ACTA FACULTATIS XYLOLOGIAE ZVOLEN, 58(1): 59−66, 2016
Zvolen, Technická univerzita vo Zvolene
DOI: 10.17423/afx.2016.58.1.07

EFFECT OF DIFFERENT FIRE RETARDANTS ON BIRCH PLYWOOD PROPERTIES

Pavlo Bekhta – Olesya Bryn – Ján Sedliačik – Igor Novák

ABSTRACT

The feasibility of applying conventional flame retardants usually used to improve fire behaviour of solid wood was evaluated in this study for the production of fire-resistant plywood panels. For making plywood the birch (*Betula verrucosa* Ehrh.) veneer and commercial phenol-formaldehyde glue resin were used. Five different standardized fire-retardants were chosen for veneer impregnation. Firstly, veneer sheets were treated by immersion in 20% aqueous solution of each fire-retardant. Diffusive and capillary impregnation was evaluated to select the most effective treatment of veneer. Absorption of impregnation solution in veneers was determined. Afterwards, five-layer plywood panels were prepared from impregnated veneers in laboratory press at the following pressing parameters: pressure of 2.0 MPa, temperature of 130 °C, time of 10 min and glue spread of 120 g/m^2. Shear strength and fire resistance of plywood were determined. It was found that diffusive impregnation of moist veneer, in comparison with capillary impregnation of dry veneer, is characterized by the less salting-out of fire-retardants on the veneer surface and their more homogeneous distribution in middle of veneer. It was proved that conventional fire-retardants for solid wood can be used for plywood and also allow re-classification of plywood from the group of increased flammability materials to the group of hard inflammable materials.

Keywords*:* birch plywood, fire-retardants, impregnation, shear strength, weight loss.

INTRODUCTION

Birch plywood is a valuable construction material which can be widely used in public buildings because has unique properties, such as advantageous strength parameters resulting from its layered structure. However, the flammability of plywood limits its applicability in many areas because of the heavy casualties or the uncountable damage of the property caused due to the fire accident. For example, according to the information of Ukrainian Research Institute of Civil Protection (2015), there were 68 879 fires in Ukraine in 2014, in which 2 246 people died and 1 450 injured, and material damages are inflicted to the amount of 55 million €. Therefore, improving the capability of fireproof of the plywood becomes one of the important issues. To reduce the flammability and/or fire emissions, wood is treated with fire retardants. Such treatment considerably reduces the rate at which flames spread the wood surface and reduces the amount of potential heat (LEVAN and WINANDY 1990, MARTINKA *et al*. 2012, ZACHAR *et al.* 2012).

There are some main ways of decreasing the flammability of plywood panels: (a) soaking, diffusion or impregnation of the individual veneers before gluing (BORYSIUK *et al.* 2011, FRANCES BUENO *et al.* 2014, GREXA *et al.* 1999, LAUFENBERG *et al.* 2006, MILJKOVIĆ *et al.* 2005, SHIM 1982); (b) incorporation of the fire retardant into the glue used for bonding (GREXA *et al.* 1999, CHENG and WANG 2011, SU *et al.* 1998); (c) impregnating the consolidated plywood with chemicals by vacuum pressure process or other methods (LEVAN *et al.* 1996, KIM 1987, KIM *et al.* 1984); (d) surface treatment by flame retardant coating (CHANG *et al.* 2011, CHOU *et al.* 2009, CHOU *et al.* 2010, CHUANG *et al.* 2010, YEW *et al.* 2015).

Many types of flame retardants are currently used for consumer products. The aim of this study was to explore the possibility of applying conventional flame retardants which are usually used to improve behaviour of wood against fire for the production of fire-resistance plywood panels.

MATERIALS AND METHODS

Rotary cut veneer sheets of birch (*Betula verrucosa* Ehrh.) with dimensions of 250 mm by 250 mm and with thickness of 1.5 mm and conditioned to moisture content of 6–7% were chosen for the experiments.

Five different conventional fire-retardants SFA, BB, BS, DA, DU (see Tab. 1) which are recommended by GOST 28815-96 to fire-proofing of solid wood were chosen for veneer impregnation. Chemical compositions of fire-retardants are shown in Table 1. The fire-retardants were applied in 20% aqueous solution. Two methods were carried out for treated veneers at environmental conditions:

(i) Diffusive impregnation. Individual layers of veneer with moisture content of 60–80% were immersed in 20% aqueous solution of each fire-retardant for 70 min at 20 °C.

