

Wood Preservative Systems Containing Copper and Borates: Efficacy and Synergy

Mike H. Freeman

Independent Wood Scientist
Memphis, Tennessee

Shane C. Kitchens

Terry L. Amburgey
Mississippi State University
Starkville, Mississippi

ABSTRACT

Wood preservative systems containing both copper and borate are discussed. They fall into three groups: (1) Remedial/supplemental treatments composed of pastes or rods containing both borate and copper compounds; (2) Dual treatment of borate-treated wood with oil-borne copper naphthenate; (3) Preservative formulations containing both copper and borate. The efficacies of the various copper-borate preservative systems are discussed together with synergistic effects resulting from combinations of copper and borate. Data presented indicate currently-accepted retentions for copper naphthenate, when utilized in a dual wood treatment system containing sodium octaborate tetrahydrate (DOT), are standardized at a higher than needed level based on 20 year test results and recent soil-block testing.

INTRODUCTION

The wood protection industry has moved from broad-spectrum preservatives towards those more closely matched to the application and exposure environment. Borates and organic biocides have gained importance, but copper remains the primary biocide component in protecting wood in ground contact or fully exposed to weather (Lebow 2007). Research over the last couple of decades has seen the commercialization of preservatives based on copper as the primary biocide, either solubilized as an aqueous amine or ammoniacal complex or in combination with co-biocides to provide protection against copper-tolerant fungi and termites. This paper reviews the efficacy and synergy of treatments that combine copper and boron compounds either in dual treatments or in one formulation containing both of them.

BORATES

Reviews on the world-wide use of borates as wood preservatives attest to their fungicidal/insecticidal efficacies and other properties (Barnes, et al 1989; Carr 1959; Cockcroft and Levy 1973; Drysdale 1994). The attributes of borates as wood preservatives, depending on the compound used, are: low mammalian toxicity, broad-spectrum fungicides and insecticides, corrosion inhibitors, water-soluble, ability to diffuse through cell walls of non-seasoned wood. However, wood treated with water-diffusible borates is not suited, when used alone, for use in ground contact or exterior above-ground exposures where leaching would be a problem. Borates available today offer a highly effective and flexible option for both stand-alone and more specialized formulations. They include formulations prepared from sodium tetraborate, sodium pentaborate, boric acid, or, usually, disodium octaborate tetrahydrate (DOT) (Groenier and Lebow 2006). The biochemical reactions responsible for biocidal activity of borates are based on the reaction of the tetra hydroxyl ion $B(OH)_4$ with polyols of biological significance in wood-attacking organisms in both fungi and insects (Lloyd 1990; Lloyd 1998). In termites, borates act as poison to gut protozoa and/or bacteria, leading to starvation as well as systemic effects.

Wood treated to a minimum retention of 0.2 pcf (pounds per cubic foot) (3.2 kcm, kilograms per cubic meter) BAE is protected from both decay fungi and insects. Table 1 shows conversion factors for converting the various methods of expressing borate retention to one another. Various studies have determined that 0.09 pcf (1.5kcm) BAE is required to inhibit decay and 0.125 pcf (2.0 kcm) BAE for sapstain. No basidiomycete has exhibited tolerance to borates (Amburgey 1990; Lloyd 1998) but they are less effective against molds. Under conditions suitable for molds, wood is non-seasoned and contains large amounts of glucose and fructose, which complex with the borates making them unavailable to complex with polyols of biological significance in the molds (Lloyd et al. 1990). The toxic threshold of boric acid for larvae of *Hylotrupes bajulus* is 0.02 pcf to 0.025 pcf (0.3 to 0.4 kcm). Against larvae of *Anobium punctatum*, 100% extermination is achieved with 0.043% BAE [~ 0.014 pcf]. Borates are highly toxic to *Coptotermes species of subterranean termites* and less toxic to *Nasutitermes species*. In laboratory tests, 0.3% BAE [~ 0.096 pcf] protected pine from significant damage by *Reticulitermes species of subterranean termites*, and >0.54% BAE [~ 0.173 pcf] is needed to protect against *C. formosanus*, the *Formosan subterranean termite* (Lloyd 1990).

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Table 1: Converting from one borate expression of retention to another

Initial retention in pcf B ₂ O ₃	Retention in Kg/m ³ B ₂ O ₃ (multiply pcf by 16)	Retention in pcf <i>Tim-bor/a</i> (multiply B ₂ O ₃ by 1/0.67)	Retention in pcf BAE (multiply B ₂ O ₃ ret. by 1/0.56)/b	Retention in Kg/m ³ <i>Tim-bor/a</i>	Retention in Kg/m ³ BAE/b
0.17pcf	2.72 Kg/m ³	0.25pcf	0.30pcf	4.0Kg/m ³	4.8Kg/m ³
0.28pcf	4.48 Kg/m ³	0.42pcf	0.50pcf	6.72Kg/m ³	8.0Kg/m ³

a = Tim-bor Industrial (DOT) is 67% B₂O₃; Boric acid is 56% B₂O₃; pcf x 16=kcm

b = BAE is boric acid equivalent

Lack of efficacy of borates to mold and soft-rot fungi (non-basidiomycetes) partly explains their poor performance in ground contact; hence, they are frequently used in combination with other biocides (Amburgey 1993). Replacing arsenic in CCA with boron, results in better protection against soft-rot fungi (Gray and Dickinson 1983). Presence of copper in formulations containing borates may be the key to increasing the efficacy of borate-treated wood to soft-rot decay fungi. Copper and borates apparently form a complex that's more fungitoxic than either copper or borates alone (Amburgey and West 1989).

COPPER NAPHTHENATE

Since the 1980's, copper naphthenate (CuN) has gained market acceptance, because of its low mammalian toxicity, for use in crossarms on utility poles, bridge timbers, utility poles, fence posts and lumber. Unlike creosote and pentachlorophenol (penta), CuN is classified by the EPA as a non-restricted use preservative. CuN test history spans several decades and involves a variety of oil-carriers, test sites in different American Wood Protection Association (AWPA) Hazard Zones, sample sizes, rating systems and exposure conditions. CuN is known to control decay fungi, molds, mildew, dry-rot fungi, certain marine growths, termites, and bacteria. CuN has been tested as a stand-alone oil-borne preservative and sometimes incorporated as an additive for creosote.

Railroad companies are continuously looking for ways to improve crosstie life in high-decay hazard areas. Studies have shown that CuN-treated crossties provide service life comparable to that of creosote-treated crossties. Wood treated with CuN, as with other organometallics, is less susceptible to decay by copper-tolerant fungi (by inhibiting oxalic acid production) than water-borne copper biocides (Green and Clausen 2005). Young (1961) and Sutter et al. (1983) postulated that the oil component in CuN physically prevents movement of precipitated copper oxalate to the exterior of the wood surface. Premature failures of CuN-treated poles in the earlier years occurred primarily while the industry was learning how to handle and apply the preservative (Brient, J.A, Freeman, M.H and McIntyre, C.R.).

