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## High-Throughput Fire Tests and Weathering-Induced Degradation Behaviour of Intumescent Coatings

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### ABSTRACT

In this work, the weathering-induced degradation of intumescent coatings was investigated by a systematic and comprehensive approach. A mechanism is revealed that is proposed to be responsible for the loss of function of intumescent coatings induced by weathering.

First, the thermal decomposition of artificially weathered intumescent coatings was examined. To get a better understanding of the weathering and ageing phenomena, the degradation behaviour of the single ingredients during the weathering process was investigated, as well as their chemical and physical interactions. For the systematic approach, the materials that are essential for intumescence (ammonium polyphosphate, pentaerythritol, titanium dioxide, melamine and the binder) are treated with moisture, elevated temperature and UV radiation.

Thermogravimetry (TG) and IR spectroscopy were used to compare the initial samples with their different grades of weathering. We demonstrate that ammonium polyphosphate, melamine and the binder are mainly responsible for the ageing process. Further, it was demonstrated that TG and IR spectroscopy are suitable measuring methods to detect the effects of weathering on intumescent coatings.

Finally, a small-scale fire test procedure is introduced. Based on the reduction of the sample size, up to 50 samples can be tested in a single fire test. The results of this fire test have the same quality as the results from standard intermediate fire tests corresponding to DIN 4102-8.

### KEYWORDS:

*Intumescent coatings; fire resistance; weathering resistance*



## INTRODUCTION

Among different kinds of fire protection materials for steel constructions, intumescent coatings are the ones preferred by architects today and thus dominate the corresponding market. With the application of intumescent coatings, the time to failure for structural steel is enhanced in the case of fire, with the steel construction remaining visible [1]. A great deal of research has been performed to optimize intumescent coatings, but there are still some shortcomings to be resolved. Solvent-free coatings, especially, are still sensitive to ageing and weathering [2]. The intumescent coatings work through the mechanism of swelling when they are heated up. When the binder gets soft, its ingredients cause chemical reactions so that the coating forms a multicellular foam. Because of the low heat conductivity of the inflating gases, the coating generates an effective insulation layer between the underlying steel and the heat source. Furthermore, the hot surface may reflect or radiate the heat so that in the case of fire the heating rate of the steel construction is reduced [1, 3].

There are three essential components for intumescent coatings: a carbon source, an acid donor and a blowing agent. The binder which bonds the ingredients together can act as a carbon source as well. In some cases, additional inorganic ingredients are added to improve the thermal resistance strength. These inorganic additives undergo chemical reactions at high temperatures, which improve the thermal stability of the char. One of the compositions that is currently common contains pentaerythritol (PER) as a carbon source, ammonium polyphosphate (APP) as an acid donor and melamine (MEL) as a blowing agent [4]. With this composition, polyvinyl acetate (PVAC) is often used as a binder. As it also acts as a white pigment, titanium dioxide ( $\text{TiO}_2$ ) is often used as an inorganic filler. Activated by heat, the carbon source, together with the acid donor, creates a high-viscous carbonaceous network (which is also phosphoric, due to the APP) by alcoholysis and esterification. Due to its thermal decomposition, the blowing agent releases nonflammable gases and the resulting bubbles produce a multicellular foam [4]. At high temperatures, when the organic compounds are already evaporated,  $\text{TiO}_2$  reacts chemically with the remaining phosphate in the APP to form a ceramic structure containing titanium pyrophosphate [5].

Some research has been done to investigate the effects of weathering on intumescent coatings [1, 5]. Until now, only the coating has been examined as a whole system. Our approach is to reveal the degradation mechanisms and main impacts of weathering by studying the degradation behaviour and interaction among the single ingredients. For the experiments, the samples are divided in two categories. The weathering-induced degradation and reactions of the ingredients are investigated on the basis of pure and mixed dry chemicals, whereas the ageing-related performance of the intumescent coatings is evaluated by coatings that have been applied to steel panels. The samples are tested at different states of the artificial weathering process by fire tests and TG. Furthermore, our task is to improve the resistance to weathering of intumescent coatings by systematically varying the formulations. The different grades of weathering and the systematic variations of the formulation call for a high number of samples. In order to deal with the high number of samples, the size of the steel panels is reduced to the scale of 75 mm x 75 mm x 5 mm. The small specimen size facilitates the storage of a sufficiently high number of samples in the ageing chamber and enables high-throughput fire tests so that up to 50 samples are evaluated simultaneously in one fire test.

