THERMAL BEHAVIOR AND TOXIC EMISSIONS OF FLAME RETARDED TIMBER IN CONE CALORIMETER TESTS

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ABSTRACT

The thermal behavior and toxic emissions of timber products common in industrial buildings in Northern Greece treated or not with flame retardants are investigated. Eight species of wood treated or not with three typical intumescent flame retardants were subjected to constant incident heat fluxes of 35, 50, 65 and 80 kW/m² in a cone calorimeter linked to the FTIR analyzer. The test results presented in this paper cover the following characteristics: (i) time to ignition, (ii) heat release rate (HRR), (iii) average (300 s) HRR, (iv) effective heat of combustion (MJ/kg), (v) smoke production and (vi) toxic species emissions. The main findings of the experimental analysis are that under the influence of the flame retardants: there was either 'no ignition' of the samples or a considerable ignition delay (at lower irradiances) compared with untreated samples. Thermal emissions significantly decrease in terms of the values of 'peak HRR' and 'First 300 s Mean HRR' (by a factor varied from 2 to 5 up to type flame retardant used). In the cases of flame retarded samples, where there was 'no ignition' or a considerable ignition delay of the samples there were similar or less toxic emissions compared with the bare samples. NH_3 was an exception, since both flame retardants contained ammonium in their chemical composition, which was released during the intumescent action of the samples.

Based on the results of this study, the application of intumescent flame retardants on wooden surfaces is proposed for the cases where 'no ignition' or considerable ignition delay occurred. This could be a safe and cost effective approach in reducing fire losses in industrial buildings.

Keywords: cone calorimeter, emissions, flame retardant, heat release rate, ignition, intumescent, wood.

1 INTRODUCTION

Wood has many good properties as a material. It is heavily used for construction and building because of its ease of processing, physical and mechanical properties, esthetic, environmental and health aspects [1–3]. Wood is also used in many applications for purposes such as surface lining material, furniture, flooring, roof, shelves, pallets, wooden scaffolding for both offshore and onshore, and packing cases [1, 4, 5]. All these surfaces may add significantly to the fire loading of a compartment, aid the spread of flame and advance the onset of flashover. For these reasons, various national and international building material regulations seek to control the use of wall and ceiling linings on the basis of the performance of such materials in standardized tests, measuring, for example, the speed of surface spread of flame [6]. The materials are classified in terms of their rate and distance of flame spread over their surface. The classification groups range from 0 to 4, class 0 – non-combustibles or materials of a suitably low surface flame spread to meet the class criteria, whereas class 4 is all materials with a surface flame spread greater than the criteria required to meet classes 0–3 [7]. Wood is normally classified as a class 3, sometimes a class 4 material. Generally, the requirement for a material, so that it can be used as a surface lining material for walls and ceilings, is class 0–1, therefore wood would be unsuitable to be used as a surface lining and if used, it would significantly add to the fire. The above clearly signals the importance of controlling the ignition resistance, and flammability of timber as used in different forms in various constructions. So, it is possible to increase the fire performance of wood, with the application of flame retardants. With the addition of a flame retardant such as an impregnation treatment and surface coatings (possibly intumescent), the classification group of wood can be raised to

class 1. Building Regulations class 0 can be achieved through the application of both types of flame retardants. Thus, it may be possible to use wood as a surface lining material, if it is treated correctly.

There has been a significant but limited amount of work looking at flame retardants for wooden surfaces. Previous research has shown that flame retardants applied to wood have had a positive effect on the burning behavior of wood, in terms of ignition and the most important variable to describe fire hazard the heat release rate (HRR) [8–10]. In the present work, the effect of three typical intumescent flame retardants (latest technology) on representative types of timber in a cone calorimeter with online effluent gas analysis equipment Fourier transform infrared (FTIR). Analysis involved thermal behavior, smoke production and toxic species analysis of the samples.

2 EXPERIMENTAL

The apparatus used was a standard cone calorimeter manufactured in accordance to ISO 5660 (1993) and ASTM E1354 (1992) supplied by Fire Testing Technology Ltd. The tests were carried out in accordance with the test procedure of ISO 5660 except in regards to the time at which the test was terminated. All tests were carried out in the horizontal orientation at heat fluxes of 35, 50, 65 and 80 kW/m^2. An edge frame was used in accordance with the standard resulting in a specimen surface area of 0.0088 m^2 exposed to the radiant source. The instrument was calibrated at the start of each day. The cabinet door was kept closed for the duration of the test to ensure that drafts from the surroundings did not affect results.

A TEMET GASMET CR-Series portable FTIR analyzer was connected to the cone calorimeter to experiment with virgin samples that were chosen to be painted with flame retardants and for all flame retarded samples at 35, 50, 65 kW/m^2. This has a multi-pass, gold-coated sample cell with a 2 m path length and volume of 0.22 L. A liquid nitrogen cooled MCT detector was used that scans 10 spectra per second and several scans are used to produce a time-averaged spectrum. For fire research that develops slowly over several minutes, an overall response time of 5 s was used and this was more than adequate to resolve the time dependent toxic gas production in the present fires which lasted for typically 10 min. The instrument was calibrated by the manufacturers (using reference gas concentrations) for all the significant species that were present in the sample. The only calibration necessary prior to the test was to zero the instrument on nitrogen. The calibration was checked for some gases, CO, CO_2, benzene and methane using certified span gases and the agreement was satisfactory.

2.1 Sample preparation

Substrates were 100 mm square and thickness varied from 19 to 22 mm and were supplied from a local timber merchant. All specimens for test were prepared in advance and allowed to 'temper' at room temperature and ambient humidity for a minimum of 24 h. Time duration of each test was in general 600 s, although, in some flame retardant samples, the duration was extended up to 1,000 s, depending on the thermal behavior of the specimen. The reason for that is that present work is interested in examining the development of fires on wooden samples painted or not with fire-retardant paints during the early stage of fire development, and for a period of time up to 10 min, which, in real fire conditions, covers the time needed for the evacuation of the industrial plant by its staff, the potential intervention of the fire-safety staff of the plant, and the arrival of the fire department to extinguish the fire [1, 5].

Three types of wood flame retardants were used to represent main classes of commercial products, i.e. water-based paint, solvent-based paint, and varnish water-based flame retardant. This selection of flame retardant was based on its chemical composition, since each one represents a large homogeneous class of products, and also on the applications for which each one has been designed. It should be emphasized, that the objective was not to determine or use the best product in the market, but to establish general patterns of behavior of timber with or without flame retardant. In particular, the following were chosen:

- 'Zero Flame', which is an intumescent water-based fire-retarding paint, copolymer dispersion. Its specific gravity is 1.31 g/cm^3. Its recommended application is done at a coverage rate of 3.7 m^2/L to achieve a dry film thickness of 230 μm in two coats. Due to its chemical composition – water-based – it is suitable for interior wooden surfaces, i.e. softwood, plywood, MDF, etc.
- 'Synto Flame', is a solvent-based intumescent flame-retarding paint. It is a thixotropic material of acryl-copolymer base. Its specific gravity is 1.4 g/cm^3. Its recommended application is done at a covering rate of 3 m^2/L to achieve a dry film thickness of 270 μm in two coats. Due to the fact that this is an acrylic-based paint, it is durable, and its application is recommended both on interior and exterior wooden surfaces.
- 'Varnish Zero Flame' consists of a two-pack waterborne base coat and spirit-based finish coat. According to information about the product's composition component A, which constitute the base, contains: formaldehyde (<1%), propanol-2-ol (1.0–5.0%), methanol (<2). Its specific gravity is about 1.21 g/cm^3 .Component B is the activator, and, according to the composition information of the product contained on the safety data sheet, it contains: phosphoric acid ester at a concentration of 70–80%. Its specific gravity is about 1.42 g/cm^3. 'The clear finish', according to the composition information shown on the safety data sheet, contains: isoparafinic hydrocarbon at a concentration of 60–70%. Its specific gravity is 0.820 g/cm^3. Its recommended application is done at a covering rate of 6.9 m^2/L of dry varnish, and 9.8 m^2/L of dry clear finish. In all cases, the average application rate was ~100 ± 4.5% of the recommended.