Numerous reports reviewing the efficacy of CuN against decay fungi when solubilized in various petroleum solvents, using both soil block and agar block techniques, have indicated excellent control over decay organisms with retentions from 0.02 to 0.044 pcf (0.32 to 0.70 kcm) (as copper) in southern yellow pine (SYP) sapwood, including efficacy against copper-tolerant fungi such as *Poria placenta* (Freeman 2002). A test using SYP stakes installed in Mississippi in 1943 compared CuN at 0.5% copper metal in naphtha and 5% pentachlorophenol (penta) in pine oil naphtha. At 20 years, 60% of the penta stakes had been removed from service while only 30% of CuN stakes had been removed due to decay and termite attack (Crawford 2000). Long-term efficacy trials indicate that CuN at 0.03 pcf(Cu as Metal) dissolved in No. 2 diesel oil gives an average predicted lifespan of over 50 years, comparable to that of either clean creosote or penta in heavy oil in the severe decay and termite AWP Hazard Zone 5 in southern Mississippi (Davidson 1977). Data compiled in USDA Forest Service Publication FPL-01 shows that CuN-treated pine round stock gives excellent service life when compared to CCA, creosote, or penta (Freeman 2002). CuN-treated SYP poles used in AWP Hazard Zone 5 require a retention of 0.13 pcf (2.08 kcm) (copper as metal), but posts treated to less than one-quarter of this retention, 0.03 pcf (Cu as Metal), in AWP Hazard Zone 5, have a calculated service life > 65 years (Freeman et al., 2005). CuN-treated hardwood stakes tested in Florida and southern Mississippi(Harrison Plot74) and rated for decay and insect attack showed that 4.5 pcf (72 kcm) creosote is roughly equivalent to 0.08 pcf (1.28 kcm)(copper as metal) in oak (Barnes et al., 2003). Similarly, Brient and Webb (2002) showed that CuN-treated railroad crossties with 0.03 to 0.05 pcf (0.48 to 0.8 kcm) copper, in service for 13 years, were equivalent to ties treated with 7.8 pcf (124.8 kcm) creosote.

Nicholas and Freeman (2000) compared the performance of CuN and penta-treated pine stakes against decay and termites in Mississippi. The depletion rate of penta was somewhat greater than that for CuN. Increasing oil content in the solvent carrier had a positive effect on efficacy. The carrier solvent facilitates the penetration of preservative into wood.

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Wooden blocks, treated with CuN or penta in a similar P9 oil, and tested in accordance to AWWA Standard M-11 for leaching, revealed slight leachability of both preservative systems: 0.49% of the CuN was leached while 1.40% of the penta was leached. Preliminary indications are that copper naphthenate is tightly bound to the wood substrate both chemically and physically, including copper-lignin bond formation, copper-holocellulose bond formation, and copper-extractives bond formation (Freeman 2002). Factors affecting the performance of CuN are the same as those affecting other oil-borne preservatives in treated wood. They include: conditioning method, soil type and soil chemistry at the site of installation of the treated wood, solvent type (carrier solvent), amount of oil in the solvent, and the presence of a co-biocide.

COMBINING COPPER AND BORON PRESERVATIVES

CuN-borate formulations combine the fungicidal effectiveness of copper-containing formulations with the fungicidal and insecticidal effectiveness of a diffusible borate. Copper and boron formulations can be combined in three different ways:

- A. Remedial/supplemental treatments composed of pastes or rods made of copper and borates.
- B. Employing a primary oil-borne wood preservative such as CuN as a dual treatment after a borate pre-treatment.
- C. Wood treated with formulations containing both copper and boron, such as ammoniacal copper borate (ACB), copper chrome borate (CCB and CCA-B)

All three result in synergistic effects with economic and ecological advantages. Application rates are considerably reduced, and it is possible to control a broad range of wood-destroying organisms. The restriction of borates to indoor applications has been overcome by use of dual treatments of oil-borne systems over borate-treated wood or the use of more complex formulations where boron is just one active ingredient in a formulation containing two or more. Research continues to develop borate formulations that have increased resistance to leaching while maintaining biocidal efficacy.

Remedial/Supplemental Treatments of Copper and Borate Compounds

Borates have been used successfully in a remedial/supplemental capacity, especially in the treatment of in-service creosote-treated poles and railway crossties, by inserting borate rods or borate/copper rods, applying borate/copper pastes, brushing with a boron/glycol solution, spraying with borate solution, and injecting borate paste or copper/creosote paste. A properly-applied diffusible boron treatment can diffuse 4 to 5 inches (11 to 12 cm) from the site of installation and can also prevent and arrest decay, primarily in utility poles and railroad ties (Barnes et al., 1989).

Several publications (Amburgey and West 1989, Amburgey and Freeman 1993a and 1993b, Freeman and Amburgey 1997 and Amburgey and Freeman 1997) document results of a field test with a CuN-borate paste (Cu-Rap 20™) for treating the ground line of poles after varying periods of exposure at the Mississippi State University (MSU) Dorman Lake test site (AWWA Hazard Zone 4) from 1987 until 2003. The tests compared performance of the paste with that of penta in a paste-type formulation, and untreated pole stubs. The pastes contained 10% penta in thixotropic paste/gel or a 2% as copper metal CuN and 40% Borax. The pastes were applied to polyethylene film-backed wraps fastened to the below-ground portions of untreated, unseasoned SYP pine pole stubs so that the 18-inch (30.5 cm) tall wraps extended two inches (50 mm) above ground. Untreated controls could easily be broken after 4.5 years by leaning on them. B-CuN treated pole stubs were protected with almost no decay after 10 years, whereas those treated with penta paste had considerable decay at ground line and at the uppermost part of the stubs exposed to rainfall and effects of puddling after just 4.5 years (Amburgey and Freeman 1993).

Sectioning the B-CuN treated pole stubs after 9 years showed that nearly the entire cross sections at ground line were sound but with limited decay. Visual examination and a push test (200 lbs mass pressure) indicated that the treated stubs continued to be protected at ground line after 10 years. The nearest to the ground line that decay was observed in unseasoned stubs treated with B-CuN paste was 18 inches (45.7 cm). Untreated SYP pole stubs that were seasoned before B-CuN treatment had decay 12 to 18 inches (30.5 to 45.7 cm) above the ground line. Penta-paste-treated stubs had some decay throughout their length. After 4.5 to 5.5 years, analysis of the B-CuN treated unseasoned stubs indicated that borate was concentrated both vertically and radially in the first 12 inches (30.5 cm) above ground at levels above those required to protect wood from both brown rot (0.5% BAE; 0.16 pcf; 2.58 kcm) and subterranean termites (0.3% BAE; 0.10 pcf; 1.61 kcm). The distribution of copper was greater than expected. Copper was concentrated 6 inches (15.2 cm) above ground in the stubs that had been seasoned prior to application of the B-CuN paste and also moved more both vertically and radially in the non-seasoned than in the seasoned stubs. After 9 years, most borate was concentrated above ground line in unseasoned stubs while greater concentrations of borate were located below ground line in seasoned stubs. Copper concentrations were greater at and below ground line in seasoned than in unseasoned stubs. Borate and copper both moved vertically and were present in sufficient amounts to protect sections of the stubs 3 ft (0.9 m) above ground. The conclusions were that in Cu-Rap 20™ a diffusible copper/borate complex is formed in the wood (Amburgey and West 1989). The borate-copper complex formed accounted for the movement of copper in these stubs. In addition, the copper-borate complex formed had a toxic threshold

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considerably below that of borate only; wood remained sound in areas where borate concentration was approximately 1/10 the estimated toxic threshold. Synergistically, copper protected against both basidiomycete and soft-rot decay fungi while the B-CuN mixture protected against both decay fungi and subterranean termites. The copper reduces borate leaching via partial fixation.