## HIGH-THROUGHPUT TESTING

### Samples and Sample Preparation

First, a primer is spread over the surface of the steel panel using a paint roller. After 12 hours of curing, the application of the first layer can be started. The coating is applied with in several steps using a squeegee. The maximum thickness of each layer must not exceed 500  $\mu\text{m}$  in order to prevent cracks in the surface of the coating. After curing, the new layer is shrunk to a dry film thickness of about 250  $\mu\text{m}$ . This means that a layer with a dry film thickness of about 1 mm consists of four layers. The tolerance of the resulting dry film thickness is about  $\pm 20 \mu\text{m}$ .

The fire tests are performed in an oil-powered furnace with a chamber size of 100 cm x 100 cm x 100 cm. A hanger welded on to the chamber connects the back side of the panels with a metal wire. This metal wire passes through a vermiculite board and is fixed on the backside of the board with screws. A pair of thermocouples (Type K, chromel-alumel, 0.5 mm diameter) is also welded to the back surface of the samples to measure the temperature during the fire test. The furnace has two open windows, in which the vermiculite boards with the mounted samples were placed (Fig. 1 (a)).

### Evaluation of the Testing Procedure

The high-throughput fire tests of the small-scale samples yield results equal to those obtained with an intermediate-scale fire test conforming with the specifications of DIN 4102-8 [6]. The dimensions of the intermediate-size steel panel are 500 mm x 500 mm x 5 mm and the chamber of the corresponding furnace is 170 cm long, 63 cm high and 40 cm wide. In both furnaces, the flame proceeds parallel to the surface of the samples. The temperature program is the UTTC in accordance with DIN EN 1363 -1 [7].

The good comparability (Fig. 1 (b)) of the result can be attributed to the fact that the thermal behaviour of the many small panels arranged close to each other is similar to the thermal behaviour of the one large panel that is used in the intermediate fire tests. The reason for the lower temperature of the intermediate-scale sample is that the distance of the small-scale sample to the furnace flame and to the thermal element of the furnace (20 cm distance) is greater than the distance of the intermediate-scale sample to the thermal element (10 cm distance) and the furnace flame. Thus the intermediate-scale sample is more strongly affected by heat radiation than the small-scale sample. In addition, the interiors of the two furnaces have different fluid properties, related to their different internal dimensions. The quality of the results, in combination with the high number of samples that are tested in one fire test, qualifies this testing procedure for future fire tests.

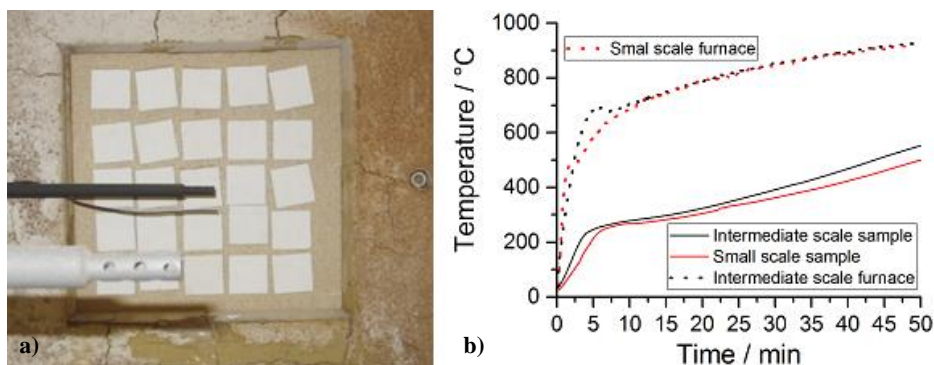


Fig. 1. High-throughput fire testing, arrangement of the small-scale samples in the furnace (a); comparison of the high-throughput small-scale fire test with an intermediate-scale fire test (b).

