

EFFECT OF BORON ADDITION TO ADHESIVE AND/OR SURFACE COATING ON FIRE-RETARDANT PROPERTIES OF PARTICLEBOARD

Mustafa Kemal Yalinkiliç

Associate Professor

Yuji Imamura

Associate Professor

Munezoh Takahashi

Professor

Wood Research Institute
Kyoto University
Uji Kyoto 611, Japan

and

Zafer Demirci

Research Associate
Faculty of Forestry
Black Sea Technical University
Trabzon 61080, Turkey

(Received August 1997)

ABSTRACT

Boron added to urea formaldehyde (UF) resin during manufacture of board from waste tea leaves was combined with a fire-retardant coating system containing boron to further reduce combustibility. Boric acid (BA) and borax (BX) were used as boron compounds separately or in a mixture of 5:1 (BA:BX, w/w) in aqueous solutions of UF resin. A BA+BX mixture was also added to a 40% aqueous solution of trimethylolmelamine (TMM) (as a binding agent) and applied to the board surface. Fire-retardant properties were determined according to the Japanese Industrial Standard JIS A 1322.

Thickness swelling and water absorption levels were not changed remarkably by boron addition to UF resin, while static bending and internal bond strengths were reduced to some extent. However, BX addition suppressed the adverse effect of BA on board strength, probably by buffering its acidic pH to almost neutral levels, while BA reduced the glowing or smoldering effect of BX. Panels with or without added boron showed no ignition after the flame source was cut off after 13 min. Surface coating with the boron-added TMM improved fire retardance. To limit the reduction of strength properties due to boron addition to the resin, fire-retardant surface coating can be applied to impart a required level of fire protection.

Keywords: Boron, bio-based composite, fire retardance, surface coating, particleboard, UF, waste tea leaves.

INTRODUCTION

Carbon-based, cellulosic materials, such as wood- and bio-based composites, will combust, pyrolyze, or otherwise burn when subjected to either radiant energy (as from a fire a short distance away) or sufficient direct heat

(as from a flame in direct contact). The designer seeking to enhance the fire resistance of a structure or assembly built with either sawn wood or bio-based engineered composite products can employ several techniques, including coating members with approved fire-proofing materials, or using fire-retardant-

treated sawn wood and engineered bio-based material products (Slifka 1997).

The borate chemicals offer substantial advantages for wood protection, providing fire resistance as well as efficacy against both fungi and insects, low cost, ease of handling and treatment. There is growing interest in their low mammalian toxicity and environmental acceptability (Laks et al. 1994). Adding boron compounds to the adhesives during board production seems one practical treatment. However, interference by the added chemicals in bond formation, which results in poor strength properties, limits this kind of application. Instead, raw materials can be immersed in a treatment solution, chemicals can be sprayed onto particles, and/or the end product can be surface coated. In the first two cases, chemical interference in the bonding is still likely to occur, while surface coating of boards with a fire retardant is not expected to impart long-term protection (Laks and Palardy 1990; White and Sweet 1992). On the other hand, borate loading sufficient to prevent damage by fungi and insects was claimed to improve fire resistance, but does not impart fire retardancy (Barnes and Amburgey 1989). Therefore, a combination of both boron addition to the adhesive and surface coating of the board might improve combustion resistance and some other important board properties. Compatibility of adhesive with boron is also important. The water-soluble borates have a strong negative effect on the bonding performance of phenol formaldehyde (PF) resins, but, in contrast, there was little or no effect with the urea formaldehyde (UF) (Laks et al. 1988; Laks and Manning 1994). Moreover, the UF-boron combination was promising in terms of flame retardancy (Kozlowski et al. 1992).

Agro-based fibers are of growing importance as a potential resource for composite products of the future. High-performance composite materials with uniform densities, durability in adverse environments, and high strength can be produced by using these fiber sources (Rowell et al. 1993; Rowell 1996). Wood is currently the major raw material

source in the board industry, but non-wood lignocellulosic sources can work just as well. Residual tea leaves of tea factories provide an abundant fiber source in tea-growing countries (Kacar 1991; Örs and Kalaycioglu 1991; Memmed et al. 1992; Kalay et al. 1993). Particle-board manufactured from the industrial wastes of tea leaves (WTLB) has recently shown high biological resistance, possibly due to the high phenolic extractive content of tea leaves (Yalinkiliç et al. 1997a; Kacar 1991). Previous studies on the matter have been conducted by Su et al. (1997a, b) and Yalinkiliç et al. (1997b).

The objective of this study was to determine the effects of boron, either added to the adhesive or as a surface treatment, on fire retardance and other properties of composite board made from waste tea leaves.

MATERIALS AND METHODS

Board manufacture and boron treatment

Waste leaves of *Camelia sinensis* L. were obtained from the biggest public sector tea-producing plant of Turkey (CAYKUR). Urea formaldehyde adhesive containing 55% solid was used with the ratio of 10% (w/w), based on the oven-dry weight of the particles. In the first of three series of treatments, boron was added to the UF as boric acid (BA) and borax (BX) at final concentrations of 0.25, 1.00, and 4.70% (w/v) and a mixture of 5:1 (BA:BX, w/w) with the same concentration levels, representing low, moderate, and high loading of the chemicals as generally required for fungal, insecticidal, and fire resistance (Yalinkiliç et al. 1996; Drysdale 1994). Ammonium chloride and paraffin wax were also added to the glue at 1% from the 33% and 40% concentrations of original solutions, respectively. Control boards were manufactured at three density levels, 0.55, 0.65, and 0.75 g/cm³, while boron added boards were of medium density (0.65 g/cm³). Boards made with the boron addition to UF resin were labeled "boron-added" boards. The thickness of all boards was adjusted to 8 mm at the press. Pressing was ap-

TABLE 1. Codes of the treatment groups at experimental design.

