Mehmet Yeniocak[1], Osman Goktas[1], Sezil Aliyazicioglu[1], Mehmet Colak[1], Sevil Yeniocak[1], Ertan Ozen[1], Mehmet Ugurlu[2]

Determination of the Effect of Liquid Glass (SiO_2) on Color Stability of Wood Stained by Natural Dyes

Određivanje učinka tekućeg stakla (SiO_2) na stabilnost boje drva obojenoga prirodnim bojama

Preliminary paper • Prethodno priopćenje
Received – prispjelo: 8. 2. 2017.
Accepted – prihvaćeno: 1. 12. 2017.
*UDK: 630*812.111; 630*829.22*
doi:10.5552/drind.2017.1707

ABSTRACT • *In this exploratory study, the effect of liquid glass (SiO_2) treatment on color stability of wood stained by natural dyes was investigated. Mixing liquid glass with natural dyes produced durable, natural, and protective wood stain as expected. For natural dyes, Licorice (<u>Glycyrrhiza glabra</u> L.), Indigo (<u>lsatis tinctoria</u> L.) and pomegranate skin (<u>Punica granatum</u> L.) were chosen and their extracts were mixed with liquid glass and applied to Scots pine (<u>Pinus sylvestris</u> L.), chestnut (<u>Castanea sativa</u> Mill.) and mahogany (<u>Khaya Ivorensis</u> A. Chev.) specimens using immersion method. Coated wood specimens were tested to evaluate the protection degree of liquid glass + natural stains against discoloration using cold check test. The treated wood specimens were exposed to cold check test for different conditions; 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles. As a result, the liquid glass treatment produced better performance against color change. However, for general definition, liquid glass was not found precisely effective on color stability.*

Key words: *Liquid glass, (SiO_2), natural plant dyes, wood protection, color stability, cold check*

SAŽETAK • *U provedenom je istraživanju ispitan učinak tekućeg stakla (SiO_2) na stabilnost boje drva obojenoga prirodnim bojama. Miješanjem tekućeg stakla s prirodnim bojama napravljen je trajni prirodni i zaštitni premaz za drvo, kako se i očekivalo. Za prirodne boje odabrani su sladić (<u>Glycyrrhiza glabra</u> L.), indigo (<u>lsatis tinctoria</u> L.) i šipak (<u>Punica granatum</u> L.), a njihovi su ekstrakti pomiješani s tekućim staklom i metodom uranjanja naneseni na uzorke drva običnoga bora (<u>Pinus sylvestris</u> L.), kestena (<u>Castanea sativa</u> Mill.) i mahagonija (<u>Khaya Ivorensis</u> A. Chev.). Na tako obrađenim uzorcima drva, primjenom testa hladne provjere, istražen je zaštitni utjecaj premaza od tekućeg stakla i prirodne boje na promjenu boje obrađenih uzoraka drva. Obrađeni su drvni uzorci bili izloženi testu hladne provjere u različitim uvjetima: 1 h pri 50±5 °C, 1 h pri laboratorijskim uvjetima i 1 h pri -20±2 °C u 20 ciklusa. Rezultati istraživanja pokazali su da je obrada tekućim staklom imala pozitivan učinak na zaštitu boje drvnih uzoraka obojenih prirodnim bojama, odnosno da nije došlo do promjene boje. Međutim, općenito se može zaključiti da rezultati istraživanja nisu dali uvjerljiv dokaz učinkovitosti tekućeg stakla na stabilnost boje obojenog drva.*

Ključne riječi: *tekuće staklo (SiO_2), prirodne biljne boje, zaštita drva, stabilnost boja, hladna provjera*

[1] Authors are professor, Ph.D. student, assistant professor, associate professor, master student and associate professor at Mugla Sitki Kocman University, Faculty of Technology, Department of Woodworking Industrial Engineering, Mugla, Turkey. [2]Author is professor at Mugla Sitki Kocman University, Faculty of Science, Department of Chemistry, Mugla, Turkey.

[1] Autori su profesor, doktorand, docent, izvanredni profesor, student diplomskog studija i izvanredni profesor Sveučilišta *Mugla Sitki Kocman*, Tehnološki fakultet, Odjel industrijske obrade drva, Mugla, Turska. [2]Autor je profesor Sveučilišta *Mugla Sitki Kocman*, Fakultet prirodnih znanosti, Kemijski odjel, Mugla, Turska.

1 INTRODUCTION
1. UVOD

Volatile organic compounds (VOCs) are chemicals used to manufacture and maintain building materials, interior furnishing, cleaning products, and personal care products. "Volatile" means that these chemicals evaporate or can easily get into the air at room temperature. "Organic" means that these chemicals are carbon based. The term "chemical emissions" refers to VOCs as they evaporate into the air from products (Greenguard, 2016).

