WATER REPELLENT EFFICIENCY OF WOOD TREATED WITH COPPER-AZOLE COMBINED WITH SILICONE AND PARAFFIN EMULSIONS

Hüseyin Sivrikaya[1], Ahmet Can[2]

[1] Turkey, Bartin University, h_sivrikaya@yahoo.com

[2] Turkey, Bartin University, 6116acan@gmail.com

ABSTRACT

Copper-azole free of chromium and arsenic is one of the potential wood preservatives against wood decay organisms being on the market as an alternative to CCA (copper, chrome, arsenic).

In this study, copper-azole solution with the concentration of 2.4 % was mixed with water repellents, 0.5 %, 1 % and 2 % of silicon emulsions as well as 5, 10 and 15% of paraffin emulsions respectively. In the first experiment Scots pine samples were treated with these solutions followed by a fixation step in a conditioned chamber (21°C , 65% RH). In the second experiment, treatment of the Scots pine specimens was done with the same formulations, but the samples were dried in an oven at 100 °C for two days in order to measure water absorption and water repellency efficiency.

Paraffin emulsions reduced the water absorption more than copper-azole alone and silicon based formulations when the samples left the fixation in the conditioning chamber. Water absorption increased in the samples dried at 100 °C compared to those left to ambient condition. The oven drying increased the water absorption to the copper-azole treated wood.

Paraffin emulsions lead to better water repellency compared to control and silicon emulsions, but the increasing in the paraffin emulsion did not improved the efficiency.

Key words: copper-azole, water repellents, silicon, paraffin, Scots pine,

1. INTRODUCTION

The first generation wood preservatives such as creosote, Pentachlorophenol (PCP) and principally CCA (copper, chrome and arsenate) were the major biocides for industrial applications because of the broad range of activity to decay fungi, insects and marine borers, in addition to low cost and long-term efficacy. However, PCP and creosote have been restricted or banned in many countries due to the health and environmental concerns as well as ultimate disposal of treated wood (Freeman et al. 2006).

The use of CCA wood preservatives was banned by US-EPA (Environmental Protection Agency) in the residential applications such as decks, fences and playground components effective as of December 31, 2003, and effectively restricted the use of CCA to the treatment of wood used primarily in industrial and agricultural applications.

Second generation copper-based formulations, such as copper azole (CA) and ammoniacal copper quat (ACQ), replaced CCA in residential applications (Green and Schultz 2003).

Copper azole primarily consists of amine copper and co-biocides such as tebuconazole to protect wood from fungal and insect attack. It was developed in different formulations; copper azole Type A (CBA-A), which contains 49 % copper, 49 % boric acid and 2 % Tebuconazole, Type B (CA-B) is comprised of 96 % copper and 4 % Tebuconazole without added boron (Lebow 2004).

The characterization and thermal behavior of copper azole (Tanalith E 3494) treated wood was studied by means of Fourier transform infrared spectroscopy (FTIR) and thermogravimetric (TG) analysis by Helsen et al. (2007). FTIR analyzing of treated wood showed the most binding sites of copper as carboxylic groups, phenolic groups and aromatic esters, and resulted in a higher charcoal.

The other experiments regarding copper azole were investigated by several authors. Barnes and Lindsey (2009) studied mechanical propertie, found that copper azole treatment did not show negative effects in comparison to the control values.

Cornfield et al. (1994) and Temiz et al. (2005) performed the weathering performance of copper azole in terms of surface roughness and color measurements, indicated resistance against weathering.

As to comparative performance with CCA; Drysdale et al. (2000) reported that copper azole outperformed CCA in the sites where fungal activity is high, whereas CCA was more effective in the sites where termite activity is severe. Further, about 1.5 times as much copper azole is required to give equal performance to CCA (Suttie et al. 2002).

On the other hand, spruce and larix displayed poor penetration and retention with copper azole while scots pine showed the best (Yıldız 2007). When Douglas-fir treated with copper azole type B according to passive impregnation method, retention and penetration varied with different incising densities and dipping times (Islam et al. (2009). The penetration was found higher with passive impregnation method than full-cell method despite the similar retention, moreover leaching of preservative was significantly higher for latter one (Ando et al. 2011).

The 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 (Green and Schultz 2003).

It was reported by Scholz et al. (2009) that water capillary uptake in wood could be reduced by paraffin treatment. In recent years, Vax treatment has been evaluated to slow photodegradation (Lesar et al. 2011a), wood durability and sorption properties (Lesar and Humar 2011b).

