Study on the Effects of the Aging by Accelerated Weathering on the Intumescent Fire Retardant Coating for Steel Elements

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Abstract: This paper reported the results of an experimental study of degradation in fire protection performance of intumescent coating for steel elements after different times of accelerated weathering aging. The physical and chemical changes of the coatings during the aging process were investigated. After aging the surface of the samples were found to become rough, powdered and embrittled; the fire resistance time decreased and the char layer morphology changed significantly. Due to the oxidation, decomposition and hydrolysis reactions in the main components of the coating, such as the resin and the fire retardant system, the content ratio and composition of the coating changed. Then the concerted expansion reaction may not occur between the ingredients when heated, which led to the deterioration of the fire resistance performance of the coating.

1 Introduction

Intumescent fire retardant coatings, a type of passive fire protection materials, are widely used due to their unique advantages, such as not affecting the intrinsic properties of other materials, their ease of processing, and their ability to be applied to several different materials [1-3]. Generally, intumescent fire retardant coatings contain “active” ingredients (an acid source, a carbon source, and a blowing agent) bound together by a binder. The optimum performance of the coating, in terms of physical and chemical properties forming an effective protective char layer, is insulating the substrate from fire [4-6].

Because the occurrence of fire is random, it may occur within one year of the application of the coating or as late as ten years or longer, whether the original performance of the fire retardant coating remains over time must be considered. The ingredients of the fire retardant coatings, especially the “active” ones, are often moisture sensitive, and when used outdoors, ultraviolet rays easily break the molecular structure of the coating [7]. Sakumoto et al. conducted accelerated tests and small-scale heat tests, and from their results, they proposed a new testing method for evaluating the durability of intumescent coatings with consideration for the high temperature and high-humidity weather conditions in Japan [8]. In the work of Roberts et al., Shell UK performed a long-term passive fire protection weathering program at a maritime test site using furnace tests to assess the fire performance of the materials [9]. Ling-ling Wang studied the degradation in the fire protection performance of two types of intumescent coatings after different cycles of accelerated hydrothermal aging tests and proposed an aging mechanism and the thermal
conductivity of the char according to the experiment results [10,11]. Jimenez et al. studied the fire performance deterioration of an intumescent coating in three different accelerated aging conditions and found that when steel plates were immersed in salt water, the fire resistant effect drastically decreased [12]. Toshiro Harada et al. evaluated the weather ability and combustibility of fire-retardant-impregnated wood following accelerated weathering tests, and they reported that the best retention was achieved by pigmented and penetrating coatings demonstrating the possibility of retaining the required fire performance for a quasi-noncombustible material, even after 2000 h of accelerated weathering [13].

The mechanism of the degradation in the fire resistance of the fire retardant coating under aging conditions by accelerated weathering, which contains the effects of UV radiation, water moisture, and high temperature, has not been reported. However, in the natural aging process, these three aspects may have the most significant effects on the coatings. In this paper, typical solvent based fire retardant coatings were treated in the accelerated aging chamber for different lengths of time. Based on the results from FTIR, XPS, TG/DTG analyses, the aging mechanism of the fire retardant coating under the accelerated weathering condition was investigated. The fire resistance time and the morphology of the coating and char layer of those aged samples were measured.

2 Experimental section

2.1 Aging scenario

An accelerated weathering aging chamber was employed to treat the coating samples. For this apparatus, UVB-313 fluorescent lamps were used as the light source. One exposure cycle lasted 12 h and included an 8-h UV exposure period at 60 ± 3 °C black panel temperature and a 4-h condensation exposure period at 50 ± 3 °C black panel temperature. The irradiance of the lamps was 0.65 W/m² nm. The relative humidity during the irradiance period was 15%, and that during the condensation period was 100%. The samples were aged in this condition for 0 h, 120 h, 240 h, 360 h, 480 h and 600 h respectively. And the location of the samples in the chamber were exchanged every 48 h.