2.2 Experimental fires configuration

The selection of the heat flux is a very important factor when undertaking cone calorimeter tests [6, 9, 11]. The current tests were carried out at heat fluxes of 35, 50, 65, 80 kW/m^2, to represent a possible range of heat fluxes to be encountered in a developing industrial fire.

The aim was to examine all bare, flame retarded samples in the same radiation in order to be able to compare them. Fewer tests have been performed at 80 kW/m^2 because of technical difficulties which did not allow to perform further experiments at such a large value of irradiance. Based on the above, eight species of wood which constitute common applications in different forms, i.e. floor, ceiling, shelves, pallets, packing cases, scaffolding, furniture, etc., were chosen for experimental investigation [1, 5]. In total, 90 tests (Table 1) have been performed at various irradiances, in order to determine various flammability characteristics of a range of virgin wood species.

Five typical types of wood, i.e. pine, MDF, chipboard faced by maple, MDF faced by maple, blockboard were chosen as representative from those used in virgin form, for painting with the typical types of flame retardants that mentioned above (Table 2). Chipboard was not tested experimentally painted with flame retardants, since its experimental processing as bare

Table 1: Virgin sample tests.

Virgin samples	Heat flux	No. of tests
Chipboard	35, 50, 65, 80 kW/m^2	12 tests
MDF	35, 50, 65, 80 kW/m^2	12 tests
Chipboard covered by maple (2–3 mm)	35, 50, 65 kW/m^2	9 tests
MDF covered by maple (2–3 mm)	35, 50, 65, 80 kW/m^2	12 tests
Chipboard covered by melamine (2–3 mm)	35, 50, 65, 80 kW/m^2	12 tests
MDF covered by melamine (2–3 mm)	35, 50, 65 kW/m^2	9 tests
European pine	35, 50, 65, 80 kW/m^2	12 tests
Blockboard	35, 50, 65, 80 k W/m^2	12 tests
Total virgin tests		*90 tests*

Table 2: Wood flame retarded tests.

Sample	Heat flux	Application	No. of tests
MDF 'Zero Flame' retarded	35, 50, 65, 80 kW/m^2	'Zero Flame' paint (2 coats)	12 tests
MDF 'Synto Flame' retarded	35, 50, 65 kW/m^2	'Synto Flame' paint (2 coats)	9 tests
Pine 'Zero Flame' retarded	35, 50, 65 kW/m^2	'Zero Flame' paint (2 coats)	9 tests
Pine 'Synto Flame' retarded	35, 50, 65, 80 kW/m^2	'Synto Flame' paint (2 coats)	12 tests
Blockboard 'Zero Flame' retarded	35, 50, 65, 80 kW/m^2	'Zero Flame' paint (2 coats)	12 tests
Blockboard 'Synto Flame' retarded	35, 50, 65 kW/m^2	'Synto Flame' paint (2 coats)	9 tests
Chipboard faced by maple 'Zero Flame Varnish' retarded	35, 50, 65 kW/m^2	One coat 'Zero Flame Varnish'+ one coat clear finish	9 tests
MDF faced by maple 'Zero Flame Varnish' retarded	35, 50, 65 kW/m^2	One coat 'Zero Flame Varnish' + one coat clear finish	9 tests
Total flame retarded tests			*81 tests*

wood showed that their behavior is not particularly different, comparing with the other wood type of similar morphology and composition, i.e. MDF. As for MDF faced by melamine and chipboard faced by melamine, they do not allow any painting, but are rather applied in their current form. Varnished timber tests were simple performed for general comparison purposes, since they do not constitute the main object of this research work. Two types of timber, mostly used in the industrial buildings in Northern Greece, i.e. pine and MDF, were chosen

for painting with varnish and for experimental examination at 35, 50, and 65 kW/m^2, so as to be able to compare them with bare and flame retarded samples.

The abbreviations are: cb 'chipboard', cb/maple 'chipboard covered by maple', cb/melamine 'chipboard covered by melamine', MDF/maple 'MDF covered by maple', MDF/melamine 'MDF covered by melamine', Bb 'Blockboard', ZF 'Zero Flame', SF 'Synto Flame', ZFV 'Zero Flame Varnish', V 'varnish'.

FTIR analyzer was connected to the cone calorimeter for only virgin samples that were chosen to be painted with flame retardants and varnish plus MDF faced by melamine and for all flame retarded samples (Table 2), at 35, 50, 65 kW/m^2. The main reason that the above samples has been chosen is to assess the concentration of toxic gasses in fires of typical wooden samples, treated or not with typical kinds of flame retardants, and finally to evaluate the overall toxicity of different kinds of fire-treated or untreated wooden samples.

2.3 Thermal behavior – experimental results

Fire development results cover: (i) time to ignition(s), (ii) HRR (kW/m^2), (iii) average (300 s) HRR, and (iv) effective heat of combustion (MJ/kg). All tests were fairly repeatable in terms of the tig and HRR values, i.e. 2–4% std. dev. (expresses the standard deviation as a percentage of the average value). Experimental results represent the mean of a minimum of three tests. 'No significant' differences were observed in thermal behavior of untreated samples (tig, HRR, MLR) [1, 5]. Some slightly lower HRR peak values (kW/m^2) were noted for homogeneous (pine) compared with composite in nature samples (e.g. MDF, chipboard). At low irradiance (i.e. 35 kW/m^2), facing types of timber, e.g. MDF, Cb, with melamine or maple increases significantly the ignition resistance of MDF and Cb by a factor of 1.5–2, due to the flame-retarding properties of melamine and maple [1, 5].
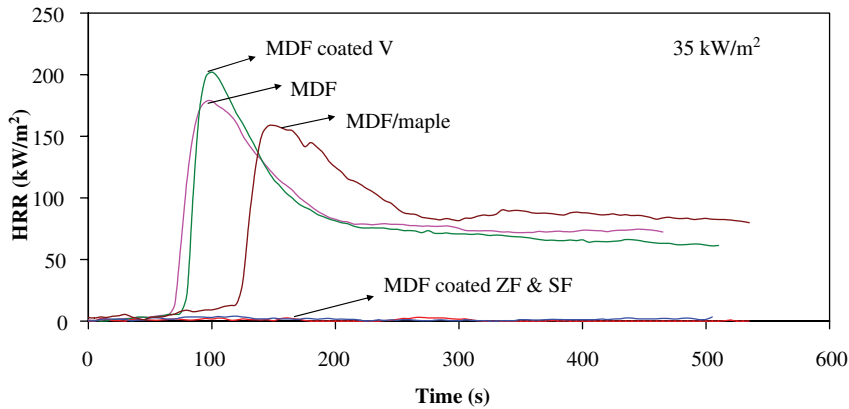
In all flame treated samples, the intumescent paint or varnish swell into thick, robust foam upon exposure to heat, thus protecting the underlying material from fire by providing a physical barrier to heat and mass transfer. First of all, in all cases, the irradiance of 35 kW/m^2 did not lead to ignition. At 50 kW/m^2 irradiance, some of the samples ignited, particularly those that had been painted with the solvent-based (Synto Flame) retardant. In all cases, the ignition delay was very long compared with bare wood data, and this suggests that the ignition process is dominated by the flame retardant coating behavior rather than the substrate. At 65 kW/m^2, all samples ignited, however, at remarkably longer ignition times than those observed in the corresponding virgin wood samples, at the same irradiance. At this irradiance levels, a direct comparison of the effect of the three flame retardants used in this work is possible and this is done in Table 3. The comparison is achieved by defining an ignition resistance factor (IRF):

$$\text{IRF} = \frac{t_{\text{ign}} \text{ Coated Sample}}{t_{\text{ign}} \text{ Bare Sample}}, \tag{1}$$