VOCs are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. The majority of VOCs found in the indoor environments originate from building materials, indoor furnishings, cleaning supplies, consumer products and processes, such as printing, cooking, hobbies, cleaning, interior renovations and pesticide applications.

The human health risks can be decreased using organic chemicals instead of highly toxic, petroleum based ones. Human health risks may include: eye, nose and throat irritation, headaches, loss of coordination and nausea, damage to the liver, kidney and central nervous system; also some organics can cause cancer in animals, some are suspected or known to cause cancer in humans (EPA, 2016).

There are three main ways how people are exposed to chemicals: ingestion, dermal absorption, and inhalation. Ingestion occurs when materials including chemical content are swallowed or placed in the mouth. Dermal absorption occurs when chemicals come into contact with the skin. While these are both significant forms of chemical exposure, the majority of everyday chemical exposure occurs through the air we breathe in our homes, offices, schools and other indoor environments. As mentioned earlier in this paper, these airborne chemicals are commonly referred to as volatile organic compounds (VOC's). EPA's Office of Research and Development's "Total Exposure Assessment Methodology (TEAM) Study" found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas (Dalsan, 2015; Greenguard, 2016).

Due to economical impacts, environmental concerns, and new regulations, paint and coating industries are significantly shifting toward water-borne formulations (Stoye *et al*., 2006; Dalsan, 2015). Nowadays, the interest in using water-borne paints or stains in furniture manufacturing has been significantly increased. Unfortunately, water-borne paints are not fully harmless because the colorants used in water-borne paints are frequently aniline based ones, where aniline is a toxic organic compound with the formula $C_6H_5NH_2$.

There is a variety of definitions like; "VOC Free Paint", "Zero VOC", "Green-Product" on paint bins. "Zero VOC" paint does not necessarily mean non-toxic, healthy, or safe. EPA allows the paint to be called "Zero VOC" even if the VOC content in it is actually not zero. EPA Method 24 allows for up to 5 g/L of VOCs as "Zero VOC" for oil-borne paints, 250 g/L as "Low-VOC" for latex paints, and 380 g/L, as "Low-VOC" for oil-borne paints (EPA, 2016).

As mentioned earlier in this study, VOCs are a cause of low indoor air quality. The United States Environmental Protection Agency (US EPA) recommended not using them in indoor environment". The synthetic dyes can be replaced with the natural ones to solve this problem. During the last few decades, growing interest in the use of natural colourants has been recognized, both in public awareness and scientific activity (Leitner *et al*., 2012; Khan *et al*. 2006). The majority of natural dyes are vegetable dyes from plant sources: roots, berries, bark, leaves, wood and other organic sources such as fungi and lichens. These alternative materials provide increased sustainability, renewable resources, environmentally friendly processing, reduced pollution, and green chemistry (Bechtold et al., 2003). Also, environmentally-friendly natural poisonous plant extracts, stains derived from natural dye plants, and water-based wood preservatives are being developed against wood damaging biotic and abiotic factors. There are scientific studies on using natural plant dye staff for wood materials. After applying natural dyes on wood specimens, color changing (Goktas *et al*., 2013; Peker, 2012; Goktas, 2009; Goktas, 2008[a]; 2008[b]), antimicrobial, and antifungal performances (Ozen, 2014) have been determined. Unfortunately, natural colorants and preservatives can be bleached and discolored by exposure to weather conditions. Therefore, introducing natural and durable colorant is a requirement that needs to be developed against bleaching and discoloration.

As a solution to this problem, applying liquid glass on wood materials was considered as a potential option. The liquid glass can be used to decrease the disadvantages of wood like lack of color stability and water interaction of wood (Lu *et al*., 2014). Also, another study showed that the addition of nano-SiO_2 modification to the wood structure provides decrease in external moisture penetration, which has a negative effect on color changes (Jiang *et al*., 2013). The liquid glass can be sprayed on the surface within seconds and can create an anti-microbial, easy-to-clean barrier that will last from one to several years, depending on the surface (Nanopool, 2012). In this study, the coated wood specimens were tested to evaluate the protection degree of liquid glass+natural stains against discoloration using cold check test.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Wood test specimens
2.1. Drvni uzorci

As wood material, Scots pine (*Pinus sylvestris*), chestnut (*Castanea sativa* Mill.), and mahogany (*Khaya Ivorensis A. Chev.*) wood specimens commonly used in furniture and decoration industries in Turkey were chosen. The specimens were prepared from the sapwood parts of the first-class wood with smooth fiber, knotless and crack-free surfaces, no color and density differences, with annual rings perpendicular to the surfaces, in accordance with TS 2470 standards (2005).

