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2 **SOME SURFACE CHARACTERISTICS OF ORIENTAL BEECH WOOD**
3 **IMPREGNATED WITH SOME FIRE-RETARDANTS AND COATED WITH**
4 **POLYUREA/POLYURETHANE HYBRID AND EPOXY RESINS**

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21 **ABSTRACT**

22 This study was made to determine surface characteristics such as colour, gloss, and
23 surface hardness changes of Oriental beech (*Fagus orientalis*). The wood specimens were
24 firstly impregnated with some fire-retardants (FRs) and primed with epoxy resin (EPR) and
25 then coated with polyurethane/polyurea hybrid resin (PUU). Oriental beech was impregnated
26 with 3 % aqueous solution of boric acid (BA), borax (BX), boric acid and borax mixture (1:1),
27 and ammonium sulphate (AS). While Sikafloor®-156 was used for epoxy coating (EPR),
28 Sikalastic®-851 R was used for polyurethane/polyurea hybrid coating (PUU). According to our
29 results, all treatment groups gave negative lightness stability values after accelerated
30 weathering. The colour stability of epoxy resin coated Oriental beech was higher than that of
31 polyurethane/polyurea hybrid resin coated Oriental beech. Except for boric acid impregnated
32 and polyurethane/polyurea hybrid resin coated Oriental beech, all fire-retardants treatment
33 before polyurethane/polyurea hybrid resin and epoxy resin coatings decreased the gloss losses
34 of Oriental beech after accelerated weathering. Fire-retardants impregnation before epoxy resin
35 and polyurethane/polyurea hybrid resin coatings improved the surface hardness values of
36 Oriental beech after accelerated weathering.

37 **Keywords:** Epoxy coating, fire retardants, oriental beech, polyurea coating, polyurethane
38 coating, surface characteristics.

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INTRODUCTION

Preserving the visual structure of wood posed a very important problem. Wood is degraded by biotic/abiotic effects, especially in outdoor conditions. Climatic changes exhibit a weathered appearance in the wood (Peker 1997). In weathering exposure, the effect of sun rays on the wood changes the wood color very rapidly, and it causes losses in hardness, brightness, and mechanical properties. This is reported to be caused by wood extractives and chemical degradation of lignin (Budakçı 2006, Anderson *et al.* 1991, Sivrikaya *et al.* 2011). The expectation of better protection of wood, which plays an important role in the world economy, especially in the field of construction and furniture, during storage, transportation, manufacturing and service continues to be up to date (González-Laredo *et al.* 2015). For this, many different methods are applied within the "wood preservation" discipline (Sögütlü and Döngel 2009). One of these methods is impregnation. Impregnation means trying to penetrate the protective materials of different character, which try to minimize the effects of the hazards in the area of use, to extend the service life of the wood, using pressurized/non-pressure methods. In this sense, simple techniques such as dipping and spraying can be used (Aslan and Özkaya 2009), as well as more advanced techniques that apply pressure/vacuum (Özgenç *et al.* 2013). The most effective method of preventing the photodegradation of wood involves treating inorganic salts with dilute aqueous solutions, particularly hexavalent chromium compounds (Evans *et al.* 1992). The most common method for protecting wood against weathering factors and photodegradation is the use of coatings such as paints with UV absorbers and/or antioxidants, varnishes, stains, organic finishes, or water repellents (Evans *et al.* 1992). It has become up-to-date in coating with top surface materials (paint, polish and varnish) in addition to impregnation to further increase the service life of wood and protect it against weathering conditions. For this reason, several studies have reported that impregnation and varnishing both contribute to the long-term protection of wood surface properties against weathering. Gündüz

66 *et al.* (2019, 2020) studied colour, gloss, and surface hardness changes of Scots pine
67 impregnated with copper-based chemicals and then varnished with polyurethane, cellulosic,
68 and water-based varnish after accelerated weathering. They found that copper-based chemicals
69 impregnation before three varnishes coating improved surface properties of Scots pine wood
70 specimens after accelerated weathering. Türkoğlu *et al.* (2015) investigated the effects of
71 natural weathering on colour stability of Scots pine (*Pinus sylvestris* L.) and Oriental beech
72 (*Fagus orientalis* L.) treated with some chemicals such as tanalith-E TN-E, adolit-KD5, and
73 chromated copper arsenate and then coated with synthetic and polyurethane varnishes. They
74 found that the color stability of treated and varnished Scots pine showed better colour stability
75 than un-treated and solely varnish coated Scots pine specimens after weathering.

