Soy Protein Combined with Copper and Boron Compounds for Providing Effective Wood Preservation

In Yang[a,*], Monlin Kuo[a], and Deland J. Myers[b]

Departments of [a]Natural Resource Ecology and Management and [b]Food Science & Human Nutrition, Iowa State University, Ames, Iowa 50011-1021

ABSTRACT: Chromated copper arsenate (CCA), an arsenic-based wood preservative, is toxic to human health and the environment. Although CCA is stable in seasoned wood, there are potential dangers during CCA manufacture, lumber treatment, and waste disposal. This research was conducted to study the effectiveness of soy products to replace toxic chromium and arsenic compounds in wood preservative formulations. Three soy products (Arpro 2100, HM 90, and Supro 760) were used as fixative agents in preservative solutions containing anhydrous $CuSO_4$ and $Na_2B_4O_7 \cdot 10H_2O$. The decay resistance of treated wood blocks was measured by a soil-block culture method. Despite the large molecular sizes of copper–protein and copper–boron–protein complexes, southern pine sapwood was treatable with these preservative formulations. Wood samples treated with >6 kg·m^{-3} $CuSO_4$ and 7.5 kg·m^{-3} soy product, and subsequently leached for 3 d and exposed to the decay fungus *Gloeophyllum trabeum* (Fr.) Mur., sustained only 0.5% weight loss over 12 wk. Wood samples needed 40 kg·m^{-3} $CuSO_4$ and 50 kg·m^{-3} soy protein to resist the copper-tolerant decay fungus *Postia placenta* (Fr.) M. Lars. & Lomb. These results suggest that soy-based wood preservatives can prevent wood products from fungal attack and can replace CCA.

Paper no. J11117 in *JAOCS 83*, 239–245 (March 2006).

KEY WORDS: Anhydrous copper sulfate, decay fungus, decay resistance, leachability, sodium borate, treatability, weight loss, wood preservatives.

Wood is susceptible to deterioration by microorganisms and insects. Biological deterioration of wood-frame buildings in the United States causes billions of dollars of damage annually (1). Wood products for exterior uses, such as poles, posts, decks, and timber bridges, must be chemically treated to extend their service lives. Chromated copper arsenate (CCA) was used for wood preservation until 2004, when the U.S. Environmental Protection Agency prohibited the use of CCA-treated products for residential purposes. Therefore, less toxic alternatives are needed to replace CCA as a wood preservative because of its toxicity to human health and the environment. Although CCA is no longer used to protect wood for residential use, it is still widely used to protect wood for exterior uses, such as residential fences or telephone poles. Consequently, there is an urgent need for effective, environmentally benign, and cost-competitive alternatives. Nicholas and Schultz (2) suggested that alkyl ammonium compounds and azoles could be used as effective and environmentally friendly alternatives. But the high cost of synthetic and organic wood preservatives relative to CCA has been an obstacle to using alkyl ammonium compounds and azoles as replacements for CCA.

The most commonly used CCA formulation contains 36.1% cupric oxide, 47.5% chromium trioxide, and 16.4% arsenic pentaoxide on a weight percent basis (CCA-type C) (3). The arsenic and copper salts are toxic to decay fungi and insects, whereas the chromium salt is used to stabilize the arsenic and copper salts to prevent leaching into the environment. Wood treated with CCA in accordance with the standards of the American Wood Preservers' Association (AWPA) has a longer, more reliable service life, and CCA chemicals are stable in seasoned, treated wood. However, CCA may be hazardous during the manufacture and treatment of lumber. The waste products may also be hazardous. Chromium and arsenic salts are extremely toxic to humans and animals, and thus have undergone close environmental scrutiny. Therefore, a viable nontoxic and nonpolluting alternative to CCA is needed as a wood preservative.

Within the last few years in the wood industry, interest has increased in developing effective and benign wood preservative systems using copper salts as a preservative. Bland (4) has shown that water-soluble copper salts react with and bind to lignin in wood. However, since wood contains only 20 to 30% lignin, some of which does not react, the amount of lignin-bound copper salt is insufficient to protect wood from fungal or insect attack. Lin (5) patented a method of fixing additional amounts of copper with lignin in wood. In this method, copper sulfate was formulated with spent pulping liquor lignin in an ammonium solution to form an insoluble lignin/copper chelate. Based on Lin's innovative concept, other systems appear theoretically possible. For example, protein is known to chelate heavy metals such as copper and zinc to form water-insoluble complexes. Thevenon *et al.* (6) investigated the effectiveness of protein borate wood preservatives prepared with egg albumin, casein, and collagen. Condensed tannins were also examined as fixative agents (7). Soy protein would be a good metal-fixing biopolymer in wood preservative formulations because it is safe to handle and is readily available in sufficient quantities.