In this study, the cold check test was used to observe and investigate the behavior of the finishing layer. The cold check test is a practical way to understand that the changes in finishing layer occured because of temperature changes (Wisnofurniture, 2013).

The cold check test specimens were prepared with dimensions of 100 mm x100 mm x10 mm and were kept under suitable temperature (20±2 °C) and suitable moisture (moisture of ±12 % and relative humidity of ±65 %) conditions until they became air-dried (the moisture value in furniture used under interior area conditions) in accordance with TS 2471, (2005).

2.2 Plant material and mordant agents
2.2. Biljni materijal i sredstva za fiksiranje boje

Plant materials were purchased from domestic markets located in Turkey. The Licorice (*Glycyrrhiza glabra* L.), Indigo (*lsatis tinctoria* L.) and Pomegranate Skin (*Punica granatum* L.) were chosen as natural dyes. In addition to creating affinity between dye and wood fibre, the use of mordants change the hue of certain dyes (Shahid, 2013). Different mordants used with the same dye may darken, brighten or drastically alter the final color of the dyed wood sample. The mordants used in this study were ferrous sulfate ($Fe_2(SO_4)_3.7H_2O$), aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) and vinegar (Kimetsan Co.,Fersan Co./Turkey). Also, a synthetic dye (woodtex - Kayalar kimya Co./Turkey) has been used for comparison to natural dyes.

2.3 Extraction of dye
2.3. Ekstrakcija boje

A weighed amount of dry plant material was extracted with distilled water in a bath (Elmasonic X-tra 150 H). According to the standard procedure, the mass / volume ratio between plant material and liquid was 1:20; extraction was performed for approximately 180 min. at 45 °C. Due to the high liquor ratio, some manual stirring was applied to distribute the plant material homogenously in the liquid during the extraction period. The expected volume loss due to evaporation was compensated by the addition of water at the end of the extraction period to obtain the initial volume.

Aqueous solutions were mordanted by adding ferrous sulfate ($Fe_2(SO_4)_3.7H_2O$) 3 %, aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) 5 %, and grape vinegar 10 % in order to stabilize the color of extracted dyes, ensure itsduralibilty on the applied material (to increase retention amount), and create color options. After mordanting, liquid glass was added to mordanted aqueous with 20 % by weight.

2.4 Dyeing experiments
2.4. Bojenje uzoraka

Air-dried wood specimens were placed into the dyebath container. The immersion method was applied for 60 min at 45 °C. Any extra solution left on the specimens was wiped with a clean cloth. Specimens were then left to air dry at 20±3 °C in a vertical position.

2.5 Cold check test
2.5. Test hladne provjere

The stain and liquid glass mixture treated wood specimens were exposed to cold check test for periods of 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles according to ASTM D 1211-97 (2001).

2.6 Color measurements
2.6. Mjerenja boje

The colors of the cold check tested coated parts were identified prior to exposure using Konica Minolta CR–10 portable color reader device. Minumum four (4) repetitions (color measurmenets) were performed to analyze the colors on each specimen due to the non-homogenous color structure of wood. The identified color values were classified according to the coordinates Commission International de I'Eclaireage-CIELAB 1976 set in ISO 2470 standards (Figure 1). The obtained colors were indicated by numerical values of L, a, and b. Where; "L" indicates lightness from 0 % (black) to 100 % (white), "a" from green (-a) to red (+a), and "b" from blue (-b) to yellow (+b). Also, the coated parts were subjected to color measure prior to cold check test and stated as "color values prior to cold check".

2.7 Determination of color change values
2.7. Određivanje veličina promjene boje

In order to determine the color changes occured due to the cold check test cycle, Konica Minolta CR–1 (Japan) portable color reader device was used. Color changes were calculated with the following equations in accordance with ISO 2470 standards.

$$\Delta L^* = L^*_f - L^*_i \quad (1)$$

$$\Delta a^* = a^*_f - a^*_i \quad (2)$$

$$\Delta b^* = b^*_f - b^*_i \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

