STUDY ON SILICIC-BORIC ACID COMBINATION AGAINST WOOD DECAYING FUNGI IN PLYWOOD

Shweta BHATT
Research Scholar - Wood Preservation Discipline, Forest Products Division, Forest Research Institute
Address: Dehradun 248006, Uttarakhand, India.
E-mail: bhattshwetafri@gmail.com

Sadhna TRIPATHI
Dr. Scientist-G - Wood Preservation Discipline, Forest Products Division, Forest Research Institute,
Address: Dehradun 248006, Uttarakhand, India.
E-mail: tripathis@icfre.org

Dwarika Prasad KHALI
Mr. Scientist-F - Composite Wood Discipline, Forest Products Division, Forest Research Institute,
Address: Dehradun 248006, Uttarakhand, India.
E-mail: khalidp@icfre.org

Abstract:
Plywood as engineered wood product is used for a number of structural and non structural applications for both interior and exterior uses. The exterior exposure creates the conditions for fungi and insects attack, which lead to the early failure of wood products. Preservative treatment is necessary for wood species to improve its resistance against biological agencies. In the present study boric acid, silicic acid and their different combinations i.e. 1:1, 2:1 and 3:1 at 2, 3 and 4% concentrations were tested against wood decaying fungi (Trametes versicolor and Oligoporus placentus) in Poplar plywood through soil block test as per IS:4873 (2008). Boric acid has provided the best protection to plywood specimens against the tested fungi. The most effective combination which improved the plywood resistance to fungi was boric acid and silicic acid in 3:1 ratio. While silicic acid was found to be least effective. The efficacy of tested chemicals has improved by using higher concentrations of compounds.

Key words: boric acid, plywood, silicic acid, wood decaying fungi.

INTRODUCTION
Wood based industries in India are growing at the rate of 4.3 per cent per annum and demand for industrial wood is expected to reach 55 million m³ by 2020 (The Hindu 2012). In India wood based industries covers three important wood based panels i.e. plywood, fiberboard and particleboard. Plywood and laminates are likely to play more prominent role in future due to fast growth of construction and furniture sector. Plywood is mostly prepared from less important and non-durable wood species. It makes plywood poorly resistant against moulds, wood destroying fungi and insects in wet conditions (Lahiry 2005, Barnes and Amburgey 1993). Decay in plywood is mostly caused by fungal attack (Reinprecht 2007). The other reason of non-durable character of plywood is use of sapwood in major portion of veneer, which is non-durable in nature (Khali et al. 2006). The life span of plywood can be enhanced by using more durable wood species or by treatment of wood with effective and ecologically safe preservatives (Brischke and Rapp 2008). However, preservative treatment of plywood is not easy due to various factors such as compatibility with manufacturing processes, adhesive and additive systems, stability and consistency of the preservatives (Ross et al. 2003).

The ideal wood preservative should have characteristics, such as high toxicity towards wood decaying agents, good fixation in treated wood, non-corrosive to metals and safe in handling (Cartwright and Findlay 1958). In recent time, environmental concerns and the energy crisis especially with regard to oil-based preservative systems had encouraged the changes in treatment technology and preservative systems worldwide. The growing public concern on environment toxicity of many wood preservatives has rendered more importance to boron based preservatives. Boric acid (H₃BO₃) is natural occurring compound containing elements boron, oxygen and hydrogen. They belong to traditional preservatives for wood protection against wood destroying fungi and insects for interior exposures (Kirkpatrick and Barnes 2006, Lin and Furuno 2001). It has flame retardant effect, low volatility and low mammalian toxicity (Hafizoglu et al. 1994). It was found its good efficacy on poplar

*Corresponding author
wood against white rot (*Trametes versicolor*) (Hashemi et al. 2010). In another study boric acid, disodium tetraborate, tributyltin naphtenate (TBTN), 2-thiocyanomethylthio benzothiazole (TCMTB) and some other commercial fungicides had been tested for antifungal protection of plywood. Tests showed that fungicides added to composites in higher amounts provided successful antifungal activity (Reinprecht 2010).