The objectives of this study were to formulate wood preservatives containing copper and boron salts with different soy products as chelating agents, to measure leachability of the soy-

*To whom correspondence should be addressed at Program in Environmental Materials Science, Department of Forest Products, Seoul National University, San 56-1 Sillim-Dong, Kwanak-gu, Seoul, South Korea 151-742. E-mail: dahadad2000@yahoo.com

TABLE 1
Formulations of Soy Product-Based Preservatives and Their Effectiveness Against Brown-Rot Fungus (*Postia placenta*)

Formulations[a] (kg·m^{-3})					Target retention	Measured retention	Treatability[b]	Leached retention[c]	Leachability[d]	Weight loss[e]
Cu	HM	Arpro	Supro	B	(kg·m^{-3})	(kg·m^{-3})	(%)	(kg·m^{-3})	(%)	(%)
		Control								54.21
		CCA-type A			1.6	0.52	32.33	0.52	0	16.66
					4	4.40	110.07	4.36	0.01	2.03
					8	10.68	133.53	10.33	0.03	0.38
8					8	4.99	62.43	4.56	8.62	54.31
16					16	14.34	89.60	9.80	31.63	55.37
24					24	23.52	97.99	12.32	47.62	57.33
32					32	30.40	94.99	16.00	47.37	56.36
40					40	38.80	96.99	15.17	60.91	52.59
8	10				18	16.64	94.90	16.00	3.85	58.30
16	20				36	37.76	97.57	28.96	23.31	45.93
24	30				54	54.88	103.79	33.92	38.19	32.27
32	40				72	71.84	101.95	33.60	53.23	19.97
40	50				90	92.16	104.71	24.96	72.92	6.30
8		10			18	17.76	100.51	16.80	5.41	56.73
16		20			36	40.48	104.68	32.96	18.58	37.55
24		30			54	52.16	98.86	40.96	21.47	22.30
32		40			72	74.72	106.24	50.72	32.12	1.31
40		50			90	90.40	102.81	53.44	40.88	0.48
8			10		18	16.48	93.23	16.32	0.97	49.65
16			20		36	41.92	108.18	36.00	14.12	30.52
24			30		54	44.48	84.18	36.80	17.27	20.96
32			40		72	76.48	108.73	53.28	30.33	14.20
40			50		90	96.16	109.35	56.96	40.77	6.15
11				5	16	13.36	83.51	12.32	7.80	48.28
19				11	30	31.11	103.71	23.04	25.95	3.47
22				14	36	37.77	104.93	24.16	36.04	6.87
26				18	44	52.83	120.07	21.92	58.51	0.88
29				21	50	59.81	119.61	20.16	66.29	0.23
32				24	56	68.57	122.44	15.04	78.07	0.04
11	14			5	30	27.00	90.01	22.24	17.64	58.18
19	22			11	52	46.90	90.20	25.76	45.08	17.88
22	30			14	66	60.53	91.71	24.96	58.76	4.89
26	34			18	78	73.53	94.27	18.08	75.41	0.72
29	40			21	90	86.81	96.45	11.36	86.91	0.83
32	50			24	106	103.63	97.76	0.80	99.23	0.77
11		14		5	30	29.43	98.11	24.80	15.74	58.98
19		22		11	52	50.76	97.61	29.60	41.68	9.33
22		30		14	66	64.75	98.11	29.28	54.78	17.35
26		34		18	78	77.46	99.31	26.24	66.13	0.52
29		40		21	90	93.69	104.10	23.04	75.41	0.50
32		50		24	106	114.37	107.90	12.48	89.09	0.44
11			14	5	30	27.60	92.00	24.32	11.88	57.10
19			22	11	52	53.45	102.78	34.24	35.93	5.53
22			30	14	66	71.79	108.78	33.28	53.65	1.06
26			34	18	78	87.54	112.23	28.48	67.47	0.26
29			40	21	90	93.90	104.33	24.00	74.44	2.45
32			50	24	106	109.31	103.12	18.40	83.17	2.79

[a]Cu, anhydrous copper sulfate; HM, Honey Mill 90 (Harvest State, Mankato, MN); Arpro, soy protein isolate Arpro 2100 (ADM, Decatur, IL; Supro, soy protein isolate Supro 760 (Protein Technologies International, Palatine, IL); B, sodium borate.
[b]Treatability refers to the percentage of actual retention to the target retention.
[c]Leached retention refers to the preservative remaining in treated specimens after hot water extraction.
[d]Leachability refers to the percentage of preservative leached from treated specimens.
[e]Weight loss refers to the percentage weight loss after exposing specimens to the brown-rot fungus for 12 wk.

