Front. For. China 2008, 3(4): 487–492
DOI 10.1007/s11461-008-0075-y

RESEARCH ARTICLE

Fengqiang WANG, Zhijun ZHANG, Qingwen WANG, Jiayin TANG

Fire-retardant and smoke-suppressant performance of an intumescent waterborne amino-resin fire-retardant coating for wood

Abstract An intumescent waterborne amino-resin fire-retardant coating for wood (C) was synthesized and its fire-retardant and smoke-suppressant properties were investigated. The main film-builder of C was urea-formaldehyde resin blended with polyvinyl acetate resin. The intumescent fire-retardant system of C consisted of guanylurea phosphate (GUP), ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL). Specimens of plywood painted, respectively, with a commercial intumescent fire-retardant coating (A), a synthesized coating (C), and the main film-builder of coating C (B), as well as an unpainted plywood (S-JHB), were analyzed by cone calorimetry (CONE). The results show a marked decrease in the heat release rate (HRR) and the total heat release (THR), an increased mass of residual char (Mass), a marked postponement in time to ignition (TTI) and a reduced carbon monoxide production rate (P_{CO}). The smoke production rate (SPR) and total smoke production (TSP) of the plywood painted with coating C were observed with the CONE test. The overall fire-retardant and smoke-suppressant performance of the synthesized coating C was much better than that of the commercial coating A. The thermogravimetric analysis (TGA) results of coating C and its film-builder B indicated that the thermal degradation process of B was slowed down by the addition of the intumescent fire-retardant system; the increase in the amount of charring of coating C was considerable.

Keywords waterborne wood coatings, intumescent fire-retardant coatings, amino-resin, cone calorimeter, thermogravimetric analysis, smoke suppression

1 Introduction

With the increase in living standards and growing concerns about environmental protection for people, wood is attracting gradually more attention for its particular characteristics and excellent environmental properties. However, its marked combustibility may cause unexpected potential fire hazards. Therefore, some wood should be treated with fire-retardants when they are used in densely populated sites. Intumescent fire retardant coatings can expand and form a thick porous charred layer to insulate the substrate from the action of heat, and protect substrates against high temperatures and exposure to oxygen over a certain period of time. These coatings have a wide application in the efficient protection of flammable materials against fire. They have received considerable attention and have been rapidly developed in recent years. Generally, intumescent coatings contain natural or synthesized polymers as film-builders, and from acid, carbon and gas sources an active intumescent fire-retardant system is formed, usually with some fillers and auxiliary agents.

Many instruments are used to investigate the fire-retardant and smoke-suppressant performance and pyrolytic behavior of materials, such as the cone calorimeter (Xu et al., 2005), TGA (Jimenez et al., 2006), DTA, DSC (Gu et al., 2007), TG-DSC, TG-MS and TG-FTIR (Kunze et al., 2002; Li et al., 2007). Because a cone calorimeter can synthetically characterize fire-retardant and smoke-suppressant performance and reveal the fire-retardant mechanism of the fire-retardant material, it has been widely used by researchers to simulate real fires. In our study, we have also used a cone calorimeter to evaluate the properties of fire retardation and smoke suppression by measuring HRR, THR, Mass, TTI, P_{CO}, SPR and TSP of the different coatings. A thermo-gravimetric analysis was carried out to investigate pyrolysis and the charring process of the synthesized waterborne intumescent amino-resin fire-retardant coatings.

Translated from *Scientia Silvae Sinicae*, 2007, 43(12): 117–121 [译自: 林业科学]

Fengqiang WANG, Zhijun ZHANG, Qingwen WANG (✉), Jiayin TANG
Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, China
E-mail: qwwang@nefu.edu.cn

2 Experiment

2.1 Materials

The binder used was a mixture of urea-formaldehyde resin (UF) and polyvinyl acetate (PVAc) resin. The film-builder was cured at ambient temperatures.