## AGEING BEHAVIOUR

### Material and Methods

In this work, two intumescent coatings, based on a common formulation, are treated with artificial weathering. Both formulations contain ammonium polyphosphate, pentaerythritol, melamine, PVAC and titanium dioxide. For the first formulation, common phase-II APP is used. For the second formulation, the common phase-II APP is replaced by an APP coated with melamine formaldehyde resin. For closer investigation of the weathering-induced reactions, the principal ingredients of the intumescent coating and selected combinations of the ingredients were treated with artificial weathering as well.

The single ingredients are: APP, PER, MEL,  $\text{TiO}_2$  and PVAC.

The combinations consist of mixtures of the dry chemicals:

APP + MEL, APP + PER and APP +  $\text{TiO}_2$ ;

$\text{TiO}_2$  + MEL and  $\text{TiO}_2$  + PER;

$\text{TiO}_2$  + APP + MEL and  $\text{TiO}_2$  + APP + PER

The coatings, the ingredients and the combination of the ingredients were treated with cyclic artificial weathering, including a humid and a warm period:

A period of 6 hours at 40 °C and 95 % relative humidity was followed by a period of 6 hours at 70 °C and 20 % relative humidity. When UV radiation is mentioned, it was applied with the power of 35 W / m<sup>2</sup> in a range from 290 nm to 400 nm. The samples were stored in the weathering chamber as shown in Fig. 2 (a).

The coatings were subjected to the artificial weathering conditions for 15 weeks. UV radiation was applied during the entire period. Every 3 weeks a pair of coated steel panels was removed from the weathering chamber for examination. Hence the coatings were available in the initial state and after 3, 6, 9, 12 and 15 weeks of artificial weathering (Fig. 2(b)). The single ingredients and the combinations were treated with the same conditions for 24 weeks. In order to investigate the influence of UV radiation on the weathering-induced effects of ageing, all ingredients and the combination of ingredients were artificially weathered with and without the exposure to UV radiation.

After the accelerated weathering tests, all dry chemicals were examined using TG and ATR. Furthermore, the weathered single ingredients were used to produce intumescent coatings. These coatings were prepared by replacing one of the usual initial ingredients with the respective weathered ingredient in each case. All coatings were evaluated by TG. Furthermore, the coatings containing the weathered single ingredients were evaluated by fire tests. The TG measurement was taken using ground coatings with a mass of 5 mg. All TG measurements took place under nitrogen atmosphere with a heating rate of 10 K / min.

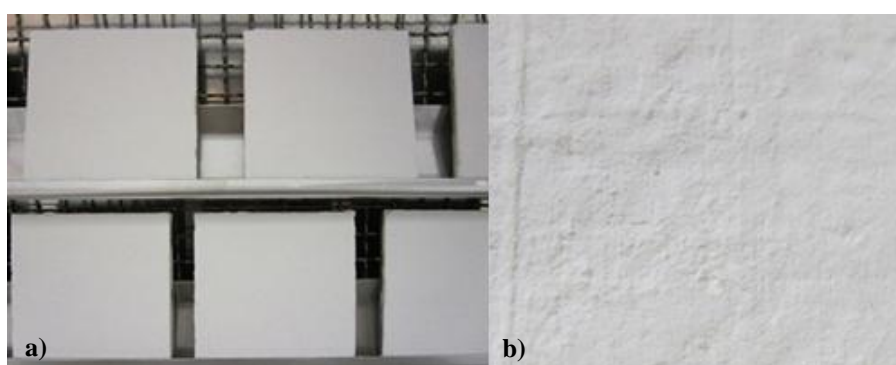


Fig. 2. Samples, first coating in the initial state (a); first coating after 9 weeks of artificial weathering (b) .