It can be seen that 'Synto Flame' paint increased tig by a factor of 2–5 depending on the substrate, whereas 'Zero Flame' paint caused an increase of ignition delay by factor 17–32. In other words 'Zero Flame' was significantly more effective in delaying ignition than 'Synto Flame' – 4–10 times more effective. The above variations may be attributed to the different basic chemical composition of the two flame retardants, i.e. the 'Zero Flame' paint is latest-generation water-based, whereas the 'Synto Flame' paint is a solvent-based flame retardant. This means that the solvent which is organic-based impregnates the substrate causing earlier ignition. Table 3 also lists the IRF for 'Zero Flame Varnish' and it is evident that this was not

Table 3: Comparative effects in t_{ign} of flame retardant coatings at 65 kW/m².

Substrate	IRF 'Zero Flame' paint	Substrate	IRF 'Synto Flame' paint	Substrate	IRF 'Zero Flame Varnish'
MDF	21	MDF	2	Chipboard/ maple	15
Pine	32	Pine	5	MDF/maple	20
Blockboard	17	Blockboard	4		

Figure 1: HRR (kW/m²) versus time for MDF, varnished MDF, MDF faced by maple, 'Zero Flame' retardant MDF, 'Synto Flame' retardant MDF at 35 kW/m².

as high as the 'Zero Flame' paint. This may be attributed to the additional organic volatile content of the varnish. Fewer tests were performed at 80 kW/m², because of the technical difficulties that occurred. At this irradiance as well, ignition was observed in all tested samples, with a significant reduction in the ignition delay. Figures 1–3 compare HRR for treated and untreated samples of MDF at 35, 50 and 65 kW/m². As we have seen in the previous, at 35 kW/m² irradiances, there is 'no ignition' in any of the flame retardant coated samples. This is reflected in the HRR for 'MDF ZF and SF' in Fig. 1.

At 50 kW/m² irradiances (see Fig. 2), in the cases where there was still 'no ignition', i.e. 'MDF ZF' paint retarded samples, the HRR curves now show some activity with an irregular fluctuation of values from 7 to 18 kW/m².

In the cases where there is ignition (at 65 kW/m²): (i) for the 'Synto Flame'-retarded samples, the HRR curves are formed with a relatively 'simple' shape with a peak and decreasing period once the peak is formed. This is due to the fact that in the case of 'Synto Flame' retarded samples, the intumescent foam 'cracks' more sufficiently so as to allow the formation of a more 'structured' shape of flame, (ii) for the 'Zero Flame' retarded samples, the HRR curves are formed with continuous small fluctuations of values, which form multiple small peaks, i.e. without any of them being absolutely 'distinguishable'.

This is due to the fact that in the case of 'Zero Flame' samples, the intumescent char cracks marginally thus allowing the formation of only thin flamelets scattered on the sample's surface, as it can be seen in Fig. 4.
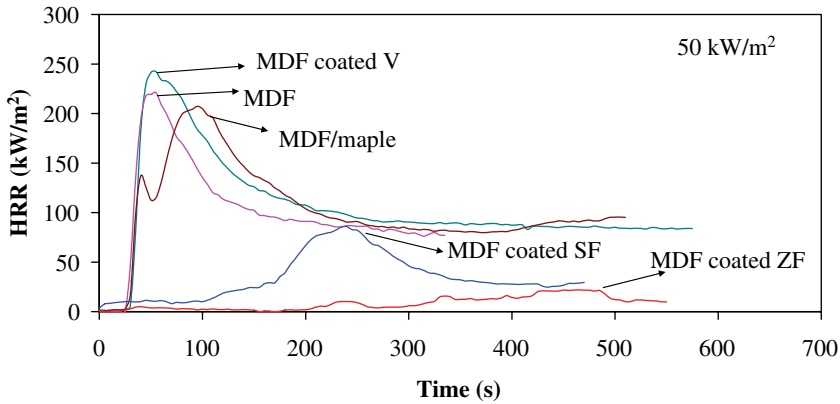
Figure 2: HRR (kW/m^2) versus time for MDF, varnished MDF, MDF faced by maple, 'Zero Flame' retarded MDF, 'Synto Flame' retardant MDF at 50 kW/m^2.
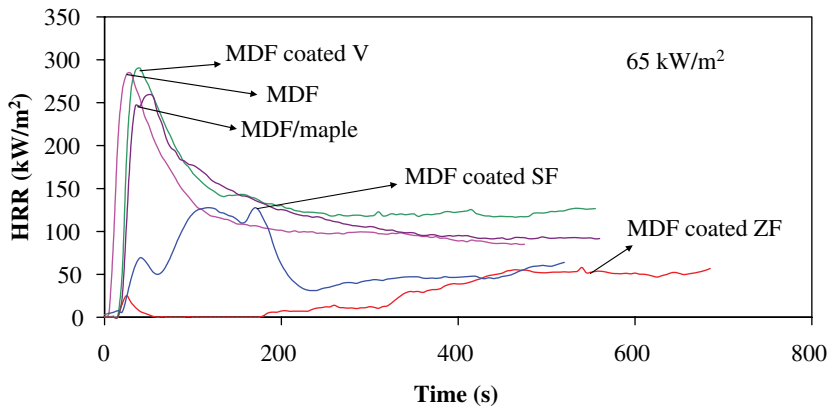

Figure 3: HRR (kW/m^2) versus time for MDF, varnished MDF, MDF faced by maple, 'Zero Flame' retarded MDF, 'Synto Flame' retardant MDF at 65 kW/m^2.

Figure 4: 'Zero Flame' treated MDF exposed at heat flux 65 kW/m^2.

At 80 kW/m^2, fewer experiments were performed for the reasons mentioned above. In these cases, the HRR was much higher than at lower irradiances, indicative a fully established flame in agreement with the observation. These tends with MDF were representative of the general qualitative behavior also shown by the other types of Timber, i.e. pine, blockboard.

2.3.1 Peak HRRs

As shown in Fig. 5, the peak HRR values increase with increasing in irradiance.