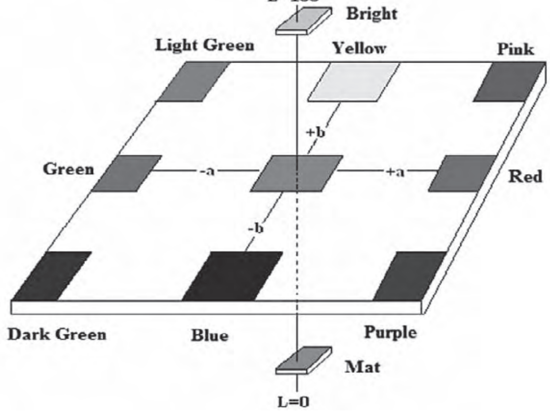

Figure 1 CIELAB–76 color system
Slika 1. Sustav boja CIELAB-76

Where; Δ*L**, Δ*a** and Δ*b** are the changes occurring between the initial state (i) and final state (f) of colors. Δ*E**, indicates total changes of colors occurring in *L*, *a*, and *b*. The highest value shows the highest color change.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The color change values of the test specimens exposed to cold check test for periods of 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles are numerically presented in Table 1, Table 2, and Table 3. Positive (+) values of Δ*L** show whitening, and negative (-) values of Δ*L** indicate the color turning to gray. Positive values of Δ*a** indicate reddening of the colors, and negative values of Δ*a** show a shift towards green. Positive values of Δ*b** represent yellowing in color, and negative values of Δ*b** represent the color turning blue.

The results showed that all wood specimens, exposed to cold check test, produced negative values of Δ*L**. This was attributed to chemical structure changes that occurred, especially in lignin, due to temperature differences applied through the cold check test.

For natural plant extracts, sensitive degrees to cold check test are Licorice (*Glycyrrhiza glabra* L.), Pomegranate skin (*Punica granatum* L.) and indigo (*Isatis tinctoria* L.) extracts. For Licorice, the best color stability (Δ*E** 3,14) was determined on chestnut wood with vinegar mordant. The biggest change (Δ*E** 49,08) for the same dyestuff was observed on chestnut wood treated with ferrous sulfate (Table 1). The best color stability (Δ*E** 3,71) for Pomegranate skin was determined on mahogany wood with vinegar mordant. The biggest change (Δ*E** 50,06) for the same dyestuff was observed on scots pinewood with ferrous sulfate (Table 2). For indigo, the best color stability (Δ*E**8,89) was determined on chestnut wood with control sample (without mordant). For indigo, the biggest change

Table 1 Color changing of wood specimens stained with Licorice (*Glycyrrhiza glabra* L.), extracts
Tablica 1. Promjena boje uzoraka drva obojenih ekstraktom sladića (*Glycyrrhiza glabra* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za fiksaciju boje*	**Mixtures** *Smjese*	**Before stain** *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			*L**	*a**	*b**	Δ*L**	Δ*a**	Δ*b**	Δ*E**	Δ*L**	Δ*a**	Δ*b**	Δ*E**
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	65.94	9.00	20.26	-2.64	-0.10	1.26	2.93	-3.14	-0.28	1.18	3.37
		B	65.18	8.80	20.48	-9.30	-1.90	-3.94	10.28	-9.66	-1.54	-2.04	9.99
	Ferrous sulfate *željezov sulfat*	A	68.26	8.10	19.54	-42.56	-8.10	-24.80	49.92	-42.08	-8.52	-20.58	47.61
		B	69.96	8.18	19.34	-45.30	-8.68	-23.74	51.88	-43.68	-8.80	-20.58	49.08
	Aluminum Sulfate *aluminijev sulfat*	A	62.54	8.80	20.54	-4.76	-1.22	2.20	5.38	-5.90	-1.28	2.36	6.48
		B	66.74	8.20	19.30	-3.22	-0.88	2.60	4.23	-4.54	-0.58	2.94	5.44
	Vinegar *ocat*	A	69.20	7.44	19.30	-3.80	0.74	2.44	4.58	-3.88	0.46	1.88	4.34
		B	65.08	9.14	20.18	-2.74	-0.46	0.80	2.89	-2.88	-0.64	1.08	3.14
	Synthetic stain *sintetičko bojilo*		70.02	8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.62	5.66	23.82	-6.42	1.26	3.46	7.40	-8.14	1.52	2.54	8.66
		B	82.74	5.16	24.64	-5.44	0.08	2.10	5.83	-6.60	0.88	1.36	6.80
	Ferrous sulfate *željezov sulfat*	A	81.60	5.64	25.80	-20.04	0.88	-1.56	20.12	-23.34	1.54	-3.30	23.62
		B	81.62	5.26	27.84	-25.80	1.84	-3.90	26.16	-28.24	3.12	-5.46	28.93
	Aluminum Sulfate *aluminijev sulfat*	A	81.58	5.82	25.52	-4.82	1.58	6.44	8.20	-8.32	4.04	6.26	11.17
		B	80.60	6.22	26.48	-3.64	1.22	4.76	6.12	-8.64	5.24	4.72	11.15
	Vinegar *ocat*	A	82.16	5.16	26.72	-5.16	1.94	1.78	5.79	-6.72	1.56	2.92	7.49
		B	83.02	4.14	24.90	-5.20	0.22	2.18	5.64	-6.92	1.22	2.60	7.49
	Synthetic stain *sintetičko bojilo*		82.36	4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	51.30	15.68	18.86	-3.72	0.16	0.32	3.74	-7.80	-1.01	-0.24	7.87
		B	48.62	15.22	18.40	-1.94	-1.44	-0.76	2.53	-3.84	-2.40	-0.90	4.62
	Ferrous sulfate *željezov sulfat*	A	50.66	16.30	18.66	-19.34	-14.42	-11.44	26.70	-20.74	-12.92	-10.92	26.76
		B	50.46	15.12	18.48	-20.20	-13.96	-12.04	27.35	-20.10	-11.76	-10.56	25.57
	Aluminum Sulfate *aluminijev sulfat*	A	50.96	16.04	19.88	-0.64	-3.76	0.26	3.82	-3.58	-4.36	-1.28	5.78
		B	50.02	15.88	18.74	-1.88	-2.98	0.80	3.61	-4.96	-3.66	0.02	6.16
	Vinegar *ocat*	A	50.70	16.24	19.34	-2.86	-0.06	0.24	2.87	-5.42	-0.98	0.54	5.53
		B	50.74	15.38	19.22	-1.46	-0.46	0.20	1.54	-3.12	-1.16	0.02	3.33
	Synthetic stain *sintetičko bojilo*		50.56	15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