| Boron compound added to UF resin | Final concentration in the resin solution % | Board density g/cm ³ | Surface coating type | | |
|----------------------------------|---|---------------------------------|----------------------|-------------|--------------------|
| | | | Non-coated | TMM-coated | TMM + boron-coated |
| Untreated | — | 0.55 | 1-1/2-1/3-1 | 1-2/2-2/3-2 | 1-3/2-3/3-3 |
| | — | 0.65 | 4-1/5-1/6-1 | 4-2/5-2/6-2 | 4-3/5-3/6-3 |
| | — | 0.75 | 7-1/8-1/9-1 | 7-2/8-2/9-2 | 7-3/8-3/9-3 |
| Boric acid (BA) | 0.25 | 0.65 | A-1 | A-2 | A-3 |
| Borax (BX) | 0.25 | 0.65 | B-1 | B-2 | B-3 |
| BA + BX | 0.25 | 0.65 | C-1 | C-2 | C-3 |
| BA | 1.00 | 0.65 | D-1 | D-2 | D-3 |
| BX | 1.00 | 0.65 | E-1 | E-2 | E-3 |
| BA + BX | 1.00 | 0.65 | F-1 | F-2 | F-3 |
| BA | 4.70 | 0.65 | G-1 | G-2 | G-3 |
| BX | 4.70 | 0.65 | H-1 | H-2 | H-3 |
| BA + BX | 4.70 | 0.65 | I-1 | I-2 | I-3 |

Note: Each code represents 4 boards manufactured with a size of 565 × 565 mm and 8-mm thickness; TMM: trimethylolmelamine.

plied by 20–22 kJ/cm² at 150 °C for 5 min. Experimental design is summarized in Table 1.

In the second series of treatments, trimethylolmelamine (TMM) was applied to the untreated and boron-added boards' surfaces by brushing. Accordingly, an amount corresponding to 50 g/m² 40% aqueous TMM solution was brushed onto the boards' surface; and after one day's air drying at ambient temperature, curing was done at 120°C overnight.

In the third series of treatments, BA+BX mixture (5:1, w/w) was added to TMM solution at the 4.70% concentration level (w/v). The amount of the applied surface coating solution was adjusted by continuous weighing of the specimens during brushing. Higher density boards needed an extra brushing for the same amount of coating.

Testing of fire retardancy

A number of WTLB panels were tested according to the Japanese Industrial Standard JIS A 1322 (1982). 210-mm-long and 70-mm-wide board panels 8 mm thick were clamped with steel holders and exposed to the heating flame at an angle of 45 degrees (Fig. 1). Liquefied petroleum gas was used as the heat source. The heating flame was adjusted to a height of 65 mm, and was applied for 13 min, based on preliminary tests in which the flame penetrated the other surface of the control pan-

els. The times for the panels to be charred and ignited were recorded. The post-flaming time (i.e., the duration of continued burning after the removal of flame source) was recorded. Flame penetration through the board, weight loss due to combustion, and char length were determined. Char length was calculated as the mean value of measurements of the exposed and unexposed surface charring dimensions by width and length of each specimen. Char was considered as decomposed parts of test boards after combustion, in this study, rather than superficial charred area, since almost all boron-added boards showed this kind of early charring.

Exposed surfaces of some representative panels were photographed after combustion to illustrate their general appearance.

Thickness swelling (TS), water absorption (WA), and mechanical tests

To reveal the effect of boron addition to UF resin on TS and WA levels of WTLB, boron-added and non-added boards were subjected to relevant tests. All the boards were conditioned at 18–22°C and 60–70 RH for 6 weeks. The TS and WA of boards were determined according to the Japanese Industrial Standard JIS A 5908 (1994) for 2 and 24 h. Specimen size was 50 × 50 mm with the given thickness. Twelve replications were made for each



FIG. 1. Testing of fire retardance according to JIS A 1322.

board type for TS and WA determinations. Specimens' edges were sealed with an epoxide resin prior to these tests. British Standard BS 5669 (1979) was followed for the static bending and internal bond resistance (SB and IB) tests by using 300-mm-long and 50-mm-wide and, 50- × 50-mm sized specimens, respectively, with the given thickness. Six replications were made for each board type for SB and IB determinations.

RESULTS AND DISCUSSION

Fire retardancy

Post-flaming and flame penetration.—All the tested WTLB panels interestingly did not show post-flaming regardless of boron treatment. This was probably due to urea in the UF adhesive or the inherent combustion behavior of the waste tea leaves owing to high tannin content. Vegetable tannin is used as corrosion and a heat-resistant coating material for metallic surfaces, especially aluminum sheets, in combination with other supplemental chemicals (Reghi 1982; Millet 1985). Interestingly, tea leaves contain almost 10 times as much Al

as higher plants (Kacar 1991), so that possible tannin-Al interaction may also be of importance in the fire-retardant properties of WTLB. Table 2 includes observations of flame penetration through the board, from the exposed to the unexposed surface, at the end of 13-min flaming time.