#### Weathering-Induced Effects on the Intumescent Coating Measured by TG

After 9 weeks of artificial weathering, depositions occurred on the surface of both types of coatings (Fig. 2(b)). This observation is consistent with the experiments of Wang [1], as it is APP, MEL and PER that migrate to the surface of the coating. The TG measurements of the weathered coatings (Fig. 3 (a) and (b)) show a mass loss at around 100 °C, which is only observed in the curves of the weathered coatings. As water evaporates at 100 °C, the mass loss can probably be attributed to water that infiltrated the coating during the weathering process. Another difference concerning the mass loss of the samples in different states of weathering is visible between 200 °C and 300 °C. According to the previous work of R. Kunze [8], where a similar coating is analysed by TG, water and ammonia are released in this temperature range and the coating starts to foam up.

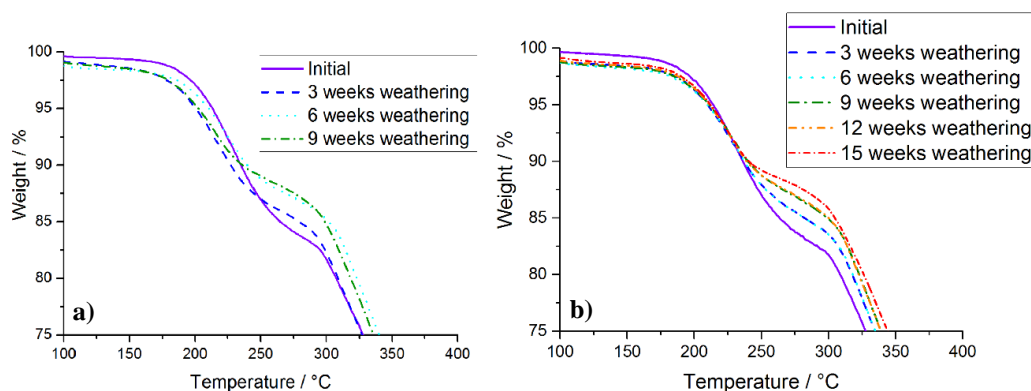


Fig. 3. TG measurements, thermal decomposition of the first coating at different states of accelerated weathering (a); thermal decomposition of the second coating at different states of accelerated weathering (b).

Both substances are released during the thermal decomposition of APP and melamine [4, 9]. The fact that the mass loss is reduced in the temperature range where the intumescence occurs indicates that the performance of the coating has deteriorated. The fact that a smaller quantity of volatile components is released leads to the

assumption that the intumescence is affected. For this, two causes are considered. During the weathering process, the ingredients that are necessary for the intumescence migrated to the surface of the coating and are no longer available for the intumescence process [1]. Furthermore, the ATR measurements (Fig. 5 (a)) and the TG measurements (Fig. 5(b)) of the artificially weathered ingredients prove that APP reacts chemically with MEL during the artificial weathering process. Our assumption is that during the artificial weathering process of the intumescent coating, the APP reacts with the MEL inside the coating. We assume that this is another reason for the weathering-induced loss of function of intumescent coatings. It is worth mentioning that there is no further change in the thermal degradation behaviour (measured by TG) of the first coating after 9 weeks of artificial weathering. We assume that the moisture diffusion in the coating and the reaction between APP and MEL is completed after this time. The results of the TG measurements of the second coating (Fig. 3 (b)) show similar behavior, but impact of weathering on the second coatings continues even after 9 weeks of weathering. This leads to the assumption that the second coating that contains the modified APP can resist the damage of weathering for a longer period. This supports the assumption that the chemical reaction of APP and MEL is responsible for the weathering-related loss of function of the intumescent coating, as the surface treatment of the modified APP slows down the chemical reaction of APP and MEL.

### Ageing Effects Caused by Weathering of Single Ingredients and Combinations

Neither the APP nor the other ingredients changed their thermal behaviour during the artificial weathering process when they were weathered separately. This was proved by ATR and TG measurements and fire tests. Only the ATR spectra of the binder changed after 6 weeks of artificial weathering (Fig. 4 (a)). The peak in Fig. 4 (a) at  $3300\text{ cm}^{-1}$  indicates adsorbed moisture. The thermal degradation behaviour of the artificially weathered APP is shown in Fig. 4 (b) and (c). The coatings for this fire test were prepared by replacing of the ingredients with the artificially weathered version one at a time.