Table 2 Color changing of wood specimens stained with Pomegranate skin (*Punica granatum* L.) extracts
Tablica 2. Promjena boje uzoraka drva obojenih ekstraktom šipka (*Punica granatum* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za fiksaciju boje*	**Mix-tures** *Smje-se*	Before stain *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	L^*	a^*	b^*	Δb^*	ΔE^*
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	64.46	10.00	21.72	-2.38	4.48	5.86	7.75	-4.14	0.72	5.16	6.65
		B	68.18	7.36	19.84	-1.72	-0.78	7.30	7.54	-2.28	-0.52	7.42	7.78
	Ferrous sulfate *željezov sulfat*	A	66.10	8.42	20.42	-36.46	-9.52	-22.58	43.93	-36.88	-9.32	-19.56	42.77
		B	68.98	8.04	19.78	-40.56	-9.22	-21.94	47.03	-38.62	-9.20	-18.70	43.88
	Aluminum Sulfate *aluminijev sulfat*	A	63.40	9.50	21.60	-3.90	-1.46	8.52	9.48	-5.76	-0.98	8.28	10.13
		B	62.76	9.12	20.62	-1.80	-1.98	9.28	9.66	-2.96	-0.90	7.96	8.54
	Vinegar *ocat*	A	67.32	8.14	19.40	-2.96	0.54	8.32	8.85	-5.04	0.78	7.60	9.15
		B	65.40	8.64	20.24	-3.22	-0.96	6.48	7.30	-3.92	-0.76	6.42	7.56
	Synthetic stain *sintetičko bojilo*			8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.46	4.64	24.80	-6.04	1.68	9.36	11.27	-8.36	2.11	8.98	12.45
		B	83.08	4.54	25.20	-6.54	0.74	11.38	13.15	-8.74	1.94	11.38	14.48
	Ferrous sulfate *željezov sulfat*	A	81.42	5.70	24.96	-45.66	-6.02	-23.42	51.67	-45.36	-5.42	-20.48	50.06
		B	82.92	4.66	24.82	-53.78	-5.86	-26.28	60.14	-21.72	4.06	10.56	24.49
	Aluminum Sulfate *aluminijev sulfat*	A	81.26	4.88	26.30	-9.92	0.90	15.56	18.48	-14.92	4.76	11.94	19.69
		B	82.32	4.90	25.60	-7.86	0.68	22.00	23.37	-43.80	-3.86	-15.36	46.58
	Vinegar *ocat*	A	82.04	5.00	25.94	-8.98	2.74	10.80	14.31	-11.34	4.16	10.72	16.15
		B	81.74	5.92	25.52	-9.26	1.48	9.50	13.35	-11.18	2.38	9.86	15.10
	Synthetic stain *sintetičko bojilo*			4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	49.28	15.92	19.50	-0.28	0.00	3.26	3.27	-2.96	-0.68	2.54	3.96
		B	51.32	16.12	18.60	-0.04	-1.42	3.12	3.43	-2.24	-3.04	2.58	4.57
	Ferrous sulfate *željezov sulfat*	A	49.90	15.60	18,44	-20.12	-13.36	-13.60	27.72	-21.36	-13.04	-13.20	28.29
		B	50.66	15.54	19.48	-24.66	-15.32	-18.54	34.45	-23.46	-13.58	-15.52	31.24
	Aluminum Sulfate *aluminijev sulfat*	A	50.76	15.24	19.04	-1.90	-3.60	6.52	7.69	-6.00	-2.92	3.98	7.77
		B	51.94	15.98	19.68	-1.54	-3.78	9.06	9.94	-4.26	-3.90	7.00	9.08
	Vinegar *ocat*	A	47.52	15.68	18.86	-1.38	-0.12	3.06	3.36	-4.06	-0.46	2.12	4.60
		B	50.46	15.50	18.98	-0.20	-1.50	3.06	3.41	-1.58	-2.12	2.60	3.71
	Synthetic stain *sintetičko bojilo*			15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

(ΔE^* 56, 74) for the same dyestuff was observed on the same wood with ferrous sulfate (Table 3).