Flame penetrated the unexposed surface of almost all the untreated boards at three density levels and boron-added boards at the fungal and insecticidal loading concentrations unless coated with the surface fire retardants. Boron-added boards showed great resistance to flame penetration after TMM coating, whereas untreated boards at the same density had no resistance. The TMM delayed the ignition time almost twofold, and char length and WL decreased remarkably with BA (Su et al. 1997a and b; Yalinkiliç et al. 1997b). Relatively late penetration of flame was observed for the untreated boards of 0.75 g/cm³ density, although flame penetrated through all the untreated panels after 13-min exposure. Flame penetration on coating with the TMM-boron mixture and, to a lesser degree with TMM of boards of 0.65

TABLE 2. *Flame penetration of each treatment group after flaming.*

| Treatment codes | Chemical in the UF solution | Board density g/cm ³ | Flame-penetrated number of specimens | | |
|-----------------|-----------------------------|---------------------------------|--------------------------------------|---------------------|---------------------|
| | | | Non-coated | TMM-coated | TMM + boron-coated |
| 1 to 3 | — | 0.55 | All | All | All |
| 4 to 6 | — | 0.65 | All | All | Two third in number |
| 7 to 9 | — | 0.75 | All | All | One third in number |
| A | BA (0.25%) | 0.65 | All | All | Two third in number |
| B | BX (0.25%) | 0.65 | All | One third in number | None |
| C | BA + BX (0.25%) | 0.65 | All | None | Two third in number |
| D | BA (1.00%) | 0.65 | All | All | All |
| E | BX (1.00%) | 0.65 | All | Two third in number | One third in number |
| F | BA + BX (1.00%) | 0.65 | All | One third in number | None |
| G | BA (4.70%) | 0.65 | None | None | None |
| H | BX (4.70%) | 0.65 | Half in number | None | None |
| I | BA + BX (4.70%) | 0.65 | Half in number | One third in number | None |

Note: Results reflect observations of 6 specimens belonging to each treatment group subjected to the test ($54 \times 6 = 324$ specimens). For abbreviations refer to Table 1.

and 0.75 g/cm³ density, was reduced. Boron-added boards with surface coatings showed excellent resistance against flame penetration (Table 2). The TMM-boron mixture was much more effective than TMM alone even in boron-added boards. As a consequence, neither separate surface coating nor sole boron addition to the adhesive yielded sufficient flame-proof property to the WTLB panels. Therefore, a combination of both treatments appeared to be necessary to improve flame-resistance.

Glowing

Glowing time (GT) duration after closing off the flame source is given in Tables 3 and 4. Glowing time decreased with increasing board density (Table 3). At lower density, hollow spaces in the board might provide sufficient air for internal combustion, though air is

known as a good insulator against heat transfer in large-scale structural boards (Slifka 1997). In the present case, boards at high densities did not allow further glowing under the charred layer. Void spaces within the boards are not desired for decay resistance. Mycelial mass of decay fungi fills such spaces and begins to severely damage surrounding parts (Imamura 1993). However, one advantage of the low density (0.55 g/cm³) that appeared in this study is the easy application of surface coating by quick absorption and drying of the brushed paste, which enables use of more coatings when required and fixation of a film layer with deeper penetration. Glowing time

TABLE 3. *Glowing time after 13 min flaming of the WTLB manufactured without boron addition to UF resin.*

| Board density (g/cm ³) | Glowing time (min) | | |
|------------------------------------|--------------------------|--------------------------|----------------------------------|
| | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD |
| 0.55 | 41.6 \pm 5.5 | 32.2 \pm 3.5 | 24.7 \pm 11.9 |
| 0.65 | 12.6 \pm 4.7 | 11.7 \pm 2.9 | 16.3 \pm 5.1 |
| 0.75 | 8.7 \pm 1.2 | 13.4 \pm 2.0 | 12.3 \pm 1.1 |

Note: SD; Standard deviation. For abbreviations refer to Table 1.

TABLE 4. *Glowing time after 13 min flaming of the WTLB manufactured with boron addition to UF resin.*

| Board type | Glowing time (min) | | |
|------------|--------------------------|--------------------------|----------------------------------|
| | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD |
| Control | 9.3 \pm 3.3 | 10.0 \pm 2.8 | 15.0 \pm 6.0 |
| A | 6.4 \pm 2.0 | 15.0 \pm 3.5 | 11.0 \pm 2.8 |
| B | 14.3 \pm 4.9 | 11.0 \pm 3.0 | 6.0 \pm 3.4 |
| C | 10.0 \pm 0.6 | 7.0 \pm 1.0 | 6.0 \pm 1.3 |
| D | 10.0 \pm 0.9 | 20.0 \pm 0.2 | 12.0 \pm 0.8 |
| E | 27.0 \pm 2.8 | 25.0 \pm 1.0 | 23.0 \pm 1.5 |
| F | 13.0 \pm 1.6 | 10.0 \pm 1.9 | 12.0 \pm 3.0 |
| G | 11.0 \pm 4.4 | 23.0 \pm 3.0 | 13.0 \pm 3.7 |
| H | 34.5 \pm 6.2 | 23.0 \pm 3.8 | 23.0 \pm 3.1 |
| I | 14.3 \pm 1.0 | 9.0 \pm 1.5 | 5.0 \pm 0.4 |

Note: For codes and abbreviations refer to Tables 1 and 2.

TABLE 5. Weight loss and char length caused by combustion of the WTLB manufactured without boron addition to UF resin.

| Board density (g/cm ³) | Weight loss (%) | | | Char length (mm) | | |
|------------------------------------|--------------------------|--------------------------|----------------------------------|--------------------------|--------------------------|----------------------------------|
| | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD |
| 0.55 | 23.3 \pm 2.2 | 18.7 \pm 3.4 | 18.6 \pm 4.0 | 74.1 \pm 7.9 | 63.4 \pm 3.7 | 59.1 \pm 10.6 |
| 0.65 | 17.8 \pm 3.0 | 16.4 \pm 1.6 | 13.1 \pm 5.6 | 44.6 \pm 2.6 | 43.8 \pm 8.7 | 33.8 \pm 21.3 |
| 0.75 | 17.8 \pm 0.6 | 14.4 \pm 0.9 | 13.5 \pm 0.8 | 48.8 \pm 2.6 | 43.2 \pm 7.9 | 24.2 \pm 2.3 |

Note: For codes and abbreviations refer to Tables 1 and 2.

was considerably shorter for TMM and TMM-boron coated boards than non-coated ones. This result is consistent with those of a previous study (Su et al. 1997a). As for the boron-added boards, BA acted to shorten the GT, while BX tended to extend it (Table 4). Borax generally reduces flame spread but promotes smoldering or glowing and BA suppresses smoldering but has little effect on flame spread (LeVan and Tran 1990; Yalinkiliç et al. 1997b, c). The mixture of BA and BX reduced glowing after flame in the present study.

