Thermal characterization of intumescent fire retardant paints

L. Calabrese[1], F. Bozzoli[1], G. Bochicchio[2], B. Tessadri[2] , S. Rainieri[1*], G. Pagliarini[1]

[1]Department of Industrial Engineering - University of Parma
Parco Area delle Scienze 181/A, 43124 Parma, Italy.
[2]National Research Council of Italy (CNR), Trees and Timber Institute – Fire Lab. Via Biasi, 75, 38010 San Michele all'Adige, Italy.

E-mail address of the corresponding Author (Sara Rainieri): sara.rainieri@unipr.it

Abstract Intumescent coatings are now the dominant passive fire protection materials used in industrial and commercial buildings. The coatings, which usually are composed of inorganic components contained in a polymer matrix, are inert at low temperatures and at higher temperatures, they expand and degrade to provide a charred layer of low conductivity materials. The charred layer, which acts as thermal barrier, will prevent heat transfer to underlying substrate. The thermal properties of intumescent paints are often unknown and difficult to be estimated since they vary significantly during the expansion process; for this reason the fire resistance validation of a commercial coatings is based on expensive, large-scale methods where each commercial coating-beam configuration has to be tested one by one. Adopting, instead, approaches based on a thermal modelling of the intumescent paint coating could provide an helpful tool to make easier the test procedure and to support the design of fire resistant structures as well. The present investigation is focused on the assessment of a methodology intended to the restoration of the equivalent thermal conductivity of the intumescent layer produced under the action of a cone calorimetric apparatus. The estimation procedure is based on the inverse heat conduction problem approach, where the temperature values measured at some locations inside the layer during the expansion process are used as input known data. The results point out that the equivalent thermal conductivity reached by the intumescent material at the end of the expansion process significantly depends on the temperature while the initial thickness of the paint does not seem to have much effect.

1. Introduction

Steel structures are widely used in building construction due to their high mechanical strength, ductility and execution times. However, due to deterioration of mechanical properties with temperature, it is essential that the whole structure and its elements have the necessary fire resistance to prevent a collapse in case of fire. One measure intended to the design of structures with the required fire resistance is to use higher cross-sectional elements or fire-resistant steels. An increase of the fire resistance time can be achieved by applying passive fire protection materials that insulate the steel structure from the effects of the elevated temperatures that are generated during a fire. They can be divided into two categories: non-reactive materials, of which the most common types are

incombustible boards and spray of a cooling fluid, and reactive materials, of which the intumescent coatings are an example. They are available as solvent or water-based systems, which are applied with a thickness of up to approximately 3 mm. The time for the steel component to reach a critical point of behavior confers the rating to the coating. Typically this occurs when the steel component reaches about 550°C, the temperature at which steel shows a considerable loss in strength. The advantages of this kind of protection include the reduced overweight compared to other materials, off-site application and a good surface finishing, which can be improved with the application of decorative films[1]. Intumescent systems consist generally of three compounds: an acid source (ammonium phosphate-APP), a carbon source (pentaerythriol - PER) and a blowing agent (melamine). These compounds are linked each other by a polymer matrix which plays a capital role in the intumescent behavior. Phosphorous polymeric binders are often used as flame retardancy. The paint layer evolves under the effect of the heating source in a complex way [2], with an interplay of physical and chemical processes that occur in a suitable sequence (in series or in parallel) [3,4].

Exposed to a heating flux, the behaviour of the intumescent coating can be described by successive steps. Initially under the effect of the thermal flux, the ablation of a part of the intumescent paint then occurs, gases are released and they cause the swelling of a part of the paint. Subsequently, a charring zone appears, which grows with time, until being stabilized in stationary state. The ablative layer goes on regressing and the expanding layer swells. The non reactive char layer grows to the detriment of the reactive layer and the ablative layer. Finally, the original intumescent paint is totally ablated, the paint stops to swell and just a stable char layer stays [2].