(ii) Capillary impregnation. Individual layers of veneer with moisture content of 7–10% at first were immersed in 20% hot aqueous solution of each fire-retardant for 30 min at 80–90 °C and after that in 20% cold aqueous solutions of the same fire-retardants for 40 min at 20 °C.

Tab. 1 Fire-retardant composition.

Fire-retardants	Component	Amount (w:w)
SFA	Sodium dichromate ($Na_2Cr_2O_7$)	1
	Ferrous sulphate ($FeSO_4$)	1
	Ammonium chloride (NH_4Cl)	10
BS	Boric acid (H_3BO_3)	1
	Sodium carbonate (Na_2CO_3)	3
BB	Boric acid (H_3BO_3)	1
	Borax ($Na_2B_4O_7$)	1
DA	Di-ammonium phosphate ($(NH_4)_2HPO_4$)	1
	Ammonium sulphate ($(NH_4)_2SO_4$)	1
DU	Di-ammonium phosphate ($(NH_4)_2HPO_4$)	1
	Urea ($CO(NH_2)_2$)	1

The treatment of veneer was carried out in the bath made from chemically proof material. Veneer was loaded into the bath in a metallic container from stainless steel for the improvement of treatment process. After finishing of treatment process, the container of veneers was removed from bath and was kept over the bath for some time for draining an excess of solution into the bath. Then veneer sheets were folded with their grain direction perpendicular to each other and maintained during 1 hour for redistribution of fire-retardant. The veneers were then subjected to a second drying process, reconditioned to 6–7% moisture content, and re-weighed.

In addition, five-layer experimental plywood panels were manufactured from impregnated and non-impregnated veneers using commercial phenol-formaldehyde (PF) glue resin. PF resin (solid content of 42 % and viscosity Ford 4/20 of 120 s) was uniformly spread onto one side of the face veneers at 120 g/m^2. The veneers were then laid-up into a plywood billet and hot pressed using a pressure of 2.0 MPa at 130 °C for 10 min in a laboratory hot press.

The following properties of impregnated veneers and plywood were determined: absorption of impregnation solution, weight loss, and shear strength (according to EN 314-1; pre-treatment for humid conditions). A salting-out of chemicals on the surface of treated and dried veneer was also fixed. Prior to mechanical testing, the specimens were conditioned at 20 °C ± 2 °C and 65 % ± 2 % relative humidity.

The absorption content per unit volume (kg/m^3) may be expressed as:

$$Absorption = \left[\left(m_2 - m_1 \right) / V \right] \times C \quad (1)$$

where, m_1 and m_2: weight of veneer sheet before and after treatment, respectively, kg; C: the concentration of fire-retardant chemical solution, and V: the volume of veneers, m^3.

To evaluate the fire behaviour of plywood panels, fire test method “Ceramic pipe” (Fig. 1) according to the GOST 16363-98 standard was carried out. The device for fire-resistance test consists of ceramic pipe (the basket) 1 with external sizes 120 × 120 × 300 mm and the thickness of wall 16 mm. The ceramic pipe was placed on metallic stand 2 with lateral windows for controlling the air supply to the burning zone. The device also consists of a gas burner 3, rheometer 10 for adjusting the natural gas speed, holder 5 of specimens 6, hood 7, exhaust hood 9, thermocouple 8 to measure the temperature of exhaust gases. The scales, potentiometer 4 and stop-watch used as ancillaries. Ten specimens with dimensions of 150 × 60 mm were used for testing. The gas burner is used as the source of the fire (duration of influence 2 min).

Specimens were weighed with an accuracy of less than 0.1 g. Test was performed in a fume cupboard with natural ventilation. Gas burner was ignited and flame height was established of 15–25 cm at the gas consumption about 1 litre/min. When the temperature reached 200 ± 5 °C, a hood was took back and fixed specimen was lowered into a ceramic box and simultaneously turns on the stopwatch. The hood was returned to the operating position. After 2 min the gas supply was stopped and the specimen was left to cool in the device, but not less than 20 minutes after the stop of specimen burning. The cooled sample was removed from a ceramic box and kept for 1 h at the room temperature and relative humidity of 70 %. Then, the specimen was weighed.

The efficiency of the treatments was assessed on the resistance of the treated plywood to weight loss (WL):

$$WL = \left[\left(W_b - W_a \right) / W_b \right] \times 100\% \quad (2)$$

Where: W_b is the initial weight before the test,
W_a is the weight after the test, g.