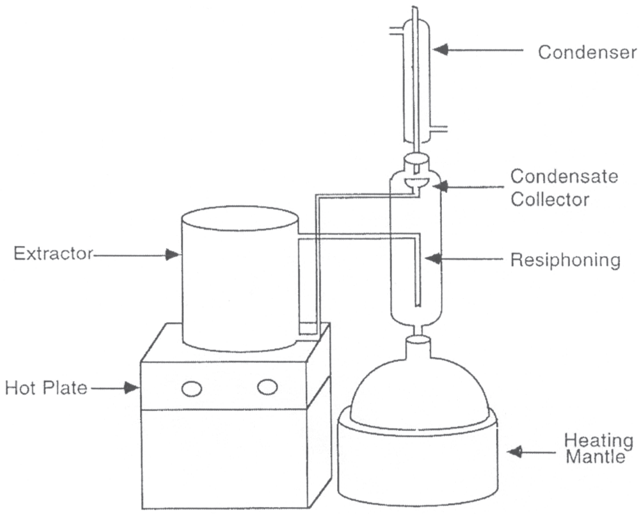

FIG. 1. Schematic of the extraction apparatus for studying the leachability of wood preservatives.

based wood preservatives in treated wood, and to determine the effectiveness of these preservatives against fungal decay.

EXPERIMENTAL PROCEDURES

Preservative formulations. Copper sulfate ($CuSO_4$: Cu) and sodium borate ($Na_2B_4O_7$-$10H_2O$: B) were used as preservative salts to protect wood against decay fungi. Defatted soy flour (Honey Mill 90; Harvest State, Mankato, MN: HM), Arpro 2100 (ADM, Decatur, IL: Arpro), and Supro 760 (Protein Technologies International, Palatine, IL: Supro) were used as chelating agents for the preservative salts. Dry HM soy flour has a typical composition of 55% protein, 37% carbohydrates, and 8% other components, mainly salts. Arpro is a soy protein isolate in granular form, obtained by a salt precipitation process and typically containing over 90% protein and 10% salts. Supro is also a soy protein isolate, obtained by spraying-drying from a neutral pH solution.

The soy products (HM, Arpro, and Supro: Pr) were dissolved in 250 mL distilled water, followed by addition of preservative salts to obtain a suspension of water-insoluble complexes (Table 1). The complexes were dissolved by adding 50 mL ammonium hydroxide (NH_4OH). The weight ratio of 1 to 1.25 Cu to Pr was used in the formulations. The concentration of prepared preservative solution varied, depending on the desired retention level of the preservative salt in treated wood specimens. Target retention of preservative salts ranged from 5 to 40 $kg{\cdot}m^{-3}$ Cu and from 5 to 24 $kg{\cdot}m^{-3}$ B in combination with Cu. Three CCA formulations of AWPA type C (2, 4, and 8 $kg{\cdot}m^{-3}$) prepared in a ratio of 18.1% CuO, 65.5% CrO_3, and 16.4% As_2O_5 were used for comparison (3). Wood samples treated with the CCA formulations also were included in tests.

Treating wood specimens. Wood blocks (19 cm^3), milled from southern pine sapwood, were treated in a laboratory pressure cylinder. The wood blocks were immersed in the treating solution for 30 min under vacuum (760 mm Hg) followed by 30 min pressure (2.5×10^3 $kg{\cdot}m^{-2}$). After being air-dried for 24 h, the treated wood blocks were oven-dried at 100°C overnight to obtain the treated dry weights and actual preservative retention of each sample. Treatabilities were calculated as the difference between the final dry weight after treatment and the original dry weight of each wood sample to give the weight gain from solution uptake.

Leaching treated wood blocks. To evaluate the stability of each treatment, treated wood blocks were subjected to hot water leaching. The treated wood blocks were evacuated with an aspirator in a desiccator for 30 min, followed by the introduction of cold water to partially saturate these wood blocks. As shown in Figure 1, saturated blocks were placed in a 3-L extractor and extracted in 70°C water for 72 h. The hot water in the extractor was replaced with fresh condensate at a rate of approximately 350 mL/h. After water extraction, wood blocks were air-dried for 24 h, oven-dried at 100°C overnight, and weighed. Leachability was calculated as the percentage of the preservative leached out of the treated specimens.

