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Formaldehyde Release from Plywood Manufactured with Two Types of Urea Formaldehyde Resins after Fire Retardant Treatment of Veneers

Oslobađanje formaldehida iz uslojene drvene ploče proizvedene od furnira obrađenih usporivačima gorenja i lijepljenih dvama tipovima urea-formaldehidnih ljepila

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ABSTRACT • *In the present study, it was aimed to investigate the formaldehyde release of plywood panels manufactured from beech, poplar, alder and scots pine veneers treated with 5 % aqueous solutions of commonly used fire retardants: zinc borate, boric acid, monoammonium phosphate and ammonium sulfate. Two types of urea formaldehyde (UF) resin with different free formaldehyde ratios (0.16 % and 0.20 %) in adhesive were used as adhesive. Formaldehyde release of plywood panels was determined according to flask method described in EN 717-3 standard. As a result of this study, it was found that formaldehyde release from panels produced by beech, poplar, alder and scots pine veneers treated with zinc borate and boric acid were higher than those of control panels, while lower formaldehyde release was obtained for panels treated with monoammonium phosphate and ammonium sulfate. This is valid for all four wood species. Treatment of monoammonium phosphate and ammonium sulfate caused considerable reduction in formaldehyde emission from manufactured plywood panels. In some usage areas, where high strength properties are not expected, plywood panels manufactured from veneers treated with monoammonium phosphate and ammonium sulfate may be used for reducing formaldehyde release.*

Key words: *formaldehyde release, plywood, veneer, fire retardant, urea formaldehyde*

SAŽETAK • *U radu je predstavljeno istraživanje oslobađanja formaldehida iz uslojenih drvenih ploča proizvedenih od furnira bukve, topole, johe i običnog bora tretiranih s 5 %-tnim vodenim otopinama najčešće upotrebljavanih usporivača gorenja: cinkova borata, borne kiseline, monoamonijeva fosfata i amonijeva sulfata. Za lijepljenje furnira upotrijebljene su dvije vrste urea-formaldehidnog ljepila (UF) različitog omjera slobodnih formaldehida*

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(0,16 i 0,20 %) u njemu. Oslobađanje formaldehida iz uslojenih drvenih ploča određeno je perforatorskom metodom opisanom u standardu EN 717-3. Istraživanja su pokazala da je oslobađanje formaldehida iz uzoraka ploča proizvedenih od furnira bukve, topole, johe i običnog bora i tretiranih cinkovim boratom i bornom kiselinom veće nego iz kontrolnih uzoraka ploča, dok je za ploče tretirane monoamonijevim fosfatom i amonijevim sulfatom ustanovljena manja količina oslobođenog formaldehida. To vrijedi za sve četiri vrste drva. Tretiranje ploča monoamonijevim fosfatom i amonijevim sulfatom rezultirala je znatnim smanjenjem emisije formaldehida iz proizvedenih uslojenih drvenih ploča. Stoga se u nekim područjima uporabe u kojima se ne zahtijeva velika čvrstoća ploča mogu upotrebljavati ploče od uslojenog drva izrađene od furnira tretiranih monoamonijevim fosfatom i amonijevim sulfatom jer se iz njih oslobađaju manje količine formaldehida.

Ključne riječi: *oslobađanje formaldehida, ploča od uslojenog drva, furnir, usporivač gorenja, urea-formaldehid*

1 INTRODUCTION
1. UVOD

Plywood is preferred as constructional material and has conventionally played an important role in light frame construction. Plywood and other wood-based materials are extensively used in the production of furniture, engineered flooring, housing, and other industrial materials (Bohm *et al.,* 2012). However, the usage and application areas of plywood are limited since the plywood is a flammable material. Therefore, there has been much interest in the fire-retardant-treatment of wood-based panels (Cheng and Wang, 2011). The plywood panels treated with fire retardant chemicals are extensively used. Especially, they are generally preferred in furniture industry and construction applications (Tanritanir and Akbulut, 1999; Winandy, 2001; Ayrilmis *et al.*, 2006).

