

WEATHERING PERFORMANCE OF WOOD TREATED WITH COPPER AZOLE AND WATER REPELLENTS

HÜSEYİN SIVRIKAYA, AHMET CAN, İBRAHİM TÜMEN, DENİZ AYDEMİR
BARTIN UNIVERSITY, FACULTY OF FORESTRY
BARTIN, TURKEY

(RECEIVED FEBRUARY 2016)

ABSTRACT

Water borne wood preservatives have been widely used for a long time in the protection of wood either in ground contact or above ground. Copper is still major biocide component used today in treatment plant for wood protection despite the environmental concerns over copper-rich preservative systems. On the other hand, water repellents are considered to be potential additives for biocides, resulting in the decreased moisture content, reduced biocide leaching and increased dimensional stabilization. In the present study, copper azole (CA) was used as wood preservatives to the natural weathering for 6, 12 and 24 months respectively. In addition, semitransparent wood stain was used as post treatment with CA, and paraffin and silicon additives were incorporated in to biocide to be water repellent. Paraffin additives reduced the retention values as compared to other formulations. The highest color change and gloss loss were obtained with Scots pine control samples within the six months. CA pretreatment before wood stain was promising by indicating the lowest color change. Color change was reduced by the increasing ratio in paraffin and silicone additives. Combination of CA with wood stain and silicon additive could reduce the copper leaching to some extent.

KEY WORDS: Scots pine, copper azole, wood stain, silicon, paraffin.

INTRODUCTION

The first generation wood preservatives such as creosote, oil-borne pentachlorophenol (PCP) and waterborne chromated copper arsenate (CCA) were widely used for industrial applications because of their broad range of activity, low cost and long-term efficacy. CCA particularly was by far the major preservative for residential applications in which it is not permitted since January 2004 due to the environmental concerns (Freeman et al. 2006). The increased concerns over CCA were arsenic and chromium exposure and disposal problems of CCA treated wood (Preston 2000, Schultz et al. 2007) that led to introduction of second generation wood preservatives.

The second-generation biocide systems include the waterborne copper-rich systems that contain amine- or ammonia-complexed alkaline copper (II) and an organic co-biocide to control copper tolerant fungi (Freeman et al. 2006, Kamdem 2008, Schultz et al. 2008). These preservatives also have some additives providing hydrophobic characteristic such as carboxylic acid, paraffin or wax emulsion (Humar et al. 2005)

Alkaline copper quat (ACQ) and copper azole (CA) are commercially available for residential applications. Both preservatives are free of arsenic and chromium, as effective as CCA for above-ground, ground contact and fresh water applications. However, high levels of copper and relatively high formulation cost compared to CCA are known to be disadvantage (Freeman et al. 2006). In the case of copper-ethanolamine treated wood, ethanolamine causes the depolymerization of lignin that results in increased leaching, but could be improved by the addition of antioxidants and fixation in oxygen free atmosphere (Humar et al. 2008).

Copper azole preservative is composed of amine Copper and a co-biocide to further protect wood against fungi and insect attack. Copper azole is produced in different formulations; CBA-A includes boric acid, CA-B contains copper (96%) and tebuconazole (4%), the other formulation CA-C, which is known synergistic, incorporates propiconazole (2%) and tebuconazole (2 %) as the co-biocides (Freeman and McIntyre 2008). The azoles, such as propiconazole or tebuconazole provide high resistance against wood decay fungi, good stability and leach resistance in wood (Schultz et al. 2007).

When the wood material is exposed to outdoor conditions without any protective treatment, it will be under the influence of degrading factors such as ultra-violet light, leaching, wood hydrolysis with water, swelling, discoloration and decay by micro-organisms. The combination of the factors chemical, mechanical and light energy is defined as weathering at the above-ground conditions (Feist 1983).

Copper slows photodegradation by UV radiation and water (Archer and Preston 2006). It was reported that copper azole showed resistance against weathering effect, prevented the deterioration caused by stain-fungi with regard to the experiments on Surface roughness, lignin loss, color measurements and microscopic examinations (Cornfield et al. 1994, Temiz et al. 2005). Penetrating coatings show water repellent property, include some additives to reduce weathering effect, for example, include pigments and UV stabilizers to protect the wood against UV rays (Kiguchi et al. 1996). Addition of water-repellent provides further protection to wood material, but photodegradation cannot be prevented completely (Feist 1988).

Investigation on the weathering properties of wood treated with copper-ethanolamine revealed that copper amine retarded the photodegradation of wood in the study of accelerated laboratory testing instrument (Zhang et al. 2009). Water repellent is one of the most common additives to above-ground biocide systems for premium decking (Preston 2003). Because, water repellents decrease the moisture content, reduce biocide leaching and increase dimensional stability of wood (Green and Schultz 2003).

