Parameter estimation approach to the thermal characterization of intumescent fire retardant paints

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Abstract Intumescent paints are widely used as passive fire retardant materials in the building sector. They swell on heating to form a highly insulating char, protecting steel members. Intumescent coatings for use in buildings are typically certified according to the standard cellulosic fire resistance test. This test is expensive, often non-representative of realistic fire conditions, and not enough versatile to gather detailed performance information on the response of reactive coatings. A promising approach, that could offer a helpful tool to the engineering community involved in fire safety, is found in the modelling of the behaviour of the intumescent coating. Under this approach, the knowledge of the equivalent thermal conductivity of the intumescent material is a fundamental issue, since it represents the main parameter that allows predicting the thermal protecting capability of the layer. The purpose of this paper is to optimize an estimation procedure intended to the restoration of the equivalent thermal conductivity of intumescent layers. The thermal stress is activated by the action of a cone calorimetric apparatus, while the estimation procedure is based on the inverse heat conduction problem approach under steady state assumption, where the temperature values measured at some locations inside the layer during the expansion process are used as input known data. This procedure was successfully applied to steel samples protected with an intumescent paint; the estimated equivalent thermal conductivity of the layer results to temperature dependent while the initial thickness of the paint does not seem to have a great effect.

1. Introduction
Structural steel is widely used in modern structural construction all over the world due to its high mechanical strength, ductility and execution time. Regarding steel-framed buildings, a sufficient fire resistance is an important and prior requirement of building regulations. A promising approach to achieve this requirement is to apply passive fire protection materials to the structural steel that are inflammable and capable of protecting the steel structure from the effects of high temperatures that are generated during a fire. They can be divided into two categories: non-reactive materials, such as incombustible boards, and reactive materials, such as intumescent coatings. Thin film intumescent coatings have become the dominant choice for passive fire protective materials because of their many advantages including: flexibility and ease of application, light-weight, thin and attractive appearance.
and high standard finishing. They are typically applied with a thickness ranging from 1 to 8 millimeters and could be solvent or water based [1-4].

Structural steel loses an appreciable part of its load carrying ability when its temperature exceeds 500 °C. The time at which the steel reaches this critical temperature is generally the quantity that has to be considered in the design of a safe evacuation of people from the building and therefore it has become a prior parameter in building regulations in many countries. Intumescent coatings are designed not to burn [5] and to perform under severe conditions with the aim of maintaining the steel integrity between 1 and 3 hours in case of fire [6]. Nowadays, many formulations are available and the basic components used in commercial intumescent paints are: inorganic acids or materials yielding acid at high temperatures, polyhydric materials, organic amines or amides and binders.

The inorganic acids act as a catalyst to speed up the formation of a carbonaceous char; ammonium polyphosphate is commonly used. The polyhydric materials, rich in carbon, form the carbonaceous backbone of the intumescent char; carbohydrates are usually used for this purpose, Pentaerythritol being one of the most common. The organic amines or amides act as a blowing agent; melamine is often used for this purpose because of its low water solubility [7]. These components are linked each other by a polymer matrix which plays a capital role in the intumescent behavior; indeed an increase in the ratio of polymer results in the most noticeable increase in flexibility. Phosphorous polymeric binders are often used as flame retardant.

These innovative coatings, when activated by the heat of a fire, react to form a thick, low-density, polymeric coating or char layer. The parameter that directly reflects the performance in the protection is the pore structure of the char. Water vapor and sulphur dioxide are released during the intumescent reaction. Two fire-protection mechanisms thus become available: the char layer retards the flow of heat, due to the extremely low thermal conductivity and water vapor and sulfur dioxide are released, providing fire-quenching properties. Moreover, if the char, due to the presence of titanium dioxide, reaches a sufficiently high temperature, much of the incident heat load can be reflected [8]. The behavior of the intumescent coating can be described by subsequent physical and chemical steps. Initially, under the effect of the thermal flux, the ablation of a part of the intumescent paint occurs, gases are released and they cause the swelling of a part of the paint. Subsequently, a charring layer 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. Eventually, the original intumescent paint is totally ablated, the paint stops to swell and a stable char layer establishes [9].