Wood materials colored with metal mordant mixes produced darker colors. However, researchers did not determine that mordant had negative effect on color change performances. This can be explained by the reactions between wood material and mordant mixes and definitely by the effect of UV irradiation on different colors. Dark colors could absorb the light up to 98 %, and transparent colors up to 11 %. Therefore, darker wood species could have undergone more color changes (Yeniocak *et al*., 2015).

Among wood specimens, high color changing values for cold check test were respectively observed on Scots pine, chestnut and mahogany. The reason for the differences between wood species may be due to the differences of chemical composition of wood species, and interaction of natural dyes and mordant mixes extract compounds with wood test specimens, resulting in different photo-degradation effects of UV irradiation. Several factors, such as anatomical differences, growing characteristics, machining properties, pre-treatments (e.g. steaming, drying, etc.), can also affect the color stability (Temiz *et al*., 2005; Goktas *et al*., 2009). In addition, the treatment parameters, such as treatment time, percentage of dyes materials, application temperature and percentage of mordant may also affect the color stability.

All wood specimens exposed to cold check showed negative values of ΔL^*, which means that the color of all wood specimens partially turned to gray. Generally, the highest negative values (ΔL^*) were observed on specimens that were treated with ferrous sulfate mordant. This result is compatible with literature studies about color changing (Yeniocak, *et al*., 2015) of natural dyes. The use of ferrous sulfate mordant produced high color

Table 3 Color changing of wood specimens stained with Indigo (*Isatis tinctoria* L.) extracts
Tablica 3. Promjena boje uzoraka drva obojenih ekstraktom indiga (*Isatis tinctoria* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za* fiksaciju boje	**Mix-tures** *Sm-jese*	**Before stain** *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			L*	a*	b*	ΔL*	Δa*	L*	a*	b*	Δa*	Δb*	L*
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	65.94	9.20	20.64	-4.30	-4.38	-3.38	7.01	-7.36	-4.08	-2.86	8.89
		B	64.96	9.82	20.30	-5.10	-7.12	-6.06	10.65	-6.58	-8.06	-6.20	12.11
	Ferrous sulfate *željezov sulfat*	A	66.76	8.00	20.20	-38.94	-8.76	-29.10	49.40	-38.00	-9.52	-23.54	45.70
		B	67.26	9.02	21.24	-5.10	-7.12	-6.06	10.65	-39.34	-39.34	-11.14	56.74
	Aluminum Sulfate *aluminijev sulfat*	A	63.86	9.50	20.72	-13.64	-12.12	-13.70	22.82	-15.34	-11.68	-12.78	23.13
		B	68.00	9.26	20.68	-13.92	-11.96	-12.64	22.28	-16.42	-11.94	-11.40	23.28
	Vinegar *ocat*	A	64.54	8.58	20.30	-16.90	-10.40	-16.56	25.85	-17.80	-10.14	-13.90	24.76
		B	64.78	9.45	21.50	-24.96	-17.35	-25.12	39.43	-25.04	-17.27	-21.60	37.31
	Synthetic stain *sintetičko bojilo*			8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.34	4.62	26.34	-11.78	-8.88	-9.56	17.58	-13.68	-7.86	-9.32	18.32
		B	82.38	7.92	25.98	-16.10	-15.18	-17.16	28.00	-19.02	-14.32	-17.42	29.50
	Ferrous sulfate *željezov sulfat*	A	80.46	5.54	27.08	-24.60	-7.86	-16.70	30.75	-28.90	-4.38	-15.86	33.26
		B	82.18	6.52	25.50	-16.10	-15.18	-17.16	28.00	-27.48	-27.48	-6.94	39.48
	Aluminum Sulfate *aluminijev sulfat*	A	82.04	4.92	24.08	-24.54	-13.98	-24.08	37.11	-26.96	-12.08	-22.20	36.95
		B	80.50	7.86	25.88	-18.96	-13.86	-19.58	30.58	-25.78	-10.26	-19.48	33.90
	Vinegar *ocat*	A	81.30	6.38	26.10	-23.86	-14.02	-22.98	35.97	-25.68	-12.42	-21.10	35.48
		B	81.60	7.36	24.82	-39.88	-20.64	-39.48	59.79	-41.86	-20.00	-39.30	60.80
	Synthetic stain *sintetičko bojilo*			4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	48.92	15.80	18.78	-3.64	-2.42	-1.94	4.78	-9.10	-5.20	-4.06	11.24
		B	47.78	16.62	18.12	-3.36	-3.84	-1.24	5.25	-7.98	-4.90	-1.86	9.55
	Ferrous sulfate *željezov sulfat*	A	51.30	16.04	18.64	-17.48	-16.50	-14.68	28.17	-18.63	-14.09	-12.94	26.70
		B	49.40	15.92	18.74	-3.36	-3.84	-1.24	5.25	-17.26	-17.26	-13.60	27.94
	Aluminum Sulfate *aluminijev sulfat*	A	48.40	15.84	18.50	-11.36	-15.90	-16.82	25.78	-13.82	-14.12	-14.32	24.40
		B	49.48	17.06	18.70	-8.38	-11.30	-8.02	16.19	-11.26	-11.74	-9.34	18.76
	Vinegar *ocat*	A	51.24	16.26	19.16	-6.94	-11.82	-9.26	16.54	-13.42	-10.10	-7.84	18.54
		B	47.72	16.84	18.28	-12.04	-18.84	-16.04	27.52	-15.82	-17.24	-14.88	27.73
	Synthetic stain *sintetičko bojilo*			15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