On the other hand, surface coating of boron-added boards reduced the GT. Trimethylolmelamine and TMM-boron appeared more effective when they were applied on the boards manufactured with the BA+BX addition. Since they are also effective in slowing down boron leaching from coated plywood surface (Su et al. 1997b), a combination of boron addition to resin solution with the boron containing surface coating would be preferable.

Weight loss (WL) and char length

Weight loss and char length due to combustion are given in Tables 5 and 6. Lower density boards (0.55 g/cm³) without boron addition lost 20–25% their original weights (Table 5). With reference to the WL levels of the boards without boron addition but coated, TMM-boron mixture coating was more effective than only TMM for the 0.65 and 0.75 g/cm³ density boards. High-density boards with the TMM-boron coating yielded the least char formations (Table 5). However, WL could only be reduced by 5 to 10% with the untreated high-density boards compared to the non-coated ones.

Boron addition to the resin, as expected, resulted in a remarkable decrease in WL of the boards (Table 6). More importantly, BA-added boards were least affected by combustion followed by BA+BX. Borax addition could not keep WL levels much lower than those of con-

TABLE 6. Weight loss and char length caused by combustion of the WTLB manufactured with boron addition to UF resin.

| Board type | Weight loss (%) | | | Char length (mm) | | |
|------------|--------------------------|--------------------------|----------------------------------|--------------------------|--------------------------|----------------------------------|
| | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD | Non-coated Mean \pm SD | TMM-coated Mean \pm SD | TMM + boron-coated Mean \pm SD |
| Control | 20.0 \pm 3.8 | 16.2 \pm 4.9 | 17.7 \pm 3.2 | 43.1 \pm 4.9 | 38.5 \pm 8.0 | 54.0 \pm 13.6 |
| A | 13.4 \pm 4.4 | 12.4 \pm 1.1 | 12.7 \pm 5.0 | 46.8 \pm 6.3 | 32.7 \pm 8.6 | 26.8 \pm 11.0 |
| B | 13.8 \pm 6.5 | 9.8 \pm 1.2 | 11.0 \pm 4.1 | 43.4 \pm 16.0 | 17.1 \pm 5.5 | 11.0 \pm 3.3 |
| C | 13.4 \pm 3.5 | 11.2 \pm 0.6 | 14.9 \pm 4.0 | 34.5 \pm 5.4 | 5.0 \pm 0.6 | 20.0 \pm 8.8 |
| D | 12.3 \pm 3.5 | 13.0 \pm 1.9 | 14.3 \pm 6.8 | 34.5 \pm 11.0 | 31.0 \pm 4.3 | 28.0 \pm 2.7 |
| E | 14.7 \pm 4.2 | 12.8 \pm 1.0 | 13.9 \pm 5.5 | 49.2 \pm 3.5 | 48.4 \pm 4.8 | 25.1 \pm 4.2 |
| F | 14.6 \pm 2.8 | 11.0 \pm 2.0 | 11.8 \pm 2.0 | 42.1 \pm 1.8 | 30.2 \pm 2.2 | 3.0 \pm 1.0 |
| G | 11.1 \pm 1.0 | 12.7 \pm 3.8 | 12.6 \pm 4.7 | 3.0 \pm 1.5 | 3.0 \pm 1.8 | 3.0 \pm 1.2 |
| H | 16.4 \pm 2.5 | 16.9 \pm 1.3 | 13.9 \pm 6.0 | 30.9 \pm 8.7 | 15.0 \pm 4.9 | 5.2 \pm 1.7 |
| I | 12.6 \pm 0.4 | 11.3 \pm 2.6 | 11.3 \pm 1.5 | 12.6 \pm 3.3 | 7.0 \pm 2.7 | 3.0 \pm 1.0 |

Note: For codes and abbreviations refer to Tables 1 and 2.

trols. Most of the thermal decomposition of BX-treated boards occurred during glowing, and no severe damage was observed in those panels at the flaming stage that can be understood from charring rates (Table 6). Although no generalization could be made on WL effectiveness of surface coatings applied onto boron-added boards, it is apparent that most of the WL and char length levels of these boards were much lower than those of boron-added but non-coated ones. Superiority of surface coating over boron-added board types can also be seen from the general appearance of representative boards after combustion (Fig. 2).

Thickness swelling (TS) and water absorption (WA)

Higher WA was recorded for higher board densities for 2-h soaking, but differences became negligible for 24 h (Table 7). Boron-added boards generally showed similar behavior to untreated ones in water soaking, and the boron effect was only distinguishable on the WA level for the high boron concentration (4.7%), which was added to the G and H groups (Table 8). Thus, increase of WA remained at reasonable levels in general, and no extreme change was recorded for TS values due to boron. It is also noteworthy that the BA+BX mixture yielded lower WA levels (C, F, and I groups) than their separate uses, supporting the previous findings on the relatively high stability of this mixture in wood (Yalinkiliç et al. 1995a, b).

Thickness swelling and water absorption ratios proved the aforementioned relation between board density and TS for 2-h water soaking (Table 7). When the soaking time was extended to 24 h, density no longer affected TS/WA ratio. As for the boron-added boards, in spite of WA increase at higher boron contents, TS remained almost unchanged (Table 8). As a result, TS/WA ratios decreased substantially for these board types. Thus, boron caused neither remarkable swelling nor attraction of water, compared with the untreated boards, within the concentration levels used.