76 In the literature, there are studies on some surface characteristics of wood impregnated
77 with some chemicals and coated with some coating materials after weathering or accelerated
78 weathering. However, there are almost no studies of fire retardants impregnated and
79 polyurea/polyurethane and epoxy resins coated wood after accelerated weathering. For this
80 purpose, this study has been tried for the first time in the literature. In order to obtain new
81 coatings materials that can improve the color, gloss and the surface hardness of the wood, a
82 two-step coating method was applied in this study. An impregnation method was applied by
83 using FRs which are boron chemicals and ammonium sulphate before coating process. Firstly,
84 the wood specimens were primed with epoxy resin by using Sikafloor®-156 (EPR), and then
85 coated with Sikalastic®-851 R, a polyurethane/polyurea hybrid resin. Some surface
86 characteristics of Oriental beech wood such as colour, gloss, and surface hardness were
87 investigated, as well.

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91 **MATERIALS AND METHODS**

92 **Preparation of test specimens**

93 Oriental beech (*Fagus orientalis* L.) wood was prepared in 6 mm x 75 mm x 150 mm
94 (radial, tangential, and longitudinal) dimensions for colour, gloss, and surface hardness tests.

95 **Impregnation procedure**

96 Boric acid (H_3BO_3 ; CAS: 10043-35-3), borax ($Na_2B_4O_7 \cdot 10H_2O$; CAS 1303-96-4; di-
97 sodium tetraborate decahydrate) and ammonium sulphate $[(NH_4)_2SO_4$; CAS: 7783-20-2] were
98 purchased from Merck and used to prepare the solutions. The impregnation of the Oriental
99 beech was carried out according to ASTM D 1413-07 (ASTM 2007). The amount of FRs
100 retention was determined from the following equation (Eq.1):

101

$$102 \text{ Retention} = \frac{G \cdot C}{100 \cdot V} \text{ (kg/m}^3\text{)} \quad (1)$$

103 Where;

104 $G = T_2 - T_1$

105 T_1 = First weight of the specimen (kg)

106 T_2 = Final weight of the specimen (kg)

107 V = Volume of the specimen (m^3)

108 C = Concentration (%)

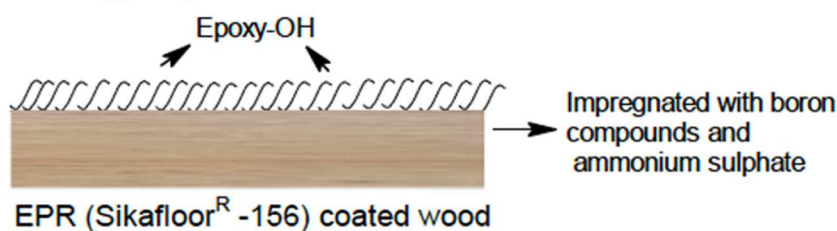
109 **Coating procedure**

110 The coatings are based on epoxy and polyurethane/polyurea hybrid resins. The
111 impregnated wood was primed with epoxy resin components (Sikafloor[®]-156) and then coated
112 with polyurethane/polyurea hybrid resin (Sikalastic[®]-851 R). Epoxy coated wood is labelled as
113 EPR (Figure 1a,b) and polyurethane/polyurea coated wood is labelled as PUU, as well (depicted
114 in Figures 2a). PUU labelled wood determine that the coatings were firstly primed with epoxy
115 resin and then coated with polyurethane/polyurea hybrid resin.

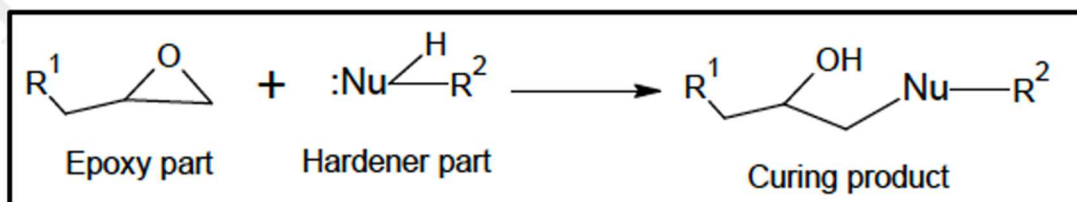
116 **EPR Coatings**

117 Sikafloor[®]-156 was used as an epoxy resin for EPR coatings. Sikafloor-156 is purchased
118 from Sika company in Turkey. Sikafloor[®]-156 is well-known as a epoxy primer with two
119 ingredients, which is consists of an epoxy part (A) and a hardener part (B), low-viscosity and
120 solvent-free (Abed *et al.* 2020). In line with the manufacturer's recommendations, 3 components
121 A and 1 component B components were combined and applied to 2 layers of wood material. It
122 was applied to the impregnated wood by the professional users of the epoxy resin manufacturer
123 company in Aydın Adnan Menderes University Furniture and Decoration Workshop (depicted
124 in Figure 1a).

