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EFFECT OF SILICIC ACID ON BORON LEACHING IN PLYWOOD MANUFACTURE

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ABSTRACT

Boric acid is a well-known wood preservative and fire retardant having low mammalian toxicity. Its efficacy is affected as it is non-fixed type, water leachable and effective only in interior conditions. In present study the effect of silicic acid and treatment methods on permanency of boron in plywood was studied through leaching test. The plywood was treated with glue line treatment as well as veneer treatment method with boric acid and three combinations of boric acid and silicic acid (1:1, 2:1 and 3:1) at 2, 3 and 4% concentrations. With a view to explore the possibility of fixation of boric acid in combination with silicic acid, the treated samples were subjected to leaching and then boron content was analyzed in leached samples. The results showed that boron was easily leached from the samples treated with boric acid only; whereas the treatment with the combination of silicic acid improved boron fixation in samples. The results of two different treatment methods showed suitability of veneer treatment to achieve sufficient boron retention in plywood. However, the leaching of boron was also high in veneer treatment than glue line treatment method.

Keywords: Boric acid, leachability, plywood, silicic acid

INTRODUCTION

Boron compounds are well established wood preservatives used for interior application (Luo *et al.*, 2005). Besides, these compounds have fire retardant effect to wood (Schoeman and Lloyd, 1998) and show low mammalian toxicity but are ecofriendly in nature (Pallaske, 2004). However, its leaching behaviour in moist or damp condition reduces its efficacy in outdoor application. Therefore, it needs to be fixed inside the wood with some fixatives to reduce its leachability and to improve the service life. Preservative fixation in wood occurs place through chemical reactions that make the preservative non leachable during service. Many efforts have been made to fix boron in wood structure through different metal salts like zinc borates (Kirkpatrick and Barnes, 2006; Lin and Furuno, 2001), organic esters (like tetramethylammonium bis/salicyl/borates) (Humphrey *et al.*, 2002), silicone gels (Furuno and Imamura, 1998; Yamaguchi, 2001) and animal proteins (Thevenon and Pizzi, 2003; Mazela *et al.*, 2007).

Ueda (1993) reported that silicon has similar structure as boron and can substitute it in wood. Yamaguchi (2002) reported the reduction of boron leaching by the use of complex compound of boric acid and silicic acid. Silicic acid forms of silicon dioxide known as silica gel on heating (Anon, 2015).

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The use of silicic acid as adhesive for bonding wood, plastics, paper, rubber and textile has been reported by Loth *et al.,* (2008). Silicon in the form of tetraethoxysilane and methyl triethoxysilane has been used to reduce boron leach-ability from modified wood and to enhance wood durability against fungi and termites (Kartal *et al.*,2009). Mahltig *et al.,* (2008) have suggested that the incorporation of silver, copper, zinc compounds, boric acid or organic biocides to alkoxysilanes to improve its biocidal properties. Previous works supported the fact that boron and silicon combination potential act as preservative, hence are used in the treatment of plywood to overcome boron leaching problem. Chemical treatment with some fixative is a method to reduce the leaching of element and second is treatment method, which also needs equal consideration. Generally, plywood is treated by three methods *viz*., glue line, veneer treatment and post-manufacturing treatment. In veneer treatment method, veneers are treated by dipping or soaking in chemicals by open tank method followed by drying and processing into a final plywood product. Whereas, in glue line treatment preservatives are incorporated into adhesive prior to pressing. Post-manufacture treatment is also practised, which include the incorporation of biocides by pressure/vacuum treatment processes, by surface coatings (dip, spray, or brush) or by direct treatment of the product. Each treatment method has its merit and demerits. Therefore, in the present study the effect of treatment method i.e. glue line and veneer on boron fixation was studied. Besides evaluation of the possible influence of test combinations of boric and silicic acid on boron leaching as compared to boric acid single treatment was studied.

