

Although this type of coatings are not exposed directly to the influence of water during the use of the structures, during the construction phase they can be subjected to adverse environments and climatic factors like water condensation and rain.

In this study, the water resistance of these coatings was evaluated after exposure to extreme high humidity environments, on a continuous condensation chamber at 40 °C and by immersion in water. The effects of the exposure conditions on the flame retardant system were analysed by Thermogravimetry (TG), Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). Furthermore, to analyse the foam layer behaviour, after exposure to the conditions mentioned above, they were submitted to 750 °C in a muffle furnace.

2. Materials and Methods

Materials

Three commercial intumescent fire protection coatings for structural steel were used in this study: one solvent-based coating designated along this document by the letter **A** and two water-based coatings, designated by the letters **B** and **C**.

Methods

In order to evaluate the water resistance of the coatings, they were submitted to the following exposure conditions:

- i) Laboratory conditions (*LC*) – the specimens were exposed to ambient room air: (23±3) °C and (50±5) %relative humidity for one month.
- ii) Continuous condensation chamber condition (*CC*) – the specimens were exposed to a saturated humidity atmosphere at 40 °C for one month.
- iii) Immersion condition (*IC*) – the specimens were immersed in demineralized water, in a room at (23±3) °C for two weeks.

Preparation of samples

The reactive coatings were applied on steel panels having dimensions of 150 mm x 75 mm x 1 mm. Three test specimens were prepared for each coating. The specimens consist of the steel panels coated with successive layers until about 3 mm of thickness (coatings **A** and **C**) and about 2 mm of thickness for the coating **B**. The layers were applied with an interval of 24 hours.

After the application of all the layers and before expose the coatings to the referred conditions, the specimens remained 48 hours at laboratory condition.

Characterization methods

After exposure the samples to the conditions mentioned above, aged test specimens of each coating were characterized by different techniques, such as FTIR, TG and DSC. Before this characterization, test specimens were conditioned in an oven at 30 °C until constant mass. The conditions of the analyses are described below.

Fourier Transform Infrared Spectroscopy (FTIR)

To compare the effects of the different exposure conditions in the chemical composition of the coatings, aged specimens were analysed by FTIR.

Infrared spectra of coatings at different exposure conditions were studied in the 400 cm⁻¹ to 4000 cm⁻¹ region using a Nicolet Magna IR spectrophotometer with a DTGS (Deuterated TriGlycine Sulfate) detector. For these measurements, samples were ground and mixed with dry spectroscopic grade potassium bromide and pressed into pellets. Thirty two scans were collected and average at a spectral resolution of 4 cm⁻¹.

Thermogravimetry (TG)

TG analysis can be used to characterize the thermal stability of the coatings. In this study, TG curves are used to confirm if the exposure to high humidity environments changes the thermal behaviour of the intumescent coatings.

The thermogravimetric analysis of the samples were performed at the apparatus *Setaram TGA-92*. The TG analyses were carried out at 10 °C/min under oxygen flow of 50 ml/min, in the temperature range 30-850 °C. The samples (about 20 mg) were placed in open alumina crucible.

Differential Scanning Calorimetry (DSC)

The DSC analysis of samples were carried out at a heating rate of 10 °C/min under Argon flow of 50 ml/min, in the temperature range 25-500 °C, using a *Netzsch – DSC 200 F3 Maia*. The samples (about 3.5 mg) were ground in powder and placed in open aluminium crucibles.

Intumescence evaluation

Additionally, to determine the foam layer behaviour, after exposure to the conditions mentioned above, the coatings were heated at 750 °C in a muffle furnace during 10 minutes. For that, a similar mass sample of each aged coating was detached from steel substrate and placed in a silica pan. Afterwards, the differences between the intumescent behaviour of each coating for the three exposure conditions were compared visually.

3. Results and Discussion

Characterization methods

The results obtained by the analytical techniques FTIR, TG and DSC are presented in the next sections.

Fourier Transform Infrared Spectroscopy (FTIR)

The Infrared spectra of coating **A**, **B** and **C** obtained for the three exposure conditions (LC, CC and IC) are presented in Figure 2, 3 and 4, respectively.