Wax and oil emulsion are used with water borne wood preservatives in order to reduce checking and improve appearance of treated wood for outdoor conditions (Evans et al. 2009). Further, wax emulsion additives reduce the cupping and checking, occurring on the treated wood during the artificial or natural weathering (Fowlie et al. 1990, Christy et al. 2005).

Several coatings or water repellents were studied with copper based preservatives for dimensional stabilization, weathering or reducing the copper leaching. Feist and Ross (1995) stated that CCA treated wood showed compatibility with various surface finished, moreover treatment especially improved the performance of semitransparent stains as well as some finishes.

Evans et al. (2009) performed the CCA incorporated with the additives 7 and 14 % of light synthetic petroleum oil and 2.5 % of wax emulsion. Wax and oil emulsion were decreased equally

the water absorption and swelling of treated wood before weathering. There was no statistical difference between wax and oil emulsion additives to reduce checking of CCA-treated radiata pine exposed to outdoor weathering.

Pretreatment of Scots pine with CCB followed by coating application such as polyurethane and an alkyd-based increased the resistance to natural weathering (Baysal 2008). In addition, compared to coating alone, both copper-based wood preservative treatment and varnish coating improved the surface properties of the samples. The reduced discoloration was attributed to the stabilization of lignin. (Baysal et al. 2013).

According to Green and Schultz (2003), copper leaching is still higher from copper- amine treated wood than the wood treated with copper-chrome. Addition of a water-repellent in to the wood biocide improves the resistance to decay above ground applications, as well as improves the weathering properties and dimensional stability of wood material. Paraffin wax can be environmentally friendly and most cost-effective additive in improving the durability of wood.

Copper-ethanolamine containing preservatives (CuE and CuEQ) and waterborne acrylic coatings were studied with spruce wood. Improved adhesion of coatings was observed on CuEQ treated samples, copper-ethanolamine treated was comparable to untreated wood with respect to properties of surface finishes, furthermore surface finishes significantly reduced the copper leaching from the preserved wood (Humar et al. 2011).

Nejad and Cooper (2011) reported that Water-based coatings on wood treated with copper-amine for exterior facades showed well performance as much as solvent based coatings. The samples treated with Copper amine had water uptake 50 % more than CCA treated woods, however overall appearance of the wood surface improved as good as CCA.

Copper-based preservatives have been extensively used for more than a century, and copper is still main biocide component used today in the protection of wood in ground contact or exposed to weather (Lebow et al. 2004).

Some of the concerns have grown in relation to waterborne copper-rich systems are as follows; hazardous effect of high levels of copper leaching into aquatic systems, corrosive problems with metals, different surface mold growth and long term disposal issue of the treated wood (Schultz et al. 2008).

Post treatment processing and coatings, adding chemical compounds to form complex with the system, some additives having hydrophobic and bonding characteristic are taken attention to be potential alternatives for this issue.

Therefore, the objective of this study was to perform copper azole and water repellents in combinations for investigating weathering properties and copper leaching of treated wood.

MATERIALS AND METHOD

Materials

Within this study, scots pine samples were prepared 15 x 7.5 x 1.5 cm in size from sapwood section (L x R x T), six replicate for each treatment. The samples were treated with copper azole (Tanalith E-3492) at concentration of 2.4 %, according to the full-cell process with vacuum (600 mm Hg) for 30 min. and pressure (6 bar) for 60 min.

Semi-transparent wood stain, silicone and paraffin emulsion were used as water repellents. Wood stain was provided from Hemel company in Istanbul, Turkey. SILRES

BS 1306, a solventless, water-thinnable emulsion of a polysiloxane modified with functional silicone resin, was obtained from the Wacker Company (Istanbul-Turkey). Paraffin emulsion, water based and contents 40 % of paraffin” was the production of Arkimya in İzmir, Turkey.

Wood stain was applied two coats by brush after CA treatment followed by 2 weeks conditioning, and 24 h was left between the coats. Silicone and paraffin emulsion were incorporated in to preservatives at 0.5, 1 and 2 % for silicone and 5, 10 and 15 % for paraffin respectively.

Methods

Retention of protective systems was calculated from the equation below.

$$\text{Retention} = \frac{G \times C}{V} \times 10 \quad (\text{kg} \cdot \text{m}^{-3})$$

where: G - uptake of preservative (kg),
C - preservative concentration (%),
V - volume of wood specimen (m³).

Treated and control wood samples were mounted on the metal panels which was established 45° inclined against the sun in the south direction, exposed to outdoor conditions for a period of 6, 12 and 24 months respectively. The test site for weathering was arranged in the province of Bartın which is located on the Western part of the Black sea region in Turkey.