The importance of water based silicones, which have already been used for masonry and concrete, as water repellents for wood was revealed by Hager (1995), achieved up to 70 % in the reduction of water uptake, then by Lukowsky et al. (1997) performed five water based silicones. Silicones were investigated to enhance water repellency (Sebe and Brook 2001, Weigenand et al. 2007) as well as silanes to the same property (Mai and Militz 2004, Hill 2004, Donath et al. 2006)

Environmental concerns also exist in relation to new copper based systems include; high levels of copper leaching, negative impact on aquatic systems, corrosion of metal fasteners since they have no chromium, mold growth, and disposal issue of treated wood (Schultz et al. 2007). Some additives having hydrophobic and bonding characteristic are proposed as potential alternatives. The aim of this study is to investigate the water absorption and water repellency properties of wood treated with copper azole combined with silicone and paraffin emulsions.

2. EXPERIMENTAL METHODS

2.1. MATERIALS

Scots pine specimens were prepared from sapwood blocks with dimensions of 6.4 x 25 x 50 mm (LxRxT) according to AWPA Standard E4-03. Six replicate was used for each formulation. Copper-Azole was used as wood preservative at 2.4 % concentration alone as well as to the same ratio with water repellents. The major constituents of the copper azole are given below (Table 1)

Table1: Constituents of the copper azole

Constituents	**%**
Copper carbonate	20,5
2-aminoetanol	< 20
Boric acid	< 5
Tebuconazole	< 0,5
Propiconazole	< 0,5
Polyethyleneimine	< 20
Organic acid	< 5
Surfactant	< 5

Silicone emulsion is a solventless, water-thinnable emulsion of a polysiloxane modified with functional silicone resin, which has approximately 1 g /cm3 density and 7 pH value. Silicone emulsion was incorporated in to copper-azole at the concentrations of 0.5, 1, and 2 % respectively, while Paraffin emulsion contents was prepared at 5 %, 10 % and 15 % solutions.

Copper-azole based solutions and pH values are given in Table 2.

Table 2: pH values of the solution

Solution	pH
CA (copper-azole) 2.4%	9,84
Paraffin emulsion	7,76
CA + 5 % Paraffin	9,74
CA + 10 % Paraffin	9,74
CA + 15 % Paraffin	9,74
Silicone emulsion	9,2
CA + 0,5% Silicone	9,93
CA + 1% Silicone	9,96
CA + 2 % Silicone	10

2.1.1. Wood treatment

Wood specimens were treated by vacuum process by applying 0,7 bar for 30 minutes. The treated samples were then allowed a fixation step in a condition chamber at 21 °C temperature and 65 % relative humidity for two weeks. The second trial was done to the same solutions with Scots pine samples, followed by oven-dried at 100 °C as distinct from the first trial.

2.2. Water absorption and water repellency efficiency

Wood specimens were soaked in distilled water for 15, 45 and 90 minutes and 3, 24, 48 hours intervals. Water absorption and water repellent efficiency were calculated according to Eq.1 and Eq. 2 given below.

Water absorption (WA)

$$WA (\%) = (W2 - W1)/W1 * 100 \quad (1)$$

W1: initial weight of the sample before water soaking

W2: weight of the sample after water soaking

Water repellent efficiency (WRE)

$$WRE (\%) = (Wu - Wt)/Wu * 100 \quad (2)$$

Wu: water absorption of untreated wood sample

Wt: water absorption of treated wood sample

3. RESULTS AND DISCUSSION

The weight percent gain (WPG %) of the copper azole treated wood and copper azole combined with water rapellents are shown in Table 4.

Table 4: The weight percent gain (WPG %) of the copper- azole and combined with water rapellents

Treatment	WPG (%) (21 °C, 65 % RH)		WPG (%) (oven-dried at 100 °C)	
	Avarage	Std.	Avarage	Std.
CA 2.4 %	79,11	18,52	82,03	17,43
CA +0,5 % Silicone	80,80	27,68	87,43	13,06
CA +1 % Silicone	89,20	13,80	85,77	17,22
CA +2 % Silicone	86,06	15,08	91,10	14,96
CA +5 % Paraffin	78,40	13,19	86,42	14,4
CA +10 % Paraffin	81,79	18,54	81,00	18,19
CA +15 % Paraffin	80,15	22,06	87,11	15,83

WPG slightly increased by the addition of silicone and paraffin, however there was no linear relationship between WPG and increase in concentration both for silicone and paraffin emulsion.