MATERIALS AND METHODS

Plywood preparation

Plywood from poplar (*Populus deltoides* Bartr Ex. Marsh) veneer was prepared in Forest Research Institute (FRI) Dehradun, India as per IS: 303 (Anonymous 1989). Green poplar logs having 125 cm average length and 150 cm girth were procured from FRI Dehradun. The logs were peeled off to veneers of 0.16 cm thickness in Forest Products Division and dried upto 10-12% moisture content. The resol based phenol formaldehyde adhesive (PF) was prepared in laboratory as process laid in IS: 848 (Anonymous, 1974). Plywood was treated with boric acid (C_1), boric acid + silicic acid (1:1) (C_2), boric acid + silicic acid (2:1) (C_3) and boric acid + silicic acid (3:1) (C_4) evaluated at three concentrations *viz*., 2, 3 and 4%. Two treatment methods (glue line and veneer treatment) were followed to treat plywood. In glue line treatment, the chemicals at test concentration were added to adhesive on the basis of its solid content just before its application on veneers. Whereas, in veneer treatment methods veneers were dipped in 2, 3 and 4% concentrations of each chemical solution for 60, 30 and 5 min, respectively, to obtain nominal retention followed by conditioning at room temperature. The prepared adhesive was then applied on both side of core veneer @ 110 g m^{-2}. After 18 h of open assemble time, three veneers including core veneer were assembled perpendicular to each other and pressed in hot press at 150^0C and 200 lbs $inch^{-2}$ pressure. Then plywood was subjected to conditioning for 24 h at room temperature. A total of 12 plywood board were prepared for four chemical compositions *viz*., C_1, C_2, C_3 and C_4 at three concentration (2, 3 and 4%). Twelve test samples of 1.9 cm x 1.9 cm x 0.45 cm size were prepared from each plywood for leaching test of boron in plywood. The samples were grouped into two set. Each set had 72 samples. Six replicates were used for each treatment including control. Thus, a total of 144 samples were prepared for testing.

Leaching test of boron

The leaching test for boron was conducted as per IS: 4873-Part 1 (Anonymous 2008). The samples were conditioned and their initial weights recorded. One set-samples were subjected to boron estimation before leaching; whereas, second set samples were placed in a beaker and pressed with a weight to prevent floating. Distilled water, approximately 9 times the volume of the samples was

poured into beaker followed by constant stirring. After 14 days the samples were removed, conditioned and the residual amount of boron was estimated in samples.

Boron estimation

The boron estimation in samples was done by method as per IS: 2753, Part I (Anonymous, 1991). All chemicals used in the study were of analytical grade and procured from SD Fine Chemicals, India. The samples were crushed into wood flour and 3 g of it was mixed with saturated barium hydroxide in a platinum crucible. The paste was dried on a water-bath, ashed slowly in muffle furnace first at low temperature and then gradually raised the temperature to dull red heat (500-600°C). The procedure was completed in about 90 min. The crucible was then filled with distilled water followed by dilute hydrochloric acid to dissolve the ash and kept covered during this process. The solution of a known volume was made in a graduated flask and used for boron estimation.

The 10 mL solution and 3 mL of sodium hydroxide (N/10) were taken in nickel crucible and kept in water bath at 100^0C for nearly dryness. The residue was ignited for 5 min in Bunsen burner till dull red and then cooled down in air. The residue was dissolved in 10 mL warm distilled water in conical flask. The pH of solution was adjusted by phenolphthalein, HCl, methyl orange and NaOH. To adjust pH the two drops of phenolphthalein and then con. HCl was added drop-wise till color fades. Two drops of methyl orange and a few drops of con. HCl were added till the solution became acidic to the indicator. Then the solution was refluxed in water bath for 15 min under air reflux condenser. The solution was cool down and pH readjusted. Glycerol (equal to one and half times the volume of solution) was added to solution and 0.5 mL phenolphthalein was used as color indicator. The solution was titrated against N/10 NaOH to the phenolphthalein end point. The boron present in water is calculated by the formula: Boron (g) = Volume of N/10 NaOH x 0.00619

Statistical analysis

The data recorded was subjected to statistical analysis to find out the variation between the treatments/factors and the relationship between the observed parameters. Each chemical with its each concentration and treatment method was considered as a single treatment to plywood. The effect of treatments/pressing time on the observed parameters was ascertained through Analysis of variance (ANOVA). In order to determine the variation between means, the least significant difference (LSD) known as the critical difference (CD) was calculated at 95% confidence level. When the difference between set of treatment means was lower than the calculated CD, an insignificant difference was obtained between the treatment and they fall under a bar. While when the difference was higher than the calculated CD a significant difference was observed and the treatments fall under separate bar.

