Experimental study on hygrothermal accelerated aging effects of transparent fire resistive wood structure coatings

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Abstract—In this paper, the durability of fire performance of a transparent fire resistive coating for wood structure was studied using hygrothermal accelerated aging. The aging effects were analysed using SEM/EDS and fire test. The results show that after 21 days of aging, the flame-retardant components gradually precipitate to the surface. The coating basically loses its expansion ability and the char layer shows a low-strength lamellar structure. The flame-retardant time of the coating decreased by 43.48% from 23 min to 13 min.

1. Introduction

Organic cultural relics, especially wood-structured buildings, are highly flammable, which will cause huge economic losses and irreparable damage to historical and cultural heritage after fire. In recent years, fires of cultural relics have occurred frequently, such as the fire of the National Museum of Brazil in 2018 and the fire of Notre Dame Cathedral Paris in 2019, which have caused extremely painful losses. Transparent fire resistive wood coatings can effectively reduce the flammability of the coated materials to delay the fire event of the substrate and prevent the rapid spread of the fire, or to delay the destruction time of the substrate structure by improving the thermal insulation\cite{1}. At present, environmentally friendly halogen-free intumescent fire resistive coatings for wood structures are mainly achieved by physically or chemically mixing intumescent flame-retardants in polymer resin substrates to achieve the purpose of fire prevention. \cite{2-6} Sol-Gel, Plasma and other surface treatment methods have also been developed and a series of transparent fire resistive coatings have been prepared. \cite{7-10}.

However, most of the chemical components in fire resistive coatings are organic, it is reasonable to infer that they react with the exposed environment and that the basic performance especially fire protection function of fire resistive coatings deteriorates over time \cite{11}. At present, there are very few reported researches on the aging performance of fire resistive wood coating, among which most of the scholars focus on the adhesion loss \cite{12, 13} after aging rather than the fire performance.

It should be noted that most of the durability and fire performance indicators of fire resistive coatings are based on independent evaluation systems. Few studies can effectively correlate the durability and weather resistance of coatings with fire performance. However, the occurrence of fire is uncertain, and it is necessary to ensure that the fire resistive coating can retain fire performance after a period of use. Therefore, it is very meaningful to study the durability of fire performance for transparent wood structure fire resistive coatings.
In this paper, experimental study on hygrothermal accelerated aging effects of transparent fire resistive wood structure coatings was carried out. Fire performance, surface morphology and distribution of element during the aging progress were characterized. The aging mechanism of transparent fire resistive coating for wood structure was tentatively proposed by analyzing the changing of fire properties and element distribution during the aging process.

2. Experimental

2.1 Materials

**Transparent coating**: two-component, water-borne fire resistive coating for wood structure, self-made.

**Specimen**: three-layer plywood with white beech veneer, commercial products

2.2 Specimen preparation

Transparent fire resistive wood structure coating was coated on three-layer plywood with white beech veneer with the dimension of 300*150*5 mm. In order to prevent side intrusion or other factors from affecting the aging behavior, a mixture of paraffin wax and rosin with the ratio of 1:1 was used to seal the edge of each specimen with a depth of at least 5 mm. After construction, all samples should be cured at a constant environment of 23±2 °C and 50±5 RH% for at least 14 days.

2.3 Test method

Hydrothermal aging was carried out by Sartec SS-7123X (SARTEC TESTING INSTRUMENTS Co., Ltd). All samples are arranged vertically at a certain distance, as shown in Figure. 1. Total aging time were set as 21 days and the sampling frequency was set as every 3 days. The aging method is shown as below.

-4 h (23±3) °C, (80±5) %RH
-16 h (40±3) °C, (50±5) %RH
-4 h (5±3) °C, (50±5) %RH

![Figure. 1 Hydrothermal aging test instrument and sample placement](image)

Scanning Electron Microscope (SEM)/ Energy Dispersive Spectroscopy (EDS) was carried out using FEI Inspect F50(FSEM, USA) and Super Octane (EDAX, USA). Fire test was carried out by a self-made test furnace and the heating curve was set as ISO 834 (T=345lg(8t+1) +20) as shown in Figure. 2. Two K-type thermocouples were used to monitor the backside temperature and the flame-retardant time was defined as the time that the average backside temperature rise reaches 220 °C.
3. Results and Discussions

3.1 Surface appearance
Digital pictures of transparent fire resistive coating after 0-21 days of accelerated aging are shown in Figure. 3. It can be seen that the transparency of the coating changed significantly after 3 days of aging and then deteriorated gradually. As the aging progresses, obvious cracks appeared on the surface of the coating and components precipitation occurred on the coating surface.

3.2 Fire performance of the coatings
Fire resistant time of coatings after 21 days of accelerated aging methods are shown in Figure.4 (a) and each specimen’s backside temperature curves are shown in Figure.4 (b). It can be seen that the fire resistant time of the coating decreased rapidly during aging and finally attenuated by 43.48% after 21 days of aging from 23 min to 13 min.