The fire resistance of a commercial coating is usually tested experimentally, by using large-scale tests (see, for instance, EN 13381-4 and EN 1363-1 standards [5,6]). Such tests are expensive and time-consuming, with a large number of tests required to cover the range of steel configurations and protection thicknesses typically required in the construction field.
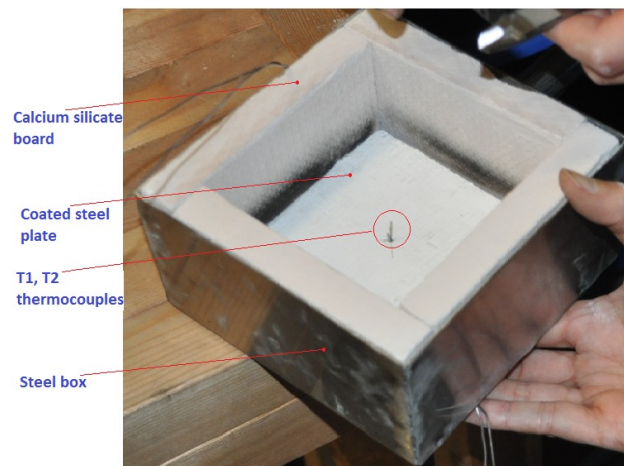
Adopting a modelling approach based on thermal properties of the intumescent paint could, instead, provide a helpful tool to make easier the test procedure and to support in the design of fire resistant structure, as well. Therefore, the knowledge of the equivalent thermal conductivity of the intumescent layer is therefore an important task, for the purpose of predicting the behavior of metal structures subject to the action of fire, when protected by intumescent paints. Some researchers [7-11] have proposed to estimate the equivalent thermal conductivity by solving the one-dimensional non-steady inverse heat conduction problem in the intumescent layer. In this procedure, the directly measured parameters are the temperature-time response of the metallic element on which the intumescent paint is smeared and the flame temperature [10] or the heat flux density produced by a cone calorimeter apparatus [8,9]. However, the determination of the net heat flux absorbed by the free surface of the intumescent layer is problematic, because of the uncertainty in parameters which characterize its thermal interaction with the surrounding environment, such as the coefficients of absorption, reflection and emission of the surface, the view factor towards the environment and its temperature, the coefficient of convection through which the surrounding air removes the heat from the surface of the intumescent layer. Others [9,12,13] have attempted an estimate of the equivalent thermal conductivity through the inversion of simple formulas, as the ones proposed in the technical regulations aimed at the determination of the temperature limit which is reached by metallic structures protected by thermally insulating coatings. However, the estimated equivalent thermal conductivity values are sometimes questionable (see, for example,[7,9,12]), since they are much lower than the thermal conductivity of air at the same temperature.

All these approaches, do not guarantee to achieve the sought result with a sufficient accuracy, due to the lack of reliable data on the thermal phenomena that occur at the free boundary of the intumescent layer. To overcome this difficulty, in this paper the temperature inside the intumescent layer is included among the variables being measured. In this way, the formulation of the inverse problem no longer requires the definition of the thermal conditions at the free surface of the intumescent layer, which is subjected to the heat flux, while the effective thermal conductivity of the intumescent layer

becomes the only unknown parameter of the protective coating to be estimated through the solution of the inverse heat conduction problem.

2. Experimental setup and estimation procedure

The considered intumescent paint consists of a polymeric PVC resin with additives: titanium dioxide, melamine and 2-butoxyethanol. The equivalent thermal conductivity of the intumescent layer was measured for two different initial thicknesses of paint, i.e. 0.8 mm (test specimen S08) and 1.2 mm (test specimen S12), evenly distributed on the face of a square steel plate with a side of 100 mm and 8 mm thick. In these conditions, the specimens were subjected to a heat flux of nominal 50 kW/m^2, produced by a cone calorimeter apparatus placed at the distance of 80 mm from its surface. The other surfaces of the specimen, both the rear and the sides, was thermally insulated with 2 cm of a calcium silicate board. The whole system was then placed in a metal box open at the top, figure 1.

Figure 1. Specimen under test.

The steel plate temperature, T_s, was measured by two K-type thermocouples, thermocouples *TS*, placed in contact with the rear face. The temperature in the intumescent layer was measured by two additional K-type thermocouples, which are protected by a metal sheath of circular cross section with a diameter of 1 mm, thermocouples *T1* and *T2*, respectively.