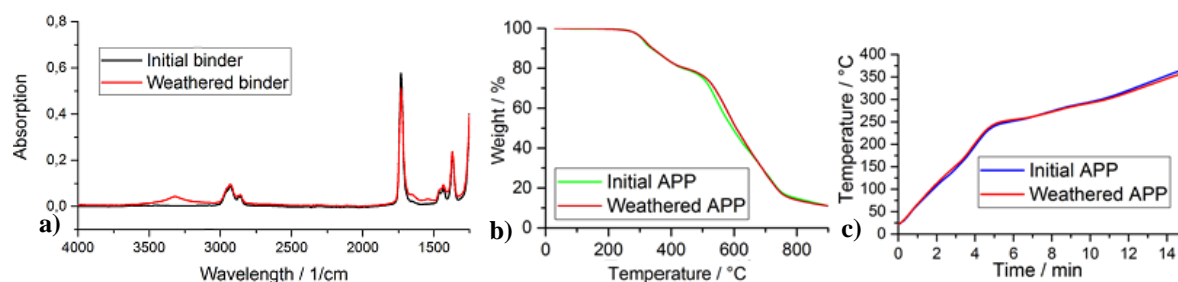


Fig. 4. Examination of the weathered ingredients, comparison of the initial binder with the artificially weathered binder (a); comparison of the initial APP with the artificially weathered APP via TG (b); comparison of the fire tests using an intumescent coating containing initial APP (blue) and artificially weathered APP (red) (c).

As to the combinations of the ingredients, only the combination of APP with MEL showed any difference between the initial and the weathered states. The differences are visible in the ATR spectra (Fig. 5(a)) and in the thermal degradation behaviour that was measured by TG (Fig. 5 (b)).

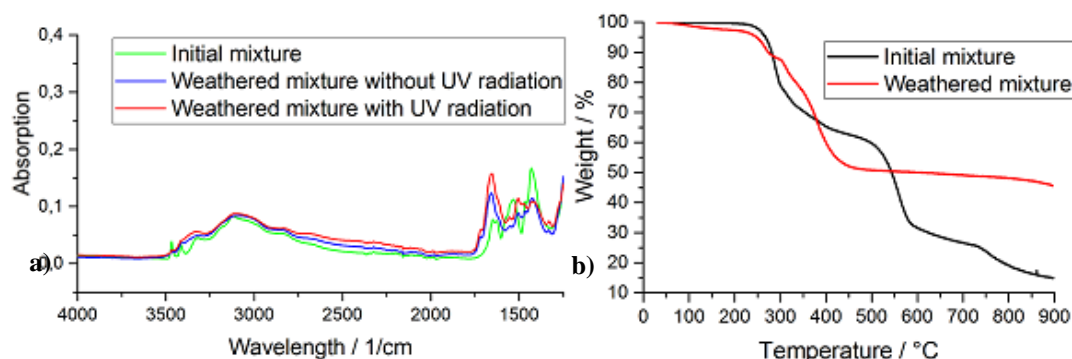


Fig. 5. Comparison of the initial APP-MEL mixture with the artificially weathered APP-MEL mixture, investigation via ATR (a); investigation via TG (b).

Neither the exposition to UV radiation nor the addition of  $\text{TiO}_2$  to this mixture made any major difference.

## CONCLUSION

Two mechanisms are considered to be responsible for the weathering-induced change of the performance of intumescent coatings. The first is the migration of the ingredients to the surface. The second is the chemical reaction of MEL with APP inside the coating. Both mechanisms are driven by moisture, so that humidity is considered to be the most relevant influence of weathering.

Further studies will be done concerning the weathering-related performance of intumescent coatings to reveal the entire mechanism of the weathering-induced loss of function of intumescent coatings. These studies include fire tests of artificially weathered intumescent coatings and coatings containing the artificially weathered combinations of APP and MEL.

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