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 [10,11]). Under this approach, each commercial coating-beam configuration has to be tested one by one. However, high operating costs, poor repeatability, unrealistic and/or inappropriate boundary conditions, and poor statistical confidence persist as common issues regarding the use of standard fire resistance tests [12].

On the other hand, performance-based structural fire engineering is increasingly common, and it is becoming more widely accepted as a method of structural fire resistance design. According to this approach, it is important to better understand the performance of reactive coatings [2]. Several methods for performance-based fire engineering design have been explored; most of them are based numerical modeling under the assumption of equivalent thermal properties of the intumescent paint. This methodology could provide a helpful tool to simplify the test procedure and to support in the design of fire resistant structure, as well. In literature, several works have been presented on this topic [13-20]. Some researchers proposed to estimate the equivalent thermal conductivity by solving the non stationary energy balance in the intumescent layer. In this procedure, the directly measured parameters are the temperature of steel substrate and the gas temperature of the gas furnace[2,16,21] or the heat flux produced by a cone calorimeter [5,14,15]. However, the determination of the net heat flux absorbed by the coating layer is difficult, 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 surrounding temperature, the convection coefficient. To overcome this difficulties, some researchers [2,15,22,23] have presented simplified models to calculate the effective thermal conductivity of the coating. However, all these approaches, do not have a sufficient accuracy, due to the weakness correlated to the determination of free boundary variables of the intumescent layer. To overcome this problem, recently Calabrese et al. [3], measured the temperature inside the intumescent layer. In this way, the formulation of the inverse problem does not require the definition of free boundary variables of the intumescent layer and the equivalent thermal conductivity of the intumescent layer becomes the only parameter of the paint that have to be estimated through the solution of the inverse heat conduction problem. In this paper the approach proposed by Calabrese et al [3] was improved: additional thermocouples were placed inside the foam; a better estimation of the heat lost was obtained by additional thermocouples on the insulating material; finally the numerical model for the thermocouple was enhanced by measuring its thermal properties.

2. Experimental setup and estimation procedure
The paint used in the here presented analysis was a water based intumescent coating (Promapaint by Promat), whose ingredients consist of a PVC polymeric resin with some additives: Titanium Dioxide, Melamine and 2-Butoxyethanol and others. The experimental tests were performed by considering two different dry film thickness (figure 1): 0.8 mm (test case label S08) and 1 mm (test case label S10), both coated on square steel plates, 4 mm thick and 100 mm wide. The specimens were subjected to a heat radiant fluxes of 50 kW/m$^2$ provided by a cone calorimeter. A specimen holder (figure 2) made of 2 cm of calcium silicate board in order to minimize and control heat losses toward the environment, was used as a cradle for the specimens.

![Figure 1](image1.png)  
**Figure 1.** Steel plate with the intumescent paint coating.

![Figure 2](image2.png)  
**Figure 2.** Specimen, thermocouples and holder.

The temperature data were acquired by K-type thermocouples sensors, where the sensing element are protected by a metal sheath of circular cross section with a diameter of 1 mm. On the base of data sheet provided by the manufacturers, it was assumed that the sensing element is located at 0.5 mm below the top of metal sheath. The temperature in the foam layer was measured by thermocouples labeled as $T1$, $T2$, $T3$. The distance between the surface of steel plate and the sensing element are reported in table 1.
Table 1. Distance of the sensing element from the metal surface.

| Specimen | Thermocouple T1 [mm] | Thermocouple T2 [mm] | Thermocouple T3 [mm] |
|----------|----------------------|----------------------|----------------------|
| S08      | 9.1                  | 19                   | 28.6                 |
| S10      | 10.6                 | 16.9                 | 25.2                 |

These temperature sensors were installed through a 1.5 mm hole, passing through the sample holder and the coated steel specimen as shown in figure 2. This arrangement prevents the movement of the thermocouples during the growth of the intumescent. The optimized horizontal distances between T1, T2, T3 were obtained by a Comsol simulation in order to minimize the reciprocal influence of thermocouples and the border effect. When the three sensors are completely covered by the char, the acquired signals start to be processed.

The temperature of steel plate T_s was acquired by two K-type thermocouples located on the non-coated surface of plate, halfway between the edge and the center of the square.

In consideration of the small thickness and the high steel thermal conductivity, the lumped capacity model can be assumed and therefore the temperature inside the plate has a spatially uniform temperature distribution.