After 15.5 years, the pole stubs treated with Cu-Rap 20™ had less decay and fewer beetle exit holes than those treated with penta paste (Pol-Nu™), and remained sound at ground line. The ground line areas of most of the stubs had varying amounts of decay, but none of them could be broken. Other studies with this formulation indicate its effectiveness in protecting standing utility poles, even in semi-arid environments. Similarly, other non-published tests at MSU in which unseasoned southern pine posts were diffusion-treated with a borate, dried, and then butt-treated with CuN have demonstrated the effectiveness of copper/borate treatments (Lonnie Williams and Terry Amburgey). While the borate eventually leached to below-threshold levels at the tops of the 6-foot (180 cm) posts, the areas receiving both the copper and borate treatment, and extending several inches above the treated area, remained sound after 10 years exposure. B-CuN paste continues to gain commercial use by both domestic and international utilities.

In another study, Freeman and Amburgey (1997) studied a paste consisting of borax and amine-solubilized CuN applied to polyethylene-backed wraps to below ground portions of pine pole stubs. The stubs remained free of decay and termite damage after 10 years. It was hypothesized that copper-borate complexes formed in the wood were responsible for the long-term protection. Despite leaching concerns, several studies show that B-CuN treated wood retains sufficient boron to prevent attack by basidiomycetes (Amburgey and Freeman 2000).

Work in the mid-1980s by Freeman and West showed that treating the ground line of untreated SYP poles with as little as 1/16-inch (1.6mm) of CuN mixed with a borate extended pole life more than 3 times that of untreated controls. Although the leaching of borates from wood in ground contact occurs, borates present in wood subsequently treated with an oil-borne envelope show a much reduced borate removal rate, and the rate of loss is less at lower moisture contents, and diminishes with lower concentrations (Dickinson, 1993).

Amburgey et al (2003) studied several supplemental treatments for in-service railroad ties. These included borate rods (Pandrol) placed in unused spike holes or in holes drilled adjacent to the tie plates or copper-borate paste applied as pads under new tie plates as rail was replaced. Water-borne or oil-borne CuN spray, or borate rods or spray, applied to the area near one tie plate were other treatments. After 14 years, random inspection concluded that the supplemental treatment with copper-borate diffused through the wood and arrested the growth of fungi that may be present, irrespective of whether it was applied as rods or pastes or spray. Borate color tests confirmed that borate was present throughout the cross-sections, in most cases at levels above the toxic threshold. Highest borate retentions were in holes drilled in the ties that contained borate rods, but placing copper-borate paste under tie plates also was effective. Placing borate rods in through-bored unused spike holes resulted in loss of borate, presumably because the borate drained from the bottoms of the holes as the rods were solubilized by rain. It was apparent that the toxic threshold of the copper-borate paste formulation was lower than that of either copper or boron alone. Overall, borate rods had higher borate retentions after 14 years than the copper borate paste or copper spray.

In a much earlier study, Highley and Ferge (1995) evaluated the distribution of boron and copper from fused rods installed into six-inch (15.2 cm) square timbers of Douglas-fir, SYP, red oak and white oak exposed aboveground for 2 years in Wisconsin. The rods were composed of sodium borate and copper salts. The BAE equivalent penetration and movement was monitored in cores or transverse sections by the curcumin/salicylic acid color test and the presence of copper was detected by the chrome azulol-S reagent (AWPA Book of Standards). Movement of copper from rods was virtually nil. Both transverse and longitudinal movement of boron from rods was greatest in SYP, which also had the highest moisture content (MC), but much lower in all the other species due to lower MC or species anatomy. Comparing this study and that of Amburgey et al., it is clear that copper only moves in the wood when combined with borate in one formulation due to the copper-borate complexes formed.

Dual Treatment Following a Borate Pretreatment

Borate-creosote

Borate dip-diffusion treatments of unseasoned pine poles or hardwood crossties protects them from fungi and insects during air seasoning and protects the interiors as checks and splits develop. Rather than using pressure to drive liquid preservative into dry wood, as with conventional treatment processes, diffusion with borates allows the salts to move through the moisture in the cell walls and lumina of moist wood.

Treating non-seasoned crossties with a DOT diffusible system, then over-coating the exterior sapwood zones has been extensively studied in the USA since 1987 when AAR/RTA/MSU (Association of American Railroads/Railway Tie Association/ Mississippi State University) began a research project to test the hypotheses that borate (DOT) treatment of non-seasoned crossties prior to drying and subsequent creosote treatment could:

- (1) Prevent decay and insect damage during air seasoning;

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- (2) Enhance durability in crossties from both easily treated and refractory species;
- (3) Reduce “spike kill” (iron degradation of both spikes and the surrounding wood) and thereby keep spikes tight and rails aligned.

This study was prompted by poor performance of ties of refractory species (e.g., white oak) in warm, humid areas of the southeastern US (AWPA Hazard Zones 4 and 5) (Amburgey et al 2003; Amburgey et al. 1987). The use of a DOT borate/oil-borne dual treatment with creosote for crossties is now a technical and commercial success in rail ties, and many of the same benefits are likely in the utility pole market with borates dual treated with oil-borne preservatives (Anon. 2003, Amburgey and Kitchens 2006, Amburgey and Kitchens 2011, Gauntt 2002).

Borate-copper naphthenate

Work in the mid-1980's showed that treating the ground line of untreated (Freeman and West 1988) SYP poles with as little as 1/16-inch (1.6 mm) thick paste of CuN mixed with a borate extended pole life more than 3 times that of untreated controls. It is suggested that the pole industry consider initial borate treatment with DOT followed by a treatment with CuN. If the pole stock is treated with a diffusible borate preservative followed by an oil-borne, non-restricted use preservative, like oil-borne CuN, the product can be truly deemed an ‘e-Pole™ (Freeman and Lloyd 2012). With both products being non-restricted and labeled for residential applications, utilization of poles and ties coming out of service in secondary applications is much more flexible. Optional uses after service would include residential landscaping, fencing or mulches. Poles treated by this procedure would have an extended service life and would be essentially free of beetle, carpenter ant and termite infestation in the heartwood, would reduce the need for remedial/supplemental treatment to arrest internal decay, and would ensure that field cuts and wounds caused by equipment installation are already treated, thus eliminating the need for *in situ* treatment (Freeman and Lloyd 2012).

A DOT-pretreated pole subsequently treated with oil-borne CuN is an even better pole than one that is solely CuN-treated. Advantages are: preventing decay during seasoning, control of soft-rot and copper-tolerant fungi (e.g., *P. placenta*), even at DOT levels as low as 0.01 pcf (0.16 kcm). Subsequent treatment with an oil-borne preservative would prevent leaching of borates and protect against soft-rot fungi. Borates, being corrosion inhibitors, retard iron degradation of wood and subsequent loosening of spikes (spike kill) in railroad crossties (Amburgey and Sanders 2009) and will prevent corrosion of fasteners in poles. Decay during air seasoning of poles, especially refractory species, prior to creosote, CuN, penta, or CCA treatment is a serious problem, especially where kiln drying is not employed. Incipient decay occurring during air seasoning can be a source of infection carried into service and/or loss of wood strength and results in highly variable and unpredictable treatments. Kiln drying is expensive and reduces the “kick back” during treatment leading to excessive bleeding after treatment.