The fire retardant system that was chosen was guanylurea phosphate (GUP), ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL). GUP was made at Northeast Forestry University, China; APP (its polymerization degree exceeds 1000) was supplied by Xinye Chemical Raw Material Company, Changsha; PER was purchased from Bazhou Chemical Industry Branch Factory, Tianjin; and, MEL was supplied by Taixing Refined Chemical Industry Company, Jinan. A few auxiliary agents for coatings were purchased from the local coatings market. A five-layer plywood was supplied by the Huatai Wood-Industry Company, China.

2.2 Equipment

An ND6 type of frequency conversion planetary ball mill was supplied by Nanjing Nanda Tianzun Electron Company. A standard type cone calorimeter was supplied by Fire Test Technology Company in the U.K, and a Pyris 6 thermo-gravimetric analytical instrument came from Perkin Elmer Company, USA.

2.3 Preparation

The technical processing of the waterborne fire-retardant coatings is as follows:

Component a: APP-GUP-MEL-PER was ground and mixed well with some water, then sifted out;

Component b: auxiliary coating agents were mixed equally with some water;

Component c: color filler and other materials were mixed equally with some water.

The mixture of UF and PVAc was stirred with component a, then placed in the ball mill for about 1.5 h. Components b and c were added to this mixture, and the intumescent fire-retardant coating was prepared by the processes of mixing, sifting and canning. The solid content was about 35% of the synthesized intumescent coating, of which the content of the film-builder (UF and PVAc) was 50%.

The fineness of the intumescent coating was tested by carrying out the test in a coating barrel. The intumescent coating was painted on the prepared plywood surface (painted twice, spaced more than 24 h apart) at least 48 h after canning, at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5%.

2.4 Cone calorimetry analysis (CONE)

Cone calorimetry analysis was carried out according to ISO 5660-1, with a heat flux of 50 kW/m^2 and a gas flow rate of 24 L/s. The samples, with dimensions of 100 mm × 100 mm × 4 mm, were placed under the conical-shaped heater that provided uniform irradiance on the sample surfaces.

2.5 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis was carried out at 10°C/min in a nitrogen atmosphere with a flow rate of 50 mL/min, using the Pyris 6 TGA. The samples (approx 10 mg) in powder form were placed in open vitreous silica pans. The measurement temperatures ranged from 50 to 800°C and the TGA curves were processed using Microsoft Excel software.

3 Results and discussion

3.1 Heat release rate (HRR)

The HRR provides a relative fire hazard assessment for materials. The HRR, especially its peak value (pk-HRR), is the primary characteristic determining the size, growth and suppression requirements in a fire environment (Charles, 2004). In general, material with a low heat release rate per unit weight or volume will do less damage to the surroundings than material with a high release rate.

The HRR profiles for different painted plywood A, B, C and S-JHB are shown in Fig. 1. Compared with S-JHB, the HRR of B decreased and its flaming period was delayed slightly; the pk-HRR of B decreased by 22% compared with S-JHB and the corresponding peak time was deferred by about 0.7 min. For the coating-painted plywood, their HRRs were far more subtle and decreased markedly: the pk-HRRs of plywood A and C were respectively lowered to 8.2% and 12.4%, and the time of occurrence was delayed 2.7 and 5.9 times, respectively, compared with S-JHB.