These thermocouples were installed through a small hole drilled in the metal plate, normally to the coated surface, with the axes at a distance of 2 mm. These arrangement prevent to possible displacements of the thermocouple during the swelling of the material under test. However it makes the exact identification of the position of the sensing element of the thermocouple problematic. In this respect, on the basis of the technical data provided by the manufacturer, it was assumed that the sensing element of the thermocouple is located at 0.5 mm from the apex of the protective metal sheath. With this assumption, the distance of the sensing element from the upper surface of the steel plate is given in table 1.

Table 1. Distance (mm) of the sensing element of the thermocouples from the metal surface of the specimen.

Specimen	Thermocouple *T1* [mm]	Thermocouple *T2* [mm]
S08	5.5	13.3
S12	8.8	15.6

After a sufficiently long time interval, thermocouples *T1* and *T2* are incorporated in the intumescent material and they begin to detect its temperature. In consideration of the relatively high thermal conductivity of the material (steel) and of the small thickness of the metal plate under test, the lumped parameter thermal model was adopted to describe its temperature behavior when exposed to the heat flux. This assumption allows to estimate transmitted to the metal plate through the protective layer, by using the energy balance of the plate itself. In fact, by denoting with q_s and q_d the heat absorbed by the plate and the heat lost through its back face, respectively, with reference to the unit surface area of the substrate plate, its energy balance gives:
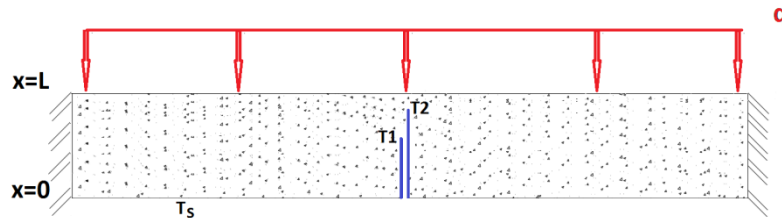
$$q = q_s + q_d = \rho_s \, c_s \, s \, \frac{dT_s}{dt} + K \, (T - T_a) \tag{1}$$

where ρ_s, c_s, s are, respectively, density, specific heat and thickness of the plate; K is the overall heat transfer coefficient which accounts for the heat lost from the back face of the specimen towards the environment, whose temperature is T_a. Anderson et al.[10] note that, once the intumescent layer has developed, q is approximately a constant. This circumstance implies that the thermal regime through the intumescent layer is almost steady and, as a consequence, the equivalent thermal conductivity of the layer could be estimated through direct application of Fourier's law for a simple plane situation:

$$\lambda_{eq} = \frac{q \cdot d}{\Delta T} \tag{2}$$

where ΔT is the temperature difference between two planes parallel to the face of the specimen, d away.
Unfortunately, with the present experimental arrangement the application of eq. 2 is not allowed, since it is expected that the thermocouples installed in the intumescent material perturb the temperature field. In fact, a non-negligible heat flux towards the base plate is established along the metal sheath of the thermocouple, which tends to depress the measured temperature, compared to the value detectable in its absence. For this reason in this paper, the inverse problem of heat conduction in the intumescent layer was formulated as shown in figure 2.

Figure 2. Thermal schematization of inverse heat conduction problem.

At x = 0 the temperature is known, as measured by the thermocouples, *TS*, placed in contact with the metal plate. Thickness *L* is set in an arbitrary way, in order to be sufficient to consider the temperature for x = L to be uniform. At x = L a Neumann boundary condition is adopted and the imposed heat flux value is estimated by eq. 1. The thermocouples were modeled in the inverse problem following the manufacturer specification. At x = L the temperature is unknown, while it is known at points 1 and 2, as measured by the thermocouples *T1* and *T2*, respectively. The side surfaces of the intumescent layer was considered to be adiabatic. The presence of thermocouples *T1* and *T2*, whose metal sheath may significantly perturb the temperature field, makes the thermal problem three-dimensional. In view of the slow variation of the thermal conditions which follow the development of the intumescent layer, the conductive thermal problem was solved in steady state.