Finally, two other K-type thermocouples were placed on at the calcium silicate-metal plate interface and between the calcium silicate and metal holder, with the aim of estimating the amount of thermal energy lost through the base of cradle.

Calabrese et al. [3] have highlighted, that after intumescent layer has completely developed, the heat flux through the paint will be approximately constant due to the negligible heat capacity of the coating. This implies that the energy balance through the foam layer is almost in a steady state and, in an ideal situation, \( \lambda_{eq} \) could be estimated through direct application of Fourier's law:

\[
\lambda_{eq} = \frac{q \cdot d}{\Delta T}
\]

(1)

The heat flux \( q \) transmitted through the protective layer (figure 3) is estimated by the energy balance of the steel plate:

\[
q = q_s + q_d = \rho_s c_s s \frac{dT_s}{dt} + \frac{\lambda_c}{s_c} (T_s - T_c)
\]

(2)

where \( q_s \) and \( q_d \) are the heat absorbed by the steel substrate and the heat lost through its back face; \( \rho_s \), \( c_s \), \( s \) are, density, specific heat and thickness of the steel respectively; \( \lambda_c \), \( s_c \), are the thermal conductivity and the thickness of calcium silicate which accounts for the heat lost from the back face of the specimen.
Unfortunately, a non-negligible heat flux along the metal sheath of the thermocouple (figure 4), may give an altered temperature field in thickness of foam, compared to the value detectable in its absence. For this reason equation (1) is not directly applicable. To overcome this problem, in this study the inverse heat conduction problem (IHCP) in the intumescent is formulated; the thermal boundary conditions at the boundaries are shown in figure 3, more specifically a Dirichlet (equation (3)) one and a Neumann one (equation (4)) are considered. At the lower boundary:

$$T|_{x=0} = T_s$$

While at the upper one:

$$-\lambda_{eq} \frac{\partial T}{\partial n}|_{x=L} = q$$

The thermocouples were modeled in the inverse problem by following the manufacturer specification, while a sheath thermal conductivity of 3.7 W/m K was estimated. The adiabatic condition on the lateral sides of the specimens was assumed. Because of the temperature field modification induced by the thermocouple sheath, the conduction problem was reformulated in three dimensions. It was then approached within a steady state IHCP solution procedure to estimate the equivalent thermal conductivity of the intumescent layer.

Even if is expected that the temperature across the intumescent layer varies by several hundreds of Kelvin, the corresponding equivalent thermal conductivity of the expanded intumescent char was assumed to be constant [24]. The optimal value of the unknown parameter then result from the minimization of the following target function[25]:

$$F(\lambda_{eq}) = \sum_{i=1}^{n} \left[ T_{exp} - T_{sim}(\lambda_{eq}) \right]^2$$

Where $T_{sim}$ and $T_{exp}$ are the simulated and experimental temperature, respectively of the three thermocouples placed within the intumescent.

3. Experimental results

The experimental tests under the heat flux of a cone calorimeter was continued until the steel plate temperature reached the value of 600°C that represents the steel critical temperature which was
reached in approximately 6000 s (for both specimens). The thermal trend of steel plate, $T_s$, is shown in figure 5.

![Figure 5. Steel plate temperature histories.](image)

Many researchers measured the histories of the substrate temperature (figure 5) [16, 26-29] to check the protective performance of an intumescent coating. The heating process of the substrate can be divided into three stages [30,31]: preheat, tumescent, and post-tumescent phases. Before the substrate temperature reaches the temperature of intumescence, the heat transfer mode within the coating is dominated by conduction and the heating process is called the preheat phase. The temperatures of the virgin coating and the substrate increase quickly in this stage. When the temperature of intumescence is approached, the rise of the substrate temperature slows because of the energy consumption of the intumescent reaction. The intumescent reaction usually occurs over a temperature range, and the heating process during this stage is called the tumescent phase. At the end of the intumescent reaction, the substrates and the char temperatures rise rapidly again, and this stage is referred to as the post-tumescent phase. Thus, the temperature curve of the substrate at the tumescent phase looks like a bending curve; this kind of bending evidence is one of the characteristics of intumescent coatings.

