International Biodeterioration & Biodegradation 70 (2012) 74–78

Contents lists available at SciVerse ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Field tests of the efficacy of zinc and fatty amine in preventing colonization by copper-tolerant fungi

Stan Lebow[a,*], Bessie Woodward[a], Steven Halverson[a], Michael West[b]

[a] USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726, USA
[b] Senatobia, MS, USA

ARTICLE INFO

Article history:
Received 20 April 2011
Received in revised form
14 February 2012
Accepted 15 February 2012
Available online 8 March 2012

Keywords:
Preservative
Field tests
Copper
Zinc
Fatty amine
Copper tolerance

ABSTRACT

Ground-contact durability of stakes treated with acidic copper formulations was evaluated. All test formulations incorporated copper, dimethylcocoamine and propanoic acid; one set of formulations also included zinc. Sapwood stakes cut from the southern pine group were pressure-treated to a range of retentions with each formulation and placed into plots within Harrison Experimental Forest in Mississippi and compared with untreated stakes and chromated copper arsenate-treated stakes. Stakes were inspected and given a visual condition rating after 1, 2, 3, 4, 5, and 7 years. Most stakes at higher retentions remained in good condition after 7 years; sporadic failures occurred in all but the highest retention of the zinc formulation. The sporadic nature of fungal attack by a fungus thought to be a strain of *Antrodia radiculosa* indicates that failures were caused by copper-tolerant fungi. At the concentrations evaluated, neither the dimethylcocoamine nor the propanoic acid offered adequate protection against copper-tolerant fungi. Addition of zinc notably increased decay resistance, and absence of failures at the highest retention may indicate that zinc can help to protect against copper-tolerant fungi. However, the sporadic nature of copper tolerance makes this finding difficult to confirm. Inspection of theses stakes will continue.

Published by Elsevier Ltd.

1. Introduction

Traditional water-based preservative formulations such as chromated copper arsenate (CCA) relied heavily on copper because of its excellent fungicidal properties. Although multiple chromium and arsenic-free alternative wood preservatives have been introduced in recent years, those intended to protect wood used in contact with soil continue to use copper as the primary fungicide. Acidic copper solutions without chromium can be highly corrosive to metal fasteners, and to lessen this concern, these alternative formulations use alkaline formulations of copper. Organic fungicides such as quaternary ammonium or azole compounds are included in these formulations to help protect the wood from attack by copper-tolerant fungi. These formulations also use higher concentrations of copper than did CCA, and there is some indication that this alkaline copper is less resistant to leaching than the acidic form used in CCA (Waldron et al., 2005; Temiz et al., 2006). Ideally, an acidic formulation would be effective at lower copper concentrations, more similar to that used in CCA. One rationale for the expected decay resistance of an acidic copper formulation is the performance of copper formate and acid copper chromate- (ACC-) treated stakes exposed at FPL's Harrison Experimental Forest test site. Although these formulations have not been as consistently effective in protecting wood as CCA, many stakes remained in good condition for over 40 years (Woodward et al., 2011). Some early failures did occur with these treatments, which may be attributable to attack by copper-tolerant fungi.

Colonization and decay caused by copper-tolerant fungi has long been recognized as a major concern for copper-based preservative treatments (Morrell, 1991). Numerous fungi have been shown to have some degree of copper tolerance in laboratory testing (Sutter et al., 1983; De Groot and Woodward, 1999; Green and Clausen, 2003), and attack of wood treated with copper formulations has also been reported in field testing (Schultz and Nicholas, 2009, 2010). The extent and severity of attack of copper-treated wood products in-service is not well understood, but commercial copper-based preservatives typically include a co-biocide to minimize this risk. Arsenic was an effective co-biocide in CCA, and most current commercial alkaline and dispersed copper formulations use quaternary amine or azole co-biocides.

In this study, we evaluated the durability of acidic copper formulations using copper concentrations below the level used in

* Corresponding author. Tel.: +1 608 231 9411; fax: +1 608 231 9592.
E-mail addresses: slebow@fs.fed.us (S. Lebow), bwoodward@fs.fed.us (B. Woodward), shalverson@fs.fed.us (S. Halverson).

0964-8305/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.ibiod.2012.02.003

Table 1
Retention of individual preservative components in treated stakes.

Solution type	Solution (%)	Retention in stakes (kg/m^3)					
		CuO[a]	Dimethylcocoamine[b]	Propanoic acid[b]	ZnO[a]	B_2O_3[a]	Total
CDP	0.45	0.63	0.69	1.68	–	–	3.01
CDP	0.89	1.14	1.25	3.03	–	–	5.41
CDP	1.34	1.65	1.80	4.39	–	–	7.85
CDP	1.78	2.04	2.23	5.43	–	–	9.70
CDP	2.23	2.33	2.55	6.21	–	–	11.09
CDP	2.67	3.04	3.33	8.11	–	–	14.48
CZDP	0.33	0.30	0.27	1.09	0.28	–	1.94
CZDP	0.66	0.78	0.65	2.59	0.61	–	4.63
CZDP	0.99	0.91	0.77	3.10	0.75	–	5.53
CZDP	1.32	1.51	1.28	5.11	1.23	–	9.13
CZDP	1.65	1.46	1.23	4.92	1.17	–	8.79
CZDP	1.98	2.01	1.71	6.85	1.66	–	12.23
CZDP + B	0.66 + 0.28 B_2O_3	0.69	0.59	2.35	0.57	1.20	5.39
CZDP + B	1.32 + 0.56 B_2O_3	1.28	1.05	4.22	0.98	2.54	10.07