Digital pictures of char layers after fire test are shown in Figure. 5. It can be seen that with the aging, the expansion performance of the coating decreases gradually, and the integrity of the char layer formed in the fire test is gradually destroyed. After 21 days of aging, the coating basically loses its expansion ability and the char layer shows a low-strength lamellar structure.
Figure 4 (a). Fire resistance times of coatings during aging progress; (b). Backside temperature

Figure 5. Digital pictures of char layers after fire test during 0-21 days of accelerated aging

3.3 Elemental analysis of the coating

SEM pictures of transparent coating after 0-21 days of accelerated aging are shown in Figure. 6. Obvious precipitation of components can be found on the surface and the surface gradually becomes unsmooth with aging. Mass fractions of main flame-retardant elements from EDS are shown in Table. 1. We can see that the mass fraction of P on the surface increased which should be caused by the precipitation of flame retardants. The mass fraction of C and O first increase with the gradually degradation of base resin. Based on these results, we can preliminarily judge that the aging mechanism is the precipitation of flame retardants which contains P such as APP. However, further extensive analysis should be done to comprehensive explain the relationship of changes in P element and the decrease of fire performance.
4. Conclusion
In this paper, the durability of fire performance of a transparent fire resistive coating for wood structure was studied using hygrothermal accelerated aging. The aging effects was analysed using SEM/EDS and fire test. The following conclusions can be drawn:

1. After 21 days of aging, the expansion capacity of the fire resistive coating is basically lost, and the char layer shows a low-strength lamellar structure. The flame-retardant time of the coating decreased by 43.48% from 23 min to 13 min.
2. The increasing mass fraction of P element proves that flame-retardant components gradually precipitate to the surface with aging. Based on this, a preliminarily aging mechanism of flame retardants precipitation is proposed.

Acknowledgments
This work was financially supported by National Natural Scientific Foundation of China (No. U19A2045).

References
[1] Shan, Y. (2010). Exploitation of ultra-thin intumescent fireproof coating for wood structure. New Chemical Materials, 28(7): 112-115
[2] Gu, J. W.; Zhang G. C.; Dong S. L.; Zhang, Q. Y.; Kong, J. (2007) Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. Surface & Coatings Technology, 201(18): 7835-7841.
[3] Shi, Y.; Wang, G. (2016) The novel silicon-containing epoxy/PEPA phosphate flame retardant for transparent intumescent fire resistant coating. Applied Surface Science, 385, 453-463.
[4] Shanshan, C.; Xiang, L.; Yang, L.; Junqi, S. (2015) Intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric. ACS Nano, 9 (4), 4070-4076.
[5] Chan, S. Y.; Si, L.; Lee, K. I.; Ng, P. F.; Lei, C.; Yu, B.; Yuan, H.; Yuen, R. K. K.; Xin, J. H.; Fei, B. (2017) A novel boron–nitrogen intumescent flame retardant coating on cotton with improved washing durability. Cellulose, 25 (1), 843-857.

[6] Radmard, B.; Poznysz, E. R.; Sargeant, J. A.; Waryold, K.; Giroux, D. J. Fire resistant coatings for wood veneer panels. U.S. Patent 9,975,314[P]. 2018-5-22.

[7] Cheng, X. W.; Liang, C. X.; Guan, J. P.; Yang, X. H.; Tang, R. C. (2018) Flame retardant and hydrophobic properties of novel sol-gel derived phytic acid/silica hybrid organic-inorganic coatings for silk fabric. Applied Surface Science, 427, 69-80.

[8] Grancarić, A.; Colleoni, C.; Guido, E.; Botteri, L.; Rosace, G. (2017) Thermal behaviour and flame retardancy of monoethanolamine-doped sol-gel coatings of cotton fabric. Progress in Organic Coatings, 103, 174-181.

[9] Farag, Z. R.; Krüger, S.; Hidde, G.; Schimanski, A.; Jäger, C.; Friedrich, J. (2013) Deposition of thick polymer or inorganic layers with flame-retardant properties by combination of plasma and spray processes. Surface & Coatings Technology, 228 (9), 266-274.

[10] Alongi, J.; Colleoni, C.; Malucelli, G.; Rosaceb, G. (2012) Hybrid phosphorus-doped silica architectures derived from a multistep sol–gel process for improving thermal stability and flame retardancy of cotton fabrics. Polymer Degradation & Stability, 97 (8), 1334-1344.

[11] Wang, L. L.; Wang, Y. C.; Li, G. Q. (2013). Experimental study of hydrothermal aging effects on insulative properties of intumescent coating for steel elements. Fire Safety Journal, 55(JAN.), 168-181.

[12] Vlad-Cristea; Riedl; Blanchet; Jimenez-Pique. (2012). Nano characterization techniques for investigating the durability of wood coatings. EUR POLYM J, 48(3) (-), 441-453.

[13] Williams, R. S. (2005). Don't get (sun) burned: exposing exterior wood to the weather prior to painting contributes to finish failure. Journal of Architectural Coatings. July: 56-60.