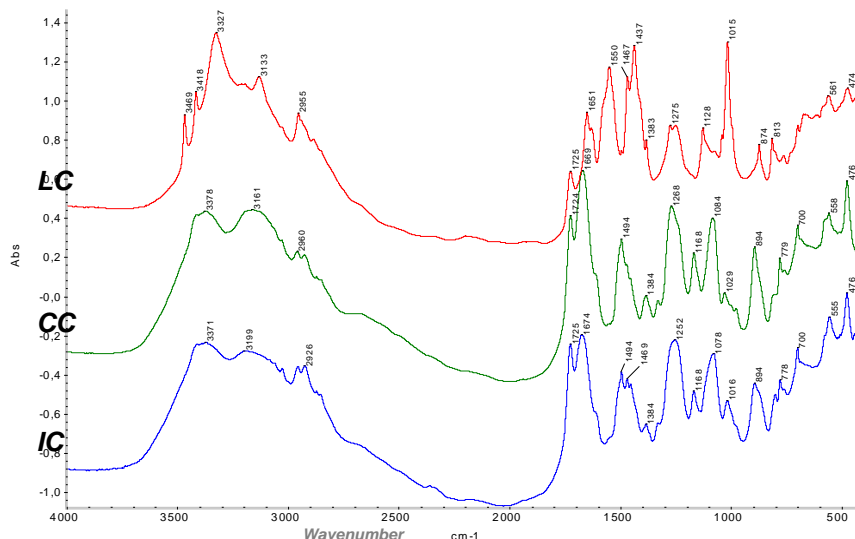


Figure 2. FTIR spectra of coating **A** after exposure condition: LC (red); CC (green); IC (blue)

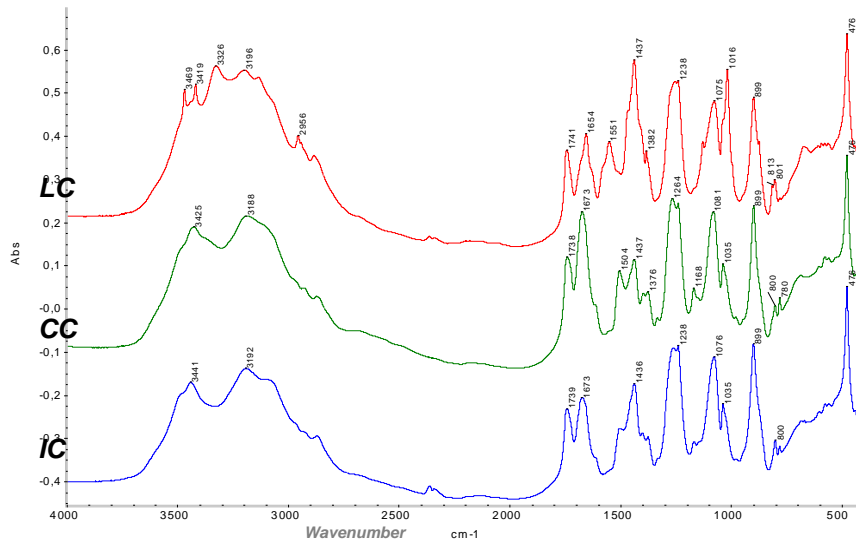


Figure 3. FTIR spectra of coating **B** after exposure condition: LC (red); CC (green); IC (blue)

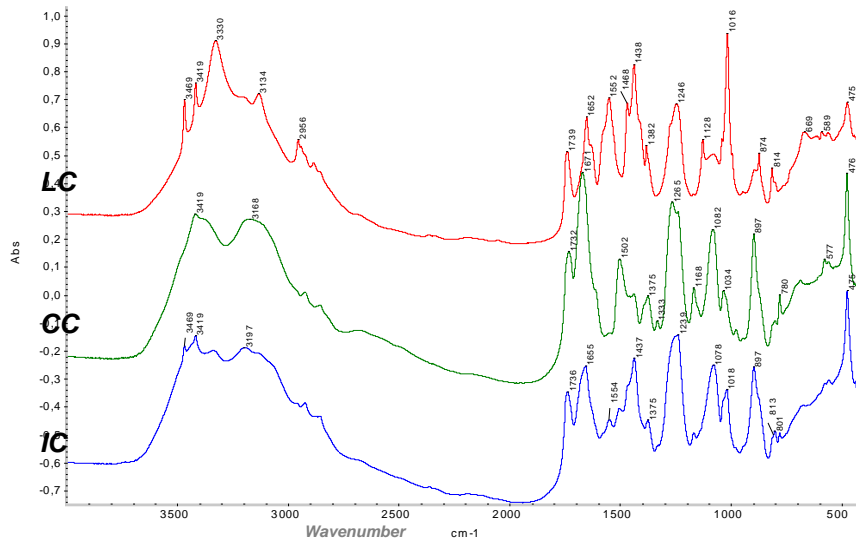


Figure 4. FTIR spectra of coating **C** after exposure condition: LC (red); CC (green); IC (blue)

The different coatings when exposed at the laboratory condition (LC), present absorption bands at 3469 cm^{-1} , 3418 cm^{-1} , 3133 cm^{-1} , 1651 cm^{-1} , 1550 cm^{-1} and 813 cm^{-1} attributed to melamine [6] and at 3327 cm^{-1} and at 1015 cm^{-1} attributed to pentaerythritol [6].