Color change

Color measuring was performed by Konica-Minolta instrument which was calibrated to the white color as of a = 4.91, b = 3.45, c = 6.00, L = 324.9. L angle is expressed in terms of color change. In case of the acute angle, the color of wood changes towards the red hue, if the angle is wide it acts close the yellow hue. L* coordinate gives the brightness level, a* and b* coordinates give the measured color. Color difference and their locations in the CIE L*a*b* system are determined based on the L*, a*, b* color coordinates. In the L* black-and-white axis (L* = 0 for black and for white the L* = 100), a* explain red-green color (positive value to the red, and negative value to the green), b* reveals the yellow-blue color (positive value to yellow, negative value to blue).

Color tone of red (a*), yellow (b*) and brightness of color (L*) values were examined independently of each other in order to determine which tone is effective in color change. Then, the total color change (ΔE) was calculated from the equation below.

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

where: i, indicates the initial value whereas f indicates the final value
 $\Delta a^* = a^*f - a^*i$, $\Delta b^* = b^*f - b^*i$, $\Delta L^* = L^*f - L^*i$

Glossiness

Gloss measurement of the specimens was determined based on their ability to reflect light. Konica-Minolta gloss meter were used to measure the brightness of the specimens. Test device is consisted of a light source and a lens directed the light parallel or converging light to test area as well as lens photocell receiver. Measurements were operated at the angle of 60° by the test device.

$$G = (Gf - Gi) / Gi \times 100 \quad (\%)$$

where: Gf - indicates the glossiness after weathering,
Gi - before weathering.

For XRF experiment, wood sections with 30 mm (width) and 15 mm (thick) were cut from the mid of the panels. The sections were ground in a mill, and sieved in the 60 mesh. The ground material was pressed up to 25 ton in 2 min. to prepare pellet. The pressed pellets were placed in to XRF device, surface of the samples were scanned with autoquantify for 30 min. the spectrums were detected and analyzed by means of the software programme in the device.

RESULTS AND DISCUSSION

Retention

Copper azole treatment alone resulted in slightly higher retention than the wood samples treated with the combination of CA and wood stain (Tab. 1). Adding of silicone emulsion increased the retention when the concentration increased. Similarly, retention gradually increased in the mixtures of CA and paraffin with the increasing in paraffin ratio. However, the mixtures of CA and paraffin resulted in considerably lower retention values than other formulations. This might be due to the molecular size of paraffin regarding penetration problems. On the other hand, this situation was not detected with the mixtures of CA and silicon emulsion.

Yildiz (2007) investigated the treatability properties of some coniferous heartwood such as Scots pine, Siberian Scots pine, Siberian larch and oriental spruce with copper azole (CBA-A, Tanalith-E 3492) at 2.4 % concentration by full cell process. Scots pine heartwood had the highest retention and penetration, resulting in 4.95 kg.m⁻³ with 60 min pressure, and 6.28 kg.m⁻³ with 120 min pressure during the impregnation. With this study, we used the same preservatives and concentration, reached to 11.38 kg.m⁻³ as average retention with Scots pine sapwood in contrast to heartwood. The retention values with Scots pine in the present study was very consistent with Temiz et al. (2005), indicating the 11.07 and 13.20 kg.m⁻³ of retention for 2 and 2.8 % of Tanalith E 3491 (copper azole) with the same wood. Tab. 1 also indicates that the additives had minor effect on pH value when compared to CA treatment alone.

Tab.1: Mean retention and pH value of the samples.

Protective	Retention (kg.m ⁻³)	pH
CA	11.38 (1.13)	9.84
WS	1.09 (0.61)	7.76
CA+WS	11.14 (1.28)	9.74
CA+S (%0,5)	10.63 (1.73)	9.74
CA+S (%1)	10.67 (3.49)	9.74
CA+S (%2)	11.48 (1.44)	9.2
CA+P (%5)	5.54 (0.80)	9.93
CA+P (%10)	6.55 (1.52)	9.96
CA+P (%15)	7.75 (1.93)	10

Color change

Change in ΔL

Tab. 2 indicates that untreated Scots pine specimens were darkened by UV irradiation during whole exposed period resulting in negative value with the samples. Previous authors reported that the darkening of wood surface might be due to the degradation of lignin and other non-cellulosic polysaccharides (Hon and Chang 1985, Petric et al. 2004, Deka et al. 2008).

Tab.2: Mean ΔL values of the samples.