In the cone calorimetric tests it is expected that the temperature across the intumescent layer varies by several hundreds of Kelvin. According to the analysis of Staggs [4], the corresponding variation of the equivalent thermal conductivity of the expanded intumescent char should then be very significant. Nevertheless, in the present investigation a uniform equivalent thermal conductivity is assumed, as representative of a first approximation estimate.
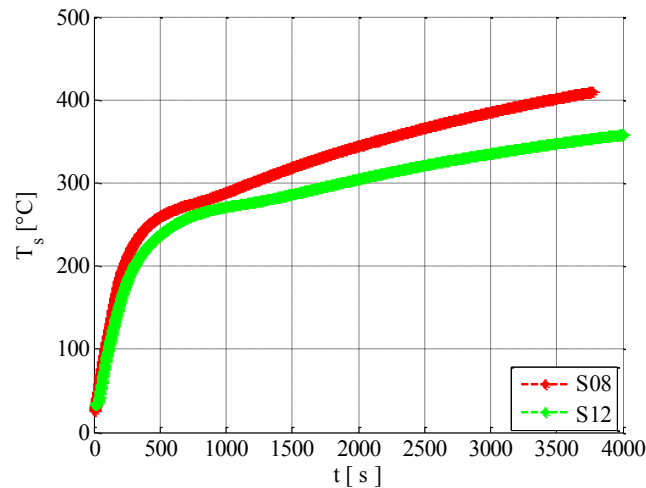
The equivalent thermal conductivity was then estimated by requiring that the following objective function have a minimum [14]:

$$\mathrm{F}(\lambda_{eq}) = [\mathrm{T_{measured}} - \mathrm{T_{computed}}(\lambda_{eq})]_1^2 + [\mathrm{T_{measured}} - \mathrm{T_{computed}}(\lambda_{eq})]_2^2 \qquad (3)$$

Where $T_{measured}$ is the temperature value measured by thermocouples *T1* and *T2*, while $T_{computed}(\lambda_{eq})$ is the corresponding temperature value given by the numerical model as a function of the equivalent thermal conductivity.

3. Experimental results
The tests under the cone calorimeter were continued for approximately 4000 s (S08 and S12). Figure 3 shows the temperature trend of the metal plate, obtained as the average value of the readings of the two thermocouples arranged in contact with the rear surface of the specimen.

Figure 3. Steel plate temperature histories acquired in the cone calorimeter test.

In the time interval considered for estimating the thermal conductivity of the intumescent layer, the two thermocouples to provided temperature values which are coincident within 1 or 2 °C, for the samples S08 and S12, respectively. As expected, the plate temperature increases monotonically, but at a varying velocity, which continues to decrease till the end of the test time. A similar behavior was detected by Anderson et al. [10]. To the opinion of these authors, the decrease of the heating velocity even after the completion of intumescence is due to the increase of the heat loss, q_d, towards the environment as the steel plate temperature increases.

The heat absorbed by the steel plate, q_s, was then calculated from the temperature time response curve, with the properties of steel specified in table 2.

Table 2. Thermal conductivity, density and specific heat for steel.

λ_s [W/m·K]	ρ_s [kg/m^3]	c_s [J/kg · K]
45	7850	$425+0.7773\,T-0.00169\,T^2+0.0000022\,T^3$

The heat lost through the back face of the specimen, q_d, was instead computed in steady state (eq. 1). By neglecting the thermal resistance of the metal box wall, the overall heat transfer coefficient, K, was defined as a series of two heat transfer resistances:

$$K = \frac{1}{R_{cs} + R_{cr}} \tag{4}$$

The first one is the thermal resistance of the calcium silicate board:

$$R_{cs} = \frac{s}{\lambda_{cs}} \tag{5}$$

while the second one is the thermal resistance from the external wall of the metallic box to the environment, whose temperature T_a was 25°C. It consists of two thermal resistances in a parallel configuration, due to heat convection and thermal radiation:
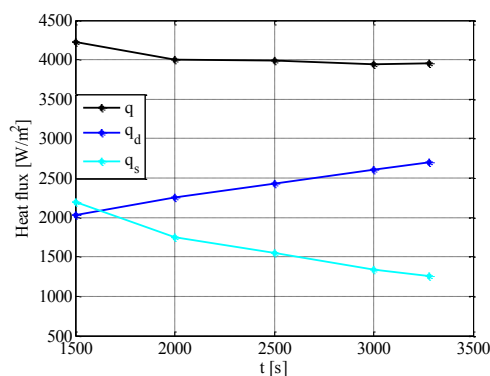
$$R_{cr} = \frac{1}{h_c + h_r} \tag{6}$$