Decay resistance of treated wood samples. Decay resistance of the treated wood blocks was evaluated in accordance with ASTM Standard D 1413-05b (8). The brown-rot fungi *Postia placenta* (ATCC No. 11538) and *Gloeophyllum trabeum* (ATCC No. 11539) were used as the test fungi. Iowa topsoil with a moisture-holding capacity of 55% was used as the soil substrate. Soil culture bottles with southern pine sapwood feeder strips on the soil surface were autoclaved at 5×10^2 $kg{\cdot}m^{-2}$ for 30 min. The bottles were inoculated with fungus cultured on potato dextrose agar. After the feeder strips were covered with fungal mycelia, sterilized wood blocks were placed onto the feed strip, two blocks per bottle. The soil-block culture was incubated at 26°C and 79% RH for 12 wk. After exposure to the fungi, wood blocks were removed from the decay chambers, cleaned of fungal mycelia, and dried in an 80°C oven overnight. Wood block decay was indicated by the percentage weight loss attributable to exposure to the decay fungus.

Data analysis. Twelve wood blocks, assigned randomly, were treated with each formulation. Effects of each variable were examined by the general linear model procedure with the Statistical Analysis System programming package (SAS Institute Inc., Cary, NC). A 95% confidence level was used in all statistical tests. Significant effects with a $P < 0.05$ were further characterized by the least significant difference test between means.

RESULTS AND DISCUSSION

Treatability of soy product-based preservatives. Treatability of each preservative formulation meant the actual percentage retention of the preservative in wood blocks. The measured retention of wood blocks treated with formulations containing Pr was very close to the target retention (Table 1). Results indicated that Pr complexed using the method described did not influence the penetration of the preservative complexes (Cu and Cu/B) into the sample wood blocks. Although southern pine sapwood has a very permeable microstructure, Pr is a large molecule and did