Protective systems	ΔL		
	6 months	12 months	24 months
Control	-29.72 (3.36)*	-31.26 (4.01)	-31.03 (6.35)
CA	-3.54 (3.20)	-3.05 (2.67)	2.77 (2.74)
WS	-5.96 (3.16)	-6.95 (1.90)	-9.07 (1.26)
CA+WS	1.08 (0.84)	2.31 (1.20)	5.62 (1.22)
CA+S(%0,5)	-2.34 (1.63)	2.52 (2.54)	3.63 (4.90)
CA+S(%1)	-2.87 (1.81)	0.27 (2.09)	1.44 (2.06)
CA+S(%2)	-1.11 (1.25)	2.49 (2.61)	1.70 (3.77)
CA+P(%5)	-11.28 (2.26)	-9.21(3.22)	-11.55 (3.19)
CA+P(%10)	-15.49 (1.68)	-7.03 (3.29)	-9.23 (3.94)
CA+P(%15)	-5.48 (1.61)	-5.10 (2.70)	-3.51 (4.19)

*Standard deviation within parentheses

However, the difference in ΔL between 6 and 12 months was very low in our study further more ΔL did not change after 12 months. It can be stated that the darkness caused by weathering was highly effective in 6 months. In addition, ΔL values of untreated samples were higher than that of other formulations for all exposure periods.

The samples treated with CA were slightly darkened by weathering during the 12 months, but after this stage the surface of the samples tended to be whiteness which was found to be the highest (5.62) after 24 months. Samples coated with wood stain had also negative values which range from -5 to -9 for 6 and 24 months respectively. But, when wood stain combined with CA, ΔL yielded positive values between 1 and 5. CA and Silicone combinations (0.5, 1 and 2 %) induced little darkness on the samples for only 6 months, whereas further exposure 12 and 24 months changed the ΔL towards whiteness. All paraffin mixtures darkened the samples higher than other combinations. It was shown also that less darkness was obtained with the samples treated with 15 % of paraffin additives rather than the additives of 5 and 10 %. The change in ΔL was different between untreated and treated samples that were also proved visually in Fig. 1. It was observed that the surface of the samples tended to be dark in different ranges with different formulations.

Change in Δa

As can be seen from Tab. 3, green hue was efficient rather than red hue on the untreated samples for 6, 12 and 24 months respectively. However, treatment with CA resulted in the red hue on weathered samples for overall exposure. In contrast to CA preservative, wood stain displayed greenish which was similar in 6 and 12 months but increased in 24 months. But, the combination of CA and WS had the lowest change in Δa that was due to the impact of CA. The combination of CA with silicone emulsion at different concentrations gave higher red hue with small differences between the ratios in comparison to combinations with paraffin additives. In spite of the red hue occurred on the samples treated with CA with paraffin additive in 6 months, the color tone then decreased to about half after 24 months.

Tab. 3: Mean Δa values of the samples.

Protective systems	Δa		
	6 months	12 months	24 months
Control	-4.46 (1.22)*	-5.16 (1.44)	-4.85 (0.90)
CA	9.81 (1.48)	7.97(2.31)	9.95 (1.39)
WS	-6.29 (1.71)	-6.14(0.69)	-10.89 (1.90)
CA+WS	0.59 (0.87)	2.06(0.80)	2.16 (0.94)
CA+S(%0,5)	10.92 (0.71)	11.33(1.07)	9.81 (1.30)
CA+S(%1)	9.69 (0.82)	10.71(1.22)	8.29 (0.94)
CA+S(%2)	9.02 (0.49)	8.75(1.87)	8.19 (1.21)
CA+P(%5)	7.41 (1.46)	6.43(1.85)	3.82 (0.77)
CA+P(%10)	7.98 (1.66)	6.91(1.37)	4.42 (0.49)
CA+P(%15)	7.91 (0.62)	7.24(0.95)	3.49 (1.28)

* Standard deviation within parentheses

Change in Δb

Blue hue dominated on untreated samples, highly changed as compared to before weathering, for all exposure periods with very small differences between the exposure times (Tab. 4), whereas, weathering led to yellow hue on the samples treated with CA. The samples coated with wood stain showed blue hue by increasing with longer periods under weathering conditions. However, the blue hue decreased when CA combined with wood stain. Yellow hue was increased on the samples treated with CA + S, for 6 and 12 months, but decreased in 24 months. In the last period, yellow hue decreased with increasing ratio in silicone emulsion. The longer exposure time increased the blue hue in the samples treated with CA +P.

The samples treated with CA and those treated with CA and silicone additives displayed reddish and yellowish after outdoor exposure. This indicates the increasing in Δa and Δb in the chromaticity coordinates.

Tab. 4: Mean Δb values of the samples.