Direct contact of boron crystals with water in the soaking tests is probably prevented by incorporating them into the structural framework of the cured resin. This may give the board long-term protection if boron leaching becomes more difficult from the cured resin than that from impregnated raw material. In addition, the stability of thickness after boron addition compared to untreated boards indicates that boron addition to a compatible adhesive in an appropriate amount that does not cause curing failure can be more practical than impregnation of the raw material. Ease of even distribution of resin among the porous leaf structure may be of additional advantage for homogeneity of board properties. However, the biological activity of boron within the cured resin and mechanical properties of end product need to be considered.

Static bending (SB) and internal bonding (IB)

Static bending and internal bonding values of WTLB with or without boron addition are shown in Tables 9 and 10. Density increase, as expected, improved both strength properties of untreated boards (Table 9). Boron addition caused some decrease in SB and IB (Table 10). However, the BA+BX mixture improved these strength properties to some extent. Evidently, BA caused more strength loss than BX and BA+BX mixture. Since, the saturation of BA solution makes it more acidic, it is likely to have had a deleterious effect on the cell wall. In an earlier study, BA-treated wood showed more mass loss after ten cycles of leaching than the retained amount of boron (Yalinkiliç et al. 1996). This was attributed to possible decomposition of cell-wall components by the acidic treatment solutions. Laks et al. (1988) found that bond strength of PF-bonded waferboard, containing biologically effective levels of sodium borates or BA, was unacceptably low. Similar cases reported for ACA and CCA waterborne preservatives have been attributed to a number of reasons, such as: pH effects, incompatibility between resin

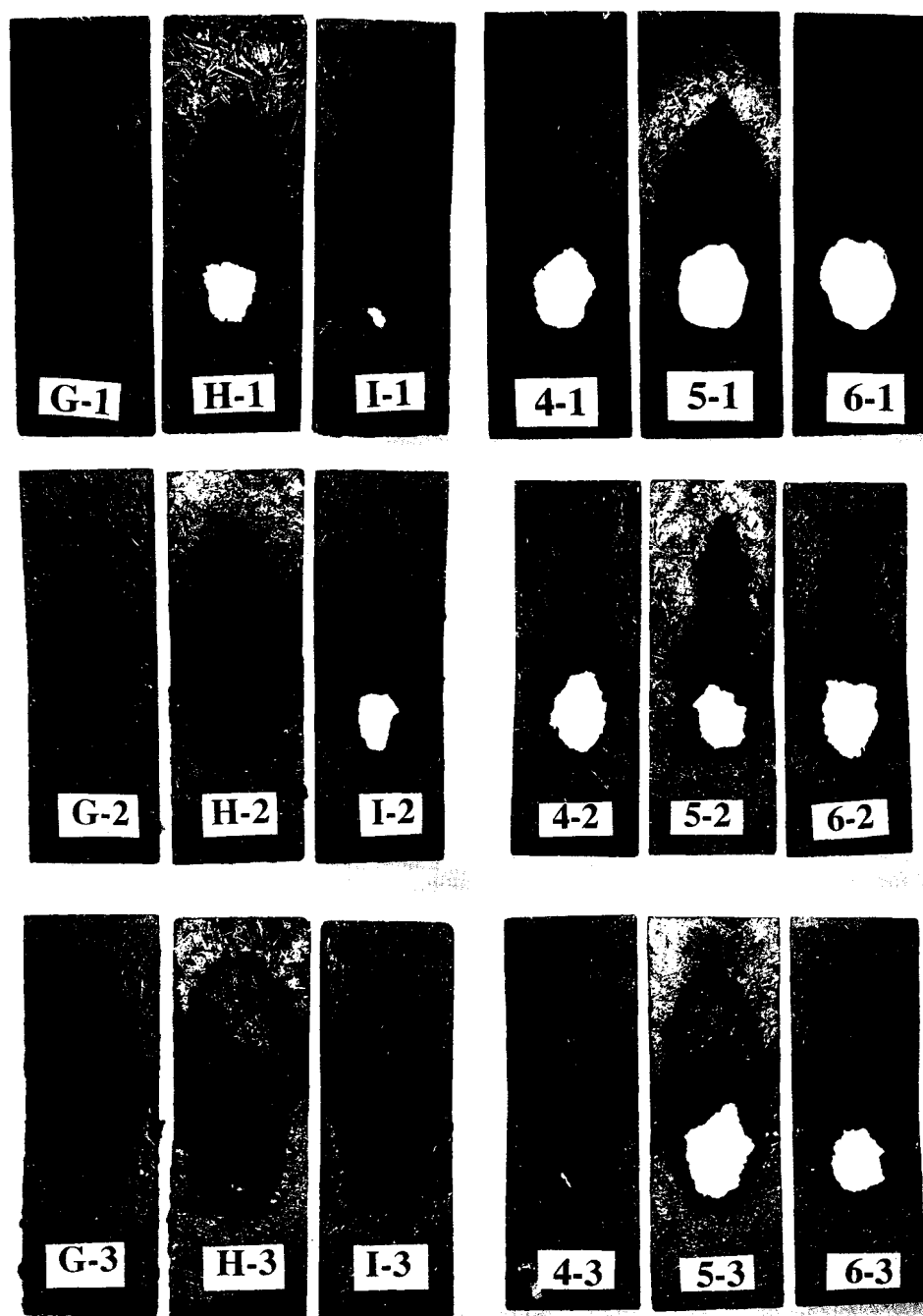


FIG. 2. Appearance of some representatively selected WTLB panels after exposure to flame according to JIS A 1322. Ashes and formed char were cleaned by a wire brush in order to show the extent of decomposition. For board types refer to Table 1.