As previously discussed at 35 kW/m^2 there was 'no ignition' and 'no distinguishable' peak HRR for any of the flame retarded samples. This was the case for the 'Zero Flame' coated samples at 50 kW/m^2 as well. The peak HRR values reported in Fig. 5 for these samples is the greatest value measured (although it did not necessarily formed as a well-defined 'peak'). For the 'Synto Flame' and 'Zero Flame Varnish' retarded samples (at 50 kW/m^2), peak values were higher, ranging from 50 to 80 kW/m^2. Thus, at 50 kW/m^2 irradiance, the type of flame-retardant coating played a more important part in the formation of the peak HRR than the physical properties of substrate. At 65 kW/m^2, all samples were ignited as mentioned before. Looking at the peak HRR values in Fig. 5 it is evident that 'Zero Flame' was much more effective than 'Synto Flame' in reducing the peak HRR values with reference to the bare wood data. At this irradiance levels, a direct comparison of the effect of the three flame retardant used in this work is possible and this is done in Table 4. The comparison is achieved by defining a 'peak HRR reduction factor' (PHRR RF),

$$\text{PHRR RF} = \frac{\text{PHRR Coated Sample}}{\text{PHRR Bare Sample}}, \qquad (2)$$

It can be seen that 'Synto Flame paint' and 'Zero Flame varnish' reduced peak HRR by a factor of 2, whereas 'Zero Flame paint' by a factor of 4–5. This may be attributed to the different chemical composition of flame retardants as mentioned before. At 80 kW/m^2, there was a smaller number of tests; in any case, even at this irradiance, the peak values are noticeably lower than the peak values of the relevant virgin samples at the same irradiances (see Fig. 5).

Existing published data on the fire resistance of intumescent coated wood are limited and inconclusive. This is explained by the fact that intumescent coating is a relevant technology in wood flame retardancy. However, important research works are found. Wladyka-Przydylak and Kozlowski [12] measured, using a cone calorimeter, thermal characteristics of uncoated
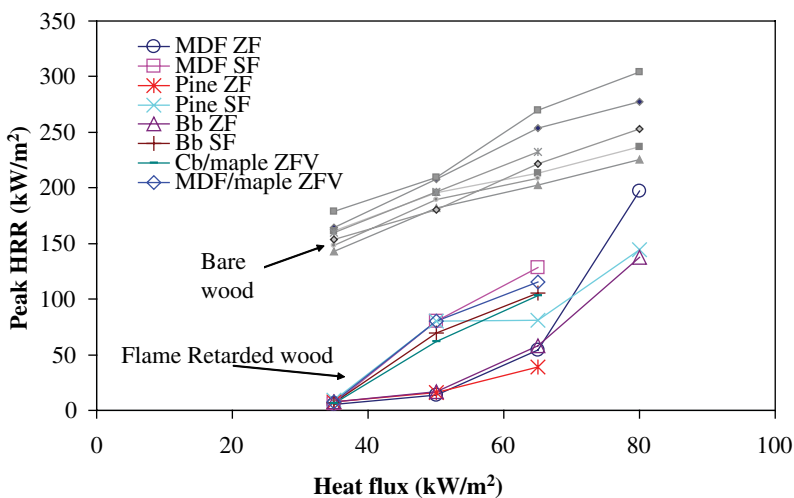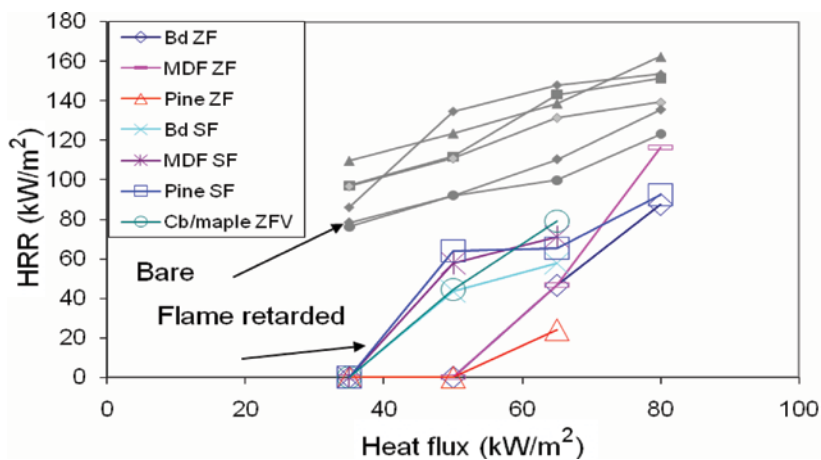

Figure 5: Peak HRR (kW/m^2) for various flame retarded samples.

Table 4: Comparative effects in peak HRR of flame-retardant coatings at 65 kW/m^2.

Substrate	PHRR RF 'Zero Flame' Paint	Substrate	PHRR RF 'Synto Flame' paint	Substrate	PHRR RF 'Zero Flame' varnish
MDF	0.2	MDF	0.5	Chipboard faced by maple	0.5
Pine	0.25	Pine	0.5	MDF faced by maple	0.5
Blockboard	0.25	Block board	0.5		

Figure 6: Average 300 s HRR (kW/m^2) versus heat flux (kW/m^2) for various flame retarded samples.

wood and coated with different flame retardants at 35 kW/m^2 in a horizontal orientation. They found that the presence of monoammonium phosphate resulted in a considerable delay in the ignition of the coatings. Uncoated wood ignited after 41 s, whereas wood coated with amino-phosphate resins ignited only after 575 and 788 s. In addition, their results indicate that coated with amino resins supplemented by monoammonium phosphate and dextrin did not ignite during entire measurement, i.e. for 30 min. These results are directly comparable with the present work with similar findings. Birgit *et al*. [3] compared 14 fire retardant treated and 13 untreated wooden products, using a cone calorimeter at 50 kW/m^2. The chemical composition of flame retardants used was not known. The values of rate of heat release were much lower for fire retardant treated than for the untreated wood-based products. Some of examined flame retarded samples had a long ignition delay with times to ignition up to 10 min and no ignition at all observed for two products. For most products, there were no HRR peaks and for others there is only one peak in agreement with the present observation.

2.3.2 Heat release rate averaged over first 300 s
Figure 6 shows the mean HRR taken over the first 300 s after observation sustained ignition for the flame retarded wooden samples. In the cases where there is 'no ignition' at 35 kW/m^2

and in some cases at 50 kW/m^2 average values are 0. HRR 300 s increases as irradiance increasing. Lower values are for 'Zero Flame' retarded (water-based) and more homogeneous samples (pine) for the reason mentioned above.

Another direct comparison of the effect of a flame retardant is achieved by defining 'First 300 s Mean HRR Ratio' (see Fig. 7),

$$\text{First 300 s Mean HRR R} = \frac{300 \text{ s Mean HRR Coated Samples}}{300 \text{ s Mean HRR Bare Samples}}, \qquad (3)$$

2.3.3 Effective heat of combustion

Average values of EHC determined for a duration of 300 s after ignition for virgin and flame retarded samples (see Fig. 8).