RESULTS AND DISCUSSION

Boron retention after treatment

Mean dry salt retention (DSR) of boron with veneer as well as glue line treatments is presented in Table 1. The samples treated with boric acid alone (C_1) showed mean retention of 16.12-28.68 and 11.32-18.52 kg m^{-3} in veneer and glue line treated samples, respectively, which is sufficient to impart resistance to wood against decay (Caldeira, 2010). Baysal and Yalinkilic (2005) reported that boric acid is low steam volatile and can be vapourized under heat, hence can be diffused thoroughly inside the wood or composite panels, when hot pressed at high temperature. The combination of boric acid and silicic acid at 1:1 (C_2), 2:1 (C_3) and 3:1 (C_4) revealed 6.15-10.77, 9.17-15.38 and 9.97-16.12 kg m^{-3} mean boron retention in veneer treated samples, respectively. Mean DSR was 5.04-8.55, 6.64-11.44 and 7.69-13.11 kg m^{-3} in the samples treated with C_2, C_3 and C_4, respectively, by glue line treatment. Statistical analysis revealed that boron retention was similar in between C_3 and C_4 at yielded only 1-4 kg m^{-3} of retention difference by both treatments. However, substantially low DSR

Table 1: Mean dry salt retention (kg m^{-3}) of boron in samples before and after treatment

Chemicals	Conc. (%)	Mean dry salt retention (kg m^{-3}) of boron			
		Before leaching		After leaching	
		Veneer treatment	Glue line treatment	Veneer treatment	Glue line treatment
Boric acid (C_1)	2	16.12	11.32	9.97	7.75
	3	24.19	14.40	12.92	9.29
	4	28.68	18.52	12.31	11.38
Boric acid & silicic acid (1:1) (C_2)	2	6.15	5.04	4.30	3.81
	3	8.06	7.44	5.54	5.23
	4	10.77	8.55	6.46	5.54
Boric acid & silicic acid (2:1) (C_3)	2	9.17	6.64	7.38	5.23
	3	12.06	8.43	9.23	6.27
	4	15.38	11.44	9.84	8.12
Boric acid & silicic acid (3:1) (C_4)	2	9.97	7.69	7.44	6.27
	3	13.85	9.78	9.97	7.94
	4	16.12	13.11	13.29	9.60
$CD_{0.05}$ =		Before leaching treatments, 1.95;		After leaching treatment, 1.44	

respective concentrations in both treatment ($p \leq 0.05$). Therefore, use of C_3 is sufficient for plywood treatment. Results demonstrated that almost 5 - 10 kg m^{-3} retention difference was observed between veneer and glue line treatment in C_1. The other combination C_2, C_3 and C_4 at all concentration levels was observed in glue line treatment than veneer treatment in all test chemicals and the difference was statistically significant ($p \leq 0.05$), except C_2 at 2 and 3%. The possible reason of high retention veneer treated samples may be because veneers were completely submerged in the chemicals and all surfaces were open to absorb the chemicals from all sides. In glue line treatment the chemicals are added to the adhesive, which was applied to core veneer only. Besides this, high preservative loss during hot pressing is one of the disadvantages of glue line treatment (Gardner *et al.* 2003). Chemical interaction of preservatives with adhesive is another aspect which may affect the preservative retention ability of veneers. It was noticed that boron absorption increased with increase in boron in combination and concentration.

Boron fixation after leaching test

The data on boron fixation in samples after leaching test revealed that C_1 treatment had mean boron fixation of 42.92-61.85 and 61.45-68.46% in veneer and glue line treated samples, respectively. In both treatment methods, boron fixation decreased with increasing boric acid concentration. It means that a threshold amount of boron could be fixed inside the wood structure and non-fixed was easily leached out. The results are in agreement with Waldron *et al.* (2005), Nair (2006) and Tondi *et al.* (2012) who reported that water soluble preservative salts leach from the treated wood according to the physical laws. Generally, the rate of leaching is concentration dependent and follows the law of mass action. After leaching test, boron retention was 7.75-12.92 kg m^{-} in C_1 treated samples which is sufficient to impart efficacy against the biological attack in service conditions (Caldeira, 2010). The present study showed more boron fixation in glue line treatment than veneer treatment, but the available dry salt retention after leaching was more in veneer treatment, depicting that veneer treatment with C_1 is more economic than glue line, even at 2% level.