2.2 Specimen preparation

The fire retardant coating employed in this study were solvent based intumescent coating for outdoor steel structure and were commercial products. The main components of the fire retardant coating were acrylic emulsion, ammonium polyphosphate (APP), melamine (MEL) and pentaerythritol (PER). The specimen substrate was a Q235 steel plate of 80 mm × 40 mm × 1.2 mm. Before brushing the coating, the steel substrates were cleaned thoroughly. The zinc rich primer based on epoxy resin was brushed prior to the fire retardant coating, and the thickness of the primer was 63.8 μm. The intervals between the coating layer and the whole thickness were set according to the instructions of the product. The fire retardant coating was brushed five times, and the thickness of the dry layer was 0.7 mm. To investigate the effect of the accelerating aging on the fire retardant coating layer directly, the top coating was not used in this study.

2.3 Testing equipment and conditions

The fire resistance of the intumescent coatings of the acid treated samples was tested by a small-scale fireproof testing furnace [14,15]. It was hypothesised that after different times of aging the compositions and the content of the coating changed. And these changes may
directly lead to the deterioration of the coating properties. To understand the changes to the molecular structure during the aging process, the elements and groups on the surface of the samples were measured using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. Furthermore, the chemical reaction process was closely related to the formation of the expanded char layer. The morphology of the foamed char layer was investigated using a stereomicroscope at a magnification of 100×.

3 Experimental results

3.1 The fire resistance of the coating after accelerated aging

When the specimens met the prescribed aging time, they were moved from the aging chamber and were air-dried. As mentioned above, the fire resistance times of the samples were tested via a small-scale fireproof furnace. After the fire test, the char layer thickness of the coating, which had a direct correlation with the fire resistance time, was measured.

Table 1 shows the fire resistance time and char thickness of the coating after different times of accelerated weather aging. The char layers of the samples shown in this table were the thickest. The aging ratio is the ratio of the fire resistance time shortening of the coating specimens after aging. The expansion factor represents the ratio of the difference between the thickness of the char layer and the initial coating layer to the initial coating layer thickness.

Table 1. Fire resistance time and char layer thickness of the coating after different aging times.

<table>
<thead>
<tr>
<th>Aging time(h)</th>
<th>Fire resistance time</th>
<th>Aging ratio(%)</th>
<th>Char layer thickness(mm)</th>
<th>Expansion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39’25″</td>
<td>-</td>
<td>29.2</td>
<td>39.6</td>
</tr>
<tr>
<td>120</td>
<td>35’12″</td>
<td>10.7</td>
<td>27.5</td>
<td>38.3</td>
</tr>
<tr>
<td>240</td>
<td>30’32″</td>
<td>22.5</td>
<td>21.9</td>
<td>30.1</td>
</tr>
<tr>
<td>360</td>
<td>25’44″</td>
<td>34.7</td>
<td>16.4</td>
<td>22.4</td>
</tr>
<tr>
<td>480</td>
<td>23’44″</td>
<td>39.8</td>
<td>14.8</td>
<td>20.1</td>
</tr>
<tr>
<td>600</td>
<td>20’12″</td>
<td>48.8</td>
<td>13.1</td>
<td>17.7</td>
</tr>
</tbody>
</table>

3.2 FTIR test results

Among the main components of the coating, the effects of the photo oxidation on the acrylic resin were the most significant because it is a high molecular weight polymer. The ultraviolet radiation, wavelengths shorter than 300nm, may have caused the homolysis of the polymer matrix, resulting in the decrease of the relative molecular weight of the polymer. It is also reported that an acrylic resin could form an inner ester in the ultraviolet aging process[16]. Furthermore, the bonds in the side chain groups could decompose and form free radicals; therefore, the most common reactions were cross-linking chain scissions. These reactions mainly depended on the functional groups chemical structure of the material[17].

To investigate the changes in the other main ingredients of the coating during aging by accelerated weathering, MEL, PER and APP were aged under the same conditions as the coating sample for 240 h. Figure 2(a) shows the FTIR spectrum of the MEL before and after aging. It can be seen from the figure that the trough positions of the virgin and aged specimens were approximately the same, and only the size of some of the troughs varied. For example, the troughs at 3470 cm⁻¹, 3420 cm⁻¹, 3340cm⁻¹, and 3130cm⁻¹ weakened. These four troughs indicate the stretching vibration of NH₂, in which the first three troughs
indicate the asymmetric stretching vibration and the last one indicates the symmetric stretching vibration of NH$_2$. Therefore, the amount of NH$_2$ present was reduced after aging. Corresponding with the trough weakening at a high wave number, the trough at 1650 cm$^{-1}$ (indicating the stretching vibration of C=N) and the trough at 1550 cm$^{-1}$ (indicating the bending vibration of NH$_2$) were weaker as well. The absorption peak at 2250 cm$^{-1}$, indicating the stretching vibration of C=N, was heightening.