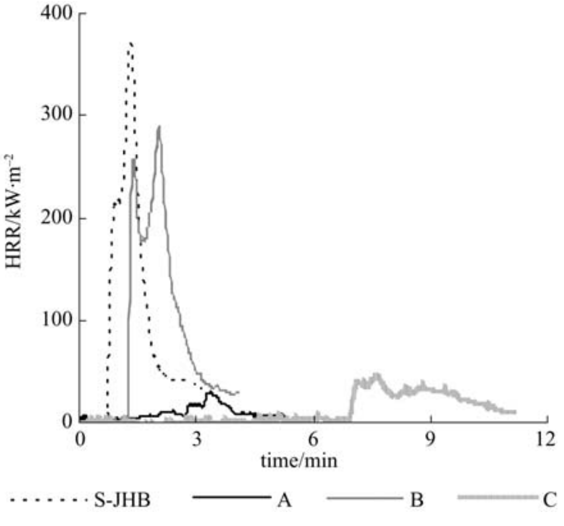

Fig. 1 HRR profiles for different painted plywood

For the plywood painted with fire-retardant coatings, the flame retardant effect was very evident. The production rate of flammable volatiles from fire-retardant coatings and plywood decreased markedly; the release time was considerably slower and later than that of S-JHB. The rate of heat transfer to plywood was decreased, and the spread of fire was deferred effectively once the fire occurred. Once the material catches fire, it is an advantage for the heat release peak to appear later, for the later the conflagration occurs, the more time is provided for personnel to evacuate the fire site and to implement fire-fighting. It is generally agreed that the fire retardant property of materials for buildings and decorations should ensure an evacuation time of at least 3.5 min after the fire starts (Wang, 2000). The heat release peak of plywood C was a little higher than that of plywood A, but the occurrence of the peak time was considerably prolonged.

3.2 Total heat release (THR)

The total heat release (THR for short) is defined as the total heat released by a material per unit area in a fire. Material with a high THR value will release more heat and, in general, the fire danger will be greater.

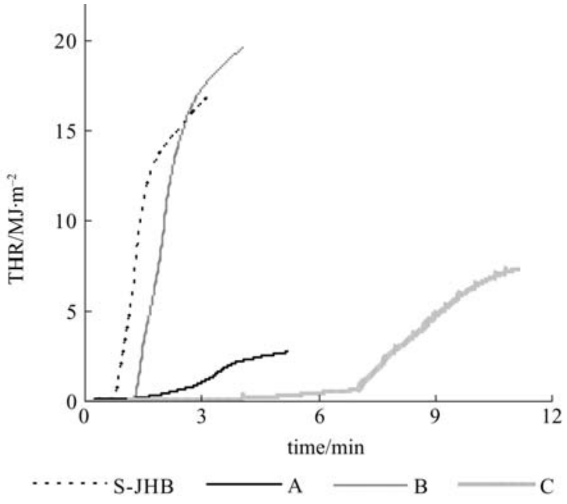

Fig. 2 THR profiles for different painted plywood

Figure 2 shows the THR curves of the differently painted plywood A, B, C and S-JHB. With time, the THRs of S-JHB and B rapidly increased and reached maximum values of 16.8 and 19.7 MJ/m^2, respectively, which meant that the samples ignited quickly and burned acutely. The THR of B was higher than that of S-JHB, resulting from the heat released from the combustion of the film-forming resin painted on the surface of B. However, for the plywood painted with fire-retardant coatings A and C, their THRs were greatly reduced to 7.2 and 2.8 MJ/m^2, respectively, and the heat release process was considerably delayed. Especially for coating C, it did not release heat during the first 6 min. Contrasting Figs. 1 and 2, it can be seen that most of the heat released from the material took place at the stage of flaming combustion. The fire-retardant coatings (both A and C) decreased the fire intensity and effectively inhibited fire combustion.

3.3 Mass

Mass refers to the amount of burning residue of material which varies over time. It is commonly expressed in terms of relative amounts, i.e., in per cent (instantaneous mass/initial mass) for a better comparison of samples with different initial masses.

The mass curves of the different coated plywood are shown in Fig. 3. The mass curve of S-JHB is similar to that of plywood B on the steeper gradient, which means that they both had a large mass loss rate and were burned out in a short time. Compared with S-JHB and B (plywood painted with film-builder), A (plywood painted with commercial intumescent coating) had a much greater final mass and a slightly longer burning-out time. However, the mass curve of the plywood painted with coating C was considerably different from that of the other three types of plywood; it had a flatter gradient, implying a lower mass loss rate. One point especially worth mentioning, is that the main mass loss of C took place 6.9 min after its exposure to the heat source, i.e., during this time combustion did not start in C; in contrast, it was precisely during these first six minutes that the other samples had already been burnt out; in fact, all of them were completely burnt in less than 5 min. Further, coating C had the largest amount of ash (about 40% of its initial mass), mainly owing to the honeycomb structure formed in the process, which plays an important role in fire prevention and heat insulation.