3.1. WATER ABSORPTION

Water absorption of copper-azole alone was slightly lower than untreated samples at the beginning of the soaking period as well as at the end. As a result of 48 hours soaking; water absorption ratio was found to be 104 % for copper azole treated wood, and ranged from 103 % to 106 % for copper azole silicon combination, and from 67 % to 73 % for copper azole paraffin formulations. In addition, it was found to be 109 % for untreated specimens.

Table 5: Water absorption rate of conditioned samples at 21 °C, 65 % RH

Water absorption (%)	Control	CA 2.4 %	CA + S (% 0.5)	CA + S (% 1)	CA + S (% 2)	CA + P (% 5)	CA + P (% 10)	CA + P (% 15)
15 min.	78,31 (19,38)	73,06 (21,13)	75,01 (26,53)	81,45 (13,15)	78,42 (11,69)	16,40 (3,01)	16,77 (3,04)	17,83 (3,20)
45 min.	81,15 (18,92)	77,28 (21,07)	78,87 (25,57)	85,33 (12,60)	84,12 (11,36)	28,57 (5,51)	27,76 (3,73)	29,95 (3,18)
90 min.	82,81 (18,73)	82,05 (20,20)	85,11 (25,05)	90,49 (12,17)	89,30 (10,62)	38,05 (5,58)	38,82 (2,99)	38,29 (2,83)
3 h.	87,40 (17,97)	85,70 (19,21)	90,00 (24,59)	94,92 (11,59)	94,15 (9,91)	41,11 (4,95)	41,00 (3,40)	41,19 (3,65)

24 h.	91,77 (15,53)	92,26 (15,50)	96,69 (19,00)	98,60 (9,22)	100,07 (7,19)	53,78 (4,26)	55,23 (2,55)	55,45 (3,10)
48 h.	109,28 (11,15)	104,58 (14,18)	105,79 (15,18)	103,79 (8,20)	106,51 (7,76)	67,93 (3,41)	72,92 (2,78)	73,48 (3,89)

Standart deviation is given in parenthesis

Paraffin emulsions showed the best performance in terms of water absorption for all soaking periods from 15 minutes to 48 hours as shown in Table 5. According to Var (2001), water absorption of wood was significantly reduced by mixture of paraffin and linseed oil. Lesar et al. (2011a) reported that wood treated with high proportions of wax reduces moisture absorption and restrains the photodegradation in accelerated weathering.