The coefficient of radiation and of convection was computed as follows:

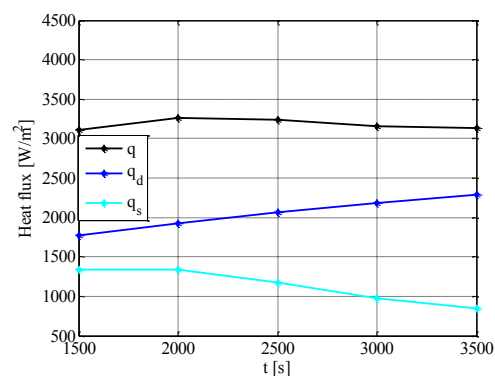$$h_r = \sigma_0 \, a \, (T + T_a) \, (T^2 + T_a^2) \tag{7}$$

$$h_c = \frac{\lambda}{l \, (Gr \cdot Pr)^{\frac{1}{3}}} \tag{8}$$

The thermal properties of air was computed at film temperature. For the wall of the metallic box the absorption coefficient a=0.7 was assumed. The overall heat transfer coefficient slightly depends from the temperature of both the box wall and the environment. In the present measurements its averaged value was 7.2 and 7.0 W/m^{2}K, for specimens S08 and S12, respectively.

For both samples, the heat flux, q, that reaches the metal plate is shown in figure 4 and 5, together with its components, q_s and q_d.

Figure 4 . Heat fluxes for sample S08.
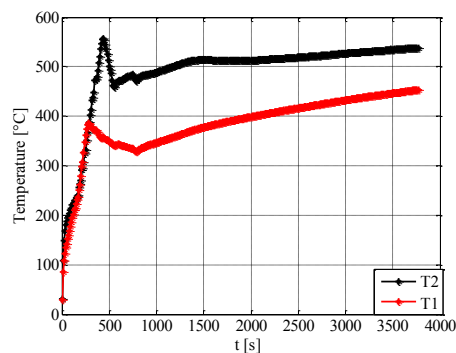

Figure 5. Heat fluxes for sample S12.

The graphs of figure 4 and 5 confirm that, after completion of intumescence, the heat flux through the intumescent layer is just constant with time. In particular, from t = 2000 s, q remains constant within ±1 and ±2% for specimens S08 and S12, respectively. Instead, q_s and q_d are not steady. In particular,

while q_s decreases with time, q_d increases, since the temperature difference between the metal plate and the environment increases.
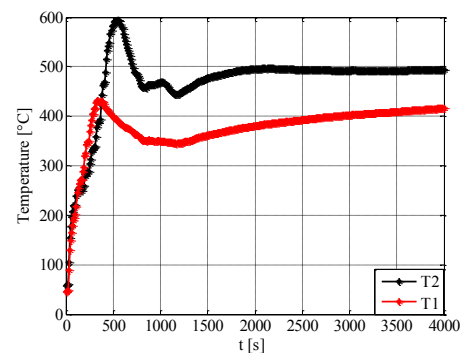
To the maximum heat flux through the metal plate it corresponds a maximum temperature difference, in the direction normal to the coated surface, of about 0.6°C, less than 0.2% of the maximum temperature difference which the plate experiences during the whole heating process. Therefore, the assumption of lumped parameters which underlies eq. 1, can be considered verified with sufficient accuracy for the purposes of the present analysis.

The assumption of negligible heat losses in the experimental test aimed to the estimation of the equivalent thermal conductivity is at the base of the procedure suggested by many researchers, see, for instance, Anderson et al. [10], Mesquita et al. [9]. Disregard the heat losses in the energy balance equation of the steel plate (eq. (1)) may result in an underestimation of the heat flux through the intumescent layer and, as a consequence, it may result in a proportional underestimate of the equivalent thermal conductivity. To the assumption of negligible heat losses may be due some unrealistically low values of the equivalent thermal conductivity which are reported in the technical literature on the subject of intumescent protective coatings.