Protective systems	Δb		
	6 months	12 months	24 months
Control	-20.99 (2.31)*	-22.06 (1.11)	-22.35 (3.82)
CA	8.86 (1.47)	7.98 (1.97)	6.33 (1.34)
WS	-13.06 (2.93)	-15.81 (2.90)	-22.26 (2.28)
CA+WS	-1.83 (1.20)	0.25 (1.43)	-0.52 (2.83)
CA+S(%0,5)	10.30 (0.78)	10.44 (1.59)	6.02 (1.56)
CA+S(%1)	8.63 (1.15)	10.47 (1.76)	4.38 (0.81)
CA+S(%2)	8.18 (1.07)	8.93 (1.67)	3.01 (1.75)
CA+P(%5)	-1.52 (1.59)	-3.30 (3.64)	-8.37 (2.38)
CA+P(%10)	-4.58 (2.11)	-0.65 (3.04)	-7.62 (1.42)
CA+P(%15)	0.33 (1.52)	-2.70 (3.55)	-8.34 (1.62)

* Standard deviation within parentheses

Baysal (2014) found that treatment with Tanalith-E (copper azole) and varnish coating turned the reddish and yellowish color on wood surface after accelerated weathering. The yellowing and reddishness were attributed to the formation of quinones and quinine-like

structures resulting from the depolymerisation and oxidation of lignin involving free radicals (Kamdem and Grelier 2002).

Change in ΔE

Tab. 5: Total color change (ΔE) of the control and treated samples.

Protective systems	ΔE		
	6 months	12 months	24 months
Control	36.65 (3.14)*	38.61 (3.12)	38.55 (5.01)
CA	13.68 (1.64)	11.68 (1.42)	12.11 (1.64)
WS	15.67 (5.50)	18.33 (3.25)	26.39 (2.69)
CA+WS	2.21 (0.94)	3.11 (1.14)	6.04 (1.63)
CA+S(%0,5)	15.19 (0.50)	15.61 (1.78)	12.07 (1.20)
CA+S(%1)	13.28 (0.70)	14.98 (2.06)	9.48 (1.24)
CA+S(%2)	12.23 (0.96)	12.75 (1.92)	8.89 (2.18)
CA+P(%5)	13.58 (2.05)	11.71 (2.62)	14.77 (3.32)
CA+P(%10)	18.02 (1.74)	9.88 (2.53)	12.76 (3.51)
CA+P(%15)	9.63 (1.00)	9.26 (2.11)	9.70 (1.74)

* Standard deviation within parentheses

As an expected result the highest color change was obtained with untreated Scots pine samples as shown in Tab. 5. While the total change observed in 6 months on control samples, no change was found between 12 and 24 months under weathering. It is demonstrated from these results that six months exposure is sufficient to obtain the total color change with unprotected wood. The similar result was available for CA treated wood which showed notable change just for 6 months. Marked increase was shown in color change of wood coated with wood stain after 12 months. In the case of CA +WS, color change increased continuously in all exposure periods. However, the best result was attained with this combination, by indicating the lowest change for all exposure times when compared to before weathering. The inhibiting effect of CA+WS in color change was also confirmed by Δa and Δb as shown in Tabs. 3 and 4. This reveals that the color is stabilized by the application of CA and wood stain that can be suggested on wooden construction for outdoor against photodegradation. These findings were also demonstrated by visually in Fig. 1, which reflected the change in color in untreated and treated samples for 6, 12 and 24 months respectively.

With regard to silicon combinations with CA, total change in color ranged from 8 to 15 depends on the silicon ratio and exposure times. When compared to paraffin combination with CA, higher concentration of paraffin (15 %) resulted in lower change than that of 5 % and 10 %. This might be explained by the higher amount of paraffin being in treated wood.

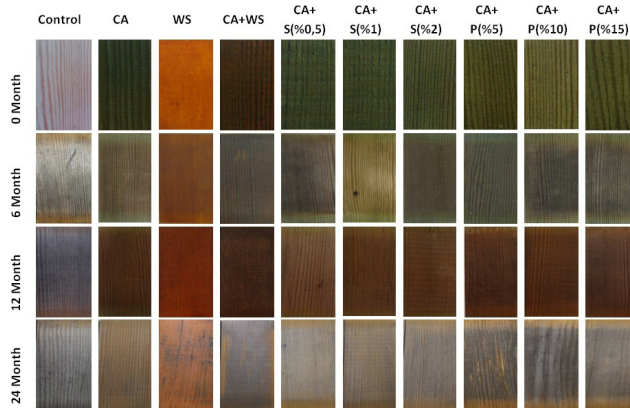


Fig. 1: The picture of control and treated samples exposed to natural weathering for 6, 12, 24 months.

The total change in color of treated samples exhibited lower values than that of control samples in all cases for 6, 12 and 24 months respectively. This reveals the effectiveness of the formulations included in the experiments of the present study against weathering. The efficacy of copper ethanalamine (CuEA) against photo degradation was reported after 500 h accelerated weathering by Deka et al. (2008), suggesting that the photostabilization of wood might be due to the reaction of CuEA with phenolic groups of lignin.