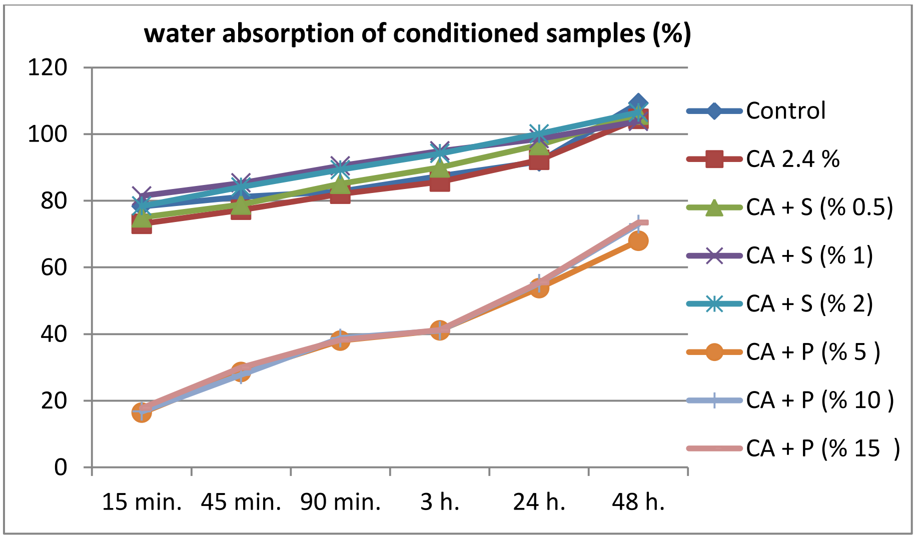

Figure 1: Water absorption rate of conditioned samples at 21 °C, 65 % RH

Table 6: Water absorption rate of oven-dried samples at 100 °C

Water absorption (%)	**Control**	**CA 2.4 %**	**CA + S (% 0.5)**	**CA + S (% 1)**	**CA + S (% 2)**	**CA + P (% 5)**	**CA + P (% 10)**	**CA + P (% 15)**
15 min.	96,51 (7,86)	97,02 (12,95)	101,23 (11,76)	102,39 (12,77)	98,52 (10,12)	43,94 (11,00)	66,05 (14,51)	70,57 (9,27)
45 min.	99,70 (7,26)	105,78 (14,37)	106,28 (10,98)	107,44 (12,31)	105,03 (9,54)	81,51 (12,98)	88,02 (18,51)	94,93 (11,34)
90 min.	99,64 (8,50)	107,91 (15,50)	108,95 (10,06)	109,89 (11,27)	107,53 (8,67)	95,87 (9,46)	91,26 (19,20)	91,36 (14,50)
3 h.	101,64 (8,43)	112,19 (14,73)	112,66 (8,66)	113,47 (9,97)	110,09 (7,63)	104,96 (9,66)	93,60 (18,51)	94,00 (13,11)
24 h.	109,05 (7,05)	121,52 (11,53)	118,52 (5,13)	118,46 (5,98)	114,94 (4,92)	115,40 (8,69)	103,44 (14,34)	103,01 (8,34)

48 h.	125,80 (7,23)	130,24 (8,66)	122,44 (4,42)	129,47 (14,81)	119,40 (1,86)	122,34 (7,44)	113,54 (9,85)	112,90 (4,79)

After oven-drying; paraffin emulsions showed lower water absorption than untreated samples and CA alone for 15 minutes, as well as similar results for 48 hours soaking.

Water absorption of paraffin treated wood gradually increased with increasing concentration for 15 minutes, but it was reversible after 48 hours soaking.

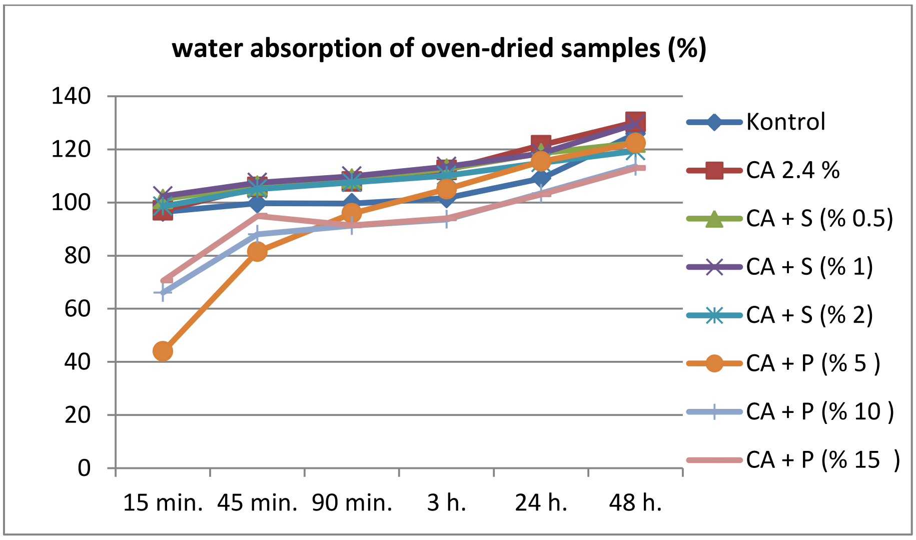

Figure 2: Water absorption rate of oven-dried samples at 100 °C

Water absorption increased in parallel with soaking time for both conditioned and oven dried samples. Copper azole-paraffin combinations showed less water absorption than others, particularly CA+P (5 %) absorbed the lowest after conditioning process. Lebow et al. (2003) used the combination of wax (1, 3 % and 5 %) mineral spirit solvent and urethane varnish at 20 % concentration for investigating the leaching of copper, chrome and arsenic from CCA treated wood. Water repellent significantly reduced the leaching of these components.

Water absorption was significantly different between paraffin and silicone combinations in 15 minutes period. It is shown from the Figure 1 and 2, oven-dried samples resulted in more water absorption than the air-dry samples. It might be atributed to negative impact of high temperature on biocide and biocide water repellent combination.