Immediate treatment of non-seasoned timber with borates controls incipient decay and protects against insects such as dampwood termites (*Zootermopsis angusticollis*) (Dickinson and Murphy 1991). To date, over 1 million railroad crossties treated with borate and subsequently dual treated with creosote have been installed in different track applications and remain efficacious against decay and termite attack for at least 20 years in AWPA Hazard Zones 4 and 5 and in “wet” climate areas, even though the DOT in their interiors remains mobile and water soluble. Borate diffusion rate and retention are maximized by incising to ½ inch (12.7mm) depth, and treating non-seasoned timber with a preferred MC of 70-90%. MC of mixed hardwoods and gums should be no lower than 40% and oaks and hickories no lower than 50% when treated with borates to maximize the rate of diffusion. A large amount of borate was lost from ties that were vapor-dried following borate treatment, rather than air-seasoned, before the creosote dual treatment (Amburgey et al. 2003).

Comparing creosote-borate and copper naphthenate-borate treatments

Amburgey and Sanders (2009) reported on a field test with railroad crossties that compared the efficacy of borate DOT dual treated with either creosote or CuN. Non-seasoned white oak, red oak and gum ties were either placed in air-seasoning piles with no treatment or given either a single or double one-minute dip in heated TimBor® (30%) or four other borate formulations, each containing 1% Busan® 1030 mold inhibitor. The borate-dipped ties were stacked and covered with polyethylene for 4 weeks of diffusion. Analysis of cores from the mid-points of treated ties confirmed borate diffusion. Double-dipping, with the treatments done on consecutive days (tarpred between dips) resulted in approximately twice the retention of borate that was obtained using a single dip. Portions of the non-seasoned borate-treated and untreated air-dried, ties were treated with creosote or CuN in fuel oil following seasoning. All ties were placed on a gravel bed at the MSU Dorman Lake field test site (AWPA Hazard Zone 4) in June 1986. A spike was driven into one end of ties within each treatment group to determine the effects of treatments on iron deterioration (spike kill). After one year, a portion of the ties in each treatment group were inoculated in holes drilled near the tie midpoints with active cultures of either *Lentinus lepideus* (brown-rot) or *Trametes versicolor* (white-rot) basidiomycete decay fungi using inoculated wooden dowels.

After 20 years of exposure, the inoculated fungi became established in the ties not pre-treated with borate. Ties given either a single or double one minute borate dip and subsequently treated with creosote or CuN had no insect damage and little

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or no internal decay, even after inoculation with *L. lepideus* and *T. versicolor*. The decay fungi in the treated dowels moved only a very short distance from the dowel before being controlled. The surfaces of the borate-creosote ties looked better than those of the borate-CuN ties because the creosote provided greater protection of the tie surfaces from soft-rot fungi under the pine straw that had accumulated on top of them than did CuN. This difference in surface appearance had no relation to internal decay of the ties (Table 2). Most of the borate-creosote or borate-CuN ties, and some of the red oak and white oak ties given only a borate treatment, retained sufficient borate after 20 years to flash red when sprayed with the AWPAA-approved curcumin boron indicator, suggesting that borates do not leach out as rapidly as they diffuse into wood. The coloration indicates presence of boron at levels equal to or greater than 0.049 pcf (0.80 kcm). Most of the ties treated with TimBor (DOT) alone were not serviceable. Untreated ties were completely destroyed except for portions of white-oak heartwood. Pre-treatment with borates protected the interiors of ties from decay fungi and insects during air-seasoning and in service, and the subsequent dual treatment minimized borate leaching and controlled soft-rot fungi. Lack of spike kill in borate pre-treated ties confirmed that borate-treated wood is not corrosive to ferrous metals. These results verify those obtained using DOT borate-treated ties subsequently treated with creosote and exposed on active rail lines (Amburgey, et al. 2003).

Table 2: Performance ratings for the ties with 20 years of exposure in AWPAA hazard zone four

Treatments	Species	Exterior Ratings	Interior Ratings	Loose Spikes
Untreated	Gum	0	0	All
	Red Oak	0	0	All
	White Oak	0	0	All
Creosote	Gum	9.8	9.4	0
	Red Oak	8.6	8.5	0
	White Oak	8.5	8.0	0
CuNap	Gum	6.0	8.0	0
	Red Oak	6.5	4.0	1
	White Oak	7.0	5.7	0
TimBor	Gum	0	0	5
	Red Oak	2.0	1.1	2
	White Oak	3.0	2.3	3
TimBor-Creosote	Gum	9.3	9.4	1
	Red Oak	8.3	10	0
	White Oak	8.8	9.6	0
TimBor-CuNap	Gum	8.0	9.7	0
	Red Oak	7.7	10	0
	White Oak	7.2	8.8	0

(Rating 10= No deterioration; 0=Failure)

New Soil Block Screening Studies

In a more recent study, Amburgey and Kitchens (2010) evaluated the performance of dual-treated borate and CuN or creosote blocks in soil-block laboratory tests (AWPA E-10) in SYP sapwood and Red Oak and exposed to *G.trabeum* for 12 weeks. Solvents studied were Diesel Oil #5 (Hunt Southland Refining Company) and toluene, which was used as a control. SYP sapwood was first treated with 0.733% B₂O₃ a.i., dried at room temperature and then treated with CuN (0.03, 0.06, 0.09, 0.12, or 0.17% a.i.) in #5 oil solvent at 3 and 5 pcf (48-80 kcm) or creosote (18.1% and 12.0%). A second set of SYP blocks was given single treatments with CuN or creosote. Red Oak was given similar treatments but at higher borate and copper concentrations: 1.16 % B₂O₃ and CuN (0.09, 0.18, 0.27, 0.36, or 0.49% a.i.) and higher retentions of creosote (53.29%, 6 pcf, 96 kcm and 35.52%, 4 pcf, 64 kcm). A summary of the results are shown in Figures 1, 2, 3 and 4.

In both SYP and red oak, samples pre-treated with B₂O₃ had much less weight loss than those not pre-treated (CuN or creosote only). These data show that copper in combination with B₂O₃, was more effective, in this test, than creosote with the same level of borate pretreatment. This supports the hypothesis that a borate-copper complex, that is more efficacious than either biocide alone, is formed between the borate and CuN when wood is dual treated with borate and copper naphthenate. The same cannot be said of the creosote-borate combination. The treatment was more efficacious in SYP as compared to red oak, which exhibited higher weight losses. The effect of oil retention level was not clear from these data, but treating samples with CuN alone, at the highest oil retention tested (7pcf, 112 kcm), was not as effective as being dual treated with borate.

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A comparison of the lowest level of copper tested versus the highest level of creosote can be seen in Figure 4. Because both sets were pretreated with borates, the higher efficacy observed in both SYP and red oak for the CuN dual treatment, is evidence of a synergistic performance not observed in borate-creosote samples.

