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Long-Term Outdoor Efficacy Trials of Wood Treated with Organic Biocides and Co-Added Non-Biocidal Additives

Tor P. Schultz
Darrel D. Nicholas
Forest Products Department/FWRC
Mississippi State University

ABSTRACT

Wood preservatives for residential applications are moving towards totally-organic systems. However, organic biocides are relatively expensive and are biodegraded over the long service life expected from treated wood. To address these two deficiencies we have employed low-cost and benign additives that enhance the efficacy of organic biocides against wood-destroying organisms, and/or reduce biodegradation by wood-inhabiting organisms such as molds and bacteria. In this paper we present efficacy results of southern pine sapwood treated with various organic biocides with and without co-added antioxidants, metal chelators, and water repellents and tested for five or more years in ground-contact or above-ground exposure. The addition of a water repellent to above-ground samples greatly enhanced the biocide's efficacy, and the greatest benefit was observed with all three additives. The addition of the antioxidant BHT also reduced biocide depletion in one ground-contact test by about 50%. Ground proximity samples treated with relatively low levels of two organic biocides, DCOI and Propiconazole:Tebuconazole, with and without co-added BHT and a metal complexing compound, have been recently installed to verify the above results.

INTRODUCTION

Wood preservation is undergoing dramatic and rapid world-wide changes. While copper-rich systems are currently employed to treat lumber for residential applications in North America, most professionals expect that totally-organic third generation systems will be required in the future. Two main concerns with organic biocides are a high cost per unit weight relative to copper and biodegradation that can occur over the long service life from various microorganisms, including wood-inhabiting but non wood-destroying organisms such as molds and bacteria. To address these problems we are employing non-biocidal additives to increase an organic biocide's efficacy and/or reduce biodegradation (Schultz and Nicholas 2008).

We selected the additives based upon the fundamental knowledge of wood-degrading mechanisms. Specifically, it is well known that wood-degrading fungi employ metal-mediated reactions (Rodríguez et al. 2003; Henry 2003) to generate free radicals that attack the wood chemical components (Reading et al. 2003; Messner et al. 2003; Goodell 2003). Further, it has long been known that many wood extractives have excellent antioxidant and metal complexing properties (Binguga et al. 2005, 2007a and 2007b, 2008; and the terpenoids provide good water repellency that lowers the decay potential. Thus, we have examined the efficacy gained by co-adding antioxidants, metal chelators, and water repellents with various organic biocides to wood (Schultz and Nicholas 2000, 2002, 2005, 2008, Schultz et al. 2005). In various laboratory and field trials efficacy increases up to three-fold were often obtained. Furthermore, the addition of BHT to ground-contact field stakes installed at two locations lowered the depletion of the organic biocide, chlorothalonil, by about 50% after 54 months' exposure (Schultz et al. 2006).

The purpose of this article is to review above-ground and ground-contact efficacy results of wood treated with various organic biocides, with and without co-added antioxidants, metal complexing compounds, and/or water repellents, and exposed outdoors for at least five years.

CHLOROTHALONIL FIELD STAKES WITH BHT

Field stakes, 19 x 19 x 457 mm made from defect-free southern pine sapwood, were treated with 0.15, 0.3 and 0.5% chlorothalonil (CTN) dissolved in toluene, with and without the additive BHT at 0, 2 and 4% levels. The stakes were treated by a full cell process then installed in ground contact at the Dorman Lake, MS, and Saucier, MS test sites. After about 3 years the controls had all failed. The results, after 105 months at Dorman Lake and 108 months of exposure at Saucier, are shown in Table 1, based on the AWPA E7 ratings. Originally 10 replicates per treatment per site were installed, but at 54 months of exposure three replicate stakes per treatment per site were destructively analyzed and the CTN and BHT depletion determined relative to an unexposed sub-sample cut from the stake before field installation.

BHT is a common antioxidant, with about 75% used in plastics and 20% added to human foodstuffs. Thus, BHT is approved for food use; more precisely, BHT is classified as a Generally Recognized As Safe (GRAS) compound. It is also relatively inexpensive in technical grade, about $1.20/lb recently, but more expensive for the high purity grades added to plastics or foods. It is also highly hydrophobic and, thus, should not leach in water.

The results show enhanced efficacy with both decay fungi and termites when BHT is co-added at both sites and at all three biocide retentions. Indeed, stakes treated with BHT alone performed about as well as stakes treated with only the biocide at the lowest level. However, the best efficacy enhancement appears to be at the two higher biocide levels employed of 0.3 and 0.5%, while the BHT level, 2 or 4%, does not appear to be important. On the lack of a BHT level effect; we believe that since BHT is not a biocide that there is no dose response curve, as long as some BHT is present it will help protect the wood. The apparent lower BHT effect at the lowest CTN treatment level of 0.15% may be due to the need to have some minimal biocide level when BHT is co-added, as BHT alone provides only some limited fungal protection.