The combination of boric acid with silicic acid increased boron fixation in plywood in both the treatment methods. The effect was more prominent in C_3 and C_4 treatments. However, C_2 treatment was not so effective in dry salt retention which exhibited 59.98-69.92 and 64.80-75.60% mean boron fixation in veneer and glue line treated samples, respectively. After leaching, only 3.81-6.46 kg m^{-3} mean boron content were in C_2 treatment, which is very low to impart protection to board against biological attack. Therefore, this combination cannot be recommended for plywood treatment. Veneer and glue line treatments by C_3 showed 63.98-80.48 and 70.98-78.77% mean boron fixation, respectively. In C_3 treatment, boron fixation was better in veneer treatment than glue line at 2 and 3%

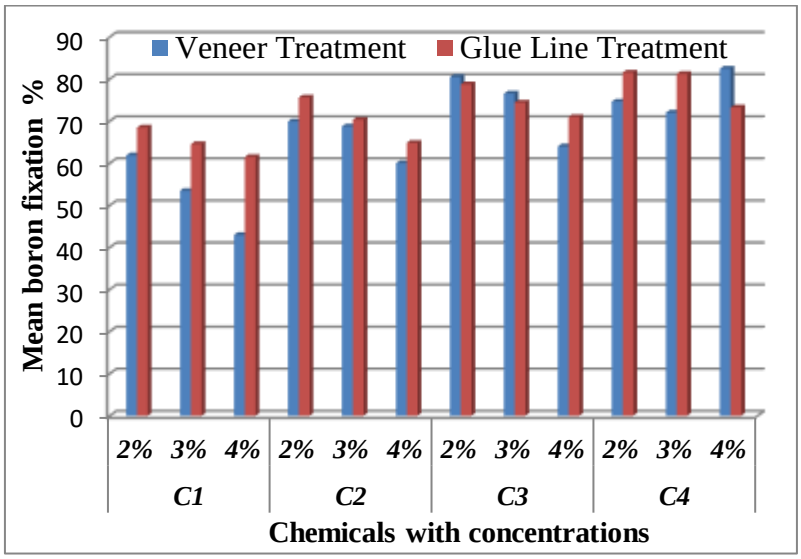

Fig. 1: Mean boron fixation percent in treated samples;
C_1 = boric acid; C_2 = boric acid & silicic acid (1:1); C_3 = boric acid & silicic acid (2:1); and C_4 = boric acid & silicic acid (3:1)

level, whereas at 4% level the trend was opposite. The dry salt retention of boron was higher in veneer treatment than glue line at all tested concentrations (Table 1). It was noted that boron leaching increased with increase in boron concentration in the combination. Contrary to our observations, Kose *et al.* (2011) found more leaching in the samples treated with low concentration of boron with water repellent compound. Lesar *et al.* (2012) reported more boron leaching with increased boron concentration in beech and decreased concentration in spruce. The maximum fixation of boron in C_3 treatment (> 75%) was achieved at 2% concentration. So, 2% concentration of C_3 treatment is highly recommendable for plywood treatment.

Results revealed mean boron fixation of 71.99-82.44 and 73.23-81.53% in veneer and glue line treatment in C_4 treated samples, respectively, whereas the substantial retention of 7.44-13.29 and 6.27-9.60 kg m^{-3} was noticed in veneer and glue line treatments in C_4 treated samples, respectively. In this combination at 2 and 3% concentration boron fixation was more in veneer treatment than glue line treatment, whereas at 4% it was higher in glue line treatment. The probable mechanism for boron fixation by silicic acid has been given by Ueda (1993) wherein it is assumed that atomic structure of the boric acid has a similar structure to silicon and each silicon atom has available three oxygen atoms of tetrahedron, due to which silicon in the crystal of high molecular-weight silicic acid can substitute for aluminum, boron and beryllium. On heating, the boric acid and colloidal silica combination changes into a glassy appearance which blocks the flow paths of wood. Altun *et al.* (2010) also observed that silica gel treatment increased leaching resistance of boron in wood samples. Our results support the theory of fixation of boric acid with silica-based compounds in wood.