Boron compounds are effective wood preservative, but the only disadvantage with boron is its leachable nature on wet exposure (Lloyd et al. 2001). Yamaguchi (2002) reported silicic acid monomer aqueous solution (SAMS) and colloidal silicic acid solution (CSAS) with combination of boric acid to reduce leaching of boron in solid wood (*Cryptomeria japonica D. Don*). The probable mechanism for fixation of boron by silicic acid was given by Ueda (1993). The combination also gave good protection against decay caused by the brown rot (*Fomitopsis palustris*) (Yamaguchi 2001). Scott (1995) reported that silicic acid is unstable in nature and rapidly condense with itself with the elimination of water forming dimers, trimers and high molecular weight polymers. It has surfactant and desiccant properties leading to wood drying and thereby protecting it from fungal attack (Willis 1954). George (2009) studied polysilicic acid formation in wood cell lumens and found efficacious against brown rot (*Gloeophyllum trabeum*) and white rot (*Trametes versicolor*). Polysilicic acid in combination with boric acid had been evaluated for fungal decay protection and it was observed that it reduced the mass loss of samples as compared to untreated (Furuno et al. 1992). In a study by Kartal et al. (2009) combinations of boron with tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) were subjected to decay resistance tests using *Fomitopsis palustris* and *Trametes versicolor* and the tests revealed that resistance of wood increased by using the combination of silane and boron compounds, when compared to untreated and only boron treated specimens.

It appears that silicon based compounds has good potential as a preservative and also can solve the problem of boron leaching. Previous research on the combination of silicic acid and boric acid has been done by Yamaguchi (2002, 2003, 2005), but its testing and performance is not evaluated in plywood so far. In the present study, the combination of boric acid with silicic acid in different ratio and concentration was studied against white rot (*Trametes versicolor*) and brown rot (*Oligoporus placentus*) on plywood. The main objective of the study was to analyse the influence of silicic acid to plywood resistance to fungi and find out the most effective combination with boric acid as eco-friendly preservative.

**MATERIAL AND METHODS**

**Phenol formaldehyde adhesive**

The resol type phenol formaldehyde adhesive (PF) was prepared according to IS: 848 (1974) in laboratory.

**Plywood preparation**

Poplar (*Populus deltoides* Bartr Ex. Marsh) veneers were used to prepare plywood panels of 3 layers with mean thickness of 0.45cm as laid in IS: 303 (1989). Poplar logs of average length of 125 cm and 150cm diameter were procured and peeled to veneers of 0.16cm thickness in the peeling lathe. The veneers were further clipped into sizes as required for plywood manufacturing. The veneers were treated with boric acid (C1), silicic acid (C2) and boric and silicic acid in different proportions i.e. (1:1) (C3), (2:1) (C4) and (3:1) (C5) in three concentrations i.e. 2, 3 and 4%. Veneers were dipped in 2, 3 and 4% of prepared solution for 60, 30 and 5 minutes respectively. The treated veneers were then dried to 8±2% moisture content prior to gluing. PF adhesive was applied at both side of core veneer at the rate of 110gm-2 and hot pressed for 10 minutes at 150°C temperature and 14.06Kg cm-2 pressure. Then plywood were removed from hot press and conditioned for 24 hours.

**Retention analysis:** The retention levels of chemicals is shown in Table 2 and were calculated by the following formula:

\[
\text{Retention of chemical (kg/ m}^3) = \frac{\text{G} \times 10^3}{\text{C} \times \text{V}}
\]

Where: G = mass of the treating solution absorbed by block (g); C = Concentration of chemical used (%); V = Volume of veneer (cm³).

**Soil block bioassay:** The test was conducted as per IS: 4873 (2008) in laboratory to test decay resistance of chemical combinations against fungi by means of soil as a medium to support fungal growth in treated samples.
Preparation of test specimens: The test blocks were prepared from the treated and untreated plywood of Poplar (*Populus deltoides* Bartr Ex. Marsh). The feeder blocks were prepared from *Bombax ceiba*. The test specimens of size 1.9x1.9x0.45 cm³ and the feeder blocks of size 0.4x1.9x3.5 cm³ were prepared along the length of grain (IS: 4873, 2008). The test specimens were marked and their initial weights were recorded. The test specimens were subjected to 100-105°C in an oven and weight was recorded till a constant weight obtained (*W₁*). Six replicates were used for each treatment as well as control.