Comparing the infrared spectra obtained at the different exposure conditions for the three coatings, it is possible to observe differences between the LC condition and the others two exposures conditions CC and IC, namely modifications in the absorption bands attributed to melamine and pentaerythritol.

For the coating **A**, in the infrared spectra of the CC condition and IC condition, the bands attributed to melamine and pentaerythritol are absent. The same is observed for the coating **B**.

For the coating **C**, the absorption bands attributed to melamine and to pentaerythritol are absent in the CC condition. In this coating submitted to IC condition, the absorption bands attributed to pentaerythritol are also absent and the absorption bands at 3469 cm^{-1} , 3419 cm^{-1} and 813 cm^{-1} attributed to melamine are present, but with lower intensity than in the LC condition.

The infrared analysis showed that some components of the coatings are lost after high humidity environments exposure.

Thermogravimetry (TG)

The thermogravimetric (TG) curves and the first derivative of the weight change (DTG) curves of the coating **A**, **B** and **C** are shown in Figure 5, 6 and 7, respectively.

The initial weight loss near $100\text{ }^{\circ}\text{C}$ is not considered, since it is probably due to the volatilization of some solvents or water.

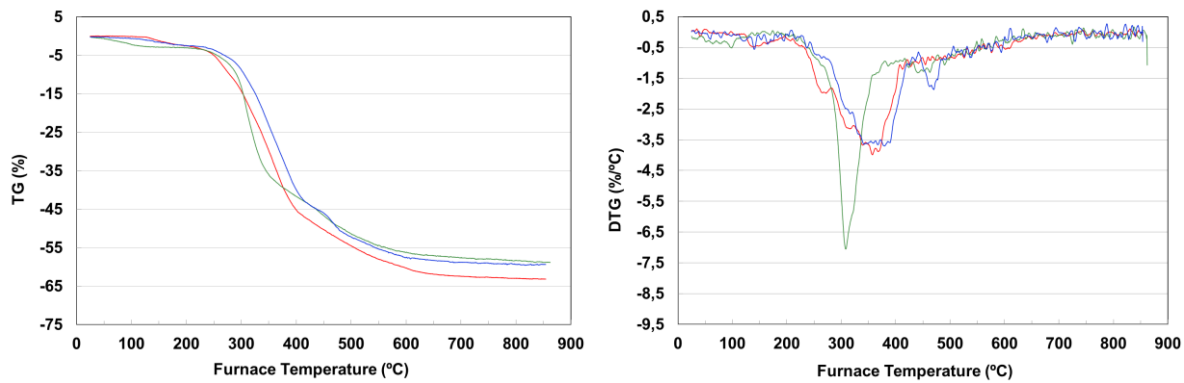


Figure 5. TG (left) and DTG (right) curves of coating **A** for the three exposure conditions: LC (red); CC (green); IC (blue)

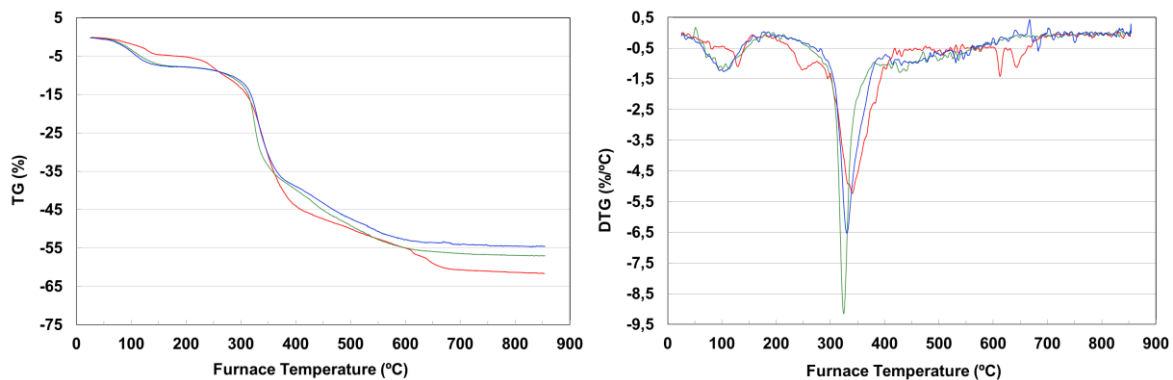


Figure 6. TG (left) and DTG (right) curves of coating **B** for the three exposure conditions: LC (red); CC (green); IC (blue)

