Liyan Wang[1]

[1]School of Petrochemical Engineering, Shenyang University of Technology, Shenyang, P. R. China

[2]Liaoning Inspection, Testing and Certification Center, Shenyang, P. R. China

Email address:

Zhengrongrong2006@126.com (Rongrong Zheng)

[*]Corresponding author

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Abstract: The water-based epoxy fire retardant coating is formed by reaction curing, which not only has good anti-corrosion performance, but also has environmental protection and flame retardant performance, which is suitable for construction machinery painting or steel structure buildings. However, the curing and cross-linking process of water-based epoxy coatings is centered on the curing agent, which gradually diffuses into the epoxy resin particles. The curing agent molecules first contact the surface of the epoxy resin dispersed phase particles and undergo a cross-linking curing reaction. As the reaction progresses, the relative molecular weight and glass transition temperature of the epoxy resin on the particle surface gradually increase, so that the diffusion rate of the curing agent molecules into the particles gradually slows down, which means that the curing reaction inside the epoxy resin dispersed phase particles Less than its surface, resulting in a low internal crosslink density, and ultimately not all epoxy groups have the opportunity to interact with the activating groups of the curing agent. Therefore, this paper studies different proportions of waterborne epoxy emulsion and curing agent. The results show that when m (epoxy emulsion): m (curing agent) = 7:3, the fire resistance and comprehensive performance of the coating are the best.

Keywords: Dosage of Curing Agent, Waterborne Epoxy Paint, Fire Performance

1. Introduction

Two-component waterborne epoxy coatings not only have essential differences in the selection of solvents, but also in the film formation process and mechanism. Waterborne epoxy emulsion and epoxy curing agent, respectively is A two-component epoxy coating part A and part B, solvent free epoxy coating for the homogeneous system, with the evaporation of the solvent, the two components are being cross linked, paint the packing was wrapped and piled into membrane, and water-borne epoxy coatings for multiphase system, general epoxy resin in the form of the dispersed phase dispersed in the aqueous phase. The water-based epoxy curing agent is dissolved in water, and the curing film forming process includes the evaporation of water, the aggregation and deformation of emulsion particles, the packaging and accumulation of pigments and fillers, and the interaction with the curing agent to form a three-dimensional spatial network structure, which finally shows strong permeability resistance [1-5].

Theoretically, the curing of epoxy resin is an activation hydrogen molecule interacting with an epoxy molecule to form a complete three-dimensional space structure [6-7]. However, the curing crosslinking process of waterborne epoxy coating takes the curing agent as the center and gradually diffuses into the epoxy resin particles [8-9]. The curing agent molecules first contact the surface of the dispersed phase particles of the epoxy resin and the crosslinking curing reaction takes place [10-11]. With the progress of the curing reaction, the relative molecular weight and glass transition temperature of the epoxy resin on the surface of the particles gradually increase, making the diffusion rate of the curing agent molecules into the particles gradually slow down. This means that less curing reaction takes place inside the dispersed phase particles of epoxy resin than on its surface, resulting in low internal crosslinking density, and ultimately not all epoxy groups have the opportunity to interact with the activation group of the curing agent [12-14]. Therefore, it is of great significance to study the effect of the amount of curing agent on the coating function in practical application. This paper mainly studies the effect of the amount of curing agent on the fire resistance of waterborne epoxy coating.