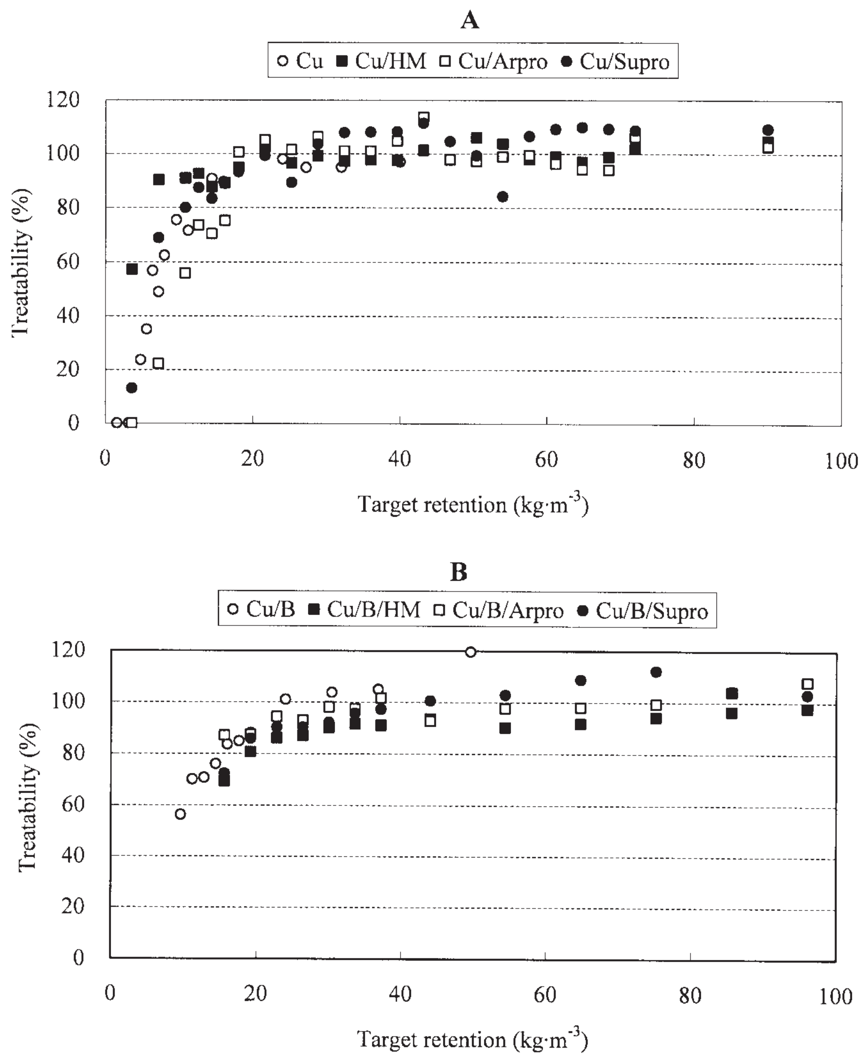

FIG. 2. Treatability of preservative formulations containing (A) $CuSO_4$-soy products (Cu/Pr) and (B) $CuSO_4$-$Na_2B_4O_7$·$10H_2O$-soy products (Cu/B/Pr). Results indicate the dry-weight gain of each wood sample from different formulations. HM (Honey Mill 90; Harvest State, Mankato, MN); Arpro (Arpro 2100; ADM, Decatur, IL): Supro (Supro 760; Protein Technologies International, Palatine, IL).

not penetrate uniformly into the wood blocks. Therefore, ammonium hydroxide was used as a dissociating agent to alleviate the penetration problem. Figure 2 shows the treatability of preservative formulations containing $CuSO_4$-soy products (Cu/Pr, panel A) and $CuSO_4$-$Na_2B_4O_7$·$10H_2O$-soy products (Cu/B/Pr, panel B). The retentions of Cu/Pr and Cu/B/Pr preservatives in wood samples increased with increasing concentration of the treating solution (Fig. 2), indicating that the molecular size of dissociated soy product-based preservatives was small enough to penetrate freely into the wood structure. A minor deviation between the target and measured retentions might have been due to the loss of soluble wood materials during the treatment. There were no significant differences in the treatabilities of Cu/Pr formulations. However, in the Cu/B/Pr formulations, the particular type of soy product influenced treatability. For instance, the treatabilities of Cu/B/HM, Cu/B/Arpro, and Cu/B/Supro formulations, were 93.40, 100.86, and 103.87%, respectively. The treatabilities of Cu/B/Arpro and Cu/B/Supro formulations were significantly higher than that of the Cu/B/HM formulation ($p = 0.02$), perhaps because of the protein content in the soy products used in this experiment. In other words, Arpro and Supro contain more protein, which chelates metal ions, causing their treatabilities to be higher than HM.

Leachability of Pr-based preservatives. The leachability of each preservative formulation was the percentage weight loss of the wood blocks treated by a preservative formulation caused by hot water leaching. Figure 3 shows the stability of Cu/Pr and Cu/B/Pr preservatives against hot water leaching. The leachabilities of Cu, Cu/HM, Cu/Arpro, and Cu/Supro were 18.76, 24.74, 15.65, and 13.23%, respectively. There was no significant difference between the leachabilities of Arpro