3.2. WATER REPELLENCY EFFICIENCY (WRE %)

Table 7: Water repellency efficiency rate of conditioned samples at 21 °C, 65 % RH

WRE (%)	CA 2.4 %	CA + S (% 0.5)	CA + S(% 1)	CA + S (% 2)	CA + P (% 5)	CA + P (% 10)	CA + P (% 15)
15 min.	6,70	4,21	-4,01	-0,14	79,06	78,58	77,24
45 min.	4,77	2,81	-5,15	-3,66	64,79	65,79	63,09
90 min.	0,92	-2,78	-9,27	-7,84	54,05	53,12	53,76
3 h.	1,95	-2,97	-8,60	-7,72	52,96	53,09	52,87
24 h.	-0,53	-5,36	-7,44	-9,04	41,39	39,82	39,57
48 h.	4,30	3,19	5,02	2,53	37,84	33,27	32,76

Paraffin emulsions initially greatly improved the water repellency which reduced in 45, 90 minutes soaking and 3, 24, 48 hours respectively as given in Table 7. The results reveals that increasing in the concentration of paraffin emulsions did not improve the water repellency. Although Paraffin treated and conditioned samples displayed better water reppellency ranged from 77 % to 79 % in 15 minutes, it reduced after 48 hours soaking to 32 % (CA+P 15%). On the other hand, Silicone emulsions exhibited poor performance at the end of the soaking periods when compared to paraffin based formulation.

Panov and Terziev (2009) did not found a clear relationship between silane and water absorption of wood. Weigenand (2007) obtained low ASE and WRE values for Scots pine treated with macro-or micro-amino-silicone emulsions although WPG ratios. De vetter(2010) indicated that organosilicones behaved as water repellents, did not reduce the maximum swelling, but influenced the rate of moisture uptake.

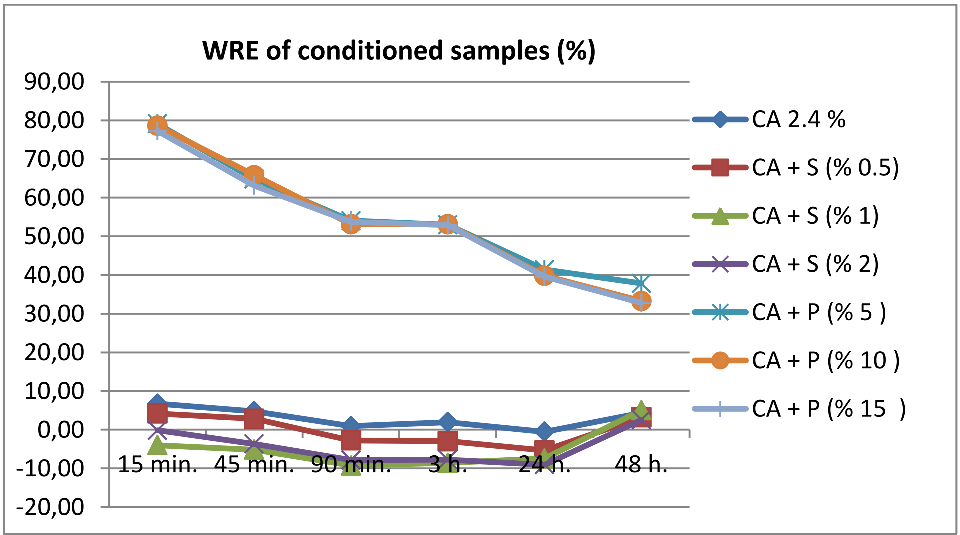

Figure 3: Water repellency efficiency rate of conditioned samples at 21 °C, 65 % RH

Table 8: Water repellency efficiency rate of oven-dried samples (100 °C)

WRE (%)	CA 2.4 %	CA + S (% 0.5)	CA + S (% 1)	CA + S (% 2)	CA + P (% 5)	CA + P (% 10)	CA + P (% 15)
15 min.	-0,53	54,47	31,56	26,88	-4,89	-6,09	-2,08
45 min	-6,09	18,24	11,71	4,79	-6,60	-7,77	-5,35
90 min	-8,30	3,78	8,41	8,31	-9,34	-10,28	-7,92
3 h.	-10,38	-3,27	7,91	7,52	-10,84	-11,64	-8,32
24 h.	-11,43	-5,82	5,14	5,53	-8,68	-8,63	-5,40
48 h.	-3,53	2,75	9,74	10,25	2,67	-2,92	5,09

WRE was found pretty low for copper azole treatment alone in the experiments in Table 8. Nejad and Cooper (2011) studied the coating properties and weathering performance of of CCA, ACQ and CA wood preservatives with coatings. They found that water repellency and visual ratings were significantly improved by CCA treatment. Although ACQ and CA treatment improved the color retention, reduced the water repellency of the coated samples.