Similar result was reported by Temiz et al. (2005), regarding the effect of accelerated weathering on coloring behavior of wood treated with some copper based preservatives such as CCA, ACQ, Wolmanit CX and Tanalith-E (copper azole). CCA and ACQ provided considerably higher stabilization in color than other copper based formulations. According to their results, photostabilization of wood by copper based treatments may be due to the retardation in the occurrence in the formation of carbonyl groups and reduction in the delignification of wood during the weathering exposure. The effect of CCA was due to the chromium content which play important role in the formation of complexes with guaiacyl lignin (Pizzi 1980). It was reported that the metal complexes between wood components and inorganic ions was important for controlling the weathering (Chang et al. 1982).

Effect of copper amine (Cu-EA) was performed in another artificial weathering test against photodegradation. Treatment with 0.25% Cu-EA was more effective in stabilizing wood color, resulting in the ΔE^* to be 8 after 1200 h exposure. Moreover, higher ratios of Cu-EA like 1.5% lowered the color change to be 4 (Zhang et al. 2009).

According to Fig. 2, untreated scots pine samples considerably lost their glossiness during two years exposure due to the natural weathering and effect of UV radiation on lignin component resulting in chromophoric groups that changes color and gloss properties. The loss of gloss was clearly proved by Fig. 1, which illustrates the samples surface after natural weathering.

CA treatment alone lost the glossiness to some extent in six months, yet had the about initial value after 12 months, and increased the glossiness after 24 months.

Change in Glossiness (%)

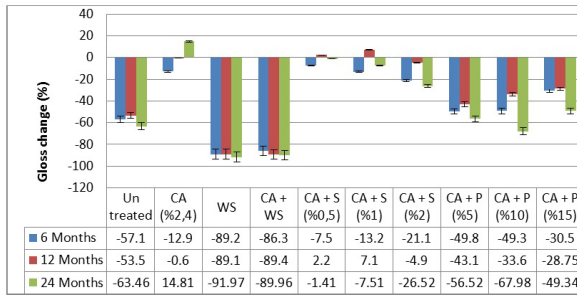


Fig. 2: Gloss change in weathered samples

However, the most change in glossiness was obtained with wood stain (WS) and mixture of CA and WS that was particularly occurred in 6 months as a loss of gloss. This heavy loss in glossiness was caused by the characteristic of wood stain, since CA treatment alone had quite lower change than its combination with WS. In contrast to this result (Baysal et al. 2014) found slight decrease in glossiness on Scots pine treated with copper-based preservatives, followed by coating of synthetic and polyurethane varnishes as a result of 500 h accelerated weathering.

CA+S noticeably differed from others like paraffin emulsion or wood stain, indicating the lowest change in glossiness. The surface gloss was the least affected by CA + S (0.5 %), and decreased for longer exposure.

The surface gloss was also affected by CA+P combinations by remarkably lowering the glossiness for not only short term but also long term weathering. It was determined that when the paraffin ratio increased to 15 %, the gloss loss was relatively less than those of 5 and 10 %.

Cu leaching

The Copper levels in control and weathered samples were presented in Tab. 6. The Copper ratio was measured to be 4.5 % in the samples treated with 2.4 % CA alone that reflects the highest amount of Cu in the samples unexposed. The adding of paraffin and silicon in to the formulation resulted in lower Cu in the control samples. The lowest Cu was determined in the combination with CA+P (10%). This can be explained by the high molecular weight of paraffin which can plug the voids, prevents the penetration of copper.

Tab. 6: The rate of remained copper (%) and total Cu amount leached out (ppm) in the samples

Variation	0 month	6 month	12 month	24 month	Total Cu amount leached out (ppm)
CA	4.5	2.24	2.28	2.24	67400
CA+WS	2.94	2.23	2.02	1.77	28000
CA+S (%0,5)	2.14	1.78	1.30	1.63	17100
CA+S (%1)	3.03	1.30	1.21	2.17	44100
CA+S (%2)	2.83	2.61	2.33	1.61	19400
CA+P (%5)	2.26	1.11	0.35	0.21	51100
CA+P (%10)	0.72	0.51	0.37	1.40	11400
CA+P (%15)	2.25	1.20	0.35	0.26	49400

The Cu level decreased about half (2.24 %) in the samples treated with CA after 6 months exposure. But, remarkable decrease was not found after this time. This indicates that most of the copper leached from the wood panels in 6 months due to the weathering. According to Humar et al. (2015), first leaching peak was observed in the initial phases of leaching. They found the Cu leaching to be 32 % from the wood treated with copper-ethanolamine, when the samples exposed to above ground for 42 months.

In addition, total leached of Cu amount was 67400 ppm in CA treated wood. Posttreatment with wood stain decreased the leached Cu compared to CA treatment alone. This was confirmed by a previous report, investigating the effectiveness of the semi-transparent coatings to reduce leaching components from the treated wood. Five commercial flooring coatings were applied on the untreated, CCA, ACQ and CA treated wood. It was found that all coatings reduced the average rates of leaching of inorganic components by 60 % during the natural weathering for 3 years (Nejad and Cooper 2010). Humar et al. (2011) found very low Cu leaching (0.2 and 0.3 %) in laboratory conditions from the wood treated with CuE which was pretreated with two different acrylic waterborne finishes.