125 The possible cure reaction between an epoxy part and a hardener part is given in Figure
126 1b. The hardeners are known the chemicals which are converted epoxy resin to thermosets,
127 have usually bear active hydrogen attached to an electronegative atom such as, N, O or S. The
128 curing reaction is a ring opening reaction between the oxirane ring and a nucleophile (Figure
129 1b). The ring opening reaction occurs via nucleophilic attack by the hardener to the oxirane
130 ring, then a second reaction follows until the remaining active hydrogens attached to the
131 hardeners are fully reacted (Babahan *et al.* 2020).



a)

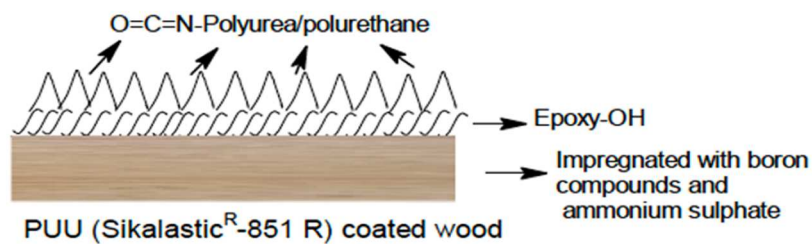


b)

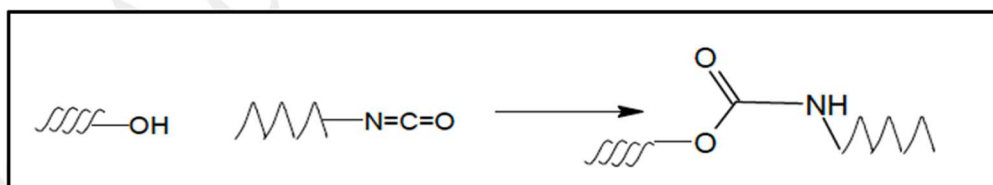
132 **Figure 1. a)** EPR coated wood **b)** Possible curing reaction between epoxy part and
133 hardener part for EPR coatings.

134 **PUU Coatings**

135 Sikalastic[®]-851 R was used for PUU coatings. Sikalastic[®]-851 R is also obtained from
136 Sika company in Turkey. PUU coated by using Sikalastic[®]-851 R resin were made after test
137 specimens were primed with epoxy resin (Sikafloor[®]-156). Sikalastic[®]-851 R is known as a two
138 component, elastic, crack-bridging, rapid-curing modified polyurethane/polyurea hybrid resin.
139 Component A consists of isocyanate derivate and component B consists of polyol/amine
140 derivative (Wagner 2015). The coating was done professionally by the manufacturer. The
141 coating was professionally made by the manufacturer firm (depicted in Figure 2a). Two layers
142 were applied to the floor using special polyurea coating machines (GAMA G-30 H) at a
143 consumption of 1,7 kg – 2,2 kg per m² and the second layer application was started within
144 maximum 6 hours after the first layer application.



a)



b)

145 **Figure 2. a)** PUU coated wood **b)** Reaction between epoxy and polyurea/polyurethane
146 moieties.

147 A possible reaction, between polyurea/polyurethane and epoxy moieties which forms an epoxy-
148 urea bond, and displayed the new interfacial chemical reaction between Sikafloor[®]-156 and
149 Sikalastic[®]-851 R, is illustrated in Figure 2b. The suggested/depicted crosslinking reaction in
150 Figure 2b that occurred between the hydroxyl groups of the epoxy resin and the isocyanate

151 groups of the polyurea/polyurethane polymers are in accord with the previous studies (Attard
152 *et al.* 2019, Chern *et al.* 1999, Chattopadhyay *et al.* 2007).

153 **Colour test**

154 The color parameters L^* , a^* , and b^* were determined by the CIEL*a*b* method. The
155 L^* axis determines the lightness, whereas a^* and b^* are the chromaticity coordinates. The $+a^*$
156 and $-a^*$ parameters show the colors red and green, respectively. The $+b^*$ parameter represents
157 yellow, whereas $-b^*$ represents blue. The L^* value can vary from 100 (white) to zero (black)
158 (Zhang 2003). The color difference, (ΔE^*) was measured according to ASTM D1536-58T
159 (ASTM 1964). The color changes were determined using Eqs. 2 to 5;

160

$$161 \quad \Delta a^* = a_f^* - a_i^* \quad (2)$$

$$162 \quad \Delta b^* = b_f^* - b_i^* \quad (3)$$

$$163 \quad \Delta L^* = L_f^* - L_i^* \quad (4)$$

$$164 \quad (\Delta E^*) = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2} \quad (5)$$

165 Where;

166 Δa^* , Δb^* , and ΔL^* represent the changes between the initial and final interval values. Five
167 replicates were made for each treatment group.