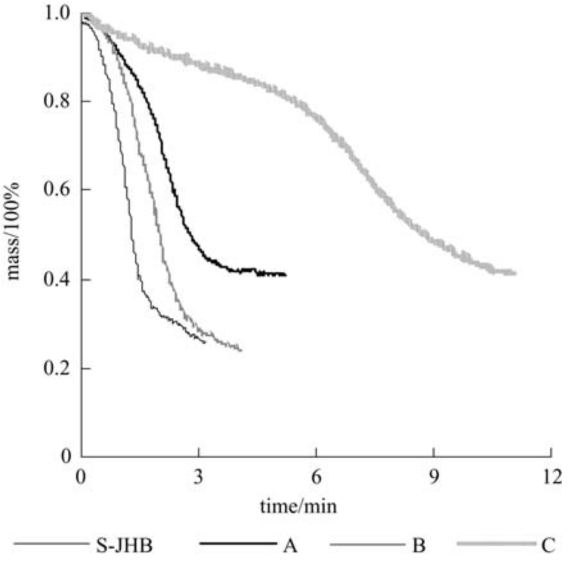

Fig. 3 Mass curves of different painted plywood

3.4 Time-to-ignition (TTI)

Time-to-ignition is defined as the duration of time for fire to ignite on the surface of material. The TTI is an important parameter for describing fire hazards of materials (Li, 2000). Materials with a long TTI will ignite with greater difficulty under the same conditions and will have better fire-retardant properties.

The TTI histograms of different painted plywood A, B, C and S-JHB are shown in Fig. 4. We can clearly see that the TTI of S-JHB is lower than that of the other plywood. The TTI of C, the longest of the four, is about 7 min, or 1.5 times longer than that of the commercial intumescent fire-retardant coating painted on plywood A. It indicates that the intumescent fire-retardant system of C fully exploited the property of thermal expansion, obstructing the heat source and deferring ignition during the heating period, consequently gaining enough time for people to escape and for fire suppression to be initiated.

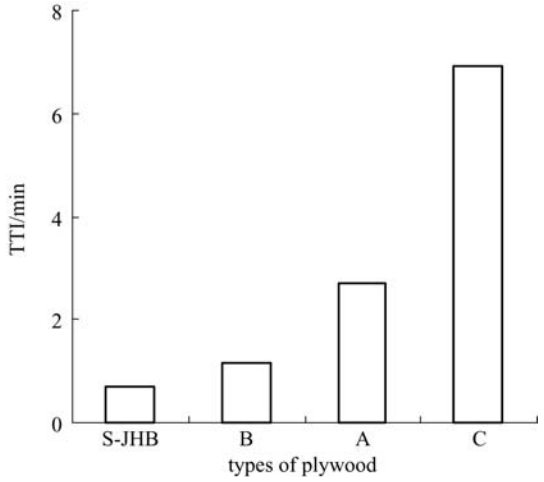

Fig. 4 TTI histogram for different painted plywood

3.5 CO release rate (P_{CO})

According to statistics, 80% of deaths in fires are attributed to smoke inhalation (Zhang, 2007). In natural fires, people often are first knocked out by smoke, dust and toxic gases and then burn to death. Especially, carbon monoxide (CO), the major toxic gas released from partial combustion of wood, is regarded as the chief offender.

P_{CO} is defined as the amount of CO released per unit time, which represents an instantaneous concentration of CO (g/s). The curves of P_{CO} of different coated plywood are illustrated in Fig. 5. Compared with S-JHB, the amount of CO release from B was not significantly different, but the release was delayed entirely. The rate of CO release from A increased markedly with a peak more than twice as high as that of S-JHB. For coating C, not only was the CO release delayed significantly, but the rate of CO production was also kept at a very low level for at least 5 min, a time longer than the 3.5 min required for evacuation, thereby decreasing the danger of fire.