The addition of silicon compound improved the leaching properties of copper component in treated wood. The better result was obtained when silicon was used at 0.5 % (17100 ppm). The higher Cu leaching in the samples treated with CA+S (1 %) might be due to the high Cu value initially being in the sample. Paraffin combinations with CA did not yield good results regarding Cu leaching, because no synergistic effect was found. The lower Cu content in the samples treated with CA+P (10 %) resulted in lower Cu leaching as well. The results indicate that some differences in copper leaching might be due to the differences in Cu retention in the wood samples.

CONCLUSIONS

Scots pine treated with the combination of copper azole and paraffin emulsion resulted in lower retention values than the combination with silicone emulsion as well as CA treatment alone. Scots pine control samples were extensively darkened by natural weathering in six months. Little increase was determined in whiteness in the case of the mixture with CA and silicone emulsion after 24 months exposure. Not surprisingly, control samples had the highest color change for each period of total exposure. Application of semitransparent wood stain after CA treatment showed synergistic effect against weathering, resulting in the lowest change in color. The increasing ratio in paraffin and silicon gradually decreased the color change. Wood satin led to negative impact on glossiness. Lower amounts of silicone inhibited the gloss change. Posttreatment application with wood stain as well as CA combination with silicon emulsion improved the leaching characteristic of Cu component. Based on the results on total color change and Cu leaching obtained from present study, wood treated with CA+WS can be suggested for above ground application as long as the glossiness is disregarded.

ACKNOWLEDGEMENT

The authors thank the Bartın University for supporting this research (Project No: BAP-2012-1-38).

REFERENCES

1. Archer, K., Preston, A., 2006: An overview of copper based wood preservatives, Wood protection 2006. <http://www.forestprod.org/woodprotection06archer.pdf>.
2. Baysal, E., 2008: Some physical properties of varnish coated wood preimpregnated with copper-chromated boron CCB after 3 months of weathering exposure in southern Aegean Sea region, Wood Research 53 (1): 43-54.
3. Baysal, E., Tomak, E.D., Ozbey, M., Altın, E., 2014: Surface properties of impregnated and varnished Scots pine wood after accelerated weathering, Coloring Technology 130 (2): 140-146.
4. Christy, A.G., Senden, T.J., Evand, P.D., 2005: Automated measurement of checks at wood surfaces, Measurement 37 (2): 109-118.
5. Chang, S.T., Hon, D.N.S., Feist, W.C. 1982: Photodegradation and photoprotection of wood surfaces, Wood Fiber Sci. 14 (2): 104-117.
6. Deka, M., Humar, M., Rep, G., Kricej, B., Sentjurc, M., Petric, M., 2008: Effects of UV light irradiation on colour stability of thermally modified, copper ethanolamine treated and non-modified wood: EPR and DRIFT spectroscopic studies, Wood Sci Technol 42: 5-20.
7. Evans, P.D., Wingate-Hill, R., Cunningham, R.B., 2009: Wax and oil emulsion additives: How effective are they at improving the performance of preservative-treated wood?, Forest Products Journal 59 (1/2):66-70.
8. Feist W.C., 1983: Weathering and protection of wood. In: Proceedings, seventy-ninth annual meeting of the American Wood – Preservers' Association 79: 195-205.
9. Feist, W.C., 1988: Role of pigment concentration in the weathering of semitransparent stain, Forest Products Journal 38 (2): 41-44.
10. Feist, W.C., Ross, A.S., 1995: Performance and durability of finishes on previously coated cca-treated wood, Forest Prod. J. 45(9): 29-36.
11. Freeman, M. H., D. D. Nicholas, T. P. Schultz, 2006. Nonarsenical wood protection: Alternatives for chromated copper arsenate, creosote and pentachlorophenol. In: Environmental Impacts of Treated Wood. T. G. Townsend and H. Solo-Gabriele (Eds.). CRC/Taylor and Francis, Boca Raton, Florida. pp. 19–36.
12. Freeman, M.H., McIntyre, C.R., 2008: A comprehensive Review of Copper-Based Wood preservatives with a focus on new micronized or dispersed copper systems, Forest Prod. J. 58(11): 6-27.
13. Fowle, D.A., Preston, A.F., Zahora, A.R., 1990: Additives: An example of their influence on the performance and properties of CCA-treated southern pine, In: Proc. Eighty-Sixth Annual Meeting of the American Wood-Preservers' Assoc. Pp 11-21.
14. Green, F., Schultz, T.P., 2003: Wood deterioration and preservation: advances in our changing world, Am. Chem. Soc. Symp. Series 845, Washington, DC. Chp. 23.
15. Hon, D.N.S., Chang, S.T., 1985: Photoprotection of wood surfaces by wood-ion complexes, Wood Fiber Sci. 17(1):92-100.
16. Humar, M., Kalan, P., Sentjurc, M., Pohleven, F., 2005: Influence of carboxylic acids on fixation of copper in wood impregnated with copper amine based preservatives, Wood Science and Technology 39 (8): 685-693.
17. Humar, M., Bucar, B., Pohleven, F., 2008: Influence of ethanolamine on lignin depolymerization and copper leaching from impregnated wood, Wood Res. 53 (4): 85-94.
18. Humar, M., Pavlic, M., Zlindra, D., Tomazic, M., Petric, M., 2011: Performance of waterborne acrylic surface coatings on wood impregnated with Cu-ethanolamine preservatives, Bull. Mater. Sci.34 (1): 113-119.