The wooden materials treated with fire retardant chemicals enable an applicable alternative to conventional non-combustible products, where a higher level of fire safety is necessary or desirable (White and Mitchell, 1992). Boron compounds are known as one of the best fire retardant chemicals due to their beneficial effects like neutral pH, protective efficiency, and less effect on mechanical strength than the others (Levan and Tran, 1990). Also, phosphorus-containing compounds like mono- and di-ammonium phosphates are considered very effective fire retardant chemicals, so they have been preferred for wooden and wood-based products for quite a long time (Grexa *et al.,* 1999).

Formaldehyde has a high risk level and it is a potential human carcinogen, so it is categorized more distinctly than most other pollutants (Salem *et al.,* 2013). Also, this chemical has adverse health effects such as eye and respiratory irritation, irritability, inability to concentrate and sleepiness (Milota, 2000; Colak and Colakoglu, 2004). The formaldehyde, one of the most significant sources, is made by people, e.g. releases from automotive exhaust not fitted with catalytic converters. The formaldehyde is also released industrially in large quantities and utilized in many processes. The products containing formaldehyde like resins, glues, insulating materials, oriented strand board (OSB), plywood, and fabrics are the major anthropogenic sources with a serious impact on people in the indoor environment (Uchiyama *et al.,* 2007). During recent years, many studies have evaluated the effects of press conditions like press temperature and time, mat moisture content, lower-molecular-weight UF resins, and formaldehyde scavengers for formaldehyde release, because wood-based panels are one of the sources of the possible formaldehyde release, and investigated the production of various wood-based panels bonding with low-formaldehyde and non-formaldehyde resins (Minemura, 1976; Hao and Liu, 1993; Grigoriou, 2000; Wiglusz *et al.,* 2002; Wang *et al.,* 2003; Aydin *et al.,* 2006; Wang *et al.,* 2007, 2008). Moreover, it was stated that plywood manufactured by adding borax ($Na_2B_4O_7$10- H_2O) (Colak and Colakoglu, 2004) and polyvinyl acetate (Kim and Kim, 2005) to the glue mixture caused the reduction of formaldehyde release. It was also determined that formaldehyde release decreased by laminating wood-based composite panel surfaces with decorative vinyl film and melamine-impregnated paper (*Groah et al.,* 1984; Nemli and Colakoglu, 2005). Also, studies have been made with tannin extracted from the bark of wattle (Vazquez *et al.,* 2000; Kim *et al.,* 2003; Santana *et al.,* 1995; Pizzi and Scharfetter, 1978), acacia (Pizzi, 2000; Jahanshahee *et al.,* 2010; Jahanshahee *et al.,* 2012) and starch (Farag, 1995; Yoshida *et al.,* 2005; Turunen *et al.,* 2003; Basta *et al.,* 2006), mangrove (Sowunmi, 2000) in co-condensed resins with phenol and formaldehyde.

The cost was a significant issue in evaluating a wood adhesive in specific implementations, its technical properties and gluing behaviour in the past. However, the environmental and health aspects of the adhesive itself have gained more significance during recent years (Aydin *et al.,* 2006). However, few published papers describing techniques for reducing formaldehyde release as an environmental pollutant from wood-based panels, such as plywood, are available. In this study, the effect of fire retardant chemicals on reducing formaldehyde release from plywood was investigated.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