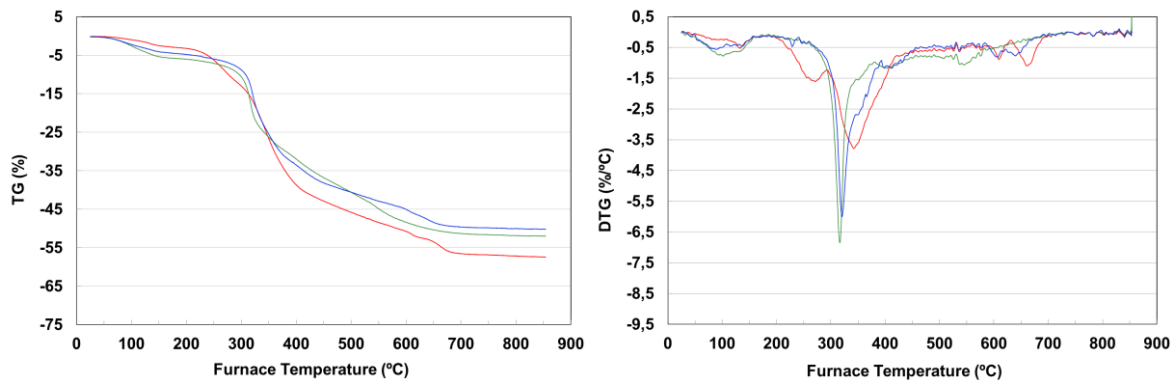


Figure 7. TG (left) and DTG (right) curves of coating **C** for the three exposure conditions: LC (red); CC (green); IC (blue)

From the data provided by the TG and DTG curves for the three coatings, it is possible to observe differences in their thermal degradation behaviour after exposure to the different environments. For the coating **A** (Figure 5) after LC condition and above 200 °C, the thermal degradation shows three steps of degradation, visible also in the DTG curve. After the CC condition the thermal degradation shows only two steps of degradation. The TG curve after IC condition presents also two steps but reveals a more slow thermal degradation than in the CC condition. The DTG curves confirm this observation. The coating **B** (Figure 6) exposed to LC condition shows in the TG curve four steps of thermal degradation above 200 °C. After the other two exposure conditions the TG curves only present two steps in the thermal degradation. The coating **C** (Figure 7) exposed to LC condition shows in the TG curve four steps of thermal degradation, while after the other two exposure conditions only present three steps in the thermal degradation. As in the FTIR analysis, TG analysis is extremely useful to confirm that high humidity environments change the behaviour of the intumescent coatings, probably because of the loss of some components responsible by the intumescent reactions. In fact, in the coatings exposed to CC condition and IC condition, the weight lost observed in the TG curves is lower than in the coatings exposed to the LC condition, confirming that some components were lost during these exposures to high humidity environments.

Differential Scanning Calorimetry (DSC)

The literature refers that pentaerythritol have an endothermic peak, due to a crystal type transition, at about 189 °C [2, 5]. The pentaerythritol was identified by FTIR as a component of the three coatings. As a consequence, it is possible to compare the DSC curves of the different exposure environments and verify the changes in the endothermic peak attributed to pentaerythritol.

The DSC curves obtained for the coatings **A**, **B** and **C** are presented in Fig 8, 9 and 10, respectively.

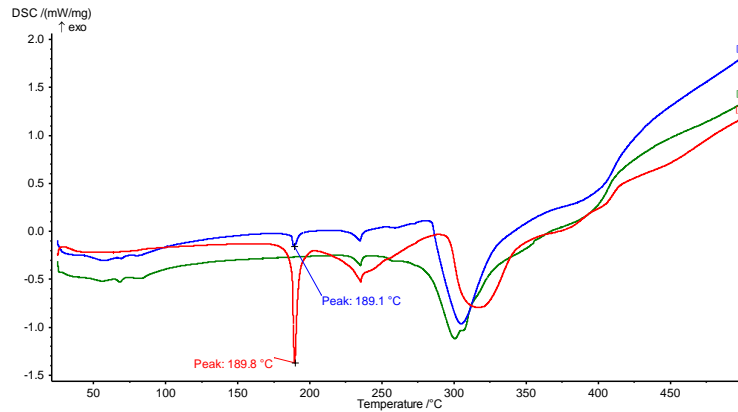


Figure 8. DSC curves coating **A** for the three exposure conditions: LC (red); CC (green); IC (blue)