19. Humar, M., Thaler N., Lesar B., Zlahtic M., Krzisinik D., 2015: Long term leaching of copper from copper-ethanolamine treated wood exposed in above and in-ground applications, The 11th Annual Meeting of the Wood Science and Engineering, 14-15 September 2015, Poznan, Poland.
20. Kamdem, D.P., 2008: Development of commercial wood preservatives: efficacy, environmental, and health issues, Am Chem Soc Symp Series 982, Washington, DC, Chp. 25.
21. Kamdem, D.P., Grelier, S., 2002: Surface roughness and colour change of copper amine and UV absorber treated red maple (*Acer rubrum*) exposed to artificial ultraviolet light, *Holzforschung* 56 (5):473–478
22. Kiguchi, M., Kataoka, Y., Doi, S., Mori, M., Hasegawa, M., Morita, S., Kinjo, M., Kadeharu, Y., Imamura, Y., 1996: Evaluation of weathering resistance of the commercial pigmented stains by outdoor exposure tests, *Mokuzai Gakkaishi* 23 (3):150-159.
23. Lebow, S., Winandy, J., Bender, D., 2004: Treated wood in transition: A look at CCA and the candidates to replace it, *Wood Design Focus*. 4–8.
24. Nejad, M., Cooper, P., 2010: Coatings to reduce wood preservative leaching. *Environ, Sci. Technol.* 44 (169):6162–6166.
25. Nejad, M., Cooper, P., 2011: Exterior wood coatings. Part-1: Performance of semitransparent stains on preservative-treated wood, *J. Coat. Technol. Res.* 8 (4) 449–458.
26. Petric, M., Kricej, B., Humar, H., Pavlic, M., Tomazic, M. 2004: Patination of cherry wood and spruce wood with ethanolamine and surface finishes, *Surf Coat Int Part B, Coat Trans* 87(B3):95–201.
27. Pizzi, A. 1980: Wood water proofing and lignin cross linking by means of chromium trioxide/ guaiacyl units complexes, *J. Appl. Polym. Sci.* 25: 2547–2553.
28. Preston, A.F., 2000: Wood preservation: trends of today that will influence the industry tomorrow, *Forest Prod J* 50 (9):12–19.
29. Preston, A.F., 2003: Wood deterioration and preservation: advances in our changing world, Am Chem Soc Symp Series 845, Washington, DC. Chp. 22.
30. Schultz, T.P., Nicholas, D.D., Preston, A.F. 2007: A brief review of the past, present and future of wood preservation, *Pest Manag Sci* 63 (8):784–788.
31. Schultz, T.P., Nicholas, D.D., McIntyre, C.R., 2008: Recent patents and developments in biocidal wood protection systems for exterior applications. *Recent Patents Material Sci* 1: 128
32. Temiz, A., Yildiz, U.C., Aydin, I., Eikenes, M., Alfreksen, G., Colakoglu, G., 2005: Surface roughness and color characteristics of wood treated with preservatives after accelerated weathering test, *App Surf Sci* 250 (1-4): 35–42
33. Townsend, T.G., Solo-Gabriele, H., 2006: Environmental impacts of treated wood, Boca Raton, FL: CRC Press Taylor & Francis Group. 520 pp June 2, 2006 Boca Raton, FL.
34. Yildiz, S., 2007: Retention and penetration evaluation of some softwood species treated with copper azole, *Building and Environment* 42 (6): 2305–2310.
35. Zhang, J., Kamdem, D.P. Temiz, A., 2009: Weathering of copper-amine treated wood, *Appl Surf Sci*, 256 (3): 842–846.

*HÜSEYİN SIVRIKAYA, AHMET CAN, İBRAHİM TÜMEN, DENİZ AYDEMİR
BARTIN UNIVERSITY
FACULTY OF FORESTRY
74100 BARTIN
TURKEY
Corresponding author: hsivrikaya@bartin.edu.tr