![Figure 2. FTIR spectrum of the MEL, PER, APP and the coating samples before and after aging.](image)

PER was also aged at the same accelerating aging conditions for 240 h. As shown in Figure 2(b), the wave number of the troughs in the FTIR spectrum were almost the same between the aged and original samples, except for a difference in the size of some of the troughs. The troughs at 3350 cm$^{-1}$ (indicating the stretching vibration of O-H), at 1380 cm$^{-1}$ (indicating the in-plane bending vibration of COH) and at 1160 cm$^{-1}$ and 1030 cm$^{-1}$ (indicating the stretching vibration of C-OH) were heightening. These changes illustrate that during aging, PER had produced a material containing more hydroxyls. The trough at 2930 cm$^{-1}$, indicating the asymmetric stretching vibration of CH$_3$, and the trough at 2280 cm$^{-1}$, indicating the stretching vibration of C-H, were heightening as well. This may be due to the breaking of the C-C bond and the subsequent production of methanol, ethanol, or other substances. The increase in the peak at 1430 cm$^{-1}$, corresponding the COH in carboxylic acid, may be the result of a small amount of acid products generated during PER oxidation.

In addition, the APP may have degraded and hydrolyzed in the presence of ultraviolet radiation and moisture. Figure 2(c) is a comparison between the FTIR spectra of the virgin and aged APP samples. The aging conditions were the same as those used for the MEL and PER. The trough at 3260 cm$^{-1}$ and the trough at 3030 cm$^{-1}$, indicating the asymmetric stretching vibration and symmetric stretching vibration of NH$_4$, respectively, disappeared after the accelerated aging. A new peak near 3030 cm$^{-1}$ formed, indicating the P-H
stretching vibration. Thus, the P-O bond in APP may break in the aging process to lose the NH$_4^+$ group and form the focal phosphate and a material containing P-H group.

To facilitate the analysis, Figure 2(d) shows the spectra of the retardant coating samples at 500 cm$^{-1}$–2000 cm$^{-1}$. The intensity of the trough at 1640 cm$^{-1}$, indicating the stretching vibration of C=O, increased with prolonged aging time. This resulted from the production of the C=O group containing acid and aldehyde generated during the photo oxidation of the resin and PER. The trough at 1400 cm$^{-1}$, corresponding to the curling vibration of C-H in the CH$_2$ and asymmetric angular vibration of NH$_4^+$, weakened due to the chain scission and the oxidation reaction of the resin and APP, which led to a decrease in containing of CH$_2$ and NH$_4^+$ groups. Compared to the origin sample, there were peaks at 1430 cm$^{-1}$ and they were slightly higher with prolonged aging times. These spectral peaks indicate the in-plane bending vibrations of C-OH in the carboxylic acid formed during the oxidation of the resin and PER. In addition to the new troughs at 1430 cm$^{-1}$, there were troughs at 1270 cm$^{-1}$, which did not appear in the origin sample spectra. These indicate the stretching vibration of C-OH in the carboxylic acid. For the oxidation of PER and the degradation of APP, the intensity of the troughs of the aged specimens at 1128 cm$^{-1}$ (indicating the stretching vibrations of PO$_4^-$ and C-O in the alcohols) weakened remarkably compared with the origin sample. Meanwhile, among these aged samples, the intensity of the troughs increased with the aging time. The causes may be that the APP was more likely to be affected by the aging conditions, such that the content of PO$_4^-$ decreased dramatically in a short period of time, and the reaction of the resin generating alcohols was relatively slow, which resulted in the irregular phenomenon of the sample ingredients during the aging process. The trough at 885 cm$^{-1}$ (not appearing in the original sample) indicates the stretching vibration of P-O-P in the pyrophosphate, which was produced by the hydrolysis of APP. The intensity of this trough increased with increasing aging time.