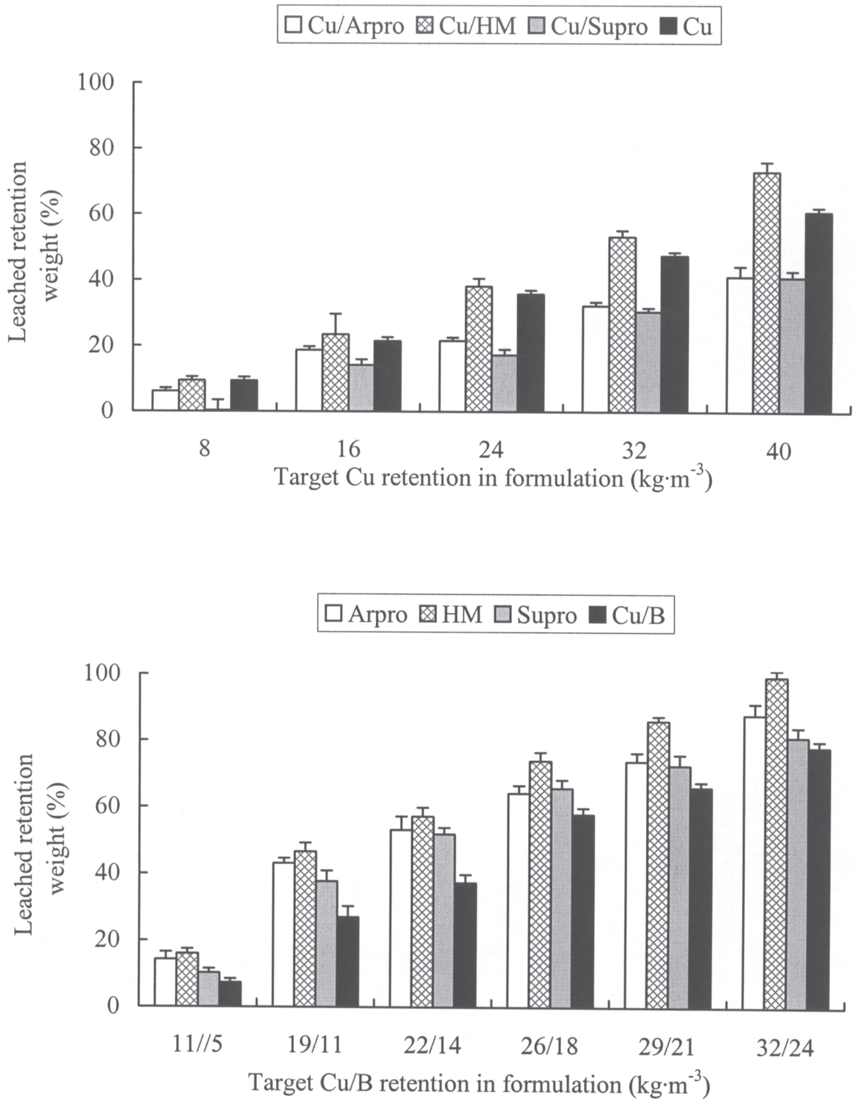

FIG. 3. Leachability of wood blocks treated with Cu/Pr and Cu/B/Pr formulations. Leached retentions were obtained by extraction in 70°C water for 72 h (sample size: 12). For suppliers and abbreviations see Figure 2.

and Supro ($p = 0.76$). However, Arpro and Supro were more effective in fixing copper than Cu alone ($p = 0.03$). For example, approximately 40% of the preservatives were leached out of wood blocks treated with 40 kg·m^{-3} Cu plus 50 kg·m^{-3} Arpro or Supro, compared with 60.8% leached from wood blocks treated with 40 kg·m^{-3} Cu (Table 1). Thus, the proteins actually fixed Cu in the wood blocks. In addition, the leachability of HM was significantly higher than that of Cu ($p = 0.04$), perhaps because of the high solubility of carbohydrates in HM.

Wood samples treated with Cu/B/Pr formulations had much higher leachabilities than wood samples treated with Cu/Pr formulations (Table 1). For example, the leachabilities of Cu/B/HM, Cu/B/Arpro, and Cu/B/Supro were 37.57, 32.78, and 30.38%, respectively. Moreover, wood samples treated with Cu/B (24.48%) showed slightly lower leachability than wood samples treated with Cu/B/Pr (Fig. 3). The higher leachabilities may be attributed to leaching SO_4^{-2}, Na^+, and soluble substances from the wood, as well as fats, minerals, and degradation products in the protein that did not chelate the copper and boron salts.

Efficacy of Pr-based preservatives. Leached wood specimens treated with Cu alone showed about 55% weight loss against *P. placenta* despite increasing the treatment amount from 8 to 40 kg·m^{-3} (Table 1). However, leached wood specimens treated with Cu/Pr showed considerably lower weight loss with increasing amounts of Cu and Pr (Fig. 4). For CCA, the weight losses of wood specimens treated with 2, 4, and 8 kg·m^{-3} were 16.66, 2.03, and 0.38%, respectively (Table 1). Leached wood specimens containing >40 kg·m^{-3} Cu and 50 kg·m^{-3} Pr showed less than 5% weight losses. As shown in Figure 4, the protein types included in