TABLE 7. Thickness swelling (TS) and water absorption (WA) values of the WTLB manufactured without boron addition to UF resin.

| Board density (g/cm ³) | Thickness swelling (%) | | Water absorption (%) | | TS/WA ratio | |
|------------------------------------|------------------------|--------------------|----------------------|----------------|-------------|-----------|
| | 2 h Mean \pm SD | 24 h Mean \pm SD | 2 h Mean \pm SD | 24 h Mean | 2 h Mean | 24 h Mean |
| 0.55 | 12.5 \pm 1.2 | 23.2 \pm 1.3 | 42.8 \pm 0.7 | 62.0 \pm 4.6 | 0.29 | 0.37 |
| 0.65 | 16.2 \pm 2.6 | 26.5 \pm 0.4 | 48.7 \pm 2.7 | 69.2 \pm 0.6 | 0.33 | 0.38 |
| 0.75 | 21.1 \pm 0.2 | 27.5 \pm 0.1 | 54.1 \pm 0.7 | 71.9 \pm 0.9 | 0.39 | 0.38 |

and preservatives, adverse effects on resin viscosity, decrease in wettability of treated particles, reduction in the number of hydroxyl groups available for hydrogen bonding, and mechanical interference by preservative salts resulting in reduced bonding (Boggio and Gertjeansen 1982; Hashim et al. 1994) and/or gelling of the phenolic adhesive by the borate before the glue droplet can wet, transfer to, and penetrate the opposite wood surface (Vick et al. 1990). Yalinkiliç et al. (1996) found that BA pretreatment remarkably reduced the ASE of vapor phase formaldehyde-treated wood, due possibly to limitation of formaldehyde cross-linking by occupation of the wood's OH- groups by boron-oxygen links. Although a similar effect was not reported for UF resin (Laks and Manning 1994), the present study showed that the tested strength values were more or less affected by boron addition to the adhesive. Improvement of SB and IB by BA+BX mixture is most likely due to buffering of the pH from acidic to neutral (F and I

groups in Table 10). Therefore, it can be speculated at this point that boron as an additive to UF should be used at around a neutral pH and at an amount that has no or reasonable adverse effects on the strength properties of the end product.

On the other hand, extractives of tea leaves are up to 30% of dry leaf weight (Kacar 1991) which is higher than many extractive-rich heartwoods of both softwood and hardwood species (Hillis 1987). They are mainly derivatives of gallic acid and catechin, which dominantly comprise flavonoid units. Since extractives provide a major contribution to many of the physical, mechanical, and biological properties of wood despite their usually limited volume (Panshin and DeZeew 1970), high tannin and non-tannin polyphenolic extractives of tea leaves may improve adhesion among leaf fibers and adhesive, if available reactive sites of phenolic rings react with the formaldehyde of synthetic resin used through condensation reactions (Subramanian 1984). The bioactive

TABLE 8. Thickness swelling (TS) and water absorption (WA) values of the WTLB manufactured with boron addition to UF resin.

| Board type | Thickness swelling (%) | | Water absorption (%) | | TS/WA ratio | |
|------------|------------------------|--------------------|----------------------|--------------------|-------------------|--------------------|
| | 2 h Mean \pm SD | 24 h Mean \pm SD | 2 h Mean \pm SD | 24 h Mean \pm SD | 2 h Mean \pm SD | 24 h Mean \pm SD |
| Control | 15.9 \pm 3.1 | 26.3 \pm 0.8 | 49.5 \pm 3.0 | 68.9 \pm 0.4 | 0.32 | 0.38 |
| A | 19.2 \pm 4.0 | 27.7 \pm 1.2 | 55.0 \pm 3.8 | 73.2 \pm 1.1 | 0.35 | 0.38 |
| B | 19.8 \pm 3.4 | 28.0 \pm 0.3 | 58.3 \pm 2.7 | 76.1 \pm 0.8 | 0.34 | 0.37 |
| C | 19.8 \pm 2.6 | 27.3 \pm 0.5 | 55.5 \pm 3.3 | 75.4 \pm 1.0 | 0.36 | 0.37 |
| D | 20.7 \pm 4.4 | 27.6 \pm 1.0 | 63.2 \pm 3.9 | 78.5 \pm 0.9 | 0.33 | 0.36 |
| E | 20.8 \pm 6.0 | 28.9 \pm 0.9 | 67.5 \pm 5.2 | 85.9 \pm 1.1 | 0.31 | 0.34 |
| F | 20.3 \pm 3.3 | 29.0 \pm 0.6 | 60.5 \pm 4.7 | 77.9 \pm 1.0 | 0.33 | 0.37 |
| G | 22.9 \pm 2.3 | 29.2 \pm 0.6 | 75.9 \pm 3.6 | 90.1 \pm 0.7 | 0.30 | 0.32 |
| H | 22.9 \pm 1.9 | 29.9 \pm 0.5 | 86.0 \pm 2.9 | 90.2 \pm 2.0 | 0.27 | 0.33 |
| I | 21.4 \pm 2.8 | 29.9 \pm 0.9 | 72.4 \pm 3.1 | 86.2 \pm 0.4 | 0.29 | 0.35 |

Note: For codes refer to Table 1.

TABLE 9. Static bending (SB) and internal bonding (IB) strength of the WTLB manufactured without boron addition to UF resin.

| Board density (g/cm ³) | SB (N/mm ²) Mean \pm SD | IB (N/mm ²) Mean \pm SD |
|------------------------------------|--|--|
| 0.55 | 6.01 \pm 0.8 | 0.30 \pm 0.02 |
| 0.65 | 9.83 \pm 0.4 | 0.59 \pm 0.05 |
| 0.75 | 12.88 \pm 1.1 | 0.64 \pm 0.03 |

effect and adhesive properties of tannin extracts of many wood barks and some other plants have already been investigated and patented (Lotz 1993; Lotz and Hollaway 1988; Laks 1991; Hartman 1977; Chibata et al. 1978). Adsorbance of formaldehyde by tannin in such a condensation reaction can also reduce formaldehyde emission of board, which is a basic environmental concern. The adhesive properties and formaldehyde adsorbance level of tannin present in tea leaves, therefore, need to be investigated.