The decrease of the heating velocity even after the completion of intumescence is due to the increase of the heat loss, $q_d$, as the steel plate temperature increases. The heat lost through the back face of the specimen, $q_d$, was calculated by equation (2); a literature value for calcium silicate thermal conductivity $\lambda_c$, was assumed.

For all specimens, the components, $q_s$ and $q_d$, of total heat flux, $q$, that reaches the intumescent are shown in figures 6 and 7.
Figure 6. Heat fluxes for sample S08.

Figure 7. Heat fluxes for sample S10.

Figure 6 and 7 show that \( q \) goes to a nearly constant value. To the aim of the present investigation, the steady state condition was assumed to be reached when the percent variation of \( q \) was lower than 5%. The assumption of negligible heat losses in the experimental test aimed to the estimation of the equivalent thermal conductivity is a fundamental hypothesis of many researchers, i.e., in , Anderson et al. [16], Mesquita et al. [15]. Disregarding the heat losses in the energy balance equation of the steel plate (equation (2)) may result in an underestimation of the heat flux through the foam layer and, as a consequence, it may result in a lower value of the equivalent thermal conductivity.

The temperature time response by thermocouples \( T1, T2 \) and \( T3 \) is shown in figures 8 and 9, for specimens S08 and S10, respectively.

Figure 8. Temperature detected by thermocouples \( T1, T2, T3 \) during the intumescence process for sample S08.

Figure 9. Temperature detected by thermocouples \( T1, T2, T3 \) during the intumescence process for sample S10.

The maximum value of temperature is reached when the intumescent layer incorporates the thermocouple, which previously is directly exposed to the heat flux emitted by the cone calorimeter apparatus.

4. Equivalent thermal conductivity estimation

The direct problem as schematized in figure 3 was solved by the numerical finite elements method, implemented inside the Comsol Multiphysics environment. The minimization of the target function (equation (5)) was performed through the Matlab Optimization Toolbox® by using as stopping criterion a relative tolerance on object function lower than \( 1 \times 10^{-4} \). The Nelder-Mead algorithm was
adopted in the minimization process. The results, in terms of equivalent thermal conductivity, obtained for the two specimens are shown in figure 10, as a function of the average temperature recorded by thermocouples installed inside the intumescent. To identify the main contributions to the uncertainty of the estimated heat flux distribution, the influence coefficient values were calculated:

$$J_{x_i}^{\lambda_{eq}} = \left( \frac{\partial \lambda_{eq}}{\partial x_i} \cdot \varepsilon_{x_i} \right)^2$$  \hspace{1cm} (6)

where $\lambda_{eq}$ is the estimated quantity and $x_i$ is the considered input parameter with an uncertainty equal to $\varepsilon_{x_i}$. For the inverse problem investigated in this work, the partial derivative present in equation (6) are calculated by a finite difference approach:

$$\frac{\partial \lambda_{eq}}{\partial x_i} = \frac{\lambda_{eq}(x_i + \Delta x_i) - \lambda_{eq}(x_i)}{\Delta x_i}$$  \hspace{1cm} (7)

Where $\Delta x_i$ is a small variation of the input parameter $x_i$. The uncertainty on the unknown parameter was estimated with the equation (8).

$$E_{\lambda} = \sum_{i=1}^{n} \left( \frac{\partial \lambda_{eq}}{\partial x_i} \cdot \varepsilon_{x_i} \right)^2$$  \hspace{1cm} (8)

The overall percent uncertainty is $E_{\lambda} \% = 12.19\%$, as reported in figure (10).

As expected, the data show that the increase of temperature of intumescence produces the increase of the equivalent thermal conductivity. Regarding the effect of the initial paint thickness, the results presented in figure 10 show a systematically higher equivalent thermal conductivity for specimen S08. However, this behavior might be due to the above reported dependence on temperature. 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
This paper, starting from the results presented by Calabrese et al. [3], proposes an improved approach for estimating the equivalent thermal conductivity of the char layer generated by the intumescence process. Experimental results were obtained through two specimens, with different initial paint thickness. The methodology is based on the solution of the inverse heat conduction problem within the system under the least-square method with temperature measured in three different locations of the intumescent layer as inputs known data.

The results confirm the conclusion of Calabrese et al. [3]: the equivalent thermal conductivity depends on the temperature, while paint initial thickness, for the experimental condition here investigated, does not seem to have great importance.

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