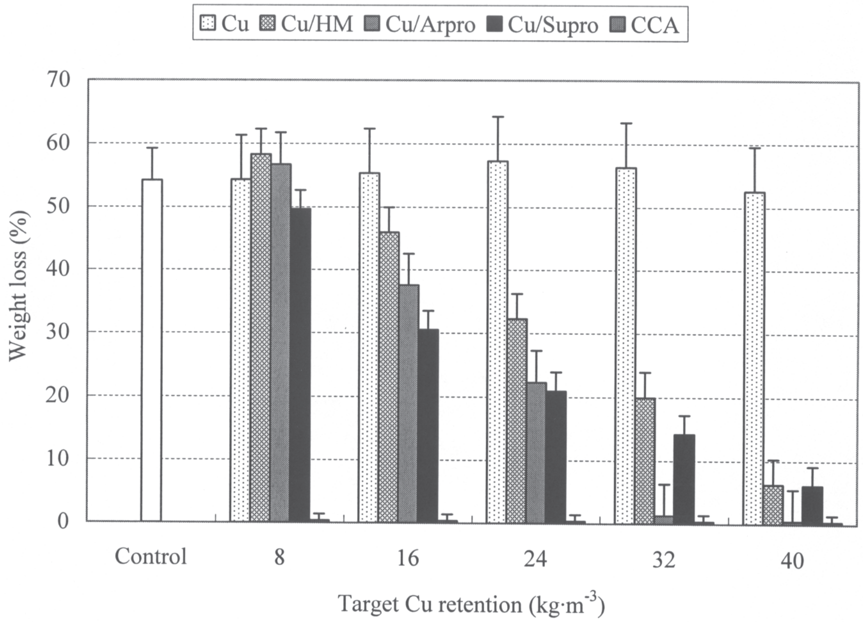

FIG. 4. Decay resistance of leached wood specimens treated with CCA, Cu, and Cu/Pr preservative formulations. Results indicate effectiveness against the brown-rot fungus *Postia placenta* for 12 wk. Each point is a mean representing 12 wood blocks treated with different formulations. For suppliers see Figure 2. CCA, chromated copper arsenate; for other abbreviations see Figure 2.

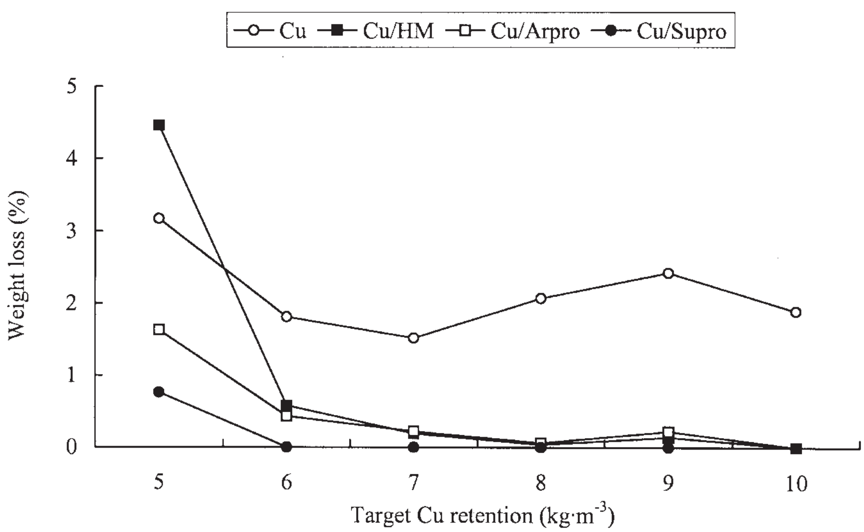

FIG. 5. Decay resistance of leached wood specimens treated with Cu and Cu/Pr preservative formulations. Results indicate effectiveness against the brown-rot fungus *Gloeophyllum trabeum* for 12 wk. Each point is a mean representing 12 wood blocks treated with different formulations.

the wood preservative formulations did not influence the decay resistance against *P. placenta* ($p = 0.47$). In addition, leached wood samples treated with >6 kg·m^{-3} Cu and 7.5 kg·m^{-3} Pr showed less than 0.5% weight loss after exposing them to the copper-intolerant *G. trabeum* (Fig. 5). The results indicate that soy-based preservative formulations protected wood samples against the decay fungi as effectively as CCA. Baechler and Roth (9) reported that wood blocks should contain at least 14 kg·m^{-3} Cu to effectively protect against decay by *P. placenta.* Our results of decay resistance for the Cu/Pr formulations differed, possibly because of the leaching test. Thus, copper sulfate/protein formulations could be used for above-ground protection of wood against brown-rot decay, but their effectiveness for ground-contact applications needs to be evaluated in field trials.