In this experimental study, 2 mm-thick rotary cut veneers with the dimensions of 500 mm by 500 mm were obtained from beech *(Fagus orientalis Lipsky)*, poplar (*Populus deltoides* I-77/51 clone), alder *(Alnus glutinosa* subsp. *barbata)* and scots pine *(Pinus sylvestris L.)* logs. A laboratory scale rotary type peeler (Valette&Garreau - Vichy, France), with a maximum horizontal holding capacity of 800 mm, was used for manufacturing veneer. While the alder and poplar veneers were manufactured from freshly cut logs, beech and spruce logs were steamed for 12 h before veneer production. The main function of steam heating is to soften the veneer log temporarily, making it more plastic, pliable, more readily peeled, and improving the quality and quantity of the material recovered from the log (Baldwin, 1995). Therefore, beech and spruce logs were steamed to make easier the rotary cutting, whereas alder and poplar veneers were manufactured from freshly cut logs because alder and poplar logs can be peeled freshly. The horizontal opening between knife and nosebar was 85 % of the veneer thickness, and the vertical opening was 0.5 mm in rotary cutting process. The veneers were then dried to 6-8 % moisture content in a veneer dryer. After drying, veneer sheets were treated with some fire retardant chemicals. For this aim, 5 % aqueous solutions of zinc borate, boric acid, monoammonium phosphate (MAP) and ammonium sulfate were used. The veneers were subjected to re-drying process at 110 °C after they being immersed in the fire retardant solution for 20 min. The retention level for each treatment solution was calculated with the following equation, and they are presented in Table 1.

$$R = \frac{G \cdot C}{V} \cdot 10, \text{ kg/m}^3 \qquad (1)$$

Where
R – Retention level, kg/m^3;
G – grams of treatment solution absorbed by the sample;
C – grams of preservative or preservative solution in 100 g treatment solution;
V – volume of sample in cm^3.

Three-ply-plywood panels, 6 mm thick, were manufactured by using two types of urea formaldehyde resin with different free formaldehyde ratios. The formulations of adhesive mixtures used for plywood manufacturing are given in Table 2. Veneer sheets were conditioned to approximately 5-7 % moisture content in a climatization chamber before gluing. The glue mixture was applied at a rate of 160 g/m^2 to the single surface of veneer by using a four-roller glue spreader. Hot press pressure was 12 kg/cm^2 for alder and beech and 8 kg/cm^2 for scots pine and poplar panels, while hot pressing time and temperature were 6 min and 110 ºC, respectively. Two replicate panels were manufactured for each test group.

Formaldehyde release of plywood panels was determined according to flask method described in EN 717-3 standard. This is a simple and inexpensive method for testing formaldehyde release and suitable for testing of uncoated boards (Aydin *et al.,* 2006). In this method, test pieces of known mass are suspended over water in a closed container at constant temperature (40 °C). The formaldehyde released from the test pieces is absorbed by the water and determined photometrically (Sundman *et al.,* 2007). The temperature and time were 40 °C and 3 h, respectively, in determining the formaldehyde release. The test apparatus shown in Figure 1 was used for the determination of formaldehyde release from plywood panels (in milligrams per 100 gram of oven-dry panel).

Table 1 Retention levels of fire retardant chemicals at 5 % solution
Tablica 1. Razine retencije kemikalija za usporavanje gorenja pri uporabi 5 %-tne otopine

Wood species *Vrsta drva*	**Fire retardant chemicals** *Kemikalija za usporavanje gorenja*	**Average retention** *Prosječna retencija* kg/m^3		**Wood species** *Vrsta drva*	**Fire retardant chemicals** *Kemikalija za usporavanje gorenja*	**Average retention** *Prosječna retencija* kg/m^3
Beech *bukva*	Zinc borate / *cinkov borat*	12.58		**Alder** *joha*	Zinc borate / *cinkov borat*	15.80
	Boric acid / *borna kiselina*	13.28			Boric acid / *borna kiselina*	13.75
	MAP / *monoamonijev fosfat*	8.71			MAP / *monoamonijev fosfat*	10.60
	Ammonium sulfate *amonijev sulfat*	9.10			Ammonium sulfate *amonijev sulfat*	10.74
Poplar *topola*	Zinc borate / *cinkov borat*	13.49		**Scots pine** *obični bor*	Zinc borate / *cinkov borat*	18.22
	Boric acid / *borna kiselina*	10.51			Boric acid / *borna kiselina*	15.97
	MAP / *monoamonijev fosfat*	10.76			MAP / *monoamonijev fosfat*	9.06
	Ammonium sulfate *amonijev sulfat*	11.03			Ammonium sulfate *amonijev sulfat*	17.94