168 **Gloss test**

169 The gloss values of Oriental beech were measured according to ASTM D 523-14
170 (ASTM 2018) with a measuring device (Micro-TRI-Gloss). The chosen geometry was an
171 incidence angle of 60°. Five replicates were made for each treatment group.

172 **Surface hardness test**

173 The surface hardness of Oriental beech was measured with the König hardness
174 according to ASTM D 4366-14 (ASTM 2014). The specimen was positioned on a panel table
175 and a pendulum was placed on the panel surface. The pendulum was deflected for 6° and

176 released, triggering the start of the timer. The time needed to decrease the pendulum amplitude
177 from 6° to 3° corresponded to the König hardness estimate. Five replicates were made for each
178 treatment group.

179 **Accelerated weathering**

180 The accelerated weathering experiment was performed according to the American
181 standard ASTM G154-06 (ASTM 2016) in a Q-Panel Company (QUV) weathering tester with
182 eight ultraviolet florescent lamps (UVA 340). The specimens were exposed to UV irradiation
183 cycles for 8 hours, followed by condensation for 4 hours in a QUV apparatus for 250 hours.
184 During the weathering period at the maximum intensity ($\lambda_{\max} = 340 \text{ nm}$), the average
185 irradiance was $0,89 \text{ W m}^{-2}$. The temperature was 50 °C during the condensation period and it
186 was 60 °C during the light irradiation period.

187 **Statistical evaluation**

188 Test results were analysed by a computerized SPSS statistical program include analysis
189 of variance and Duncan test applied at 95 % confidence level. Statistical evaluations were made
190 on homogeneity groups (HG) where different letters reflected statistical significance.

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RESULTS AND DISCUSSIONS

193 **Colour test**

194 The results regarding the color change values of the Oriental beech FRs impregnated
195 and coated with PUU and EPR before and after accelerated weathering for 250 hours are given
196 in Table 1 and Figure 3.

197 Table 1 shows L^* , a^* , and b^* values of un-treated and non-coated (control) group, solely
198 coated, and impregnated with FRs (boron chemicals and ammonium sulphate) and coated
199 Oriental beech specimens and also shows the values of change ΔL^* , Δa^* , and Δb^* , as well as
200 ΔE^* of the Oriental beech after 250 h accelerated weathering. The retention values of Oriental
201 beech wood impregnated with FRs were changed from $9,00 \text{ kg}\cdot\text{m}^{-3}$ to $12,31 \text{ kg}\cdot\text{m}^{-3}$. Before
202 accelerated weathering, all of the treatment groups were observed a decrease in L^* values than

203 that of un-treated and non-coated (control) group. While the L^* value of the un-treated and non-
 204 coated (control) group was 68,19, it was changed from 49,75 to 58,29 for the impregnated and
 205 coated Oriental beech wood. L^* value of the EPR coated Oriental beech was higher than that
 206 of PUU coated Orietal beech. The decrease in the L^* value of Oriental beech showed that the
 207 wood became darker after the EPR and PU coated. These results are consistent with those of
 208 Baysal (2012), Üstün *et al.* (2016), and Şimşek and Baysal (2012). Our results showed that a^*
 209 and b^* values of un-treated and non-coated (control) group were 9,89 and 20,94. While a^* and
 210 b^* values were -1,02 and -0,43, respectively for PU coated Oriental beech, a^* and b^* values
 211 were 14,38 and 24,96, respectively for EPR coated Oriental beech. Moreover, while FRs
 212 impregnated and PU coated Oriental beech gave negative L^* values, it gave positive L^* values
 213 for FRs impregnated and EPR coated Oriental beech. Our results showed that L^* values of EPR
 214 coated Oriental beech were highly higher than that of PUU coated Oriental beech.

215 **Table 1:** Colour change values of Oriental beech before and after 250 hours of accelerated
 216 weathering.