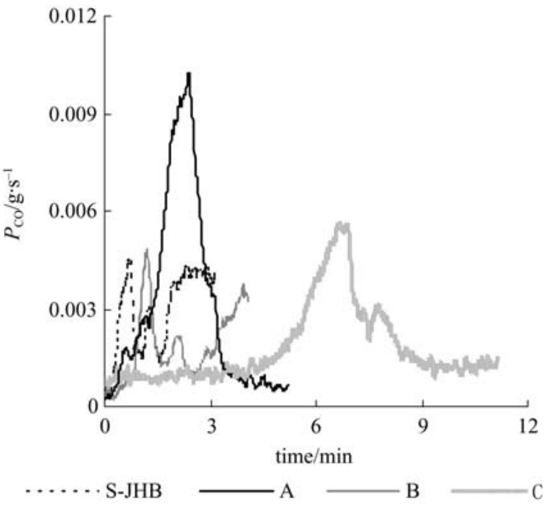

Fig. 5 P_{CO} curves of different painted plywood

Carbonaceous organic materials can generate a large amount of gaseous volatiles and form diffusion flames during violent combustion processes. Both can dilute the oxygen of the combustion atmosphere and obstruct the oxygen supply from the surroundings. Under such conditions and as a consequence, this will lead to oxygen deficiency of the combustion atmosphere and the carbonaceous pyrolysates would burn incompletely and quickly generate much CO gas (Wang et al., 2006).

For fire-retardant coating C, at the flaming combustion stage, its carbon source produced a large amount of char, which, along with some carbonaceous pyrolysates, generated much CO gas quickly due to incomplete combustion under the condition of oxygen deficiency formed in a violent combustion process.

3.6 Smoke producing rate (SPR)

The smoke producing rate (SPR, m^2/s) refers to the amount of dense smoke released per unit time that can be calculated from the division of a specific extinction area (SEA) by the mass loss rate (MLR).

Figure 6 shows the SPR profiles of different painted plywood. It can be seen that all four tested samples have a similar release process. The profile can be split artificially into three stages: in the first stage (before ignition occurs) a small amount of smoke is released, in the second stage (flaming combustion period) heavy smoke is released, and in the third stage (after-glow combustion period) a small amount of smoke is released. In our experiment, it was found that the main source of dense smoke release was the second stage (flaming combustion period); a small amount of dense smoke was produced in the first stage and hardly any dense smoke was released in the third stage. The SPR of the plywood coated with intumescent fire-retardant coating C was clearly reduced because the guanylurea phosphate in coating C, which has a decomposition temperature of about 200°C, decomposed before the plywood did during the first stage, to avoid or lessen the decomposition of the plywood, in turn further suppressing the release of volatile pyrolysates, i.e., the release of smoke was suppressed in an efficient manner. In contrast, the commercial intumescent coatings A and B increased the SPR of plywood markedly, especially plywood A. Its pk-SPR was almost the highest among the specimens, about the same level as the pk-SPR of S-JHB, and 13 times higher than plywood C.

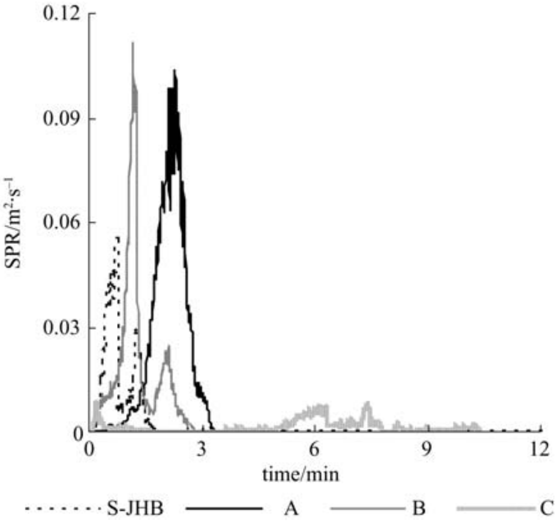

Fig. 6 SPR profiles of different painted plywood

3.7 Total smoke product (TSP)

The total smoke product (TSP, m^2) is defined as the total amount of smoke released by material in the process of burning and pyrolysis. It can be calculated by a process of integration of SPR over time; it is also called the cumulative smoke release product.