After oven-drying process, silicon based formulations initially resulted in much better water repellency than paraffin emulsions, but then decreased gradually at the following soaking periods. Water repellency increased from 2.75 % to 10.25 % with increasing silicon content in 48 hours duration. It is shown from the Table 8, heating process led to adverse impact on copper-azole and paraffin emulsion in improve the water repellency .

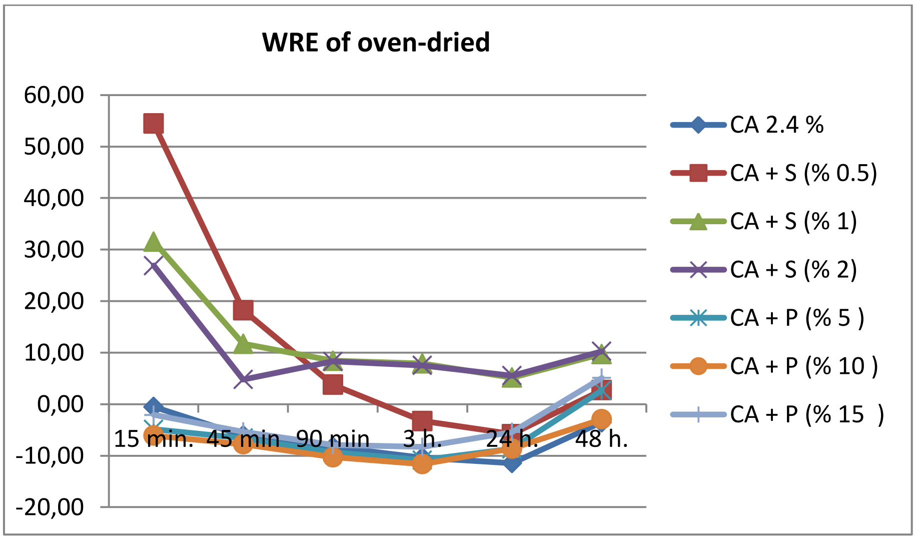

Figure 4: Water repellency efficiency rate of oven-dried samples (100 °C)

4. CONCLUSIONS

Oven-drying process increased the water absorption not only for copper azole tretaed wood alone, but also paraffin and silicon combinations. Wood specimens showed lower water absorption after 15 minutes soaking when they treated with paraffin combinations.

The subsequent soaking periods led to higher water absorption of wood tretaed with paraffin and silicone combinations. The higher water absorption might be resulted from the leaching of paraffin and silicon and thus removal of those in the following soakings.

Even though water repellent efficiency decreased by increasing soaking time for conditioned and oven dried samples, paraffin combinations showed well performance for conditioned samples. Further researches are needed with silicon emulsions at higher concentrations to achieve less water absorption and more water repellent efficiency. In addition, paraffin and silicon emulsions should be used alone to compare with their combinations with copper azole.

REFERENCES

Ando, K., Islam, Md.N., Yamauchi, H., Hattori, N. 2011. Preservative Leaching from Copper Azole–Treated Lumber: A Comparison between the Full-Cell Method and the Passive-Impregnation Method, Forest Prod. J. 61(3):270–272

AWPA E4-03. 2010. Standard Method of Testing Water Repellency of Pressure Treated Wood

Barnes, H.M., Lindsey, G.B. 2009. Bending properties of wood treated with a new organic wood preservative system. Bioresource Technology, 100: 778–781

Cornfield, J.A., Hale, M., Fettis, G. 1994. A comparison of analytical and visual techniques used for assessment of weathering properties of chromium and copper azole treated timber, Presented at the 25th annual IRG Meeting, Nusa Dua, Bali, Indonesia, Document IRG/WP 94-20023

De Vetter, L., Van den Bulcke, J., Van Acker, J. 2010. Impact of organosilicon treatments on the wood-water relationship of solid wood. Holzforschung 64:463–468.

Donath, S., Militz, H., Mai, C. 2006. Creating water repellent effects on wood by treatment with silanes. Holzforschung 60(1):40–46

Drysdale, J.A., Hedley, M.E., Loh, E., Hong, L.T. 2000. Comparative performance of copper azole and copper chrome arsenate treated rubber wood in Australian, Malaysian and New land test sites, Presented at the 31st Annual IRG Meeting, Kona Surf, Hawaii, USA, Document IRG/WP 00-30213.