FRs and coating materials	Retention (Kg/m ³)	Colour values before accelerated weathering						Colour values after 250 hours accelerated weathering			Total colour changes	
		L^*		a^*		b^*		ΔL^*	Δa^*	Δb^*	ΔE^*	Homogeneity group
		Mean	SD	Mean	SD	Mean	SD					
Un-treated and non-coated (control) group	-	68,19	2,34	9,89	0,69	20,94	1,16	-6,79	2,71	5,22	8,98	BC
PUU	-	53,66	0,11	-1,02	0,01	-0,43	0,08	-9,45	4,91	14,89	18,30	A
BA+PUU	12,13	53,70	0,30	-1,04	0,08	-0,36	0,06	-7,73	2,50	14,65	16,75	A
BX+ PUU	9,00	53,40	0,45	-1,03	0,01	-0,25	0,08	-8,57	3,29	15,60	18,10	A
AS+PUU	12,30	53,32	0,25	-1,03	0,01	-0,38	0,04	-8,95	4,37	15,61	18,51	A
(BA+BX)+PUU	9,34	53,76	0,12	-1,03	0,08	-0,29	0,09	-9,40	4,58	15,14	18,46	A
EPR	-	55,83	7,60	14,38	3,38	24,96	0,92	-7,38	2,98	2,15	8,24	BC
BA+EPR	11,27	49,75	7,55	14,80	0,69	23,37	3,74	-6,00	0,50	0,40	6,03	CD
BX+EPR	10,80	55,78	1,17	15,09	1,95	27,55	1,19	-3,39	1,10	3,37	4,90	D
AS+ EPR	12,31	51,78	1,98	13,54	1,51	26,13	2,44	-4,88	1,43	0,41	5,10	D
(BA+BX)+EPR	12,05	58,29	6,30	13,32	2,85	23,16	1,91	-7,30	3,94	7,10	11,21	BC

Note: PUU: Polyurea/Polyurethane hybrid resin, EPR: Epoxy resin, BA: Boric acid, BX: Borax, AS: Ammonium sulphate. SD: Standard deviation. Five replicates were made for each group. Homogeneity group was realized at 95 % confidence level.

217
 218 After 250 h of accelerated weathering, the negative (ΔL^*) values for un-treated and non-
 219 coated (control) group and other all FRs impregnated and coated Oriental beech were occurred.
 220 Therefore, the wood became rougher and darker after accelerated weathering. The darkening

221 of Scots pine may be due to the degradation of lignin and other non-cellulosic polysaccharides
222 (Hon and Chang 1985, Grelier *et al.* 2000, Petric *et al.* 2004).

223 The surface cellulose layer has the potential to stabilize the wood surface against
224 discolouration. However, it can be affected by UV lights. Under the UV lights, a decrease in
225 lignin content and at the same time an increase in crystalline cellulose content appears at the
226 surface (Evans *et al.* 1996) . Lignin produces carbonyl groups when it exposes to singlet oxygen
227 under the UV lights. The new carbonyl derivatives enable the absorbance of moisture that can
228 decrease the resistance of wood against environmental effects (Varganici *et al.* 2021, Evans *et*
229 *al.* 1996, Catto *et al.* 2016).

230 The main important consequence of wood photodegradation is surface color
231 modification, accompanied by changes in the mechanical behavior (Varganici *et al.* 2021, Leary
232 1968). Photodegradation is formed by atmospheric oxygen via free radicals. The radicals
233 formed during photodegradation are oxidized to yellow colored quinoid structures or to
234 secondary chromophores which ensure further photodegradation (Leary 1968, Olsson *et al.*
235 2014, Varganici *et al.* 2021). Photodegradation produces a series of the most damaging effects
236 on untreated wood, therefore coatings (EPR or EPR+PUU coatings) in this study have been
237 used to protect wood surface against discoloration. Impregnated with FRs and coated with EPR
238 or EPR+PUU coatings, as shown in Figure 3 and coatings protection on wood surface against
239 discoloration are detailed in the literature (Varganici *et al.* 2021, Evans *et al.* 1996, Catto *et al.*
240 2016, Cogulet *et al.* 2018;).

241 In order to covalently link the PUU coatings, epoxy resin (EPR) firstly applied to the
242 wood surface. All wood components contain UV cleavable moieties: carboxyl, hydroxyl,
243 carbonyl, double bonds. Coated with epoxy resin (EPR) process avoids occurring free radicals
244 and produce the crosslinking between epoxy resin (EPR) and polyurea/polyurethane moieties.
245 Interaction of EPR and PUU coatings stabilizes the wood surface against photoyellowing.

246 Treated the surface impregnated with FRs and coated with EPR resin or impregnated with FRs
247 and coated with EPR+PUU coatings led to a decrease in wood surface hydrophilicity and
248 enhancement in fire resistance. (Rosu *et al.* 2016, Bodirlau *et al.* 2013) The effect was
249 demonstrated by color differences decrease and an inhibition of surface darkening after
250 exposure (Figure 3). This aspect is also reflected in the variation of chromatic coordinates a^*
251 and b^* values (Table 1).