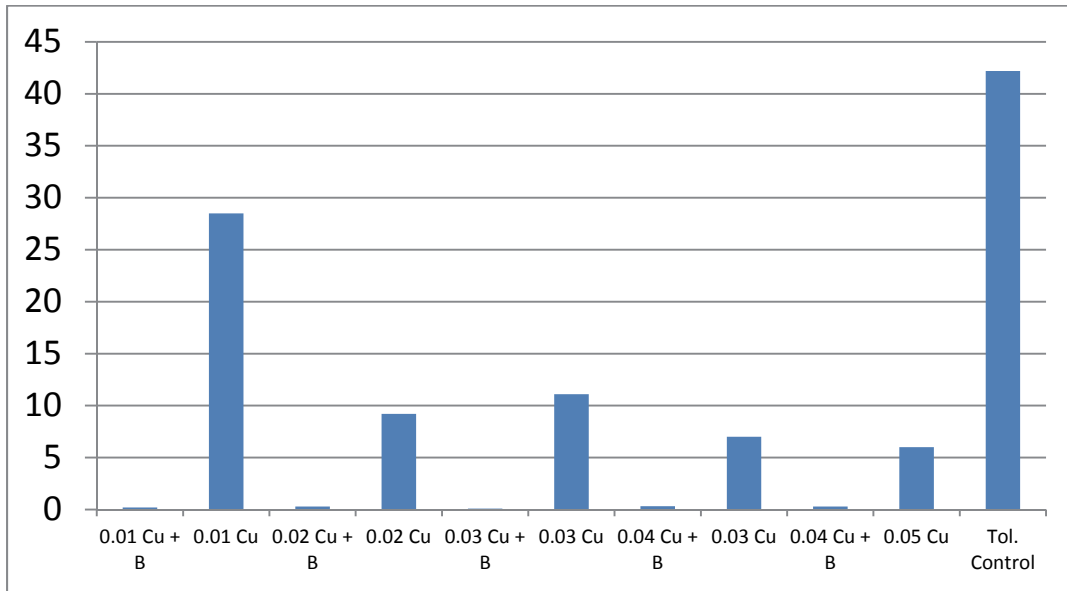


Figure 1: Percent weight losses in southern pine sapwood blocks treated with copper naphthenate and oil (5 pcf) that had either been pre-treated with borate or untreated prior to copper naphthenate treatment. Blocks were exposed to *Gloeophyllum trabeum* in a soil-block test. Controls were treated with toluene.

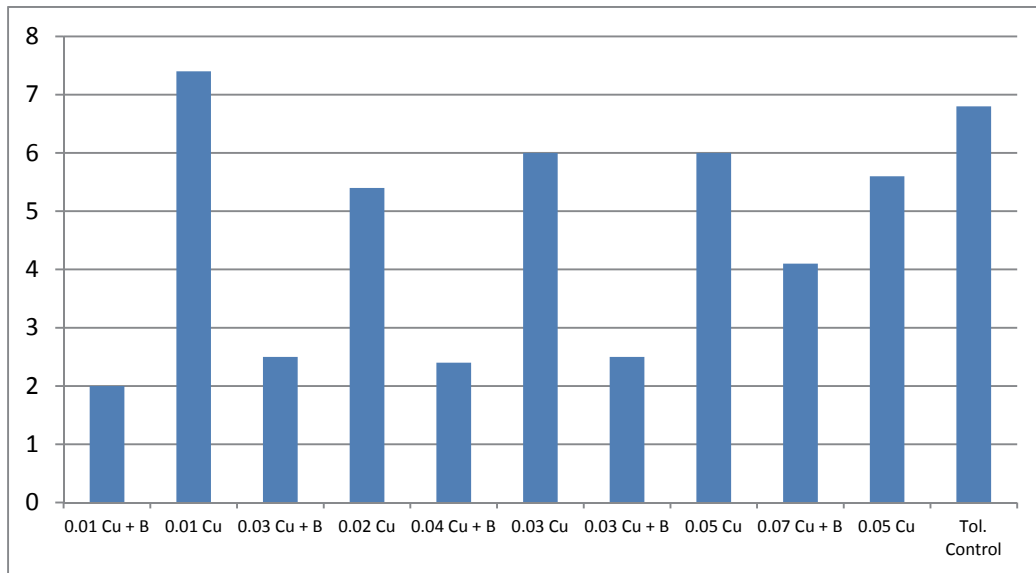


Figure 2: Percent weight losses in red oak blocks treated with copper naphthenate and oil (5 pcf) that had either been pre-treated with borate or untreated prior to copper naphthenate treatment. Blocks were exposed to *Gloeophyllum trabeum* in a soil-block test. Controls were treated with toluene.

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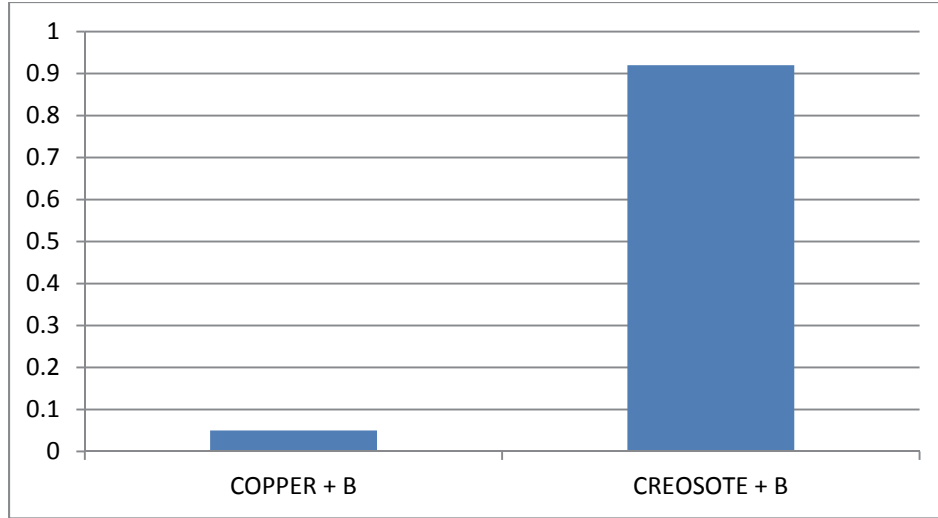


Figure 3A

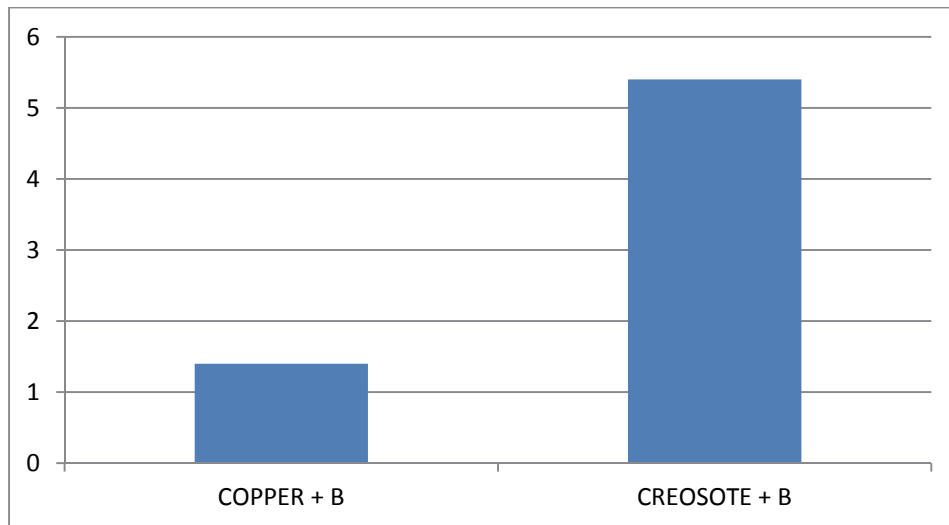


Figure 3B

Figure 3: Weight losses of pine (3A) or red oak (3B) blocks treated with copper naphthenate in oil (3 pcf) after pre-treatment with borate. Blocks were exposed to *Gloeophyllum trabeum* in a soil-block test