From a comprehensive analysis of Figs. 1, 6 and 7, it is seen that the TSP of the samples can be largely attributed to the smoke released during the initial smoldering and flaming combustion stages. The TSPs of the plywood painted with film-builder B and commercial intumescent coating A were very high, respectively about 2 and 3.3 times that of S-JHB. However, for the plywood painted with intumescent coating C, its TSP was about 54.9% that of S-JHB. In other words, the intumescent fire-retardant coating C not only reduced the SPR and TSP effectively, but also delayed the entire smoke release process for more than 5 min, so that it decreased the instantaneous degree of damage from smoke and could save enough time for people to evacuate and for fire to be suppressed.

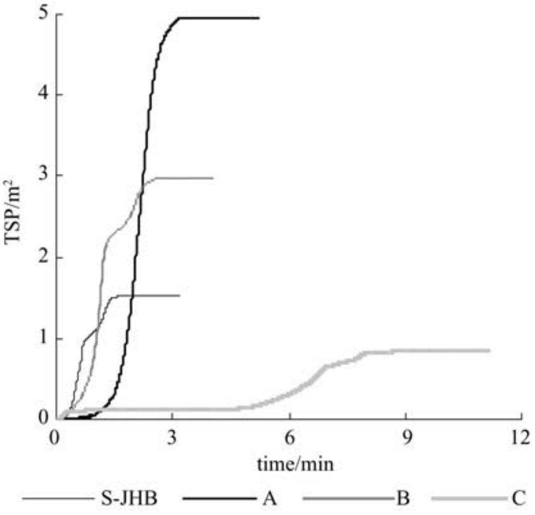

Fig. 7 TSP profiles of different painted plywood

3.8 Thermo-gravimetric analysis (TGA)

TGA is a thermal analysis technique used to measure qualitative changes in material as a function of temperature. TGA is commonly used for evaluating the combustibility and combustion stability of materials (Hu, 1999). During the degradation process, the weight loss curve (TG curve) is recorded and its first derivative (DTG curve) is obtained to show the rate of change as the apparent weight loss. Both the TG and DTG curves, typical parameters of TGA (Wang, 2000; Li, 2003), can reveal the thermal degradation process of materials and provide the value of the residual mass, used as a standard for assessing the fire-retardant effect of materials (Zhang, 2001).

TG and DTG curves of samples B (film-builder) and C (the synthetic intumescent coating) are shown in Fig. 8. It can be seen from Fig. 8 that the rate of thermal weight loss relaxed, and the thermal decomposition process became more gentle because of the use of the intumescent fire-retardant system. Further, the initial thermal decomposition temperature was advanced to about 101°C, lower than that of the film-builder, and is attributed to the release of free water and some small molecular additives with a low boiling point, largely emitted from the coatings, by which the combustion atmospheric concentration was effectively diluted and the ignition time prolonged.

GUP in the intumescent fire-retardant system began to decompose at about 185°C. With increasing temperature, the decomposition of other fire retardants accelerated. When the temperature increased to 250°C, PVAc started to decompose and emitted acetic acid. Rapid decomposition of coating C began at 354°C and tended to remain mild until 450°C. At 760°C, the temperature that we arbitrarily regarded as the end-point, the residual masses of B and C were, respectively, 10.3% and 26.8% of their initial masses. This indicated that the charring effect of the intumescent fire-retardant system was excellent, owing mainly

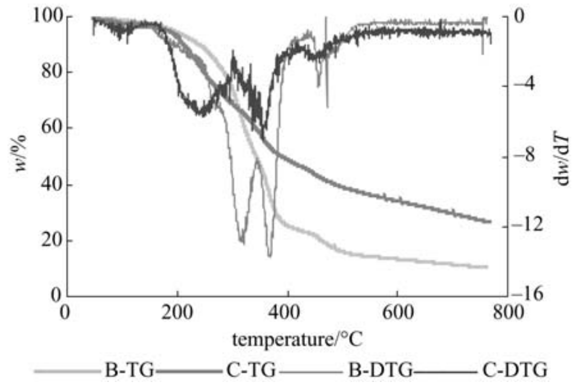

Fig. 8 TG and DTG curves of sample B and C

to the combined action of the composite sources of acid (GUP & APP), gas (MEL) and carbon (PER) mixed in proper proportions in the intumescent fire-retardant system, as well as to the catalytic charring action on the film-builder of the protonic acid, formed by the decomposition of APP and GUP under different temperature ranges.