252 FRs impregnation caused increasing in the lightness than that of only coated Oriental
253 beech in this study. It might be the FRs impregnation improved the stabilization of wood color
254 in the visible region through a reduction in the lignin degradation that resulted from UV light,
255 since the FRs impregnation process avoids occurring free radicals (Grelier *et al.* 2000). After
256 250 h of accelerated weathering, Δa^* and Δb^* values of un-treated and non-coated (control)
257 group were found to be as 2,71 and 5,22, respectively. Un-treated and non-coated (control)
258 group and all treatment groups showed positive Δa^* and Δb^* values after accelerated
259 weathering. Positive Δa^* and Δb^* values determine that wood specimens surface maintained
260 reddish and yellowish tone. While total color change (ΔE^*) was 8,98 for un-treated and non-
261 coated (control) group, it was changed from 4,90 to 18,51 for all treatment groups after
262 accelerated weathering. Colour change values showed that the best colour stability was
263 observed with BX impregnated and EPR coated Oriental beech. In our study, except for
264 BA+BX impregnation and EPR coating, other all impregnation and EPR coating caused
265 decreasing ΔE^* of Oriental beech than that of un-treated and non-coated (control) group. The
266 reduction in ΔE^* of FRs impregnated and EPR coated Oriental beech showed a positive effect
267 to colour stability in previous studies (Yalınkılıç *et al.* 1999; Baysal 2008). In our study, only
268 PUU coated and FRs impregnated and PUU coated Oriental beech showed higher (ΔE^*) values
269 than that of un-treated and non-coated (control) group. Therefore, FRs impregnated and PUU
270 coated Oriental beech showed the worst results in terms of (ΔE^*) values. There was a

271 statistically significant difference in ΔE^* values between PUU coated and un-treated and non-
 272 coated (control) group ($p \leq 0,05$).

FRs and coating materials	Before accelerated weathering	After 250 hours accelerated weathering
Control		
PUU		
EPR		
BA+PUU		
BX+PUU		
AS+PUU		
(BA+BX)+PUU		
BA+EPR		
BX+EPR		
AS+EPR		
(BA+BX)+EPR		

273 **Figure 3:** Colour changes of Oriental beech impregnated with FRs and coated with PUU and
 274 EPR after 250 h accelerated weathering.

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278 **Gloss**

279 Gloss values of Oriental beech measured before and after accelerated weathering, and
280 statistical test results are given in Table 2. Except for BA+BX impregnation before EPR
281 coating, other FRs treatments before EPR coating caused to decrease gloss values of Oriental
282 beech in some extent. It may be due to impregnation with solutions might limit the glossiness
283 up to a point in Oriental beech before weathering, probably owing to absorption and dispersion
284 of reflected rays by salt crystals prominent in the large lumens of the vessels in the wide
285 earlywood sections of the grains. Photoactive ions on the wood surface were assumed to cause
286 some loss in gloss of FRs impregnated and EPR coated Oriental beech wood surfaces before
287 weathering (Yalınkılıç *et al.* 1999). This result is consistent with the glossiness values of CCB
288 impregnated Scots pine before varnish coating (Yalınkılıç *et al.* 1999). However, gloss values
289 were highly increased for FRs impregnated and PUU coated of Oriental beech than that of only
290 PUU coated Oriental beech before accelerated weathering.

291 Accelerated weathering decreased gloss values of un-treated and non-coated (control)
292 group and FRs impregnated and PU and EPR coated Oriental beech. Çakıcıer *et al.* (2011)
293 reported that decreases in glossiness of wood species coated with one and two component
294 water-based varnishes after accelerated weathering for 216 h and 432 h. Türkoğlu *et al.* (2015)
295 investigated gloss changes of copper based chemicals impregnated and then polyurethane and
296 synthetic varnishes coated Scots pine (*Pinus sylvestris*) and Oriental beech (*Fagus orientalis*)
297 after 3 months of weathering. Our results showed that except for BA impregnated and PUU
298 coated Oriental beech, other all FRs impregnation before PUU and EPR coating showed
299 protective effect in terms of preventing loss of gloss after accelerated weathering. However,
300 while there was a statistically significant difference in gloss losses values between EPR coated
301 Oriental beech and FRs impregnated and EPR coated Oriental beech, there was no statistically

302 significant difference between in gloss losses values between PUU coated Oriental beech and
 303 FRs impregnated and PUU coated Oriental beech.

304 **Table 2:** Gloss change values of test specimens before and after 250 hours of accelerated-
 305 weathering.