Table 2 Formulations of UF1 and UF2 glue mixtures used for manufacturing plywood panels
Tablica 2. Formulacije ljepila UF1 i UF2 upotrijebljenih za proizvodnju ploča od uslojenog drva

Glue type / *Vrsta ljepila*	**Ingredients of glue mixture** / *Sastojci smjese ljepila*	**Parts by weight** *Težinski udjel*
UF1 Free formaldehyde max. 0.16 % *slobodni formaldehid, najviše 0,16 %*	UF resin (with 55 % solid content) / *UF smola (55 % suhe tvari)*	100
	Wheat flour / *pšenično brašno*	30
	Hardener - NH_4Cl (with 15 % concentration) *otvrdnjivač - NH_4Cl (koncentracija 15 %)*	10
UF2 Free formaldehyde max. 0.20 % *slobodni formaldehid, najviše 0,20 %*	UF resin (with 65% solid content) / *UF smola (65 % suhe tvari)*	100
	Wheat flour / *pšenično brašno*	30
	Hardener - NH_4Cl (with 15 % concentration) *otvrdnjivač - NH_4Cl (koncentracija 15 %)*	10

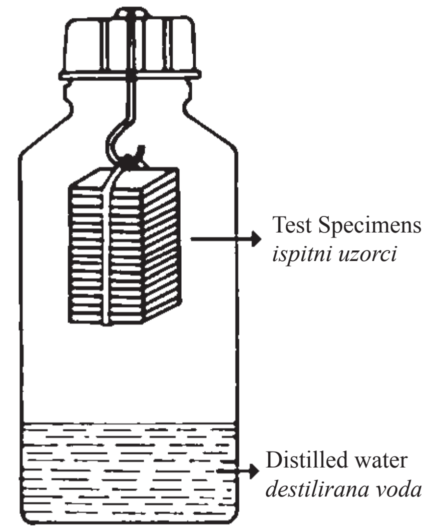

Figure 1 Test apparatus used for the determination of formaldehyde release of plywood panels (Aydin *et al.,* 2006)
Slika 1. Uređaj za određivanje formaldehida oslobođenog iz ploče od uslojenog drva (Aydin *et al*., 2006.)

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Formaldehyde release test results are presented in Fig. 2 and Fig. 3. As can be seen, the poplar plywood panels had the highest formaldehyde release for both UF types. The highest formaldehyde release of poplar plywood panels may be due to high permeability of veneers. The lowest formaldehyde release was found with alder for UF1 and beech for UF2. Also, the formaldehyde release results obtained from UF2 were higher than those obtained from UF1. In literature, it was stated that formaldehyde release increased with increasing free formaldehyde ratio in adhesive (Roffael, 1982).

The treatment processes with fire retardant chemicals evidently affected the formaldehyde release of the panels. Monoammonium phosphate and ammonium sulfate showed a decreasing effect on the formaldehyde release, whereas zinc borate and boric acid showed an increasing effect for both UF types. The lowest formaldehyde release values were obtained for plywood treated with ammonium sulfate. Treatment with ammonium sulfate decreased the formaldehyde release values of the panels produced from treated veneers by 69.53 % and 71.65 % for beech, 18.41 %, and 74.43 % for poplar, 55.94 % and 74.74 % for alder, 19.61 % and 68.70 % for Scots pine panels bonded with UF1 and UF2, respectively.