The temperature time response by thermocouples *T1* and *T2* is shown in figures 6 and 7, for specimens S08 and S12, respectively.

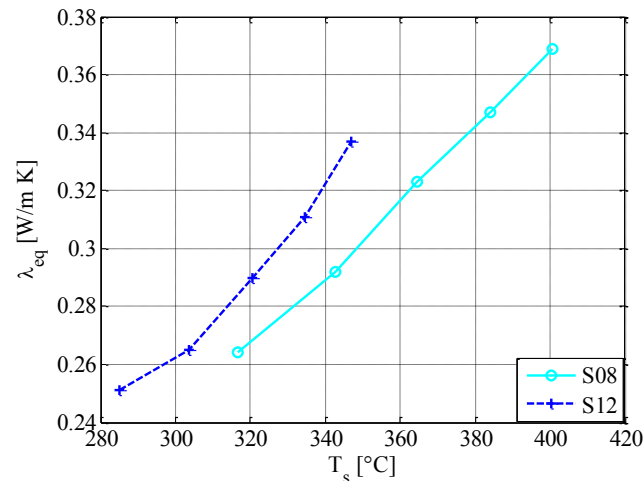**Figure 6.** Temperature detected by thermocouples T1 and T2 during the intumescence process for sample S08.

Figure 7. Temperature detected by thermocouples T1 and T2 during the intumescence process for sample S12.

The maximum value of temperature is likely reached when the intumescent layer incorporates the thermocouple, which previously is directly exposed to the heat flux emitted by the cone calorimeter. The graphs show that the intumescent layer had already reached the thickness of almost 14 mm (about 35% of the final thickness (40 mm)) at t = 500 s, for specimen S08, while, for specimen S12, the thickness of 16 mm (about 27% of the final thickness (59 mm)) was reached at t = 750 s.

4. Equivalent thermal conductivity estimation

The steady thermal problem schematized in figure 2 was solved by the numerical finite elements method, implemented inside the Comsol Multiphysics environment. The objective function (eq. 3) subject to the given constraints was then minimized through the Matlab Optimization Toolbox® by using Nelder-Mead minimization algorithm. The results, in terms of equivalent thermal conductivity, obtained for the two specimens are shown in figure 8, as a function of the temperature of the substrate metal plate.

Figure 8. Equivalent thermal conductivity, obtained for the two specimens versus the steel temperature.

As expected, the data show a great effect of temperature. An increase in the plate temperature of hundred Kelvin produces an increase of about fifty per cent in the effective thermal conductivity. Therefore, a proper data reduction procedure should account for the temperature variation across the intumescent layer, since a temperature variation of several hundreds of Kelvin is expected between the free surface of the protective layer and the surface in contact with the metal plate.

Regarding the effect of the initial paint thickness, the results presented in figure 8 show a systematically higher equivalent thermal conductivity for specimen S12. However, this behavior might be due to the above cited dependence on temperature. Indeed, in spite of the higher plate temperature for specimen S08 as shown by figure 3, it is expected that the average temperature across the layer thickness is higher for specimen S12 than for specimen S08. This circumstance derives from the estimated heat flow rate through the layer, q, and from the layer thickness, as measured at the end of the test. The average difference between the mean temperature through each layer is about between 25°C to 30°C. Shifting the curve for specimen S12 on the right of this temperature interval reduce the difference between the estimated λ_{eq} values. As a consequence, the initial thickness of the paint seems to have a quite negligible effect on the effective thermal conductivity of the intumescent layer.

5. Conclusion
A method for estimating the equivalent thermal conductivity of the char layer generated by the intumescence process has been presented and assessed through its application to two specimens, with different initial paint thickness. The method is based on the heat conduction inverse problem approach, with temperature measured in two different point of the intumescent layer as inputs known data.
The results have confirmed that the equivalent thermal conductivity highly depends on the temperature, while paint thickness does not seem to have great importance.

6. Acknowledgements

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