CONCLUSIONS

Boron addition to UF and fire-retardant coating was studied as a combined treatment process in order to further fire resistance. BA and BX or their mixture (BA+BX, 5:1, w/w) were added to the UF adhesive in manufacturing particleboard from waste tea leaves as a new bio-based resource. Fire test results showed that BA shortens the glowing time, while BX extends it. As a consequence, WL was less with BA addition than with BX addition. Mixture of these boron compounds improved their fire-retardant effectiveness as well. On the other hand, TMM and TMM-boron surface coatings were quite effective on almost all tested combustion properties of boards, when they were used as fire-retardant coating, especially for the boron-added boards. However, boron addition caused some decrease in bending and internal bond strengths at higher concentrations. Thickness swelling and WA levels did not change remarkably for boron added boards. The BA+BX mixture appeared effective in maintaining TS and strength properties.

TABLE 10. Static bending (SB) and internal bonding (IB) strength of the WTLB manufactured with boron addition to UF resin.

| Board type | SB (N/mm ²) Mean \pm SD | IB (N/mm ²) Mean \pm SD |
|------------|--|--|
| Control | 9.82 \pm 0.6 | 0.59 \pm 0.01 |
| A | 8.60 \pm 0.6 | 0.52 \pm 0.01 |
| B | 8.32 \pm 0.6 | 0.47 \pm 0.02 |
| C | 8.43 \pm 0.8 | 0.50 \pm 0.04 |
| D | 7.64 \pm 1.3 | 0.36 \pm 0.02 |
| E | 8.25 \pm 1.0 | 0.44 \pm 0.02 |
| F | 8.33 \pm 1.0 | 0.49 \pm 0.06 |
| G | 7.27 \pm 1.4 | 0.34 \pm 0.01 |
| H | 8.00 \pm 1.9 | 0.38 \pm 0.05 |
| I | 8.20 \pm 1.8 | 0.40 \pm 0.005 |

Note: For codes refer to Tables 1 and 2.

In conclusion, a combination of boron addition to UF as BA+BX mixture with a surface coating containing a sufficient amount of boron can be applied to improve fire resistance of a particleboard. When mixing BA and BX and adding them to UF and TMM, one must consider the possible side effects of BA on strength properties at high concentrations as well as increase of glowing by BX.

ACKNOWLEDGMENTS

The authors thank Dr. Hulya Kalaycioglu and Research Associate Gokay Nemli for their valuable help during board manufacture, and Dr. Wen-Yu Su for her kind help during the fire tests.

REFERENCES

- BARNES, H. M., AND T. L. AMBURGEY. 1989. Borates as wood preserving compounds: The status of research in the United States. Doc. No. IRG/WP/3542. Int. Res. Group Wood Preserv. Stockholm, Sweden. 16 pp.
- BOGGIO, K., AND R. GERTJEJENSEN. 1982. Influence of ACA and CCA waterborne preservatives on the properties of aspen waferboard. Forest Prod. J. 32(3):22–26.
- BRITISH STANDARD-355669. 1979. Wood chipboard 2nd methods of test for particleboard. British Standards Institution, London, UK.
- CHIBATA, I., T. TOSA, T. MORI, T. WATANABE, R. SANO, AND Y. MATUO. 1978. Water insoluble tannin preparation for immobilization of proteins. U.S. Patent No. 4,090,919.
- DRYSDALE, J. A. 1994. Boron treatments for the preservation of wood—A review of efficacy data for fungi