During the hot pressing, ammonium sulfate and monoammonium phosphate were partially decomposed and produced ammonium in gas. Gao *et al.,* (2015) stated that the released ammonium gas would react with free formaldehyde to produce hexamethylenetetramine, which would be stable in cured glue line and was probably related to the reduction of formaldehyde release levels. In their study, they observed that ammonium pentaborate caused decreasing of free formaldehyde content and formaldehyde release levels, which were mostly reduced by 79.0 % and 81.4 %, respectively (Gao *et al.,* 2015). In literature, it is also stated that the released ammonium could produce N-H functional groups on the surface of the veneer sheets, which contributes to reducing the formaldehyde release (Zhang *et al.,* 2013; Schroder *et al.,* 2001; Wen *et al.,* 2006). Also, Zhang *et al.,* (2013) found for plywood panels that formaldehyde release values decreased with cold-ammonia plasma pretreated veneer sheets and stated that this could result from some etching effect and a large number of free radicals generated after the cold-ammonia plasma treatment, which could develop the wetting and interfacial contact between the

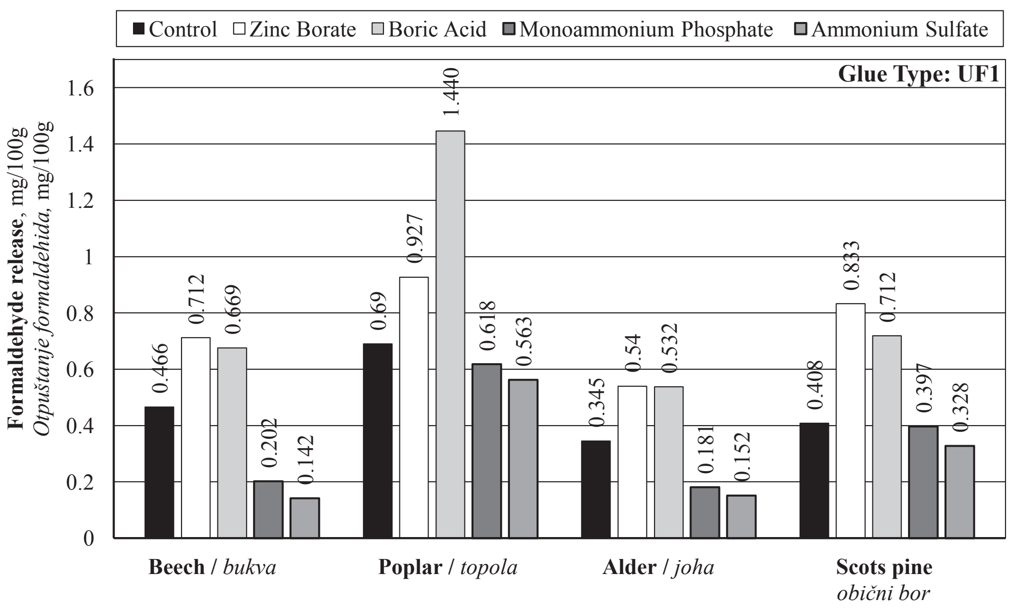

Figure 2 Effect of fire retardant chemicals on formaldehyde release of plywood panels manufactured with UF1 glue
Slika 2. Utjecaj kemikalija za usporavanje gorenja na oslobađanje formaldehida iz ploča od uslojenog drva proizvedenih uz uporabu UF1 ljepila