For weight loss and shear strength properties, all multiple comparisons were first subjected to an analysis of variance (ANOVA), and significant ($\alpha \leq 0.05$) differences between mean values of control and treated plywood specimens were determined using Duncan’s multiple range test.

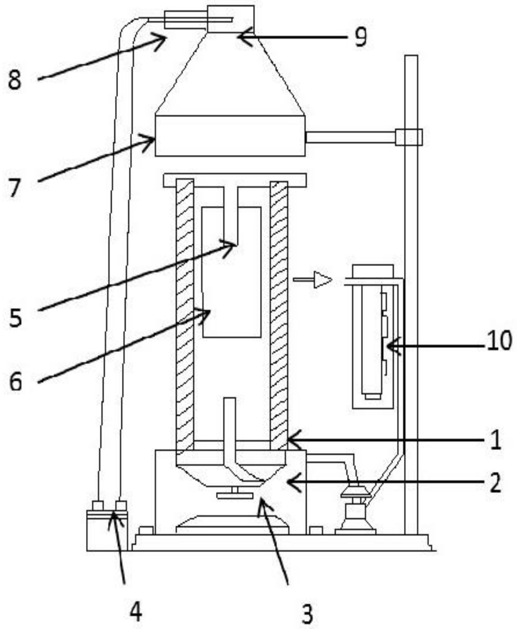

Fig. 1 A device for testing of fire-resistance of plywood specimens (GOST 16363-98): 1 – ceramic pipe; 2 – metallic stand; 3 – gas burner; 4 – potentiometer; 5 – holder; 6 – specimen; 7 – hood; 8 – thermocouple; 9 – exhaust hood; 10 – rheometer.

RESULTS AND DISCUSSION

Absorption of impregnation solution by the veneers, weight loss and shear strength of plywood panels are shown on Figures 2, 3 and 4. Analysis of variance showed that type of fire-retardants and impregnation method has significant effect on the absorption of impregnation solution by the veneers, weight loss and shear strength of plywood panels.

Absorption of impregnation solution was significantly affected both by the fire retardants and method of impregnation. During capillary impregnation the veneer absorbs solution of fire-retardant in 1.3–2.0 times more than during the diffusive impregnation. This can be explained by higher temperature of fire-retardant solution during capillary impregnation and therefore improvement of diffusion, which leads to a more intense absorption of solution.

It is known that lower total weight loss implies higher resistance against thermal degradation of fire. The outcomes of weight loss for the treated plywood samples are given in Figure 3. As can be seen, all investigated fire-retardants provide fireproof properties of plywood transferring it into the group of hard inflammable materials (I^{st} group) (WL < 10%) according with the requirements of GOST 16363-98. Fire-resistance of plywood from capillary impregnated veneers was a little bit higher than in the case of using diffusive impregnated veneer. It can be explained by less fire-retardants content in the diffusive impregnated veneer. Although both impregnation methods provide the I^{st} group of heat-resistance, it should be noted that diffusive impregnation is carried out at room temperature and accordingly the less energy is needed.

Moreover, it was found that diffusive method of impregnation of moist veneer is characterized by less salting-out of fire-retardants on the veneer surface and their more homogeneous distribution in the middle of veneer, in comparison with capillary method of impregnation of dry veneer.

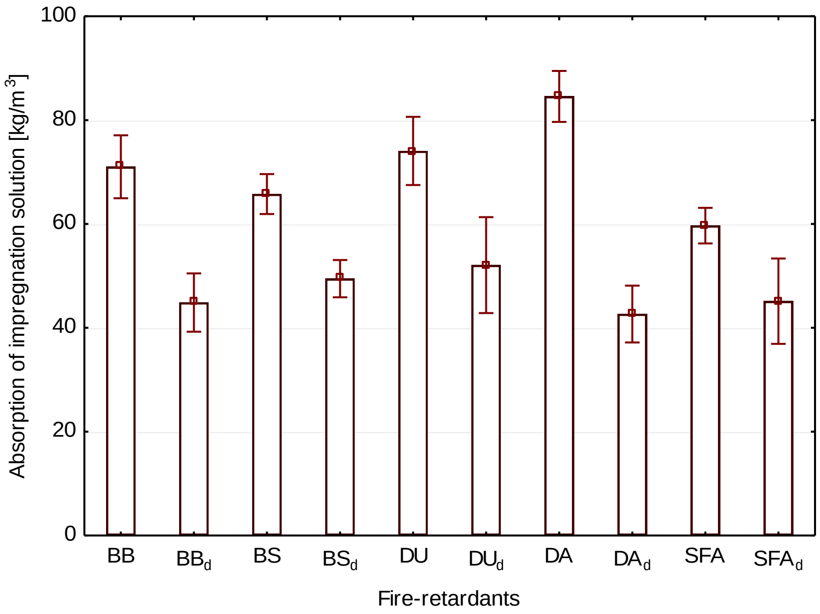

Fig. 2 Absorption of impregnation solution in veneers for different fire-retardants ("without index" – values for capillary method; "with index d" – values for diffusive method).