- and termites. Doc. No. IRG/WP 94-80037. Int. Res. Group Wood Preserv. 21 pp.
- HARTMAN, S. 1977. Alkali-treated bark extended tannin-aldehyde resinous adhesives. U.S. Patent No. 4,045,386.
- HASHIM, R., R. J. MURPHY, D. J. DICKINSON, AND J. M. DINWOODIE. 1994. The mechanical properties of boards treated with vapor boron. *Forest Prod. J.* 44(10):73-79.
- HILLIS, W. E. 1987. Heartwood and tree exudates. Springer Series in Wood Science. Springer Verlag, Berlin and Heidelberg, Germany. 268 pp.
- IMAMURA, Y. 1993. Estimation of the fungal resistance of wood composites for structural use. Pages 75-84 in N. Shiraishi, H. Kajita, and M. Norimoto, eds. Recent research on wood and wood-based materials. CURRENT JAPANESE MATERIALS RESEARCH, Vol., 11. Elsevier Appl. Science Pub. Ltd., New York, NY.
- JAPANESE INDUSTRIAL STANDARD(-) JIS A 1322. 1982. Testing method for incombustibility of thin materials for building. Approved version of JIS A 1322 (1966), Japanese Industrial Standard, Japanese Standards Institution, Tokyo.
- . JIS A 5908. 1994. Particleboards. Japanese Industrial Standard, Japanese Standards Institution, Tokyo.
- KACAR, B. 1991. Tea analysis. Fac. Agric., Ankara Univ., Ankara, Turkey. 289 pp.
- KALAY, H. Z., M. K. YALINKILIÇ, AND L. ALTUN. 1993. Mushroom production from waste tea leaves substrate and utilization of waste compost as organic fertilizer. Project of Research Fund of Black Sea Technical Univ., Code 89.113.001.1. 127 pp.
- KOZŁOWSKI, R., M. HELWIG, A. PRZEPIERA, AND A. MICIUKIEWICZ. 1992. Flame-retardant composite particleboards based on by-products of fibrous plants and other materials. Pages 320-325 in Proc. First Pacific Rim Bio-Based Symp., Roturua, New Zealand.
- LAKS, P. E. 1991. Method for treating wood against fungal attack. U.S. Patent No. 4,988,545.
- , AND R. D. PALARDY. 1990. Bonding and processing considerations for preservative containing waferboard. Pages 150-154 in Wood adhesives, Forest Products Research Society, USA.
- , AND M. J. MANNING. 1994. Inorganic borates as preservative systems for wood composites. Pages 236-244 in Proc. Second Pacific Rim Bio-Based Symp., Vancouver, Canada.
- , B. A. HAATAJA, R. D. PALARDY, AND R. J. BIANCHINI. 1988. Evaluation of adhesives for bonding borate-containing flakeboards. *Forest Prod. J.* 38(11/12):23-24.
- , X. QUAN, AND R. D. PALARDY. 1994. Preservative system for OSB panels. Proc. Structural Board Assoc., Athens, GA. 15 pp.
- LEVAN, S. L., AND H. C. TRAN. 1990. The role of boron in flame-retardant treatments. Pages 39-41 in Proc. First Int. Conf. on Wood Protection with Diffusible Preservatives.
- LOTZ, W. R. 1993. Wood preservation systems including halogenated tannin extracts. U.S. Patent No. 5,270,083.
- , AND D. F. HOLLOWAY. 1988. Wood preservation. U.S. Patent No. 4,732,817.
- MEMED, R., S. WIJANDI, AND Y. A. KUNDADI. 1992. Tea waste as a raw material for particleboard. Proc. Pacific Rim Bio-Based Symp., Roturua, New Zealand. 311 pp.
- MILLET, G. H. 1985. Cyanoacrylate adhesive composition containing tannins. U.S. Patent No. 4,511,686.
- ÖRS, Y., AND H. KALAYCIOĞLU. 1991. Cay fabrikasi atik-larinin yonga levha uretiminde degerlendirilmesi. *Turkish J. Agric. Forestry* 15:968-974.
- PANSHIN A. J., AND C. DE ZEEUW. 1970. Textbook of wood technology. 3rd ed. vol. 1. McGraw-Hill Book Co., New York, NY. 705 pp.
- REGHI, G. A. 1982. Coating composition and method. U.S. Patent No. 4,338,140.
- ROWELL, R. M. 1996. Chemical modification of nonwood lignocellulosics. Pages 229-245 in D.N.-S. Hon, ed. Chemical modification of ligno-cellulosic materials. Marcel Dekker, Inc. New York, NY.
- , B. A. CLEARY, J. S. ROWELL, C. CLEMONS, AND R. A. YOUNG. 1993. Results of chemical modification of lignocellulosic fibers for use in composites. Pages 121-127 in M. P. Wolcott, ed. Wood fiber polymer composites: Fundamental concepts, processes, and material options. Forest Products Society, Madison, WI.
- SLIFKA, M. J. 1997. Fire protection design and engineered wood products Pages 173-191 in S. Smulski, ed. Engineered wood products: A guide for specifiers, designers, and users. PFS Research Foundation, Madison, WI.
- SU, W.-Y., SUBYAKTO, T. HATA, Y. IMAMURA, AND S. ISHIHARA. 1997a. Improvement of the fire retardance of strandboard by surface treatment with melamine and boric and phosphoric acids. *Mokuzai Gakkaishi* 43(1): 75-81.
- , M. K. YALINKILIÇ, T. HATA, Y. IMAMURA, AND S. ISHIHARA. 1997b. Enhancement of leach and termite resistance of plywood treated with boric compounds. *Mokuzai Gakkaishi* 43(7):595-601.
- SUBRAMANIAN, R. V. 1984. Chemistry of adhesion. Pages 323-348 in R. M. Rowell, ed. The chemistry of solid wood. Advances in Chemistry Series 207, American Chemical Society.
- VICK, C. B., R. C. DEGROOT, AND J. YOUNGQUIST. 1990. Compatibility of non-acidic waterborne preservatives with phenol-formaldehyde adhesive. *Forest Prod. J.* 40(2):16-22.
- WHITE, H., AND M. S. SWEET. 1992. Flame retardancy of wood: Present status, recent problems, and future fields. Pages 250-257 in Proc. 3rd Annual BCC Conf. on Flame Retardance, Stamford, CT.
- YALINKILIÇ, M. K., E. BAYSAL, AND Z. DEMIRCI. 1995a. Leachability of boron from treated Douglas fir wood and alleviation of leachability by various water repellents. Pages 501-511 in Proc. Environment Symp. Erzurum, Turkey.

- , ———, AND ———. 1995b. Effect of boron preservatives on hygroscopicity of *Brutia* pine wood. Eng. Sci. J. Pamukkale Univ. 1(2–3):161–168. Denizli, Turkey.
- , S. YUSUF, T. YOSHIMURA, M. TAKAHASHI, AND K. TSUNODA. 1996. Effect of vapor phase formalization of boric acid treated wood on boron leachability and biological resistance. Pages 544–551 in Proc. 3rd Pacific Rim Bio-Based Comp. Symp., Kyoto, Japan.
- , Y. IMAMURA, M. TAKAHASHI, H. KALAYCIOGLU, G. NEMLI, Z. DEMIRCI, AND T. OZDEMIR. 1997a. Biological, physical, and mechanical properties of particleboard manufactured from waste tea leaves. Int. Biodeterioration and Biodegradation 41(1):75–84.
- , W.-Y. SU, Z. DEMIRCI, E. BAYSAL, M. TAKAHASHI, AND S. ISHIHARA. 1997b. Oxygen levels and thermal analysis of wood treated with melamine formaldehyde-boron combinations. Doc. No. IRG/WP 97-30135. Int. Res. Group Wood Preserv. 15 pp.
- , E. BAYSAL, AND Z. DEMIRCI. 1997c. Fire resistance of Calabrian pine (*Pinus brutia* Ten.) wood treated with some boron compounds and/or water repellents. Turkish J. Agric. Forestry 21:423–431.