EHC values of virgin samples are independent of heat flux demonstrating that the EHC is an intrinsic material property. This is in agreement with the work by McCready [11]. In case
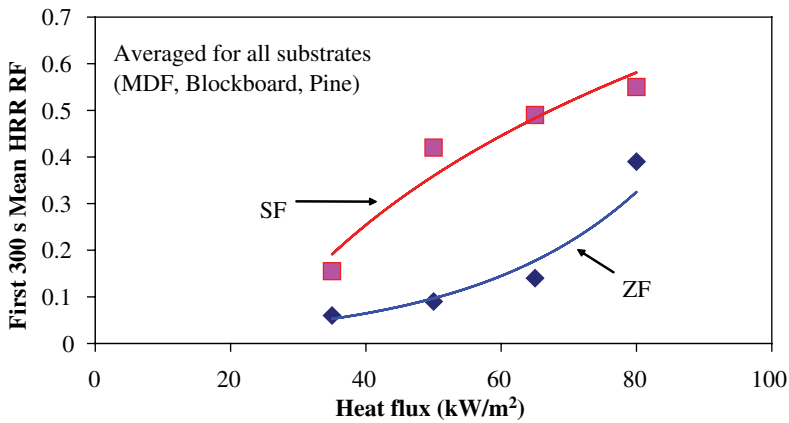

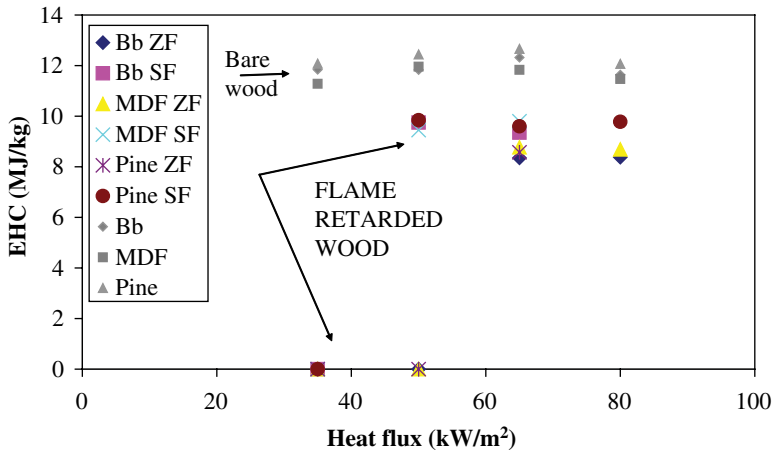Figure 7: Comparative effects in First 300 s Mean HRR of flame retardant coatings.

Figure 8: Average EHC over 300 s after ignition – the grayed out are from uncoated samples.

of flame retardant samples at 35 kW/m^2 as seen before there is no ignition, thus, there is no average value determined. In the other examined irradiances, average of EHC values were only depended by the type of flame retardant used. Thus lower values measured for 'Zero Flame' than 'Synto Flame' samples and this may be attributed to their different chemical composition.

2.4 Emissions – experimental results

2.4.1 Smoke production
In this section, we present the findings from the cone calorimeter tests using different types of wood: (i) untreated or (ii) treated with three types of market representative flame retardant coatings or (iii) coated with a common varnish. To compare the smoke production of the samples, the smoke extinction coefficient (Ks) was used which is a measure of the attenuation of light by the smoke [5, 11]. All samples produced only one initial peak, which formed faster in flame retardant-treated samples and was lower in the case of 'Zero Flame' than all the other samples. Despite 'no ignition' of the flame retardant-treated samples at 35 kW/m^2 they did produce smoke concentrations as a result of the chemical reactions that activated the flame retardant coating and liberated gaseous products of mainly ester decomposition [12]. These values are higher for 'Synto Flame' and longer period. A direct comparison of the effect of the two flame retardant used in this work is given in Table 5. The comparison is achieved by defining a 'peak smoke extinction coefficient ratio' (PSECR),

$$PSECR = \frac{PSEC \ Coated \ Sample}{PSEC \ B \ are \ Sample}, \tag{4}$$

Values below unity are seen only in the cases of 'Zero Flame' at 35 and 50 kW/m^2 where there is 'no ignition'. This means that only in these cases peak values are less than corresponding virgin samples by a factor ranging from 0.4 to 0.9. In all cases, PSECR values are higher for 'Synto Flame' than 'Zero Flame' samples. This may be attributed in their different chemical composition as discussed earlier.

1.1.1 Toxicity
In this section, we present the findings from the cone calorimeter/FTIR tests using virgin samples that were chosen to be painted with flame retardants and varnish plus MDF faced by melamine and for all flame retarded samples.

Table 5: Comparative effects in peak smoke extinction coefficient of flame retardant coatings at 35, 50, 65 kW/m^2.

Substrate	35 kW/m^2		50 kW/m^2		65 kW/m^2	
	PSECR 'Zero Flame'	PSECR 'Synto Flame'	PSECR 'Zero Flame'	PSECR 'Synto Flame'	PSECR 'Zero Flame'	PSECR 'Synto Flame'
MDF	0.4	1.4	0.5	1.5	1.2	2
Pine	0.5	1.5	0.9	2.5	1.8	2.5
Blockboard	0.4	1.5	0.8	2	1.1	2.3

2.4.2.1 CO emissions. Figures 9–11 compare CO emissions (ppm) of treated and untreated samples of MDF at various irradiance levels. Looking at the MDF CO emissions data, the following general comments can be made. Bare and varnish coated MDF samples gave a peak CO of amount 60–90 ppm and this did not change significantly with increasing incident heat flux. In the presence of flame retardants, the CO emissions were strongly dependent on whether or not the sample ignited. Where 'no ignition' was achieved (i.e. for both flame retardants at 35 kW/m^2 and for 'Zero Flame' at 50 kW/m^2) the CO emissions maximum levels were approximately half of those of bare MDF.

However, when the flame retarded samples were ignited, the CO emissions were more than doubled (compared with the Bare MDF) results and moreover they appeared to increase with
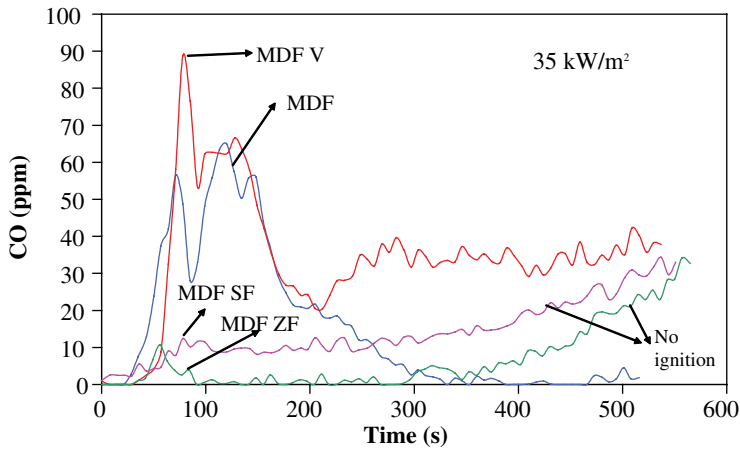

Figure 9: CO emissions (ppm) versus time for MDF, varnished MDF, 'Zero Flame' retarded MDF, 'Synto Flame' retarded MDF at 35 kW/m^2.
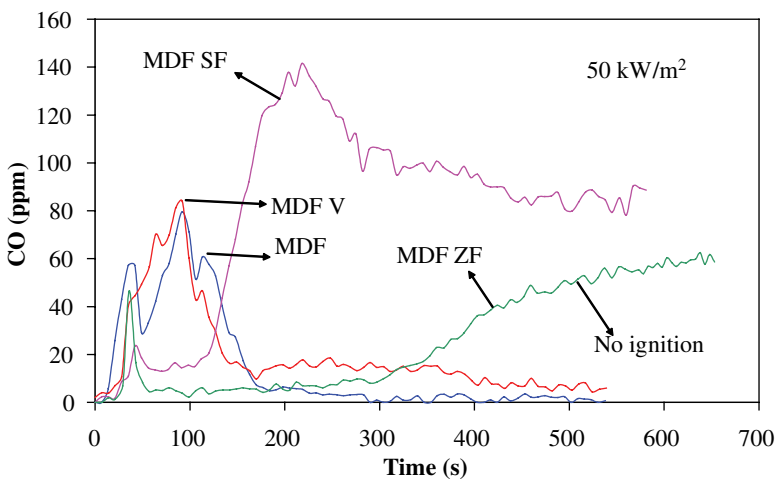