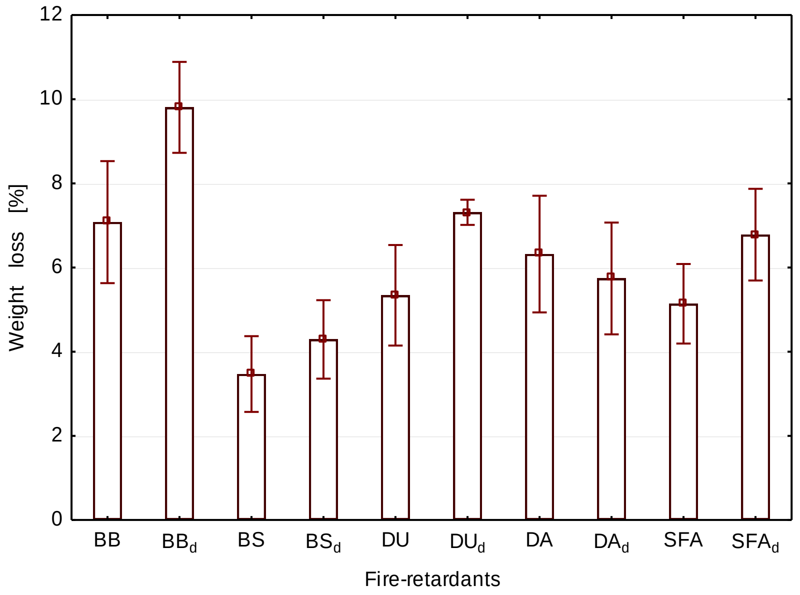

Fig. 3 Weight loss of plywood samples for different fire-retardants ("without index" – values for capillary method; "with index d" – values for diffusive method).

The shear strength test is commonly used as a fundamental indicator of the adhesive performance in plywood. Investigated fire-retardants have different effects on the shear strength of plywood (Fig. 4). Plywood specimens from veneer impregnated by BB were destroyed during their boiling. Shear strength values of plywood from veneer impregnated by BS and DU were low and don't meet the requirements of EN 314-2 standard. It can be explained by the negative influence of boric acid on the PF resin consolidation. Moreover, as reported by AYDIN and COLAKOGLU (2007) the layer of borax and boric acid crystals on the veneer surfaces after drying might have been an obstruction to intimate contact between veneer surfaces and adhesive molecules; the other reason for poor bonding after treatment may be the second drying process applied to veneers. Similar results were found in previous studies (BORYSIUK *et al.* 2011, LEBOW and WINANDY 1999). Studies conducted on fire retardant treated plywood (LEBOW and WINANDY 1999) revealed that the treatment improved the flame spread rating of the treated material but caused a reduction in the mechanical properties of this product. Fire retardant induced strength loss depends on the composition and pH of fire retardant chemicals that are used in treatment. Modulus of rupture values showed a very strong correlation between the pH of the fire retardant and strength loss in the plywood test specimens (LEBOW and WINANDY 1999). Therefore, due to the highly acidic or alkaline nature of fire retardants, the pH of the wood veneer that are used in the production of the plywood panels can be affected to the point that sufficient bonding cannot occur during pressing.