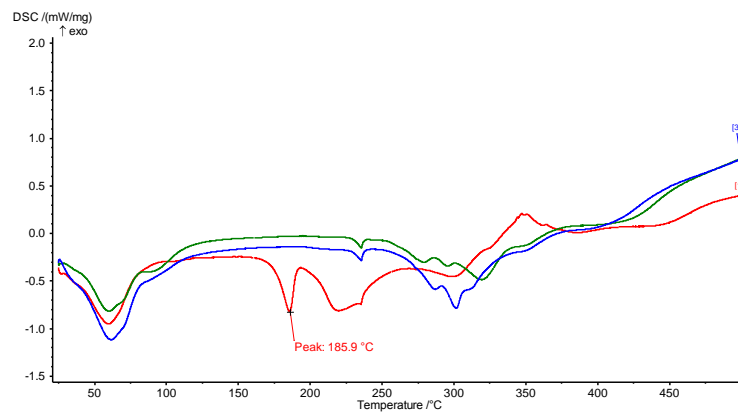


Figure 9. DSC curves coating **B** for the three exposure conditions: LC (red); CC (green); IC (blue)

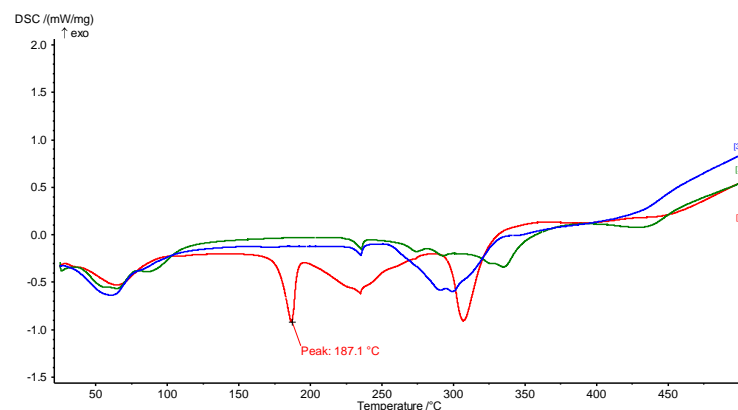


Figure 10. DSC curves of coating **C** for the three exposure conditions: LC (red); CC (green); IC (blue)

From the DSC curves of the coating **A** (Figure 8), it can be seen that the endothermic peak is present in LC condition. This endothermic peak can be also observed in exposure condition IC with lower intensity than in LC condition. In exposure condition CC the peak is not observed.

From the DSC curves of the coating **B** (Figure 9) and **C** (Figure 10), it can be observed that there is an endothermic peak, in LC condition, at 185.9 °C and at 187 °C, respectively. In CC condition and IC condition is not observed in these coatings.

Therefore, it is possible confirm that when the coatings are subjected to high humidity conditions it can lose the pentaerythritol.

In the other parts of the DSC curves, it can be seen that a series of complex changes occurred at the temperature range analysed.

Intumescence Evaluation

The photos of the coatings **A**, **B** and **C** before and after the intumescence evaluation for the three exposure conditions are presented in Figures 11, 12 and 13, respectively.

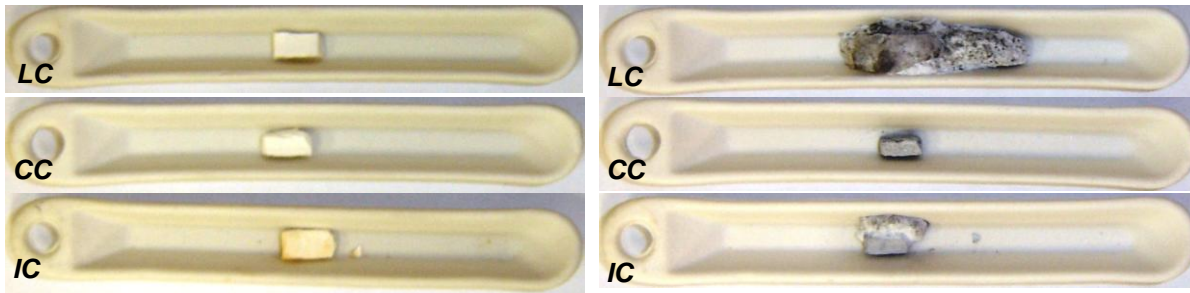


Figure 11. Coating **A** before (left) and after (right) the intumescence evaluation for the three exposure conditions: LC (red); CC (green); IC (blue)