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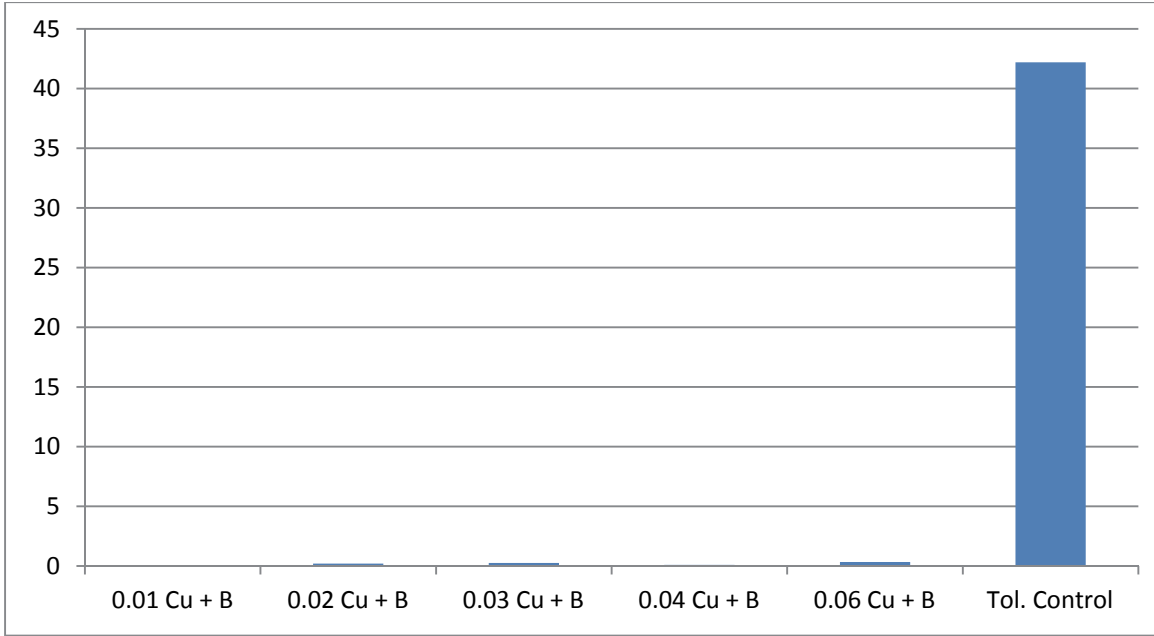


Figure 4A

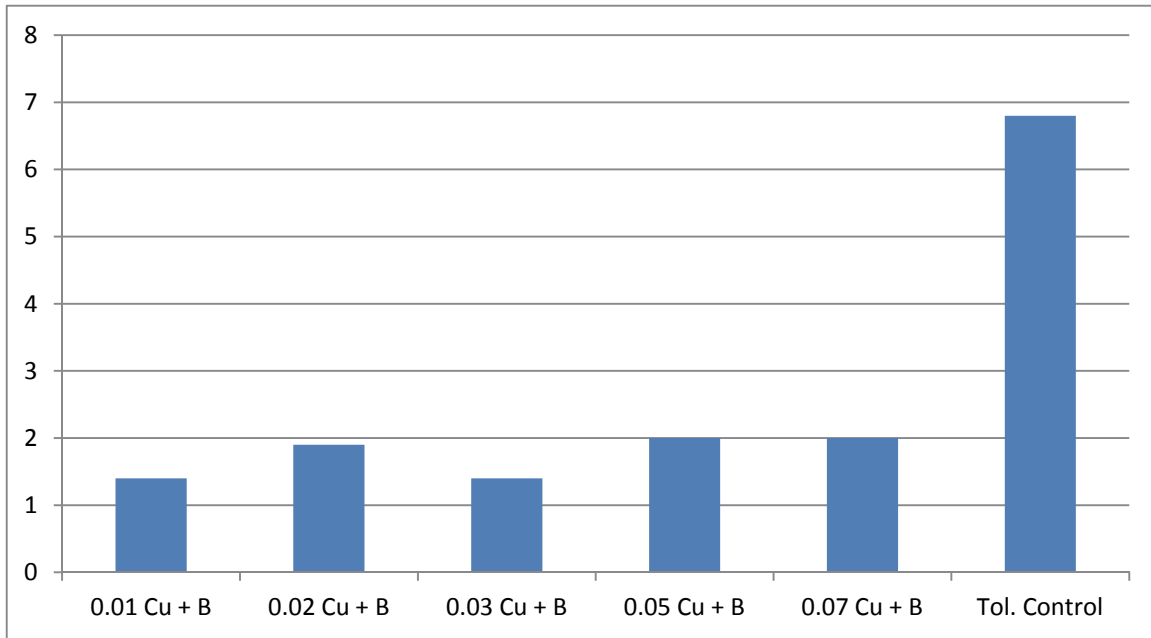


Figure 4B

Figure 4: Comparing the efficacies of the lowest retention of copper naphthenate plus borate (Cu + B) compared to the highest retention of creosote plus borate in red oak (4A) or southern pine (4B) blocks exposed to *Gloeophyllum trabeum* in a soil-block test

Formulations Containing Copper and Boron

The restriction of borates to indoor applications has been overcome by use of more complex formulations where boron is just one active ingredient in a formulation containing two or more biocides. From environmental, health and safety considerations, a number of copper-chrome formulations were developed and co-existed with CCA. These include ammoniacal copper borate (ACB) and formulations in which the arsenic component of CCA was replaced with borate, phosphate or fluoride. Penetration, fixation and efficacy were different from CCA, and none of them showed evidence of a

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copper–borate complex. However, increased efficacy is exhibited because borates control copper-tolerant fungi and soft-rot fungi in environments where this is a problem. The text below will discuss some of these inorganic formulations that contain copper and borate.

Ammoniacal copper borate (ACB)

ACB is formulated with 5% copper sulfate, (1.25% Cu) and 2% ‘TimBor’ (DOT) (2.38% H_3BO_3 ; 0.42% B). The preservative solution is best prepared with slight excess of ammonia to prevent copper precipitation. Vinden and McQuire (1984), using freshly-sawn radiata pine sapwood boards treated by soaking in ACB, showed that during treatment or diffusion storage, copper borate tended to precipitate in solution and settle on boards, thereby blocking wood capillaries. Copper penetrated 0.12 to 0.16 inches (3 to 4 mm) whereas boron penetrated the total cross-section. Partial fixation of copper by ion exchange on fixation sites in the cell wall limited its penetration and distribution. Before copper diffusion can proceed, fixation sites must be filled. Increase in storage period would not result in better copper distribution. There is no evidence of a copper-borate complex in this formulation.

During most of the last decade, the volume of wood treated annually in the United States with waterborne salts such as chromated copper arsenate, copper quat, copper azole, micronized copper and ammoniacal copper zinc arsenate has increased markedly while the total volume of pressure-treated wood has remained relatively constant, with the exception of the market drop in 2008. This growth in the use of waterborne salts may be attributed in part to the treated wood’s attractive appearance, cleanliness, and freedom from odor, but also is due to the price increase in carrier solvents for penta and the 7 + times price increases for creosote-containing systems.