FRs and coating materials	Retention (Kg/m ³)	Gloss values before accelerated weathering		Gloss values after 250 hours accelerated weathering		Gloss losses values after 250 hours accelerated weathering (%)	
		60°		60°		60°	Homogeneity group
		Mean	SD	Mean	SD		
Un-treated and non-coated (control) group	-	2,88	0,08	2,49	0,15	-13,54	CDE
PUU	-	28,06	10,16	25,00	9,51	-10,90	BC
BA+PUU	12,13	39,72	12,69	33,65	7,91	-15,28	CDE
BX+ PUU	9,00	69,62	12,19	64,86	10,17	-6,83	B
AS+PUU	12,30	69,66	4,91	65,07	9,98	-6,58	B
(BA+BX) +PUU	9,34	77,96	4,53	69,60	8,83	-10,72	BC
EPR	-	39,68	11,67	30,95	14,76	-22,00	E
BA+EPR	11,27	13,30	4,32	11,65	3,75	-12,40	C
BX+EPR	10,80	29,56	7,64	25,15	7,47	-14,91	CD
AS+ EPR	12,31	29,30	8,67	27,60	6,41	-5,80	A
(BA+BX)+EPR	12,05	59,68	15,96	55,65	10,19	-6,75	B

Note: PUU: Polyurea/Polyurethane hybrid resin, EPR: Epoxy resin, BA: Boric acid, BX: Borax, AS: Ammonium sulphate. SD: Standard deviation. Five replicates were made for each group. Homogeneity group was realized at 95% confidence level.

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307 Surface hardness

308 The surface hardness values of Oriental beech before and after 250 h accelerated
 309 weathering and the percentage change in surface hardness are given in Table 3. The pendulum
 310 hardness test was used to measure the surface hardness values. The simple principle for
 311 pendulum hardness test is that the harder surface displays the greater the oscillation time of the
 312 pendulum.

313 While the surface hardness value of un-treated and non-coated (control) group was
 314 34,60, it was 37,40 and 67,20 for PUU and EPR coated Oriental beech wood specimens before
 315 accelerated weathering. There was not a statistically significant difference in surface hardness
 316 changes between PUU coated Oriental beech and un-treated and non-coated (control) group
 317 after accelerated weathering. FRs impregnation before PU and EPR coating caused to slightly
 318 decrease surface hardness of Oriental beech before accelerated weathering, however, after
 319 accelerated weathering 250 h, there were an increasing affect for EPR coatings and decreasing

320 affect for PUU coatings, except impregnated with borax (BA) for PUU coatings. Baysal *et al.*
321 (2012) investigated the effect of the surface hardness changes of Scots pine specimens treated
322 with wolmanit-CB, tanalith-E, and adolit-KD5 and coated with synthetic varnish. They found
323 that impregnation with chemicals before synthetic varnish coating caused to decrease surface
324 hardness values of Scots pine. Our results showed that while FRs impregnation before coating
325 caused to decrease surface hardness values of Oriental beech before accelerated weathering,
326 FRs impregnation increases the surface hardness for both EPR and PUU coatings, except BX-
327 PUU and AS-PUU, after accelerated weathering. The effect of FRs treatment on surface
328 hardness was probably due to their different compositions. Active constituents in the
329 formulations might have some influence on the curing process of PUU and EPR. Surface
330 hardness values of FRs impregnated and EPR coated wood were higher than that of FRs
331 impregnated and PUU coated wood after accelerated weathering. The surface hardness values
332 of PU and EPR coated and un-treated and non-coated (control) group were decreased after 250
333 h accelerated weathering. Yalınkılıç *et al.* (1999), Baysal (2008), and Türkoğlu *et al.* (2015)
334 studied the surface hardness values of some weathered wood species. They found that
335 weathering caused to decrease the surface hardness values of the wood. The combined effect of
336 moisture, UV light, and temperature could degrade lignocellulosic structure of the wood.
337 Therefore, the degradation products became water-soluble and were leached out resulting in
338 erosion of the wood surface (Meijer 2001). BA impregnation before PUU coating resulted in
339 2.58% increase of the surface hardness of Oriental beech after 250 h accelerated weathering.

340 Moreover, other FRs treatment on PUU caused to decrease surface hardness loss. For
341 example, surface hardness decrease was 16.22 % for only PUU coated Oriental beech, it was
342 changed 2,77 % to 15.84 % for other FRs treatment on PUU.

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345 **Table 3:** Surface hardness values of test specimens before and after 250 hours of accelerated
 346 weathering.