2. Experimental Section

2.1. Preparation of Two-component Waterborne Epoxy Coating

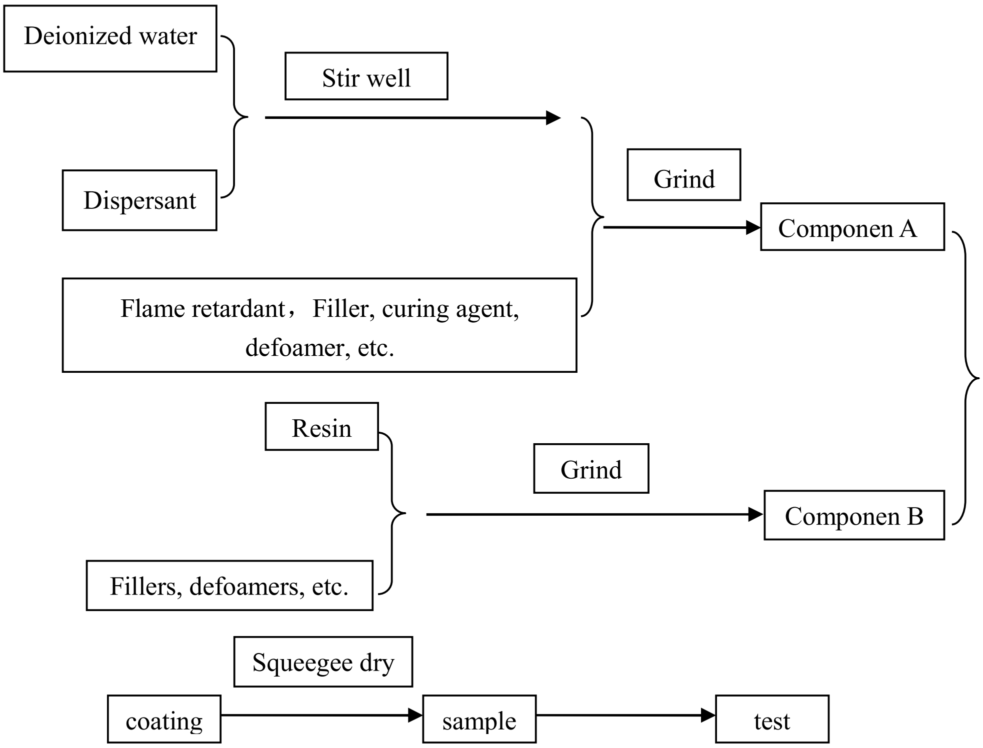


Figure 1. *Preparation process of water-based epoxy fire-retardant coating and flame-retardant coating samples.*

2.2. Characterization

2.2.1. Fire Resistance Test

Combustion heat insulation test: The size of the coated sample substrate steel plate is 100 mm×100 mm×0.9 mm, and 3 samples are prepared in parallel. Use a liquefied gas spray gun to burn the sample at the front of the flame, the flame temperature is about 800-1000°C; the distance between the flame and the coating sample is about 10cm, three thermocouples are fixed on the back of the coating sample, the computer outputs the flame retardant coating sample back temperature Time-varying data.

2.2.2. Scanning Electron Microscope Test

The DZ2 electron microscope (SEM) of UNION OPTICAL was used to observe and analyze the surface or internal micro-pore structure and distribution of the expanded carbon layer after the combustion and heat insulation test of the fireproof coating.

3. Results and Discussion

3.1. Analysis of the Amount of Curing Agent

The paint is applied on the steel plate to form a coating with a thickness of 1 mm and dried for ten days. The combustion back temperature tester was used to test the combustion and fire resistance performance of the dried samples. Use the test results to draw a curve of the steel back temperature (T) versus time (t). Figure 2 shows the influence curve of the amount of curing agent on the fire resistance of the coating.

It can be seen from Figure 2 that as the proportion of curing agent decreases, the refractory curve exhibits different laws in the low temperature and high temperature stages. Between room temperature and back temperature of 270°C, the lower the amount of curing agent, the faster the back temperature curve of the steel plate will rise, that is, the fire resistance of the coating will be worse. As shown in Table 1, it can be seen that the fire resistance of the 1# coating sample in the low temperature stage is the best, and the fire resistance time at 250°C is as long as 215s. The fire resistance curve of the coating crosses at 300°C, and the fire resistance of the 3# coating is the best at 400°C, and the fire resistance time is 3356s. If the fire resistance time when the back temperature rises to 400°C is used as the criterion, the fire resistance of 3# coating is the best, and the best amount of curing agent is 27%.

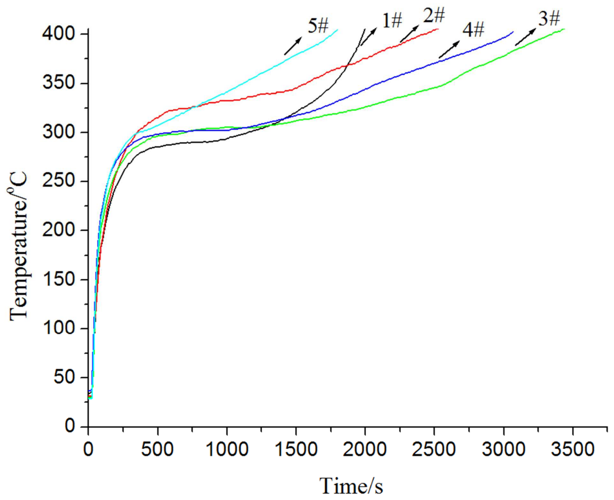


Figure 2. *The effect of the amount of curing agent on the fire resistance of the fire-retardant coating (1# 45%; 2# 30%; 3# 27%; 4# 24%; 5# 20%).*