changing (Δ*E**) values, too. These changes can be explained by the interaction of ferrous sulfate ions and wood components. Metal mordant produced color stability. Metal ions promote free radical formation (Feist and Hon, 1984; Peker *et al*., 2012) of wood components even when they are exposed to light. The stabilization of lignin by ferrous was reported to occur through the formation of complex (Kamdem and Grelier, 2002).

4 CONCLUSIONS
4. ZAKLJUČAK

The natural dyes produced lower color changes than the synthetic dyes with a few exceptions. This is a very promising result for the use of natural dyes as alternative colorants in near future.

The vinegar mordant applications provided resistance as much as other mordant applications. The natural dyestuff for wood surfaces was successfully developed by using natural mordant in natural dye application. Ferrous sulfate was observed to be the mordant type with the highest color change among all wood species in general. Sometimes this property is desired on decorative applications. It is worth noting that ferrous sulfate mordant should be avoided for some wet and hot environment, or that it can be preferred in places where the color change is not important.

The future work will be focused on the use of various natural dyes and mordants in the production of wooden products, especially for the children's furniture and wooden houses.

Acknowledgement – Zahvala

This manuscript is the outcome of the project supported by TÜBİTAK TOVAG "1001 - The Support Program for Scientific and Technological Research Projects". Project number: 213 O 185 was also orally presented at the II[nd] International Furniture Congress, 13-15 October 2016 held in Mugla/Turkey.