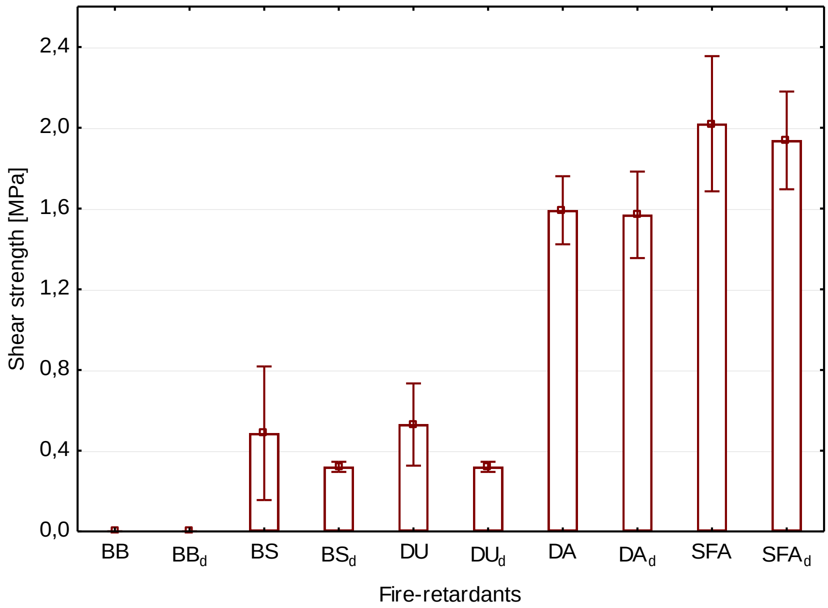

Fig. 4 Shear strength of plywood samples for different fire-retardants ("without index" – values for capillary method; "with index d" – values for diffusive method).

The plywood panels from veneer impregnated by DA and SFA fulfil the EN standard requirements. But, since ammonium chloride, as basic component part of SFA, is toxic and carcinogenic substance, then the usage and exploitation of such fire-retardant and plywood are undesirable in industry. The DA fire-retardant provides the necessary fire-resistance and shear strength properties of plywood, but it is characterized by an increase corrosive activity (which is caused by the content of ammonium sulphate). Therefore, to reduce corrosion of metals it can be recommended to replace of ammonium sulphate by a less active corrosive substance.

CONCLUSIONS

The obtained result showed that capillary impregnation of birch veneers is the most effective treatment to achieve a good penetration of fire retardants. Although the diffusive impregnation of moist veneer, in comparison with capillary impregnation of dry veneer, is characterized by the less salting-out of fire-retardants on the veneer surface and their more homogeneous distribution in middle of veneer. Moreover, the diffusive method is more energy saving.

The standardized fire-retardants for solid wood can be used for production of fire-resistant plywood. The outcomes revealed that all investigated fire-retardants improved the flammability of plywood but caused, except DA and SFA, a reduction in the shear strength of material. The treatment of birch veneers with DA and SFA aqueous solution is the most effective to improve the fire behaviour of plywood. As future works it would be interesting to analyse the effect of adding substances on the reduction of corrosive activity of DA.

REFERENCES

AYDIN, I., COLAKOGLU, G. 2007. Variation in surface roughness, wettability and some plywood properties after preservative treatment with boron compounds. Building and Environment, 2007, 42: 3837–3840.

BORYSIUK, P., KRAJEWSKI, K., BORUSZEWSKI, P., JENCZYK-TOLLOCZKO, I., JABLONSKI, M. 2011. Bonding quality of veneers protected with fireproofing preservation based on diammonium hydrogen phosphate, citric acid and sodium benzoate. Ann. WULS-SGGW, Forestry and Wood Technology, 2011, 73: 158–161.

CHANG, H., KUO, Z.H., TSAI, K.C., CHEN, T.L. 2011. Analysis on properties of water-based fire-retardant nano-coatings. Advanced Materials Research, 2011, 8: 311–313.

CHENG, R.-X., WANG, Q.-W. 2011. The influence of FRW-1 fire retardant treatment on the bonding of plywood. Journal of Adhesion Science and Technology, 2011, 25(14): 1715–1724.

CHUANG, C.-S., TSAI, K.-C., YANG, T.-H., WANG, M.-K., KO, C.-H. 2010. Effects of intumescent formulation of vinyl acetate-based coating on flame-retardancy of thin painted red lauan (*Parashorea* spp.) plywood. XXIII World Congress Seoul, Korea 23–28 August 2010.

CHOU, C.-S., LIN, S.-H., WANG, C.-I., LIU, K.-H. 2010. A hybrid intumescent fire retardant coating from cake and eggshell-type IFRC. Powder Technology, 2010, 198(1):149–156.

CHOU, C.-S., LIN, S.-H., WANG, C.-I. 2009. Preparation and characterization of the intumescent fire retardant coating with a new flame retardant. Advanced Powder Technology, 2009, 20: 169–176.

EN 314-1: 2005. Plywood. Bonding quality. Part 1: Test methods. Brussels: European Committee for Standardization. 2005.