However, there has been growing concern about the chronic toxicity of inorganic arsenicals, which manifested itself in a large way with the industry voluntary cancellation of residential uses in Dec 2003, and including a proposed Occupational Safety and Health Administration Standard for exposure to inorganic arsenic published in the Federal Register (January 21, 1975). These concerns stimulated JH Baxter to look at alternatives for arsenic in ACA, including boron; hence, the USDA-FPL began testing ACB in 1975 as a result of growing interest in the substitution of boron for arsenic in ammoniacal copper arsenate. Gordon (9) apparently envisioned such a possibility when he obtained a patent on boron, copper, and zinc salts in ammoniacal solution as wood preservatives in 1940.

The toxicity to wood-destroying fungi of borax ($Na_2B_4O_{10}H_2O$), boric acid (H_3BO_3), and other boron compounds has been recognized for many years (Freeman et al). Borates are used extensively today worldwide, but their use began predominately in New Zealand and Australia, primarily in diffusion treatments, where the treated wood was not exposed to leaching. In the United States, borates continue to be used in substantial amounts in fire-retarding preservative formulations.

They have also been widely used in the U.S. in interior exposures because of their lower level of leach resistance. Comprehensive literature reviews of boron as a wood preservative or component thereof have been published. Studies were undertaken by Bruce Johnson at the USDA-FPL to determine the decay and termite resistance of leached and unleached wood treated with solutions of ammoniacal copper borate.

By laboratory evaluation, the resistance of ACB-treated wood to termites and decay fungi was excellent. Leaching of the treated blocks caused some loss in preservative, with a consequent increase in the amount of the preservative needed to prevent damage by termites or decay fungi. The retention required was not greatly different from ACA, which is commercially used and generally regarded as very effective under severe decay and termite conditions (Johnson, B. and Foster, D. 1991).

ACB-treated blocks, without prior leaching, were more resistant to decay by the arsenic-tolerant fungus, *Gloeophyllum trabeum*, than were ACA-treated blocks. The two were equally effective when the blocks were leached prior to decay testing. The two preservatives were quite comparable in resistance to the copper-tolerant fungus, *Poria placenta*, when the treated blocks had been leached. Without leaching, ACB-treated blocks were only moderately less resistant to this fungus than ACA-treated blocks. Analysis of leachate by atomic absorption suggested that less boron is leached from ACB-treated blocks than might be expected with diffusion-type boron wood preservatives (Johnson and Foster 1991).

Although results of the ongoing field tests will be needed for verification, it appears that ammoniacal copper borate could quite satisfactorily replace ammoniacal copper arsenate for ground contact exposure of preservative-treated wood. Recommendation of this preservative for aboveground exposure does not seem premature.

ZiBOC

Tripathi et al (2005) studied the fixation of a water-insoluble composition prepared by reacting zinc chloride, borax and copper sulphate in a fixed ratio that resulted in slightly green-colored compound-ZiBOC. Although boron was retained because of chemical bonding in the new compound formed, there is no mention of reduced efficacy in this report. In poplar (*Populus deltoides*) blocks (0.75 inch or 1.9 cm cubes), scanning electron micrographs showed a difference in the structure of parent constituents and ZiBOC. Boron has rhombohedral shapes, copper has face-centered cubic shapes, and zinc has hexagonal close packed crystals, but ZiBOC was shown to have rhombohedral hexagonal shapes, completely different from

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the original components. Fixation may be based upon the simple precipitation of ZiBOC in wood structure as the solvent/co-solvent evaporates. In poplar, ZiBOC exhibited only 23.6, 13.1 and 12.1 % leachability of copper, zinc and boron, respectively, after 168 hrs of leaching. In *Pinus roxburghii*, leachability was 53.5, 6.5 and 5 %, respectively. Only 0.01% of the salt caused 60-65% growth inhibition of the white-rot fungus *Polyporus (Trametes) versicolor* and the brown-rot fungus *Poria monticola*. At 0.03% ZiBOC, 98% inhibition in growth of both fungi took place, while 0.05% killed the fungi. Only 0.50% of the salt (0.20 pcf, 3.13 kcm) protected Poplar completely against the white rot fungus *P. versicolor* and the brown rot *P. monticola*; untreated control samples had 52.1% weight loss. In pine, 0.2% (0.09 pcf, 1.39 kcm) and 0.1% (0.04 pcf, 0.68 kcm) of ZiBOC the blocks were completely protected when exposed to *P. versicolor* and *P. monticola*; untreated blocks had weight losses of 54% and 11.4%, respectively.

Chromated Copper borate (CCB)

In view of arsenic toxicity, CCB used in India and parts of Western Europe was the first non-arsenic containing formulation introduced as a safer alternative for CCA. The first CCB formulation contained 35.3% copper sulphate, 47.1 % sodium dichromate and 17.6 % boric acid. Modifications of the formulation contain potassium dichromate and chromium trioxide (Hedley 1992). CCB has wide application ranging from high-exposure situations such as marine applications, ground contact in fencing posts and rails, and also is used for indoor applications such joinery and furniture. There is evidence of improved copper penetration in the presence of borate (Kumar and Morrell 1998; Gray and Dickinson 1983), although there is no evidence of a copper-borate complex in this formulation.

Kumar and Morrell (1988) evaluated the gross absorption and penetration of CCA, CCB, CCAB and boric acid at retentions normalized to 2.5% in sawn boards of three U.S. western wood species. Penetration was measured using chrome azurol S for copper, curcumin/salicylic acid for boron, and ammonium molybdate/O-anisidine/stannous chloride for arsenic. As shown in Table 3, of the five formulations tested, CCB and CCB-A produced the highest retentions and preservative depth of penetration. CCB and CCB plus arsenic also produced the deepest penetration. Boron completely penetrated the cross section and also appeared to enhance copper penetration. Penetration depth was less in formulations with no borate, reflecting wood-chemical interactions that result in preservative being deposited near the wood surface, blocking pits and restricting fluid flow. The presence of boron appeared to retard copper precipitation, resulting in deeper penetration of both copper and arsenic. Boric acid buffers the treating solution, retarding fixation and permitting deeper preservative penetration. Small amounts of borate may significantly improve penetration of copper-based preservatives.

Table 3: Gross preservative absorptions as measured by weight gain after a full-cell treatment with 2.5% CCA or CCB

Preservative	Drying method	Location	Average retention (Kg/m ³) for 30 replicates		
			Douglas Fir	Pacific Silver Fir	White Fir
CCA-C (oxide)	Air drying	Sapwood	6.58 (0.51)	9.59 (0.20)	6.8 (1.00)
	Air drying	Heartwood	3.02 (0.70)	9.32 (3.05)	
	Kiln drying	Sapwood	8.75 (1.32)	8.24 (1.60)	5.65 (0.65)
	Kiln drying	Heartwood	4.14 (0.62)	6.48 (0.87)	
CCB	Air drying	Sapwood	8.17 (1.81)	9.88 (0.73)	7.65 (1.36)
	Air drying	Heartwood	3.62 (0.70)	8.41 (1.77)	
	Kiln drying	Sapwood	10.20 (1.97)	10.41 (1.46)	7.57 (0.74)
	Kiln drying	Heartwood	5.46 (1.52)	7.66 (0.21)	
CCB +A	Air drying	Sapwood	7.00 (1.70)	9.09 (0.55)	6.23 (2.13)
	Air drying	Heartwood	3.05 (0.50)	7.51 (1.80)	
	Kiln drying	Sapwood	9.40 (0.88)	9.08 (0.65)	7.03 (0.71)
	Kiln drying	Heartwood	6.80 (0.53)	5.93 (0.43)	

*(SD) in parenthesis

Efficacy of CCB in comparison with CCA

Several studies have shown that CCA is only superior to CCB where copper-tolerant brown-rot decay fungi are present, since arsenic controls copper-tolerant fungi. CCB is superior to CCA in controlling soft-rot fungi because greater amounts of copper are absorbed during treatment and because the boron component has a higher efficacy against soft rots (Gray and Dickinson 1983; Wakeling 1991). A better distribution of Cu across the cell wall, and penetration and mobility of boron, in hardwoods is achieved using CCB; hence it performs better in hardwoods tested in non-leaching environments (Gray and Dickinson 1983; Wakeling 1991; Hedley 1992; Hedley et al. 1996). Boron is lost during leaching, but the leaching occurs very slowly and the residual boron has a significant effect on soft-rot fungi. In field situations, the increased performance

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against soft-rot fungi is diminished because the wood becomes susceptible to copper-tolerant brown-rot fungi as boron is leached (Gray and Dickinson 1983).