Table 1. *The effect of the amount of curing agent on the fire resistance time.*

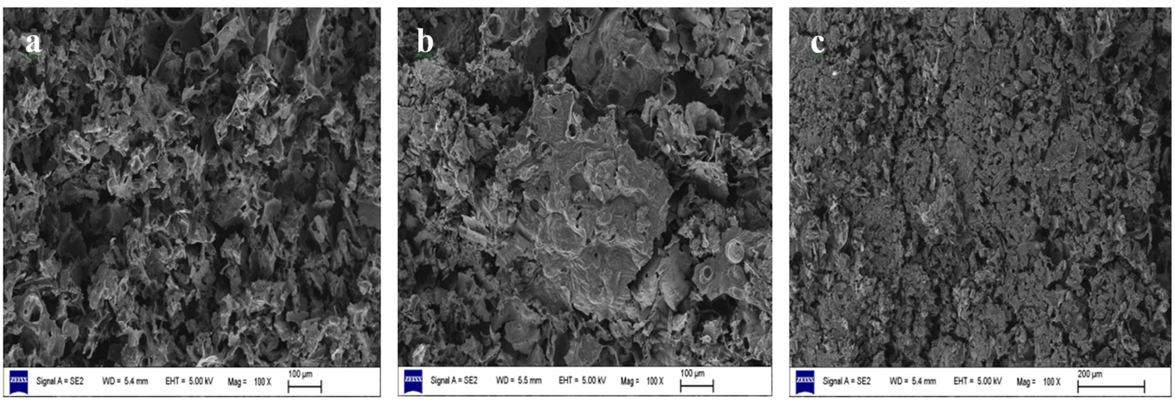
Sample serial number	1#	2#	3#	4#	5#
Fire resistance time/s (250°C)	215	182	172	137	139
Fire resistance time/s (300°C)	1170	350	675	600	362
Fire resistance time/s (400°C)	1982	2437	3356	3061	1760
Expansion ratio of carbon layer	22	21	18	16	10

Expansion ratio of the carbon layer: the maximum height of the carbon layer when the fireproof coating is heated to expand/the thickness of the original coating.

The reasons for the changes in the above two stages are as follows:

It can be seen from Table 1 that the dosage of 1# coating curing agent is 45%, the epoxy resin is fully cross-linked, and the coating film is dense. From 2# to 5# resin cross-linking degree decreases successively, the content of linear epoxy increases, and the coating film is looser. Therefore, the 1# coating can better resist the impact of external flames at the initial stage, and the fire resistance is better.

When the coating is heated and burned, the acid source in the intumescent flame retardant will quickly lose water and ammonia and undergo dehydration reaction with the carbon source to cross-link into char. If the softening temperature range and viscosity of the epoxy cross-linking system can be matched with the thermal decomposition process of the intumescent flame retardant, a denser carbon layer can be formed and better heat insulation. The 1# and 2# coatings expand rapidly at the initial stage of heating, and the expansion ratios of the carbon layer are 22 and 21 (see Table 1), which is related to the dense coating, the gas is not easy to escape and the expansion height increases. The gas decomposed from the coating can not spread evenly because of the large crosslinking degree, high softening temperature and high viscosity of the system, resulting in large pore size of the carbon layer, which is relatively loose, so the fire resistance of the coating is reduced. 5# the crosslinking degree of the coating is small, the heat resistance of the coating decreases and the melt viscosity is too small when the coating is heated, which can not effectively wrap the gas generated by the decomposition of the coating, resulting in low expansion rate and general fire resistance. The crosslinking degree of coating is moderate, and the overall fire resistance is outstanding. The 3# coating has moderate cross-linking degree, and the overall fire resistance is outstanding. Relevant studies have shown that when the amount of curing agent is too much, there will be some residual curing agent after the coating is cross-linked and cured. The curing agent has strong hydrophilicity and provides a channel for water vapor to penetrate into the coating, so it is resistant to neutral salts. The fog time is shorter, and some air bubbles and rust spots appear on the board earlier. When m (epoxy emulsion): m (curing agent) = 4.5: 1, the neutral salt spray resistance time is the longest, and the board surface has no blistering, rust spots and other phenomena [15].



a: 1# coating; b: 3# coating; c: 5# coating

Figure 3. *Scanning electron micrograph of the inside of the coated carbon layer (×100).*

3.2. Analysis of the Microscopic Morphology of the Carbon Layer

Figure 3 is a scanning electron microscope picture of the internal carbon layer after the coating combustion back temperature test. It can be seen from the figure that a coating with a higher or lower degree of cross-linking cannot form a good foamed carbon layer. Among them, 3# carbon layer has relatively uniform carbon pores on the surface, and the carbon layer is also relatively dense. Therefore, only when the degree of cross-linking of the epoxy curing system is moderate, the coating can expand uniformly after being heated and melted and softened, forming moderately sized cells, obtaining a dense and insulating carbon layer, ensuring a reduction in heat transfer speed and better fire resistance performance. This is consistent with the laws and inferences studied earlier in this article.