Figure 10: CO emissions (ppm) versus time for MDF, varnished MDF, 'Zero Flame' retarded MDF, 'Synto Flame' retarded MDF at 50 kW/m^2.
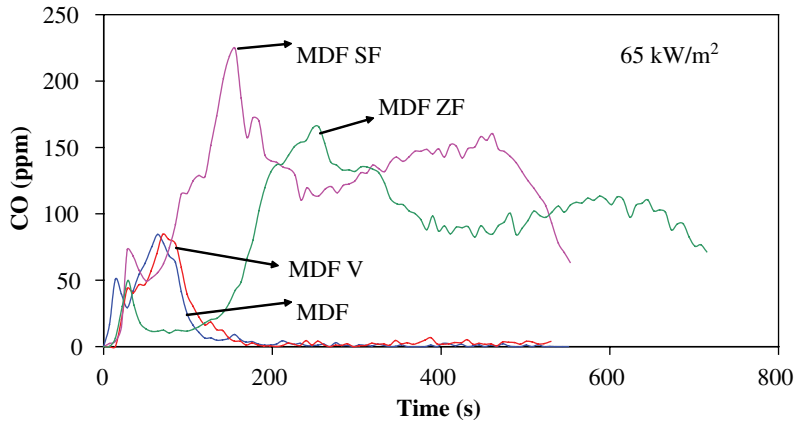
Figure 11: CO emissions (ppm) versus time for MDF, varnished MDF, 'Zero Flame' retarded MDF, 'Synto Flame' retarded MDF at 65 kW/m^2.

higher heat fluxes (see Figs 10 and 11). Similar behavior occurred for the other kinds of timber that have been tested. This behavior is further compared and quantified below (Table 6).

The peak CO emission values tended to increase as irradiance increased (see Fig. 12) for various treated samples and this attributes to more involvement of flame retardant in the combustion process as irradiance increases. At 35 and 50 kW/m^2 irradiance levels, where 'no ignition' occurred, the peak values were <80 ppm. Highest peak (at 50 kW/m^2) values were measured for 'Zero Flame Varnish' and 'Synto Flame' retarded samples, with flaming combustion. Nevertheless, the measured emissions levels are insignificant, at <200 ppm (15 min exposure limit COSHH) [13]. At 65 kW/m^2, the peak CO emission values were further increased for all flame-retarded treated samples. In all these cases (at this heat flux), both the flame retardant paint and the substrate were seen to be more involved in the combustion process. Peak values of CO (ppm) over 200 ppm were generally observed at 65 kW/m^2 for all composite-in-nature 'Zero Flame Varnish' and 'Synto Flame' retarded samples. That is, varnish- and solvent-based products seem to result in less complete combustion than the water-based retardants. Smaller CO emissions values are observed again with the pine samples.

Figure 12 compares peak CO emissions (ppm) for various flame retarded wooden samples.

A direct comparison of the effect of the two flame retardant types used in this work is given in Table 6. The comparison is achieved by defining a 'peak CO emission coefficient ratio' (PCOR),

$$\text{PCOR} = \frac{\text{PCO Coated Sample}}{\text{PCO Bare Sample}}, \tag{5}$$

This ratio takes values below unity in all cases where there is 'no ignition' of the flame retardant-treated samples. This means that, in these cases, peak CO emission (ppm) values are less than or equal to the corresponding emissions of the virgin samples. In the cases where flaming combustion occurred, the flame retardant-treated samples increased peak CO emissions by a factor of 1.5–2.9. Highest values were measured for the 'Synto Flame' samples, for the reasons mentioned before.

Table 6: Comparative effects in peak CO emissions (ppm) of flame retardant coatings at 35, 50, 65 kW/m².

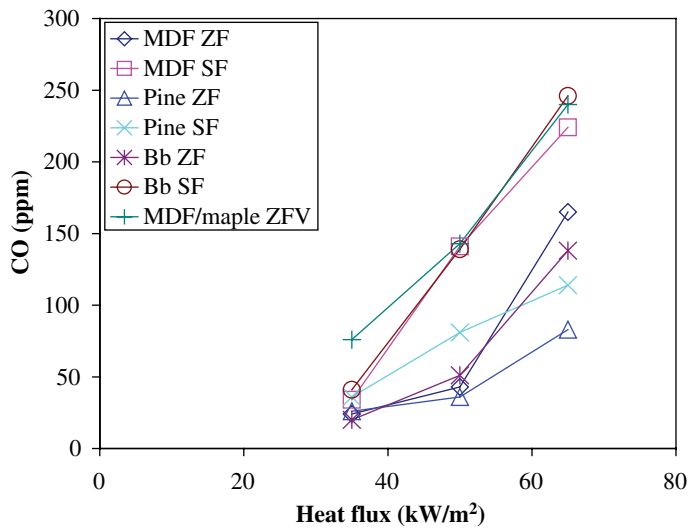| Substrate	35 kW/m²		50 kW/m²		65 kW/m²	
	PCOR 'Zero Flame'	PCOR 'Synto Flame'	PCOR 'Zero Flame'	PCOR 'Synto Flame'	PCOR 'Zero Flame'	PCOR 'Synto Flame'
MDF	0.5	0.7	0.6	1.7	2.2	2.7
Pine	0.7	0.9	0.8	1.5	2.2	2.6
Blockboard	0.5	0.8	0.7	2.0	1.8	2.9

Figure 12: Peak CO emissions (ppm) versus irradiances for various flame retarded samples.
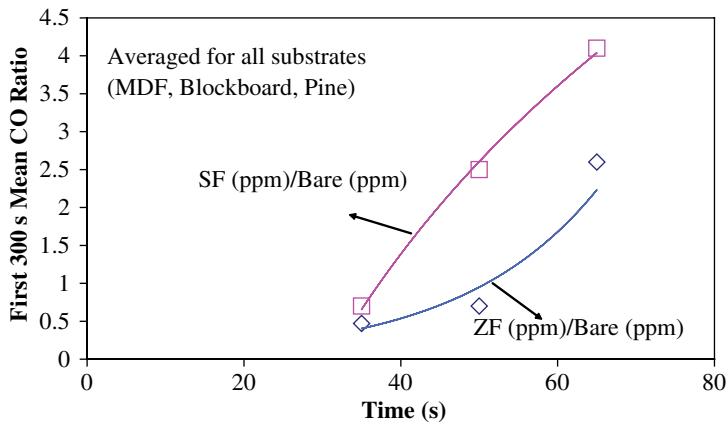

Figure 13: Comparative effects in First 300 s Mean CO emissions of flame retardant coatings.

Another comparison of the effect of the two types of flame retardants used in this work is achieved by defining a 'First 300 s Mean CO emission Ratio',

$$\text{First 300 s Mean CO R} = \frac{\text{First 300 s Mean CO Coated Sample}}{\text{First 300 s Mean CO Bare Sample}}, \quad (6)$$

Higher values of 'First 300 s Mean COR' are obtained for SF samples for the reasons mentioned above (Fig. 13).