Preparation of soil culture bottles: Sieved, air-dried garden soil amounting to 125g with pH between 5-7 was filled (compacted by tapping) in screw capped bottles. Distilled water was added to the bottles so as to obtain near 130 percent of water holding of soil. Two feeder blocks of size 0.4x1.9x3.5 cm³ were placed directly on the surface of the soil. The prepared bottles with caps loosened were sterilized in an autoclave at a pressure of 1kg cm⁻² for 30 minutes (IS: 4873, 2008).

Selection of test fungi: The test fungi selected for the present study were (IS: 4873, ASTM 1999).
1) *Oligoporous placente* Murr;
2) *Trametes versicolor* Linn.

Preparation of test culture: Sterilized culture bottles were thoroughly cooled. The fungus inoculum from freshly grown culture approximately 8-10mm in diameter was placed on the edge of the feeder blocks. The inoculated bottles were incubated in B.O.D. (Biochemical oxygen demand) with slightly loosened lids at 25±2°C and 70±4% relative humidity for approximately 21 days till the feeder blocks were completely covered by the test fungi (IS: 4873, 2008).

Introduction and incubation of the test blocks in culture bottles: Two specimens were placed on feeder blocks in contact with mycelium in each culture bottle. The bottles containing the test blocks were incubated for a period of 14 weeks in the incubator maintained at 25±2°C and a relative humidity of about 70±4% (IS: 4873, 2008).

At the end of the incubation period the specimens were removed from the culture bottles and cleaned off. The specimens were dried in the oven and weighed till the constant weight (*W₂*) was obtained.

Calculation of weight loss: Weight loss (%) was calculated from the conditioned weight of the blocks before and after testing.

\[ \text{Weight loss} \% = \frac{(W₁ - W₂) \times 100}{W₁} \]

where: *W₁* = Conditioned weight of the blocks before test (g);

*W₂* = Conditioned weight of the blocks after test (g).

Statistical analysis: Weight loss of treated and untreated (control) plywood specimens was statistical analyzed using the analysis of variance (ANOVA) test calculated by SPSS 16.0 software at 5% significance level. CD (Critical difference) values were calculated for treatment, concentration and fungus types to find whether the effect of different combinations on weight loss is significant or not (Table 1).

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>MSS</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>4</td>
<td>674.04</td>
<td>.000</td>
</tr>
<tr>
<td>Concentration</td>
<td>2</td>
<td>96.40</td>
<td>.000</td>
</tr>
<tr>
<td>Fungus</td>
<td>1</td>
<td>1149.35</td>
<td>.000</td>
</tr>
<tr>
<td>Chemical * Concentration</td>
<td>8</td>
<td>7.67</td>
<td>.074</td>
</tr>
<tr>
<td>Chemical * Fungus</td>
<td>4</td>
<td>6.33</td>
<td>.200</td>
</tr>
<tr>
<td>Concentration * Fungus</td>
<td>2</td>
<td>22.22</td>
<td>.006</td>
</tr>
<tr>
<td>Chemical * Fungus * Fungus</td>
<td>8</td>
<td>4.88</td>
<td>.321</td>
</tr>
<tr>
<td>Error</td>
<td>160</td>
<td>4.17</td>
<td></td>
</tr>
</tbody>
</table>