Conclusion: Boron compounds reportedly are more effective in terms of preservative efficacy with the only disadvantage of being leachable under wet conditions. The present study revealed that silicic acid in combination with boric acid can reduce boron leaching from plywood and is so suggested for plywood treatment. The mechanism needs to be addressed in future studies.

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REFERENCES

Altun, S., Ozcifci A., Şenel A., Baysal, E. and Toker, H. 2010. Effects of silica gel on leaching resistance and thermal properties of impregnated wood. *Wood Research*, **55**(4): 101-112.

Anonymous. 1974. *Specification for Synthetic Resin/Adhesives for Plywood (Phenolic and Amino-plastic). IS: 848.* Bureau of Indian standards, Bahadur Shah Zafar Marg, New Delhi, India.

Anonymous. 1983. *Specification for the Methods of Test for Plywood. IS: 1734*. Bureau of Indian standards, Bahadur Shah Zafar Marg, New Delhi, India.

Anonymous. 1989. *Plywood for General Purposes-Specification. IS: 303.* Bureau of Indian standards, Bahadur Shah Zafar Marg, New Delhi, India.

Anonymous. 1991. *Methods for Estimation of Preservatives in Treated. Timber and in Treating Solutions. IS: 2753,* Bureau of Indian Standards. Bahadur Shah Zafar Marg, New Delhi, India.

Anonymous. 2008. *Method of Laboratory Testing of Wood Preservatives against Fungi. IS: 4873.* Bureau of Indian Standards. Bahadur Shah Zafar Marg, New Delhi, India.

Anonymous. 2014. *Silicone Resins – Hard, Insulating, Water-Repellent*. Retrieved on 10 Nov., 2014. from *http://www.chemiedidaktik.uniwuppertal.de/disido_cy/en/info/structure/resins.html.*

Anonymous. 2015. *Boring Boron and Adhesives*. Retrieved on 20 August 2015 from *http://www.adhesivesmag,com/articles/93226-boring-boron-and-adhesives.*

Baysal, E. and Yalinkilic, M.K. 2005. A new boron impregnation technique of wood by vapor boron of boric acid to reduce leaching boron from wood. *Wood Science Technology*, **39**: 187-198.

Caldeira, F. 2010. Boron in wood preservation: A review in its physicochemical aspects. *Silva Lusitana*, **18**(2):179-196.

Furuno, T. and Imamura, Y. 1998. Combinations of wood and silicate. Part 6: Biological resistance of wood-mineral composites using water glass-boron compound system. *Wood Science and Technology*, **32**: 161-170.

Gardner, D.J., Tascioglu, C. and Wålinder, M.E. 2003. Wood composite protection. pp. 399-419. **In**: *Wood Deterioration and Preservation: Advances in Our Changing World* (eds. B. Nicholas and J.P. Schultz). ACS Symposium Series 845, American Chemical Society, Washington, USA.

Humphrey, D.G., Duggan, P.J., Tyndall, E.M., Carr, J.M. and Cookson, L.J. 2002. New boron-based biocides for the protection of wood. pp. 1-11. **In**: *The Conference of the International Research Group on Wood Preservation. IRG/WP Document No. 02-30283,* 12-17 May 2002, Cardiff, Wales, UK [*https://www.irg-wp.com/irgdocs/details.php?77808c5f-88c1-4985-a021-51d286e8bedf*].

Kartal, S.N., Yashimura, T. and Imamura, Y. 2009. Modification of wood with Si compounds to limit boron leaching from treated wood and to increase termite and decay resistance. *International Biodeterioration and Biodegradation*, **63**(2): 187-190.

Kirkpatrick, J.W. and Barnes, H.M. 2006. Biocide treatments for wood composites – A review. pp. 1-21. **In**: *The Conference of the International Research Group on Wood Preservation. IRG/WP Document No. 06-40323*, 18-22 May 2006, Tromso, Norway. [*https://www.irg-wp.com/irgdocs/details.php?2ee445e3-1ba5-4de8-952c-8d3bdc2b1193*].