4 Conclusions

An intumescent waterborne fire-retardant coating for wood was synthesized in which the main film-builder was urea-formaldehyde resin blended with polyvinyl acetate resin; the intumescent fire-retardant system consisted of guanyl-urea phosphate (GUP), ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL).

1) CONE and TGA tests proved that coating C could give rise to much char and suppress after-glowing effectively and markedly. When the coating thickness was about 0.3 mm, the pk-HRR value was reduced to just 12.4% that of S-JHB; the TTI was 10 times longer than that of S-JHB and 1.5 times longer than that of commercial coating A. The THR value was 16.8 MJ/m^2, about 42.9% that of S-JHB. The heat released by the burning material and the fire intensity were decreased by using coating C.

2) Our experiment shows that the smoke suppression effect of coating C was well demonstrated, for the CO release was clearly delayed and SPR and TSP obviously reduced, implying that the fire hazard was effectively weakened by coating C, gaining enough time for saving lives and property from the emerging fire.

Acknowledgements This work was supported by the National Natural Science Foundation of China for the Mechanism of Smoke Suppression on Wood Fire Retardant (No. 30371127) and the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (FANEDD) for support of "Applied Fundamental Research of N-P-B Fire-retardant System for Lignocellulosic Materials (No.200457)".

References

Charles A H (2004). Handbook of Building Materials for Fire Protection. America: McGraw-Hill, 450–460

Gu J W, Zhang G C, Dong S L, Zhang Q Y, Kong J (2007). Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. Surf Coat Tech, 201(18): 7835–7841

Hu Y, Li C, Shi H, Lu H D (1999). Application of thermal analysis in flame retardant materials. Fire Safe Sci, 8(1): 74–77 (in Chinese)

Jimenez M, Duquesne S, Bourbigot S (2006). Characterization of the performance of an intumescent fire protective coating. Surf Coat Tech, 201(3–4): 979–987

Kunze R, Schartel B, Bartholmai M, Neubert D, Schriever R (2002). TG-MS and TG-FTIR applied for an unambiguous thermal analysis of intumescent coatings. J Therm Anal Calorimetry, 70: 897–909

Li B (2000). Smoke Suppression and Fire-Retardant of Poly (Vinyl Chloride). Harbin: Northeast Forestry University Press, 85–204 (in Chinese)

Li G X, Liang G Z, Zhou W Y (2007). Testing and analysis techniques used to study the thermal degradation of flame retardant coatings. Paint Coat Ind, 37(4): 50–54 (in Chinese)

Li J (2003). Spectroscopy of Wood. Beijing: Science Press, 259–263 (in Chinese)

Wang Q W (2000). Principle on Fire-Retarding Technology of Wood. Harbin: Northeast Forestry University Press, 141–154 (in Chinese)

Wang Q W, Zhang Z J, Chen L, Wang F Q (2006). Effects of oxygen concentration on the smoking property of fire-retardant treated Wood. Sci Silv Sin, 42(12): 95–100 (in Chinese)

Xu X N, Xu W Y, Wu T (2005). Research on fire retardant coatings coutaining expandable graphite using cone calorimeter. Fire Safe Sci, 14(1): 11–15 (in Chinese)

Zhang L, Wang J Q (2001). A new kind of halogen-free fire retardant coatings made from expandable graphite. J Beijing Inst Tech, 21(5): 649–652 (in Chinese)

Zhang Z J (2007). Influence of oxygen concentration on the flammability characteristics of fire-retardant cellulose. Master's Dissertation. Harbin: Northeast Forestry University, 35–47