df= degree of freedom, MSS= Mean sum of square
RESULTS AND DISCUSSION

Table 2 exhibits the average retention rates and the performance of plywood specimens against *Trametes versicolor* and *Oligoporus placentus* in terms of mean percent weight loss of specimens. The mean weight loss of 34.03 and 25.46% was observed on untreated control sets due to *Trametes versicolor* and *Oligoporus placentus* respectively. The mean retention of 8.25, 11.08 and 13.76kg/m³ was recorded in specimens treated with aqueous solution of boric acid (C₁) at 2, 3 and 4% concentration respectively. Specimens treated with C₁ at 2% showed 12.82% and 8.17% mean weight loss due to *Trametes versicolor* and *Oligoporus placentus* respectively. It was noted that C₁ treatment provided sufficient protection to plywood against test fungi as compared to untreated specimens, even at 2% concentration. The guidelines of IS: 303 (1989) also recommend minimum 2% of boric acid for treatment of general purpose plywood. Freeman *et al.* (2009) reported that minimum retention of 3.2kg/m³ of boric acid equivalent (BAE) are sufficient to protect wood from both decay fungi and insects. It was observed that weight loss was further decreased by increasing concentration of C₁. It confirms the proper anti-fungal characteristics of boric acid against wood decaying fungi (Yalinkilic *et al.* 1999). Specimens treated at 3 and 4% concentration of C₁ revealed 9.49 and 7.13% mean weight loss caused by *Trametes versicolor* respectively and 7.37 and 5.17% mean weight loss caused by *Oligoporus placentus* respectively. The results are supported by Kartal *et al.* (2007), where plywood treated with 3% of boric acid exhibited less than 5% average mass loss against *Fomitopsis palustris* and *Trametes versicolor*.

Silicic acid (C₂) exhibited remarkably low retention almost half than C₁ (Table 2). The probable reason for that may be the formation of impervious layer of silicic acid powder on the sample surface, which was visually observed during experiment. Samples treated with C₂ revealed 43.57-49.17% and 41.51-58.35% higher weight loss against *Trametes versicolor* and *Oligoporus placentus* respectively as compared to C₁. However mean weight loss was reduced as compared to untreated samples (Table 2). It is due to water repellents and hydrophobic behaviour of silicones, which may have caused physical blocking of water flow paths in specimens (Hager 1995, Lukowsky et al. 1997). These characters of silicon based compounds may restrict the favorable conditions for fungal growth and provide protection against test fungi.

The good efficacy was observed only for C₃ and C₄ at higher concentrations (3-4%). The average retention achieved for C₃ and C₄ was found comparable and were lower than C₁ about 17.51-33.93%. The adverse effect on retention of chemicals in veneers was observed after adding silicic acid in boric acid. The reason may be again the formation of layer of silicic acid powder on veneers during treatment, which reduced the opening space in wood and decreased the chemical intake. The protection against *Trametes versicolor* and *Oligoporus placentus* was comparable at 2% concentration of C₃. The combination tested at 1:1 ratio (C₃) at 2, 3 and 4% concentration showed mean weight loss of 19.86, 15.65 and 13.27% by *Trametes versicolor* and 19.35, 15.05 and 10.05% by *Oligoporus placentus* respectively. Similar mass loss was achieved at 2 and 3% concentration for C₃ against test fungi (Table 2). The reason for the same is difficult to narrate. It was observed that the protection achieved at C₃ treatment was more than C₂, but less than C₁, which probably may be correlates with amount of boric acid in combination. It is reported that sufficient mobility of boron ion in veneers may have protecting effect. Baysal and Yalinkılıc (2005) reported that boric acid is low steam volatile and can be vaporized under heat, hence can be diffused thoroughly inside the wood or composite panels, when hot pressed at high temperature.

There was slight increase of retention in C₅ as compared to C₄ and C₃, which is reflected weight loss (Table 2). Better results concerning weight losses was obtained for C₅ compared to C₃ and C₄ but still showed lower efficacy than C₁. Treatment with C₁ revealed 15.28-22.06% higher mean weight loss due to *Trametes versicolor* and 25.38-33.43% due to *Oligoporus placentus* compared to C₁. Treatment with C₅ had resulted maximum protection at 4% concentration and it was found comparative to C₁ at 3% concentration (Table 2). It was found that boric acid exhibited best protection against both fungi followed by the combination in 3:1, 2:1 and 1:1 ratio. The least effective treatment against wood decaying fungi was found C₂ (silicic acid) for all concentrations. The results showed that the potential of chemical combinations against test fungi depends on the amount of boron used in combinations.