2.4.2.2 NH_3 emissions. The effect of the coatings on the NH_3 production is shown in typical Fig. 14 for coated and uncoated MDF samples at 65 kW/m². A main distinguishable peak is formed at the beginning of the intumescent action (at around 35 s) for the flame retardant samples. The NH_3 emissions then decreased to an almost constant rate significantly higher than that from untreated samples. It is evident that the bulk of the ammonia production and release occurs over a short duration at the early stages of the exposure.

Low values are obtained for 'non-flame retarded samples'. 'Significant' values were measured for 'Zero Flame' paint and 'Synto Flame' since these contained ammonium in their chemical composition. Peak values of NH_3 emissions did not present any clear trend with increasing heat flux. Higher peak values occurred for composite in nature samples (i.e. MDF, blockboard) and this is attributed to the coupling effect between flame retardant paint and substrate as mentioned before. By contrast, pine gave the lowest peak NH_3 emissions. A direct comparison of the effect of the two flame retardant types used in this work is given in Table 7. The comparison is achieved by defining a 'peak NH_3 emission coefficient ratio' (PNH_3R),

$$PNH_3R = \frac{PNH_3 \text{ Coated Sample}}{PNH_3 \text{ Bare Sample}}, \quad (7)$$

As shown in Table 7, flame retardant coatings increase peak NH_3 emissions considerably, for the reasons mentioned before. 'Zero Flame' gives constantly lower NH_3 emissions than 'Synto Flame'.
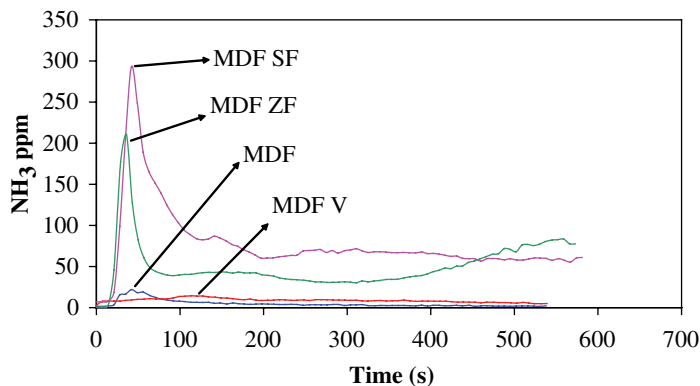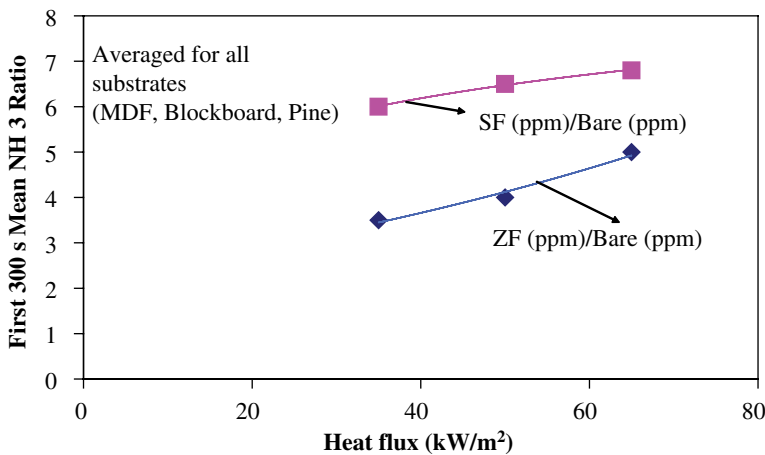

Figure 14: NH_3 (ppm) versus time for MDF, varnished MDF, 'Synto Flame' retarded MDF, 'Zero Flame' retarded MDF at 65 kW/m².

Table 7: Comparative effects in peak NH_3 emissions (ppm) of flame retardant coatings at 35, 50, 65 kW/m^2.

Substrate	35 kW/m^2		50 kW/m^2		65 kW/m^2	
	PNH_3R 'Zero Flame'	PNH_3R 'Synto Flame'	PNH_3R 'Zero Flame'	PNH_3R 'Synto Flame'	PNH_3R 'Zero Flame'	PNH_3R 'Synto Flame'
MDF	4	6	6	9	6	8
Pine	5	6	6	7	8	9
Blockboard	4	7	7	8	6	7

Figure 15: Comparative effects in First 300 s Mean NH_3 of flame retardant coatings.

A direct comparison of the effect of the two flame retardants used in this work is achieved by defining a 'First 300 s Mean NH_3 emission Ratio',

$$\text{First 300 s Mean } NH_3R = \frac{\text{300 s Mean } NH_3 \text{ Coated Sample}}{\text{300 s Mean } NH_3 \text{ B are Sample}}, \qquad (8)$$

From Fig. 15, a distinctive behavior between the two categories of retardants is observable. Higher values of 'First 300 s Mean NH_3 R' are obtained for SF samples as expected.

2.4.2.3 Acrolein emissions. The acrolein emission signals were 'messy' showing a 'discontinuous' behavior, oscillated between 0 and 25 ppm. The STEL limit for acrolein is reported as 0.3 ppm while the 5 min tenability limit is given as 2 ppm [13]. 'Significant' peak values ≫0.3 ppm are measured (15 min exposure limit as specified in STEL) for all samples. A tendency toward a reduction in peak values is observed with an increase in irradiance for untreated samples. The reason for this was the slower fire development at low irradiances which favors partial oxidation of released hydrocarbons to aldehydes, such as acrolein. No particular trend was followed for flame retarded samples, although at lower irradiances (35 and 50 kW/m^2) where 'no ignition' of the samples occurred, lower concentrations

measured. A direct comparison of the effect of two flame retardants used in this work is given in Table 8. The comparison is achieved by defining an 'Peak Acrolein emission Ratio' (PAR),

$$\text{PAR} = \frac{\text{P Acrolein Coated Sample}}{\text{P Acrolein Bare Sample}}, \qquad (9)$$

Values below unity are seen in the cases where 'no ignition' of the samples occurred. In the cases of flaming combustion flame retardants increased acrolein emissions by a factor from 1.1 to 1.6.

Another comparison of the effect of the two flame retardants used in this work is achieved by defining a 'First 300 s Mean Acrolein emission Ratio',

$$\text{First 300 s Mean Acrolein R} = \frac{\text{300 s Mean Acrolein Coated Sample}}{\text{300 s Mean Acrolein Bare Sample}}, \qquad (10)$$

A distinctive behavior between two categories of flame retardants is observable only at 50 and 65 kW/m^2. At 35 kW/m^2, it seems that both flame retardants decease 'First 300 s Mean Acrolein emission Ratio' by average factor 0.3 (Fig. 16).

Table 8: Comparative effects in peak acrolein emissions (ppm) of flame retardant coatings at 35, 50, 65 kW/m^2.