In a 16 year field study, Hedley et al. (1996) further demonstrated the influence of climate and fungal flora. CCB performed better than CCA in a waterlogged site where soft-rot fungi dominated. In conditions which favor the occurrence of brown-rot fungi (low rainfall and sandy soil), CCA was superior and showed steady deterioration, whereas CCB showed sudden failures. Table 4 shows the results of a study by Yamamoto and Rokova (1991) comparing the effectiveness of CCA, CCB and boric acid against the brown-rot fungus *Tyromyces palustris*. CCA maintained good efficacy both in softwoods and hardwoods, while CCB lost effectiveness after leaching.

Table 4: Weight losses (%) in unleached and leached blocks after exposure to the brown rot fungus *Tyromyces palustris* (Results of leached blocks in parenthesis)

Preservative	Treating solution (%)	Wood species			
		<i>Cryptomeria japonica</i>	<i>Tsuga heterophylla</i>	<i>Sterculia Parkinsonii</i>	<i>Anthocephalus cadamba</i>
Control	0.0	55.3 (56.0)	56.8 (61.6)	62.3 (53.7)	37.8 (61.4)
CCA-type C	0.1	2.5 (12.8)	33.9 (44.2)	32.7 (44.0)	4.5 (34.3)
	0.6	0.0 (0.7)	8.1 (5.0)	6.6 (6.3)	1.1(5.5)
	1.8	0.0 (0.0)	0.1 (1.4)	0.6 (1.3)	0.6 (3.0)
CCB	0.1	27.2 (52.1)	47.5 (82.7)	61.1 (60.3)	23.9 (57.3)
	0.6	0.5 (12.5)	24.1(31.5)	33.1 (24.0)	6.0 (46.8)
	1.8	0.4 (13.8)	5.0 (15.6)	9.9 (18.3)	2.6 (27.0)
Boric acid	0.1	0.0 (48.4)	13.4 (51.2)	3.5 (56.9)	1.2 (46.0)
	0.6	0.0 (49.0)	0.1(49.0)	2.3 (60.2)	1.7 (50.1)
	1.8	0.5 (45.9)	0.6 (52.7)	1.0 (62.7)	2.1 (45.4)

Yamamoto and Rokoba (1991).

Copper tolerance in CCB

As in other copper-based formulations, the tolerance of fungi to CCB formulations is exhibited by formation of insoluble non-toxic copper oxalates. Boron in CCB influences the growth of copper-tolerant fungi after the other heavy metals are inactivated through the formation of oxalates in non-leached samples (Humar et al. 2004). Copper tolerance is also likely due to lowering of the pH of the substrate by boric acid rather than the low solubility of copper oxalate (Humar et al., 2005). Attempts to combine the efficacies of CCA and CCB to control both basidiomycetes and soft-rot fungi used CCAB formulated by substituting 50% of arsenic in CCA with boric acid. In a soft-rot trial, and in a field test, this formulation was found less effective than CCA. This was attributed to poor fixation of Cu and As and confirms that CCB is ineffective against copper-tolerant brown-rot fungi (Gray and Dickinson 1983).

Comparing fixation and leaching of CCA and CCB

Chromium-containing formulations undergo fixation when the Cr^{6+} is reduced by wood components to Cr^{3+} and combines with copper and arsenic to form the insoluble complexes CrAsO_4 , CuCrO_4 , Cu(OH)CuAsO_4 (Gray and Dickinson 1987; Pizzi 1990). Arsenic catalyzes chromium-reduction, and its absence in CCB slows fixation and prevents formation of the insoluble complexes CrAsO_4 and Cu(OH)CuAsO_4 . Only insoluble CuCrO_4 is formed, reducing fixation. Boron does not take part in fixation reactions and remains wholly unchanged and leachable. The proportion of initially-adsorbed copper in wood is higher in CCB-treated timber because of higher pH and lack of arsenic interference with initial copper adsorption due to lowering of pH by arsenic acid (Gray and Dickinson 1983). The retention and distribution CCB in wood tissues of full-cell treated light red meranti (*Shorea leprosula*), studied by Electron Probe Microanalyser (EPMA), before and after exposure for 72 months, detected Cr concentrated in vessel walls while Cu was concentrated in the rays; boron was well-distributed in all tissues. While Cu and Cr leach at an exponential rate, Boron leaches at a rather constant and higher rate because it remains unchanged. After three years of field exposure, CCB-treated poles had a loss of 30% of boron, 1.3% of copper and 0.05% of chromium (Peylo and Willeitner 1997).

SUMMARY & CONCLUSIONS

Copper and borate treatments can be combined by use of formulations containing both copper and boron (e.g., CCB) or using oil-borne CuN as an envelope biocide over a borate diffusible pretreatment. This combines the fungicidal effectiveness of copper-containing formulations with the fungicidal and insecticidal effectiveness of a diffusible borate. A review of numerous studies shows that in CCB and CCB-A, boron completely penetrates the cross section and enhances copper

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penetration. Trace amounts of borate can and do significantly improve penetration of copper-based preservatives. The presence of boron retards copper precipitation, resulting in deeper penetration and distribution of copper across the cell walls. There is some evidence of a copper-borate complex being formed, but most of the boron remains unchanged and subject to leaching. The evidence points to the fact that the leaching occurs very slowly and the residual amounts of borate remaining are sufficient to protect against soft-rot and basidiomycete decay fungi, and insects such as Formosan subterranean termites.

In a CuN-borate paste used at ground line for remedial/supplemental pole treatments, the distribution of copper has been greater than expected. Both borate and copper diffused vertically and horizontally, suggesting that a borate-copper complex formed accounts for the movement of copper. This complex has a toxic threshold considerably below that of either borate or copper alone. The copper reduces borate leaching via partial fixation. In formulations with no borate, diffusion of copper is virtually nil. In a dual treatment of hardwood crossties with CuN following a treatment of non-seasoned wood with DOT borate, and seasoned prior to CuN treatment, borate remained biologically efficacious after 20 years. The efficacy of the treatment was higher than that of CuN only. This supports the hypothesis that a borate-copper naphthenate complex that is more efficacious than either biocide is formed between the borate and CuN but not with the creosote-borate combination. Besides formation of copper-borate complexes, wood treated with B-CuN exhibits less susceptibility to copper-tolerant fungi than that observed in inorganic copper formulations. Young (1961) postulated that the oil component in CuN physically prevents movement of precipitated copper oxalate to the exterior of the wood surface. There is strong evidence that, when used in combination with borate, AWWPA-recommended CuN retentions should be lowered.

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