[a] Determined by ICP analysis of milled wood.
[b] Estimated from solution composition and assayed concentration of CuO and/or ZnO.

conventional alkaline-copper formulations. A fatty amine (dimethylcocoamine), and in some cases zinc oxide, were included in the formulation to provide protection against copper-tolerant fungi and to lessen concerns with corrosion (Williams et al., 1994; West, 2004). Previous research has shown that fatty amine salts exhibit toxicity to microorganisms through cell membrane disruption (van Ginkel et al., 2008) and can inhibit decay by some types of fungi (Butcher et al., 1977; Preston, 1983). Although zinc is a somewhat less effective fungicide than copper (Barnes et al., 2004; Woodward et al., 2011) it has been widely used as a component of wood preservative formulations (Richardson, 1993). Propanoic (propionic) acid was also used in the formulations, primarily to improve solubility. However, propanoic acid does have efficacy against mold fungi in crop storage and food products (Sheaffer and Clark, 1975; Suhr and Nielsen, 2004), and may also contribute to the formulations' performance. To evaluate these formulations, stakes treated with a range of retentions were placed into the ground at a test site in Harrison Experimental Forest in southern Mississippi. The presence of copper-tolerant fungi at this site has been reported previously (Lebow et al., 2003; Schultz and Nicholas, 2010). This report discusses the decay and termite resistance of the treated stakes after 7 years of exposure.

2. Materials and methods

2.1. Preservative formulations

Two sets of formulations were tested. All formulations used copper hydroxide, dimethylcocoamine, and propanoic acid solubilized in water. One set of formulations also contained zinc oxide.

CDP: The CDP formulation had a composition of 21% copper (CuO basis), 23% dimethylcocoamine, and 56% propanoic acid. Specimens were treated with 0.45, 0.89, 1.34, 1.78, 2.23, and 2.67% solution concentrations.

CZDP: CZDP was composed of 18% copper (CuO basis), 12% zinc (ZnO basis), 14% dimethylcocoamine, and 56% propanoic acid. Specimens were treated with 0.33, 0.66, 0.99, 1.32, 1.65, and 1.98% solution concentrations. Two additional treatments were included to evaluate the value of adding boron to the CZDP. These were 0.66% CZDP + 0.28% B_2O_3 (0.5% boric acid) and 1.32% CZDP + 0.56% B_2O_3 (1.0% boric acid). In this paper these treatments are referred to CZDP + B.

Reference preservative: A 1% solution of chromated copper arsenate Type C (CCA-C) was included as an established reference preservative for both types of formulations. Based on AWPA Standard P5 (American Wood Protection Association Standards, 2011a), the CCA-C had an actives composition of 47.5% chromium (CrO_3 basis), 34.0% arsenic (As_2O_5 basis), and 18.5% copper (CuO basis).

2.2. Stake preparation and treatment

Twenty-five stakes (19 × 19 × 457 mm) per treatment group were cut from clear sapwood of the Southern Pine species group and conditioned to constant weight in a room maintained at 23 °C (74 °F) and 65% relative humidity. As described in AWPA Standard E7 (American Wood Protection Association Standards, 2003), the stakes were sorted by weight to minimize differences in density between treatment groups. Each set of 25 stakes was treated with one of the preservative formulations using a full-cell pressure process. The initial vacuum was maintained at −75 kPa (gauge) for 30 min; the pressure was maintained at 1.03 MPa for 1 h. Following treatment, the stakes were stacked in plastic bags for one week and then allowed to air-dry under room conditions. Five of the stakes from each of the test formulations were randomly selected and set aside for chemical analysis of preservative retention. Sections cut from these stakes were milled and digested in accordance with AWPA Standard A7 (American Wood Protection Association Standards, 2011b) and concentrations of copper and/or zinc and boron (as appropriate) were determined by inductively coupled plasma emission spectrometry (ICP–AES) (Table 1). The ICP analysis revealed that stakes treated with the 1.65% CZDP solutions had unexpectedly low copper and zinc retentions (Table 1). The cause of this anomaly is unclear, but it must be considered when reviewing the durability of this treatment group. An additional 20 untreated stakes were also prepared for installation in the plots.

Table 2
Typical rating scheme for evaluation of stakes.

Rating	Description of condition
10	No evidence of attack
9	Slight attack, up to 3% of cross-sectional area
8	Moderate attack, up to 10% of cross-sectional area
7	Moderate to severe attack, up to 30% of cross-sectional area
6	Severe attack, up to 50% of cross-sectional area
4	Very severe attack, up to 75% of cross-sectional area
0	Failure, can be broken easily by hand or the evaluation probe can penetrate through the stake