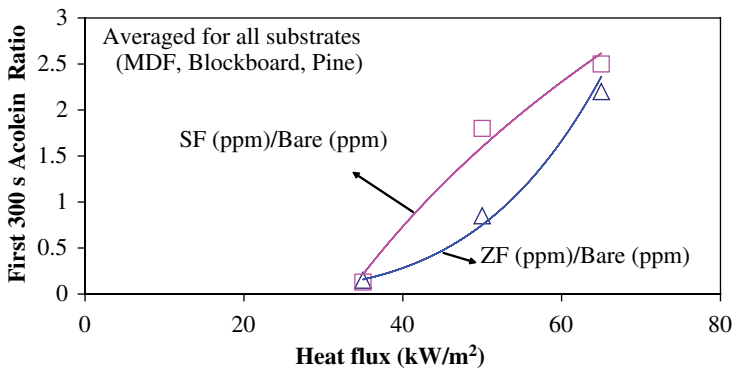| Substrate	35 kW/m^2		50 kW/m^2		65 kW/m^2	
	PAR 'Zero Flame'	PAR 'Synto Flame'	PAR 'Zero Flame'	PAR 'Synto Flame'	PAR 'Zero Flame'	PAR 'Synto Flame'
MDF	0.4	0.4	0.6	1.5	1.4	1.6
Pine	0.4	0.5	0.5	1.0	1.3	1.1
Blockboard	0.5	0.4	0.7	1.1	1.1	1.2

Figure 16: Comparative effects in First 300 s Mean Acrolein of flame retardant coatings.

Table 9: Comparative effects of flame retardant treatment on major exhaust emissions (averaged for all substrates, i.e. MDF, blockboard, pine).

Coated Emission/ Bare Emission	35 kW/m² heat flux		50 kW/m² heat flux		65 kW/m² heat flux	
	Zero Flame	Synto Flame	Zero Flame	Synto Flame	Zero Flame	Synto Flame
Peak CO (ppm) ratio	⇓	⇓	⇓	⇑	⇑	⇑
First 300 s Mean CO (ppm) Ratio	≈	≈	≈	⇑	⇑	⇑⇑⇑
Peak HCN (ppm) ratio	≈	≈	≈	≈	⇑	⇑
First 300 s Mean HCN (ppm) Ratio	≈	≈	≈	≈	⇑	⇑
Peak Acrolein (ppm) ratio	⇓	⇓	⇓	≈	≈	⇑
First 300 s Mean Acrolein (ppm) ratio	⇓	⇓	≈	≈	⇑	⇑
Peak NH$_3$ (ppm) ratio	⇑	⇑⇑⇑	⇑⇑	⇑⇑⇑	⇑⇑	⇑⇑⇑⇑
First 300 s Mean NH$_3$ (ppm) ratio	⇑⇑	⇑⇑	⇑⇑	⇑⇑	⇑⇑	⇑⇑

2.4.2.4 HCN emissions. For all virgin samples at all irradiances examined, 'no significant' HCN concentrations were released (<1 ppm). The exception to this rule was MDF faced by melamine where, due to the nitrogen content of melamine, higher HCN concentrations were released during burning, especially, at 50 and 65 kW/m², i.e. 5 and 10 ppm, respectively. These concentrations of HCN exist only for short period probably only during combustion of thin layer of melamine (2–3 mm). At 35 and 50 kW/m², irradiance levels insignificant HCN concentrations are released <1 ppm for flame retardant samples. At 65 kW/m², where there was more involvement of the flame retarded paint in the combustion, an increase in peak values was observed in all cases, however, still <10 ppm (15 min exposure COSHH limit) [13]. The creation of HCN was due to the fact that the flame retarded samples contain ammonium (NH$_4$), which during its thermal decomposition releases nitrogen, which is a major source of HCN.

2.4.2.5 SO$_2$ emissions. 'Significant' peak SO$_2$ concentrations were formed for MDF/maple 'Zero Flame Varnish' retarded samples at the beginning of the intumescent action, i.e. 7 ppm (>5 ppm, 15 min COSHH exposure limit [13]) at 65 kW/m². This could come from S contained in the isoparafinic hydrocarbon of clear finish (see Section 2.1), which releases significant SO$_2$ concentrations with the application of high irradiances. In the other virgin and flame retarded samples, 'no significant' concentrations are released, since they do not contain S in their chemical composition.

2.4.2.6 Other toxic gases. For flame retardant samples only, an increased trend for NO and NO$_2$ emissions were measured at 65 kW/m², however, still quite smaller than COSHH limits [13] (as HCN emissions). There was 'no significant' values of Toluene peak and average values were <20 ppm (≪150 ppm 15 min COSHH exposure limit [13]). Insignificant values of HCI, HF were measured since in those flame retardants there are no contained halogen acids, fluorinated resins or other chemical substances capable to release such toxic gases during combustion.

3 DISCUSSION

The effects of FR treatments on major toxic emissions in small-scale experimental work compared with the bare samples are shown in Table 9. In the cases of flame retarded samples, where there was 'no ignition' of the samples (at 35 and 50 kW/m^2), there were similar or less toxic emissions compared with the bare samples. NH_3 was an exception, since both flame retardants contained ammonium in their chemical composition, which was released during the intumescent action of the samples. Insignificant amounts of NO_2 and HCN were released, even at 65 kW/m^2 (despite the fact that both flame retardants contain N), due to the fact that thin flamelets are only formed on the surface of the samples; thus, there is an insignificant involvement of the flame retardant paint in flaming combustion.

Overall, with the exception of NH_3, lower toxics were released at low irradiances when the timber was treated. At high irradiances the benefit was reduced or reversed. It should be noted that irradiances of the order of 40 kW/m^2 or more are generally associated with the receiver being in close proximity (<1 m) to a large fire (>1 MW) or actually engulfed by it. So, in these circumstances, the fire is well established and the data show that the retardants would be ineffective at this stage.

4 CONCLUSIONS

Eight types of wood, the most widely used in Greek industries, were chosen for experimental testing in a cone calorimeter (small-scale). 'No significant' differences were observed in its thermal behavior (tig, HRR, EHC). The effects of three typical intumescent flame retardants (latest technology) on four types of timber, i.e. the most representative ones in terms of thermal behavior were tested in a cone calorimeter linked to the FTIR analyzer subjecting to constant incident heat fluxes of 35, 50, 65 and 80 kW/m^2. The main findings are the following:

- 'No ignition' of all flame retarded samples was observed at 35 kW/m^2. At 50 kW/m^2, there was 'no ignition' only for 'Zero Flame' (water-based) samples. In these cases, lower SEC values are seen compared with virgin samples, thus, there is an increase in smoke visibility.
- In other cases, a considerable ignition delay is seen at 50 and 65 kW/m^2 from 15 to 30 for 'Zero Flame', and from 2 to 5 for 'Synto Flame', as well a reduction in peak HRR from 4 to 5 for 'Zero Flame' and two times for 'Synto Flame'; this is attributed to their different chemical composition (water-based vs. solvent-based). An increase in SEC values compared with virgin samples is seen in all cases where there is flaming combustion of the treated samples. The effect of flame retardant in toxic emissions compared with untreated samples has also been assessed:
- In most cases of samples with 'no ignition', there is either reduction in toxic emissions by a factor of 2 ('Zero Flame' paint) or almost equal to unity ('Synto Flame' paint). As irradiance increases, increasing values of toxic emissions are seen during flaming combustion.

5 SUGGESTIONS/FUTURE WORK

- Performing of more small- and medium-scale experiments, treated with the updated technology of the intumescent paints (different parts of wooden cribs or some other form of samples), and using various ventilation rates to achieve both establishing and documentation of the contribution of intumescent technology in fire suppression.
- Different coatings should be evaluated in terms of durability, impact resistance, weatherability, etc.

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