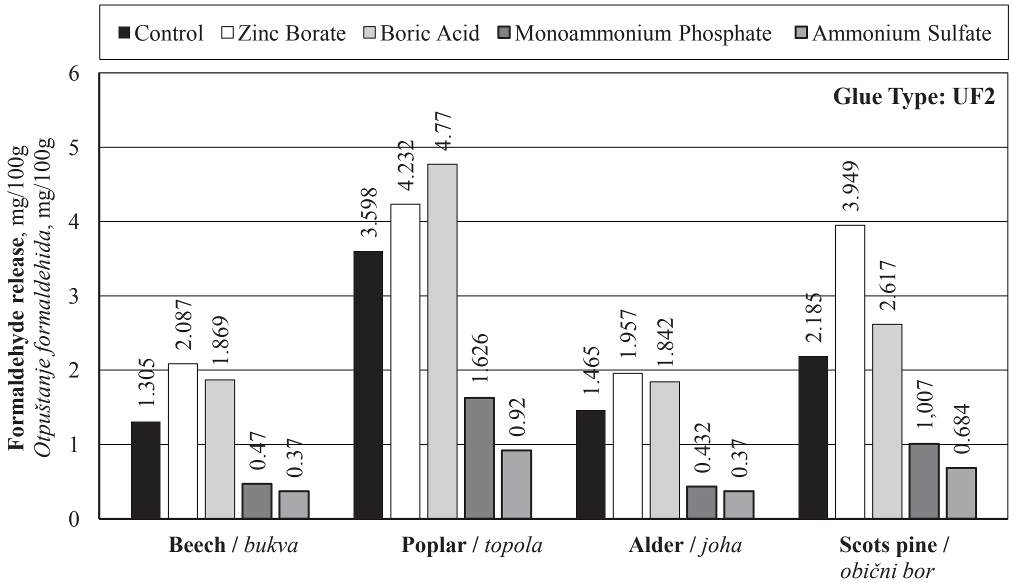

Figure 3 Effect of fire retardant chemicals on formaldehyde release of plywood panels manufactured with UF2 glue
Slika 3. Utjecaj kemikalija za usporavanje gorenja na oslobađanje formaldehida iz ploča od uslojenog drva proizvedenih uz uporabu UF2 ljepila

UF resin and the veneer sheets (Rehn *et al.,* 2003; Wolkenhauer *et al.,* 2008; Blanchard *et al.,* 2009). The development of the wetting and contact increased the shear strength and obstructed the channels preventing the release of formaldehyde (Zhang *et al.,* 2013).

Some studies have also indicated that, when wood was treated with ammonium acetate solution, the formaldehyde release from the wood composites was reduced (Colak *et al.,* 2002; Myers, 1986). Aydin (2004) stated that the ammonium acetate behaves as a formaldehyde scavenger especially when urea-formaldehyde glue was used as adhesive in the manufacturing of wood composites. In addition, Junyou and Shengyou (2010) found that the formaldehyde release from poplar plywood was significantly decreased with the addition of ammonia (Junyou and Shengyou, 2010). Wang *et al.,* (2010) stated that combinations of ammonia and sodium sulfite as formaldehyde scavengers had positive effects on the formaldehyde release of plywood panels.

The boron compounds used in this study increased the formaldehyde release of all wood species for both UF types. Colak and Colakoglu (2004) found that the boric acid increased the formaldehyde release of the panels and explained it by the fact that acetic acid arisen from boric acid reacted with free formaldehyde in the resin. Due to the increase of pH values of veneers, the ability of UF resins to undergo hydrolyses in acidic environment may have decreased (Colak and Colakoglu, 2004; Pizzi, 1989). Also, Demir *et al.,* (2014) found that the zinc borate increased the formaldehyde release of the panels.

4 CONCLUSIONS
4. ZAKLJUČAK

This study investigated the effect of fire retardant chemicals on the formaldehyde release of plywood panels. As a result of this study, for both UF types, formaldehyde release contents of the panels produced from veneers treated with zinc borate and boric acid were higher than those of the control panels, while lower formaldehyde release values were obtained for the panels treated with monoammonium phosphate and ammonium sulfate when compared to the control panels. UF2 type resin, which had a high free formaldehyde ratio, gave higher release values than UF1 type resin. Treatment of monoammonium phosphate and ammonium sulfate caused considerable reduction in formaldehyde release from manufactured plywood panels. In some usage areas, where high strength properties are not expected, plywood panels manufactured from veneers treated with monoammonium phosphate and ammonium sulfate may be used for reducing formaldehyde release.

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