The findings were supported by Freeman *et al.* (2009) and Jonge (1987). It was reported that the efficacy of boron based salts depend on the quantity of boron applied to wood irrespective of salts. The higher proportion of boron or borate ion determines the efficacy of boron based combinations against decaying fungi. The results are in conformity with the findings reported by Yamaguchi (2002, 2003 and 2005) where, silicic acid in combination with boric acid was found effective against wood decay fungi and termites. The great efficiency could be obtained with higher boric acid concentrations especially in case of uses in severe conditions. The effect of treatment and concentration on weight...
loss was found significantly different (p<0.05) (Table 1). It was noted that *Trametes versicolor* has caused more decay in specimens as compared to *Oligoporus placens*. The difference was found statistically significant (p<0.05). These findings are similar with those found in Gusse et al. (2006). The possible reason for this is the similar molecular structure of phenol formaldehyde adhesive with lignin. He observed that reported that white rot attacks lignin as well as cellulose and the molecular structure of lignin is similar to phenol formaldehyde adhesive, due to which white rot may decompose the phenolic adhesive same as lignin. It is further reported that biodegradability of phenolic formaldehyde adhesive was only caused by white rot (*Phanerochaete chrysosporium*), whereas, brown rot (*Oligoporus placens*) had no affect on it.

Table 2

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentrations of chemicals</th>
<th>Retention (Kg/m²)</th>
<th>Mean weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td><em>Trametes versicolor</em></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>34.03</td>
</tr>
<tr>
<td>Boric acid (C₁)</td>
<td>2</td>
<td>8.25</td>
<td>12.82</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11.08</td>
<td>9.49</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>13.76</td>
<td>7.13</td>
</tr>
<tr>
<td>Silicic acid (C₂)</td>
<td>2</td>
<td>3.77</td>
<td>23.75</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.57</td>
<td>21.17</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.40</td>
<td>17.48</td>
</tr>
<tr>
<td>Boric acid and Silic acid (1:1) (C₃)</td>
<td>2</td>
<td>6.20</td>
<td>19.86</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.32</td>
<td>15.65</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10.83</td>
<td>13.27</td>
</tr>
<tr>
<td>Boric acid and Silic acid (2:1) (C₄)</td>
<td>2</td>
<td>6.47</td>
<td>16.45</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.43</td>
<td>14.73</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>11.35</td>
<td>12.04</td>
</tr>
<tr>
<td>Boric acid and Silic acid (3:1) (C₅)</td>
<td>2</td>
<td>6.50</td>
<td>15.39</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.65</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12.66</td>
<td>9.76</td>
</tr>
</tbody>
</table>

Mean weight loss (Control) - 29.75%, (C₁) - 8.36%, (C₂) - 20.80%, (C₃) - 18.49%, (C₄) - 15.61% and (C₅) - 13.09%
Mean weight loss (2%) - 17.12%, (3%) - 13.99% and (4%) -11.43%
Mean weight loss (*Trametes versicolor*) - 16.90% and (*Oligoporus placens*) - 13.84%
CD (0.05) (Treatment) - 0.94, (Concentration) - 0.73, (Fungus) - 0.59

CONCLUSION

Results revealed that the combination of boric acid and silicic acid increase the plywood resistance to test fungi i.e. *Trametes versicolor* and *Oligoporus placens*. Silicic acid itself had no antifungal characteristics; however in combination with boric acid it had provided substantially protection to plywood. A concentration dependent effect was observed, as efficacy of combination increased with increasing concentration of chemicals and amount of boric acid. It is shown that the boric and silicic acid combinations can provide alternate to conventional wood preservatives, which are mammalian toxic and are restricted in preservative application on wood. A better understanding of plywood treatment will help the scientific community to design more effective systems to increase resistance to biodegradability in outdoor exposure of wood based composites.

ACKNOWLEDGEMENT

The authors are thankful to Director, Forest Research Institute, Dehradun, India for providing facilities. The authors are also grateful to the staff of the Wood Preservation Discipline and Composite Wood Discipline, F. R. I. Dehradun, for providing necessary help during the experimental work.

REFERENCES