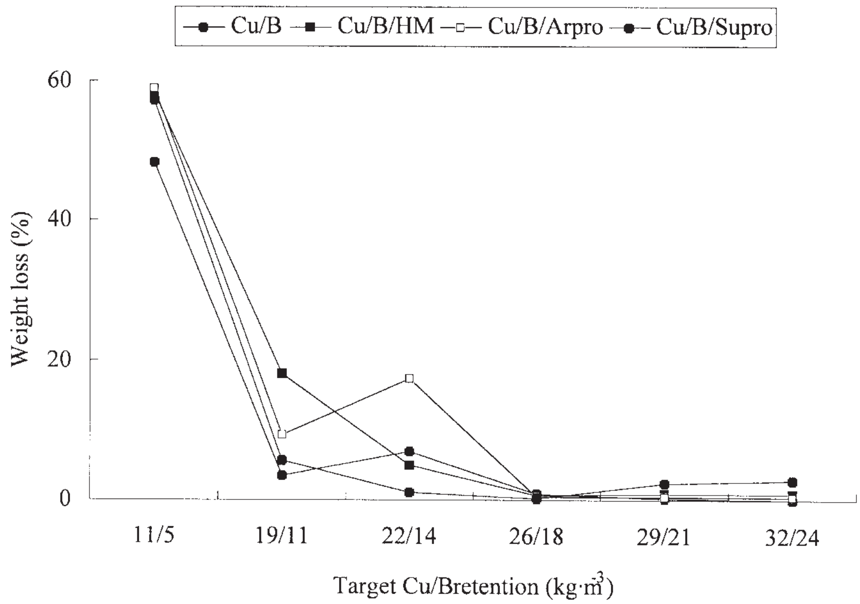

FIG. 6. Decay resistance of leached wood specimens treated with Cu/B/Pr preservative formulations. Results indicate effectiveness against the brown-rot fungus *Postia placenta* for 12 wk. Each point is a mean representing 12 wood blocks treated with different formulations.

Leached wood samples treated with Cu/B/Pr formulations showed good decay resistance against *P. placenta* (Fig. 6). For instance, leached wood specimens containing more than 26 $kg \cdot m^{-3}$ Cu, 18 $kg \cdot m^{-3}$ B, and 34 $kg \cdot m^{-3}$ Pr showed approximately 2% weight loss (Table 1). No significant differences were found between Cu/B and Cu/B/Pr formulations (p = 0.02). Cu/B/Pr formulations showed less weight loss than the Cu/Pr formulation as a result of the boron salts giving the wood excellent decay resistance (Table 1). Johnson and Gutzmer (10) reported that a Cu/B formulation (ammoniacal copper borate: ACB) was very effective against brown-rot decay in laboratory evaluations. However, in their study, wood treated with ACB and exposed in the ground for 6 yr failed to protect the wood against decay and termites because of gradual leaching of boron into the soil. The remaining copper salts were insufficient to protect the wood sample (11). Based on our study, we believe that soy proteins could be used in the ACB formulations to fix the copper component and prolong the service life of the treated wood after the boron has leached out. To demonstrate this assumption, further study is required to analyze the quantity and composition of the leachates and wood specimens used in our study.

Although wood samples treated with Cu/B/Pr formulations showed good decay resistance to *P. placenta*, no apparent advantage was observed in laboratory evaluations. Therefore, the speculated role of soy proteins in ACB formulations needs to be evaluated by field trials. The use of soy products as chelating agents may result in reduced environmental impact compared with CCA, but the soy-based formulations should be evaluated by long-term ground-contact testing.

REFERENCES

1. Preston, F.A., Wood Preservation: Trends of Today Will Influence the Industry Tomorrow, *For. Prod. J. 50(9)*:12–19 (2000).
2. Nicholas, D.D., and T.P. Schultz, Biocides That Have Potential as Wood Preservatives—An Overview, Wood Preservation in the 90s and Beyond, Proceeding No. 7308, Forest Products Society, Madison, WI, 1994, pp. 169–173.
3. American Wood Preservers' Association (AWPA), All Timber Products—Preservative Treatment by Pressure Processes, in *AWPA Book of Standards*, AWPA, Granbury, TX, 1999, pp. 23–32, C1-99.
4. Bland, D.E., Sorption of Copper by Wood Constituents, *Nature 200*:267 (1963).
5. Lin, S.Y., Method for the Treatment of Wood with Metal-Lignin Salts, U.S. Patent 5,246,739 (1993).
6. Thevenon, M.F., A. Pizzi, and J.P. Haluk, Protein Borates as Nontoxic, Long-Term, Wide-Spectrum, Ground-Contact Wood Preservatives, *Holzforschung 52*:241–248 (1998).
7. Laks, P.E., P.A. Mckaig, and R.W. Hemingway, Flavonoid Biocides: Wood Preservatives Based on Condensed Tannins, *Ibid. 42*:299–306 (1998).
8. American Society for Testing and Materials (ASTM), Standard Test Method for Wood Preservatives by Laboratory Soil Block Cultures, in *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2005, pp. 3–4, method D 1413-05b.
9. Baechler, R.H., and H.G. Roth, Laboratory Leaching and Decay Tests on Pine and Oak Blocks Treated with Several Preservative Salts, *Proc. Am. Wood Preserv. Assoc. 52*:24–33 (1956).
10. Johnson, B.R., and D.I. Gutzmer, Ammoniacal Copper Borate: A New Treatment for Wood Preservation, *For. Prod. J. 28(2)*:33–36 (1978).
11. Johnson, B.R., Field Trials with Ammoniacal Copper Borate Wood Preservative, *Ibid. 33(9)*:59–63 (1983).

[Received April 20, 2005; accepted December 12, 2005]