5 REFERENCES
5. LITERATURA

1. Bechtold, T.; Turcanu, A.; Ganglberger, E.; Geissler, S., 2003: Natural Dyes in Modern Textile Dye Houses – How To Combine Experiences of Two Centuries to Meet the Demands of the Future. J Clean Prod, 11: 499-509. https://doi.org/10.1016/S0959-6526(02)00077-X
2. Dalsan, 2015: The Greenguard Certicates, www.dalsan.com.tr (Accessed: 18. 6. 2015).
3. Feist, W. C.; Hon, D. N. S., 1984: Chemistry of weathering and protection. In: Rowell RM (ed.). The chemistry of solid wood. Am Chem Soc, Washington, pp. 401-451. https://doi.org/10.1021/ba-1984-0207.ch011
4. Goktas, O.; Baysal, E.; Ozen, E.; Mammadov, R.; Duru, E. M., 2008a: Decay Resistance and Color Stability of Wood Treated With Juglans Regia Extract. Wood Research, 53 (3): 27-36.
5. Goktas, O.; Duru, E. M.; Yeniocak, M.; Ozen, E., 2008b: Determination of the Color Stability of an Environmentally Friendly Wood Stain Derived from Laurel (*Laurus nobilis* L.) Leaf Extracts Under UV Exposure. Forest Products Journal, 58 (1/2): 77-80.
6. Goktas, O.; Ozen, E.; Duru, M. E.; Mammadov, R., 2009: Determination of the Color Stability of an Environmentally-Friendly Wood Stain Derived From Oleander (*Nerium oleande*r L.) Leaf Extracts Under UV Exposure. Wood Research, 54 (2): 63-72.
7. Goktas, O.; Çolak, M.; Uğurlu, M.; Ozen, E.; Yeniocak, M., 2013: Determination Of Leaching Performance And Color Stability Under UV-Accelerated Weathering Conditions for Wood Surfaces that were Treated with Natural Stain by Ultrasonic Assisted Dyeing Method. (TÜBİTAK-TOVAG Project no: 110 O 141.)
8. Kamdem, D. P.; Grelier, S., 2002: Surface Roughness and Color Change of Copper Amine and UV Absorber-Treated Red Maple (*Acer rubrum*) Exposed to Artificial Ultraviolet Light. Holzforschung, 56 (5): 473-478. https://doi.org/10.1515/HF.2002.073
9. Khan, M. A.; Khan, M.; Srivastava, P. K.; Mohammed, F., 2006: Extraction of Natural Dyes from Cutch, Ratanjot and Madder, and their Application on Wool. Colourage, 53 (1): 61-68.
10. Jiang, Y.; Wu, G.; Chen, H.; Song, S.; Pu, J., 2013: Preparation of Nano-SiO_2 Modified Urea-Formaldehyde Performed Polymer to Enhance Wood Properties. Rev. Adv. Mater. Sci. 33: 46-50.
11. Leitner; Binder, C. F.; Mahmud-Ali, A.; Bechtold, T., 2012: Production of a Concentrated Natural Dye From Canadian Goldenrod (*Solidago canadensis*) Extracts. Dyes and Pigments, 93: 1416-1421. https://doi.org/10.1016/j.dyepig.2011.10.008
12. Ozen, E.; Yeniocak, M.; Colak, M.; Goktas, O.; Koca, I., 2014: Colorability of Wood Material With *Punica granatum* and *Morus nigra* Extracts. BioRes, 9 (2): 2797-2807. https://doi.org/10.15376/biores.9.2.2797-2807
13. Peker, H.; Atılgan, A.; Ulusoy, H.; Goktas, O., 2012: Usage Opportunities of the Natural Dye Extracted from Acorn (*Quercus ithaburensis* Decaisne) In the Furniture Industry Upper Surface Treatment. Int J Phys Sci, 7 (40): 5552-5558.
14. Shahid, M.; Shahid-ul, I.; Faqeer, M., 2013: Recent Advancements In Natural Dye Applications: A Review. Journal of Cleaner Production, 53: 310-331. https://doi.org/10.1016/j.jclepro.2013.03.031
15. Stoye, D.; Funke, W.; Hoppe, L., 2006: Paints and Coatings, Ullmann's Encyclopedia of Industrial Chemistry. https://doi.org/10.1002/14356007.a18_359.pub2
16. Temiz, A.; Yildiz, U. C.; Ismail, A.; Morten, E.; Gry, A.; Colakoglu, G., 2005: Surface Roughness and Color Characteristics of Wood Treated with Preservatives after Accelerated Weathering Test. Appl Surf Sci, 250 (1-4): 35-42. https://doi.org/10.1016/j.apsusc.2004.12.019
17. Yeniocak, M.; Goktas, O.; Colak, M.; Ozen, E.; Ugurlu, M., 2015: Natural Coloration of Wood Material by Red Beetroot (*Beta Vulgaris*) and Determination Color Stability Under UV Exposure. Maderas, Ciencia Technology, 17 (4): 711-722. https://doi.org/10.4067/S0718-221X2015005000062
18. ***ASTM D 1211-97: 2001: Standard Test Method for Temperature-Change Resistance of Clear Nitrocellulose Lacquer Films Applied to Wood, American Society For Testing and Materials. Annual Book of ASTM Standards, West Conshohocken.
19. ***EPA (https://www.epa.gov//volatile-organic-compounds-impact-indoor-air-quality).
20. ***Greenguard http://greenguard.org/en/indoorAirQuality/iaq_chemicals.aspx) (accessed: 2. 4. 2016).
21. ***Greenguard, 2016: http://greenguard.org/en/indoorAirQuality/iaq_chemicals.aspx (accessed: 7. 6. 2016).
22. ***ISO 2470, 2008: Measurement of Diffuse Blue Reflectance Factor – Part 2: Outdoor Daylight Conditions (D65 Brightness).
23. ***Nanopool, www.nanopool.eu (access date: 13. 11. 2012.).
24. ***TS 2470. 2005: Wood – Sampling Methods and General Requirements for Physical and Mechanical Tests. TSE, Ankara.
25. ***TS 2471. 2005. Wood, Determination of Moisture Content for Physical and Mechanical Tests. TSE, Ankara.
26. ***Wisnofurniture, 2013, www.wisnofurniturefinishing.com/ Cold check for the finishing layer (accessed date: 17. 10. 2017.).

Corresponding address

Prof. Dr. OSMAN GOKTAS, Ph.D.

Mugla Sitki Kocman University
Faculty of Technology
Department of Woodworking Industrial Engineering
48000, Mugla, TURKEY
e-mail: ogoktas@mu.edu.tr