3.3. Cone Calorimeter Analysis

The cone calorimeter test (radiation power of 50 kW) mainly evaluates the fire protection performance of the coating from the aspects of heat release, smoke release, and CO and CO_2 release. The heat release rate curve and other data of the coating are shown in Figure 4 and Table 2.

It can be seen from Figure 4 and Table 2 that while the fire resistance of 3# coating is outstanding, its fire safety is also improved to a certain extent. Its peak heat release rate is 120 kW/m^2, while the peak heat release rate of 1# coating Up to 176 kW/m^2, 5# coating is 130 kW/m^2. In addition, the smoke production, CO and CO_2 production of the 3# coating are the lowest.

The photo of the residual carbon after the cone calorimeter test is shown in Figure 5. It can be seen that the carbon layer formed by the 1# coating with a higher degree of crosslinking is not uniform enough, and a similar situation exists with the 5# coating with a lower degree of crosslinking. This phenomenon is consistent with the previous back temperature test rules and the test results of the scanning electron microscope.

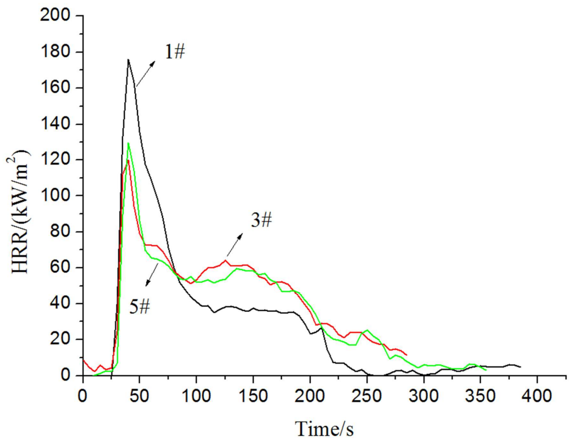
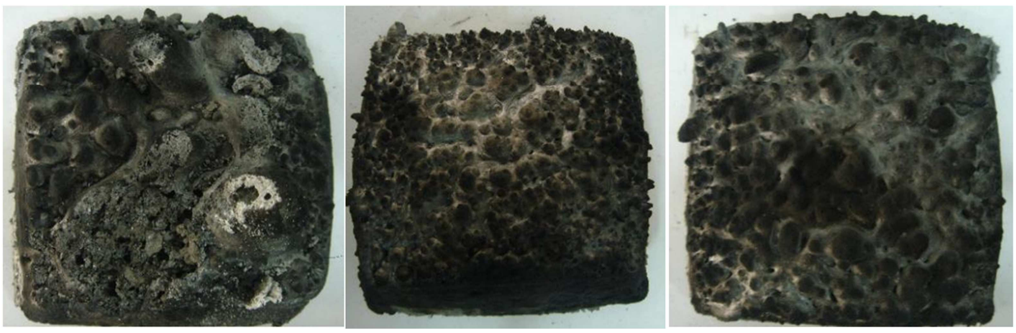


Figure 4. *Heat release rate curve of fireproof coating.*

Table 2. *Cone calorimeter test data of fireproof coating.*

Performance parameter	pkHRR/(kW/m^2)	TSR/(m^2/m^2)	TSP/(m^2/s)	avCO/(kg/kg)	avCO_2/(kg/kg)
1#	176	264	2.33	0.10	2.62
3#	120	254	2.24	0.09	2.53
5#	130	260	2.30	0.11	2.90



a 1# coating; b 3# coating; c 5# coating

Figure 5. *Photograph of residual carbon after testing by cone calorimeter.*

4. Conclusions

The research in this paper found that when the amount of curing agent is 27%, the fire resistance of 3# coating is the most prominent, and when the coating thickness is 1mm and the steel back temperature is 400°C, the fire resistance time is as high as 3356s. TGA and DTA tests indicate the degree of crosslinking. Moderate 3# coating has a softening temperature range that matches the thermal decomposition process of the intumescent flame retardant when heated, which is beneficial to the interaction between the epoxy curing system and the flame retardant. Scanning electron microscopy tests show that the carbon layer formed by the coating is more dense The cells are uniform, which can play a better heat insulation effect. The test results of the cone calorimeter show that while the coating has outstanding fire resistance, its heat release rate is the lowest, and the release of smoke and toxic gases is also the lowest.

Acknowledgements

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