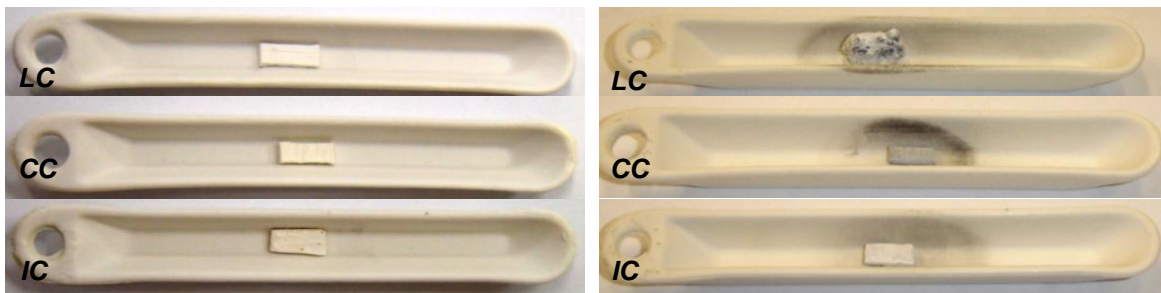


Figure 12. Coating **B** before (left) and after (right) the intumescence evaluation for the three exposure conditions: LC (red); CC (green); IC (blue)

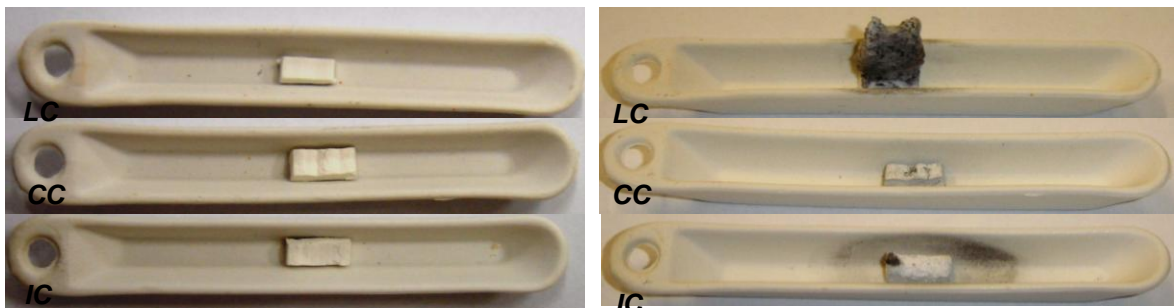


Figure 13. Coating **C** before (left) and after (right) the intumescence evaluation for the three exposure conditions: LC (red); CC (green); IC (blue)

In the coating **A** (Figure 11) submitted to LC condition, there is an expected expansion of the layer, which is not verified in the CC condition. For the IC condition it is observed a slight expansion in the layer. Coating **B** (Figure 12), at LC condition, presents also an expected expansion of the layer. This expansion of the layer are absent in the other two exposure conditions, where the layers remain with the same thickness. On the other hand, in coating **C** (Figure 13) it is observed a strong expansion and a slight expansion for the LC condition and IC condition, respectively. Finally, in the CC condition the expansion of the layer is not verified. The results obtained demonstrate that after exposure the coatings to the CC condition and IC condition, their intumescent performance is considerable different from that correspondent to the exposure to laboratory conditions (LC).

4. Conclusion

The FTIR analysis confirmed that active components, such as melamine and pentaerythritol, are lost when both solvent and water-based coatings are exposed to continuous condensation condition (CC) and immersion condition (IC).

The loss of pentaerythritol after exposure to these conditions was also confirmed by DSC analysis.

The change on the thermal behaviour of the coatings exposed to CC and IC conditions was identified by TG analysis and its adverse effect was confirmed by the intumescence evaluation test.

The characterization methods and the intumescence evaluation showed that when subject to high humidity environments the coatings can lose the components responsible for the intumescence, with adverse consequences to the formation of insulate barrier layer that protects the steel structure. To have the expected performance, the intumescent coatings should be applied in closely controlled environmental conditions and be protected from adversely high humidity conditions until the end of all the works.

References

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