FRs and coating materials	Retention (Kg/m ³)	Surface hardness values before accelerated weathering		Surface hardness after 250 hours accelerated weathering (%)		Surface hardness changes (%) after 250 hours accelerated weathering	
		Mean	SD	Mean	SD	Mean	Homogeneity group
-	-	34,60	4,21	41,80	1,48	-14,62	E
Un-treated and non-coated (control) group	-	34,60	4,21	41,80	1,48	-14,62	E
PUU	-	37,40	5,54	31,33	9,60	-16,22	E
BA+PUU	12,13	36,80	3,56	37,75	3,77	2,58	CD
BX+ PUU	9,00	35,00	1,87	29,87	10,11	-14,65	E
AS+PUU	12,30	35,47	3,13	29,85	5,77	-15,84	E
(BA+BX) +PUU	9,34	34,20	1,78	33,25	2,98	-2,77	D
EPR	-	67,20	7,69	30,75	2,06	-54,24	G
BA+EPR	11,27	51,35	5,27	60,25	7,80	17,33	A
BX+EPR	10,80	61,40	14,48	82,75	11,78	34,77	A
AS+ EPR	12,31	53,49	7,70	57,00	1,82	6,56	C
(BA+BX) +EPR	12,05	61,60	5,81	70,89	10,81	15,08	B

Note: PUU: Polyurea/Polyurethane hybrid resin, EPR: Epoxy resin, BA: Boric acid, BX: Borax, AS: Ammonium sulphate. SD: Standard deviation. Five replicates were made for each group. Homogeneity group was realized at 95% confidence level.

347

348 However, FRs treatments on EPR coated caused to increase surface hardness values of

349 Oriental beech after 250 h accelerated weathering. While the surface hardness decreases of only

350 EPR coated Oriental beech was 54,24 % after accelerated weathering, it increased from 6,56 %

351 to 34,77 % for FRs impregnated and EPR coated Oriental beech after accelerated weathering.

352 There was a statistically significant differences in surface hardness changes between EPR

353 coated and FRs impregnated and only EPR coated Oriental beech wood after accelerated

354 weathering. Türkoğlu *et al.* (2015) investigated the surface hardness changes of Oriental beech

355 and Scots pine impregnated with chromated copper arsenate and some copper-based chemicals

356 such as adolit KD-5 and tanalith-e and then coated with polyurethane and synthetic varnishes

357 after weathering. They found that the surface hardness values of impregnated and varnish

358 coated wood surface were higher than that solely varnish coated wood surface after weathering.

359 This was because the impregnation materials increased hardness and wood samples had a harder

360 varnish layer (Keskin *et al.* 2011). Our results are compatible with these researcher's findings.

361 In our study, while FRs impregnation before PUU coating decreased surface hardness loss, it

362 increased the surface hardness values of Oriental beech after accelerated weathering. It can be

363 concluded from our results that FRs impregnated epoxy coatings (EPR+FRs) have better

364 hardness values compared to FRs impregnated polyurethane/polyurea coatings (PUU+FRs).
365 This could be the reason of crosslinking density of the epoxy coatings is higher than
366 polyurethane/polyurea coatings.

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CONCLUSIONS

370 In this study, colour, gloss, and surface hardness changes of Oriental beech wood
371 impregnated with FRs and EPR and PUU coated Oriental beech wood were investigated after
372 accelerated weathering.

373 FRs impregnation and EPR and PUU coatings caused decreasing L^* values of Oriental
374 beech. While un-treated and non-coated (control) group and all treatment groups showed
375 negative ΔL^* values, they gave positive Δa^* and Δb^* values after accelerated weathering.
376 Colour stability of EPR coatings of Oriental beech were higher than that of PUU coated Oriental
377 beech. The best colour stability was obtained with BX impregnated and EPR coated Oriental
378 beech. Coating with PUU and EPR increased gloss values of Oriental beech before accelerated
379 weathering. Weathering caused decreasing gloss values of control and PUU and EPR coated
380 Oriental beech. However, except for BA impregnation and PUU coating, FRs impregnation
381 before PUU and EPR coating caused decreasing gloss losses after accelerated weathering.
382 While FRs treatment before PUU coating decreased the surface hardness losses, it increased
383 the surface hardness of EPR coated Oriental beech after accelerated weathering.

384 In conclusion, FRs treatments before PUU and EPR coatings generally resulted in higher
385 colour stability, lower gloss losses, and higher surface hardness values after accelerated
386 weathering. Thus, Oriental beech wood surfaces can be impregnated with FRs (boron chemicals
387 and AS) before PUU and EPR coatings for improving surface characteristics of wood surface
388 in weathering conditions.

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