FRANCES BUENO, A.B., NAVARRO BANON, M.V., MARTINEZ DE MORENTIN, L., MORATALLA GARCIA, J. 2014. Treatment of natural wood veneers with nano-oxides to improve their fire behaviour. 2nd International Conference on Structural Nano Composites. 2014, 64.

GOST 16363-98. Fire protective means for wood. Methods for determination of fire protective properties. Moscow, 1998, 6p.

GOST 28815-96. Aqueous solutions of wood protective means. Specifications. Kyjiv, 1998, 36p.

GREXA, O., HORVÁTHOVÁ, E., BEŠINOVÁ, O., LEHOCKÝ, P. 1999. Flame retardant treated plywood. Polymer Degradation and Stability, 1999, 64(3): 529–533.

KIM, J.M. 1987. Studies on press drying and dynamic elastic modulus of plywood treated with boric acid. Journal of the Korean Wood Science and Technology, 1987, 15(3).

KIM, J.-M., CHUNG, W.-Y., LEE, P.-W. 1984. A comparative study on the mechanical properties of plywood treated with several fire retardant chemicals (I) - Effect of soaking time on the static bending strength of treated plywood. Journal of the Korean Wood Science and Technology, 1984, 12(2).

LAUFENBERG, T.,·AYRILMIS, N.,·WHITE, R. 2006. Fire and bending properties of blockboard with fire retardant treated veneers. Holz als Roh- und Werkstoff, 2006, 64: 137–143.

LEBOW, S.T., WINANDY, J.E. 1999. Effect of fire-retardant treatments on plywood pH and the relationship of pH to strength properties. Wood Science and Technology, 1999, 33(4): 285–298.

LEVAN, S.L., KIM, J.M., NAGEL, R.J., EVANS, J.W. 1996. Mechanical properties of fire-retardant-treated plywood after cyclic temperature exposure. Forest Products Journal, 1996, 46(5): 64–71.

LEVAN, S.L., WINANDY, J.E. 1990. Effects of fire retardant treatments on wood strength: a review. Wood and Fiber Science, 1990, 22(1): 113–131.

MARTINKA, J., KAČÍKOVÁ, D., HRONCOVÁ, E., LADOMERSKÝ, J. 2012. Experimental determination of the effect of temperature and oxygen concentration on the production of birch wood main fire emissions. Journal of Thermal Analysis and Calorimetry, 2012, 110(1): 193–198.

MILJKOVIĆ, J., GRMUŠA, I., ĐIPOROVIĆ, M., KAČAREVIĆ-POPOVIĆ, Z.M. 2005. The influence of fire retardants on the properties of beech and poplar veneers and plywood. Bulletin of the Faculty of Forestry, 2005, 92: 111–124.
SHIM, C.S. 1982. The effect of pretreatment of veneer on the improvement of plywood quality. Journal of the Korean Wood Science and Technology, 1982, 10(3).
SU, W.-Y., SUBYAKTO, HATA, T., NISHIMIYA, K., IMAMURA, Y., ISHIHARA, S. 1998. Improvement of fire retardancy of plywood by incorporating boron or phosphate compounds in the glue. Journal of Wood Science, 1998, 44(2):131–136.
UKRAINIAN RESEARCH INSTITUTE of CIVIL PROTECTION. 2015. Report. Available online: http:// www.undicz.mns.gov.ua.
Zachar, M., Mitterová, I., Xu, Q., Majlingová, A., Cong, J. Galla, Š. 2012. Determination of Fire and Burning Properties of Spruce Wood. Drvna Industrija, 63(3): 217–223.
YEW, M.C., RAMLI SULONG, N.H., YEW, M.K., AMALINA, M.A., JOHAN, M.R. 2015. Eggshells: A novel bio-filler for intumescent flame-retardant coatings. Progress in Organic Coatings, 2015.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0506 "ENPROMO".

Author's address:

Prof. Ing. Pavlo Bekhta, DrSc.
Assist. Prof. Olesya Bryn, CSc.
National University of Forestry and Wood Technology of Ukraine
Department of Wood-Based Composites
Zaliznyaka 11
79057 Lviv
Ukraine
bekhta@ukr.net
chupylo_olesya@ukr.net

Prof. Ing. Ján Sedliačik, PhD.
Technical University in Zvolen
Department of Furniture and Wood Products
Masaryka 24
960 53 Zvolen
Slovakia
sedliacik@tuzvo.sk

Ing. Igor Novák, PhD.
Polymer Institute
Slovak Academy of Sciences
Dúbravská cesta 9
845 41 Bratislava
Slovakia
upolnovi@savba.sk