### 3.3 XPS test results

To further understand the possible changes in the aging process of the fire retardant coatings, the amounts of five elements (C, O, N, P, Cl) on the sample surface were tested. Table 2 show the XPS test results of the samples. It can be seen that the content of different elements differed obviously during the aging process. The content of C in the coating surface decreased with aging time, and the change was more significant in the early aging stage; the contents of O and N increased with the aging time; similar to the C element, the changes were remarkably in the early aging process. The content of the Cl element fluctuated in the aged samples, and decreased slightly compared with the untreated sample. After aging, the content of the P element increased, and there were no distinct differences among the aged samples.

Due to the oxidation reaction, acids, alcohols, and aldehydes may be produced, enhancing the amount of O in the coating. Some small molecular weight products formed in the chain scission of the resin may have been lost or evaporated under condensation and high temperature conditions, which would lead to a decrease in C. From the data listed in table 2, the chlorinated paraffin had almost no change under the aging conditions of this study. During the aging process, the APP and MEL may have oxidized and hydrolyzed, producing some water soluble materials. The APP and MEL in the inner layer would have migrated to the surface of the coating and increased the contents of the N and P elements in the surface materials. Consistent with the first condition, after a certain aging time the ingredients of the surface material did not change and the contents of N and P elements changed only slightly.
Table 2. Elemental content in the samples for different times of aging.

<table>
<thead>
<tr>
<th>Element</th>
<th>Origin sample</th>
<th>Aged for 120 h</th>
<th>Aged for 240 h</th>
<th>Aged for 480 h</th>
<th>Aged for 600 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>79.45</td>
<td>52.79</td>
<td>45.19</td>
<td>43.81</td>
<td>37.46</td>
</tr>
<tr>
<td>O</td>
<td>10.53</td>
<td>29.55</td>
<td>32.08</td>
<td>36.31</td>
<td>36.73</td>
</tr>
<tr>
<td>Cl</td>
<td>5.82</td>
<td>3.48</td>
<td>5.15</td>
<td>3.51</td>
<td>4.6</td>
</tr>
<tr>
<td>N</td>
<td>2.60</td>
<td>9.58</td>
<td>13.28</td>
<td>11.24</td>
<td>15.41</td>
</tr>
<tr>
<td>P</td>
<td>1.60</td>
<td>4.60</td>
<td>4.3</td>
<td>5.13</td>
<td>5.78</td>
</tr>
</tbody>
</table>

3.5 The morphology of the char layer after aging

Figure 3 shows a longitudinal section of the char layer after different aging times at 100× magnification using a stereomicroscope. The char layer of the untreated sample appeared spongy and fluffy, and the pores were small and relatively consistent in size. There were ‘cement’ parts (like a hard shell, and not fluffy) in the char layer of the 120 h aged specimen. The char layer of the samples aged for 240 h were completely ‘cement’, forming brittle shells. During the aging period, although the internal coating layer may not have been affected by the radiation and oxidation, the water may penetrate into the interior of the coating from the powdered surface more easily, which may have resulted in the hydrolysis or migration of the fire retardant system. The proportion of the coating components changed, and when heated, a synergistic reaction could not occur, and the dense char layer could not be formed.

![Figure 3](image)

Figure 3. Longitudinal section morphology of the char. (a) untreated sample, (b) aged for 120h, (c) aged for 240h.

4 Conclusion

The fire resistance time decreased as the aging time increased, and a sample aged for 600 h hardly had any protection effect for the substrate. The morphology changed significantly after aging, and the dense and puffy char in the untreated sample turned into ‘cement’ and looser char in the aged samples.

Based on the results of the FTIR and XPS tests, the aging mechanism of the coating in aging by accelerated weathering was that the main components in the coating, such as the resin and the fire retardant system, had oxidation, decomposition, and hydrolysis reactions by the effects of radiation, oxygen, water, and high temperature. These reactions resulted in changes in elemental content ratios of the coating. The concerted expansion reaction may not have occurred when heated, which could have led to the deterioration of the fire resistance performance of the coating.
References