Kose, C., Terzi, E., Kartal, S.N., Erilkun, B. and Imamura, Y. 2011. Preliminary evaluation of boron release and biological resistance of wood treated with disodium octoborate tetrahydrate (DOT) and a water-repellent compound. *African Journal of Biotechnology*, **10**(10): 1833-1839**.**

Lesar, B., Budija, F., Kralj, P., Patric, M. and Humar, M. 2012. Leaching of boron from wood impregnated with preservative solutions based on boric acid and liquefied wood. *Holz-als Roh und werkstoff*, **70**(1): 365-367.

Lin, L. and Furuno, T. 2001. Biological resistance of wood-metaborate composites using the borax solution system. pp. 1-24. **In**: *The Conference of the International Research Group on Wood Preservation. IRG/WP Document No. 01-30259,* 20-25 May 2001, Nara, Japan. [*https://www.irg-wp.com/irgdocs/details.php?c0897f74-ee25-41aa-b88d-e3ab57db6054*].

Loth, H., Schmidt, O., Schmidt, J., Beck, H. and Sumser, M. *2008. Silane-Crosslinking Adhesive, Sealant or Coating with a Silicic Acid Filler and Use Thereof. United States Patent Application 20080245476*. Patent publication date 9.10.2008. [*https://patentimages.storage.googleapis. com/49/bc/9a/005da76ed9c197/US20080245476A1.pdf*].

Luo, J., Chen, H. and Morrell, J.J. 2005. Effect of borate on uptake and efficacy of an anti-sap stain treatment. pp. 1-11. **In**: *The Conference of the International Research Group on Wood Preservation. IRG/WP Document No. 05-30380*, 24-28 April 2005, Bangalore, India. [*https://www.irg-wp.com/irgdocs/details.php?19cb4e52-f97c-424f-8139-8205124f6825*].

Mahltig, B., Swaboda, C., Roessler, A. and Böttcher, H. 2008. Functionalising wood by nanosol application. *Journal of Material Chemistry*, **18**: 3180-3192.

Mazela, B., Bartkowiak, M. and Ratajczak, I. 2007. Animal protein impact on fungicidal properties of treatment formulations. *Wood Research*, **52**(1): 13-22.

Nair, S. S. 2006. *Effectiveness of Copper-Boron Diffusion Treatments for Wood*. M. Sc. thesis. College of Graduate Studies University of Idaho, Moscow, Russia.

Pallaske, M. 2004. Chemical wood protection: Improvement of biocides in use. pp. 1-11. **In**: *COST Action E22 - Environmental Optimisation of Wood Protection*, 22-23 March 2004, Lisboa, Portugal.'

Schoeman, M.W. and Lloyd, J.D. 1998. International standardization: A hypothetical case study with stand-alone borate wood preservatives. **In**: *The Conference of the International Research Group on Wood Preservation.* IRG/WP Document No. 98-20381407, IRG Secretariat, Stockholm Sweden.

Thevenon, M.F. and Pizzi, A. 2003. Poly-borate ions influence the durability of wood treated with non-toxic protein borate preservatives. *Holz als Roh-und Werkstoff*, **61**: 457-464.

Tondi, G., Weiland, S., Lemenager, N., Petutschnigg, A., Pizzi, A. and Thevenon, M.F. 2012. Efficacy of tannins in fixing boron in wood: Fungal and termite resistance. *Bioresource*, **7**(1): 1238-1252.

Ueda, S. 1993. *Jikken Kagaku Kouza (Text of Experimental Chemistry).* (4th edn.), Maruzen Co. Ltd., Tokyo, Japan.

Waldron, L., Cooper, P. A. and Ung, T.Y. 2005. Prediction of long-term leaching potential of preservative-treated wood by diffusion modelling. *Holzforschung*, **59**: 581-588

Yamaguchi, H. 2001. Silicic acid-boric acid complexes as wood preservatives. **In**: *The Conference of the International Research Group on Wood Preservation. IRG/WP Document No. 01-30273*, 20-258 May 2001, Nara, Japan [*https://www.irg-wp.com/irgdocs/details.php?ac7e7f6b-5e20-4028-bd12-d8fa95fb5bfd*].

Yamaguchi, H. 2002. Low molecular weight silicic acid- inorganic compound complex as wood preservative. *Wood Science and Technology*, **36**(5): 399-417.