Freeman, M.H., Nicholas, D.D., Schultz, T.P. 2006. Non-Arsenical Wood Protection: Alternatives for CCA, Creosote, and Pentachlorophenol. In: Environmental Impacts of Treated Wood. Townsend, T.G., Solo-Gabriele, H. Taylor&Francis Group , CRC Press, 520 p. June 2, 2006 Boca Raton, FL.

Green III, F., Schultz, T.P. 2003. New Environmentally-Benign Concepts in Wood Protection: The Combination of Organic Biocides and Non-Biocidal Additives. In: Wood Deterioration and Preservation Advances in Our Changing World. Goodell B., Nicholas, D.D., Schultz, T.P. ACS symposium series 845, 482 p.,

Hager, R. 1995. Waterborne silicones as wood preservatives. IRG/WP/30062.

Helsen, L., Hardy, A., M.K. Van Bael, M.K., Mullens, J. 2007. Tanalith E 3494 impregnated wood: Characterisation and thermal behaviour J. Anal. Appl. Pyrolysis 78: 133–139

Hill, C.A.S., Farahani, M.R.M., Hale, M.D.C. 2004. The use of alkoxysilane coupling agents for wood preservation. Holzforschung 58(3):316–325

Islam, Md.N., Ando, K., Yamauchi, H., Hattori, N. 2009. Preservative treatment of Douglas-fir lumber by the passive impregnation method with copper azole. Eur. J. Wood Prod. 67: 77–81

Lebow, S., Williams, R.S., Lebow, P. 2003. Effect of Simulated Rainfall and Weathering on Release of Preservative Elements from CCA Treated Wood. Environ. Sci. Technol. 37, 4077-4082.

Lebow, S. 2004. Alternatives to Chromated Copper Arsenate (CCA) for Residential Construction. Proceedings of the Environmental Impacts of Preservative-Treated Wood Conference Orlando, Florida

Lesar, B., Pavlic, M., Petric, M., Skapin, A.S., Humar, M. 2011a. Wax treatment of wood slows photodegradation. Polymer Degradation and Stability 96: 1271-1278.

Lesar, B., Humar, M. 2011b. Use of wax emulsions for improvement of wood durability and sorption properties . Eur. J. Wood Prod. 69: 231–238

Lukowsky, D., Peek, R.D., Rapp, A.O. 1997. Water based silicones on wood . IRG/WP 97-30144

Mai, C., Militz, H. 2004. Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds – a review. Wood Sci Technol 37(6):453–461

Nejad, M., Cooper, P. 2011. Exterior wood coatings. Part-2: Modeling correlation between coating properties and their weathering performance. J. Coat. Technol. Res., 8 (4) 459–467.

Panov, D., Terziev, N. 2009. Study on some alkoxysilanes used for hydrophobation and protection of wood against decay. Int. Biodeterior. Biodegradation 63:456–461.

Schultz, T.P., Nicholas, D.D., Preston, A.F. 2007. Perspective A brief review of the past, present and future of wood preservation. Pest Manag Sci 63:784–788.

S`ebe G, Brook, M.A. 2001. Hydrophobation of wood surfaces: covalent grafting of silicone polymers. Wood Sci Technol 35(3):269–282

Suttie, E.D., Bravery, A.F., Dearling, T.B. 2002. Alternatives to CCA for ground contact protection of timber: a perspective from UK on performance and service life expectations, Presented at the 33rd Annual IRG Meeting, Cardiff, Wales, UK, Document IRG/WP 02-30289.

Weigenand, O., Militz, H., Tingaut, P., Sebe, G., de Jeso, B., Mai, C. 2007. Penetration of amino-silicone micro- and macro-emulsions into Scots pine sapwood and the effect on water-related properties. Holzforschung 61:51–59.

Yıldız, S. 2007. Retention and penetration evaluation of some softwood species treated with copper azole. Building and Environment 42 : 2305–2310

Var, A. A. 2001. Reductıon by paraffın wax / linseed oil mixture of water uptake in wooden materials Süleyman Demirel Üniversitesi, Orman Fakültesi Dergisi Seri: A, Sayı: 2, ISSN: 1302-7085, Sayfa: 97-110.

Acknowledgement: This study was supported by the Bartin University, Project No BRT-2012-1-38