While the antioxidant concept was developed for decay fungi, it also increased termite efficacy. A later depletion study (Schultz et al. 2006) showed that BHT reduced CTN depletion by about 50%. Consequently, at first we thought that the increased termite efficacy may be due to the greater biocide present in stakes with co-added BHT as compared to the CTN levels in stakes without BHT. However, stakes treated with BHT alone also had greater termite resistance. Subsequent laboratory AWPA E1 termite choice tests with BHT-treated wafers showed that BHT alone will repel termites and, surprisingly for a food additive, greatly increase termite mortality (AWPA Poster at this meeting.)

QUAT MINI LAP-JOINTS WITH ANTIOXIDANT, METAL CHELATOR AND WAX

Mini-lap joints made with defect free southern pine sapwood were installed at Viance's Hilo, HI, site. The samples were treated by a full-cell process with a quat formulation of Barlox and DDAC. Additives included propyl gallate, BHT, phenanthroline, and a paraffin wax water repellent, in various combinations.

Propyl gallate is an antioxidant also employed in food, and is a semi-synthetic derivative of gallic acid obtained from hydrolysable tannins with the carboxyl group modified with a propyl group to increase hydrophobicity. It is relatively expensive, and in prior ground-contact field tests poor results were obtained which was likely due to its slight water solubility, 0.35% at room temperature, causing slow leaching over a few years. Propyl gallate also has unusually good metal chelating properties (Bubgina 2005) and in laboratory decay tests gave very good results (Schultz and Nicholas 2002), likely due to its combined antioxidant and metal chelating properties.

While we were able to identify a low-cost, benign and non-leachable antioxidant, BHT, we could not identify a non-leachable metal complexing agent. Laboratory studies were conducted with EDTA salts that showed our concept was sound (Schultz and Nicholas 2002), but EDTA is very soluble. Thus, we selected an oil-borne metal complexing agent, phenanthroline, for outdoor exposure tests. However, this compound is relatively expensive and toxic.

The average decay ratings after six years of above-ground exposure at Viance's Hilo, HI, research site are given in Table 2. The addition of wax had a large impact. For example, at the lowest quat level with 1.0% propyl gallate the average ratings was 0.9, but with 1% wax added the average ratings increased to 8.2 When all additives were employed ratings were above 9.0 for all quat retentions. This is similar to laboratory experiments where the best results were obtained when both an antioxidant and metal chelator were employed (Schultz and Nicholas 2002).

PROPICONAZOLE/WAX MINI LAP-JOINT WITH PROPYL GALLATE

Mini lap-joint samples were constructed from defect-free southern pine sapwood, treated with a full-cell process and installed five years ago at both Viance's Hilo, HI and MSU's Saucier, MS test sites. The organic biocide was propiconazole with and without propyl gallate co-added, with 1% paraffin wax added to all formulations to reduce propyl gallate leaching. The wax had a large effect on reducing decay; the average decay rating of the wax-only treated controls was 6.9 and 3.8 after 4 and 5 years of exposure, respectively. The control samples in Saucier, which has a lower decay hazard than Hilo, had an average ratings of about 8.5 after five years of exposure and none of the propiconazole-treated samples had any decay. Thus, only the Hilo results are shown.

Table 3 shows the decay ratings after 4 and 5 years of exposure in Hilo. The addition of propyl gallate increased the efficacy of samples treated with the two lowest levels of propiconazole. For example, samples treated with only 0.05 or 0.1% propiconazole and wax had decay ratings of 9.0 and 9.1 after five years, while the samples with co-added 0.5 or 1% propyl gallate all had higher decay ratings of 9.4 to 10.0. As with the BHT:CTN ground-contact field stakes, employing a higher level of propyl gallate did not result in greater efficacy.

A relatively rapid decrease in efficacy was noticed for samples treated with the two lower levels of propiconazole without propyl gallate in the 5th year. This may be due to biodegradation of the organic biocide, which concerns the authors.

FUTURE TRIALS

As mentioned above, while metal complexing compounds were found to improve efficacy in laboratory decay experiments we were unable to identify a safe, benign, economical and hydrophobic compound that would be suitable for wood preservation. However, we recently reported that resin acids, isolated from the chemical pulping of southern pine and called tall oil rosin, or TOR, may serve this purpose. One commercial use of TOR is to complex metals, and TOR also has a GRAS classification. TOR costs about $0.40/pound, and is extremely hydrophobic and so does not leach from wood. Furthermore, in a waterborne emulsion formulation TOR imparts some water repellency to wood, increasing the dimensional stability in above-ground exposure.

To verify the effectiveness of TOR, and conduct tests with additional biocides, the authors initiated a study that employed the organic biocide DCOI or Propiconazole:Tebuconazole. Relatively low biocide levels were employed so that decay would occur relatively quickly and the effect of the additives determined. Ground-proximity samples, made from defect-free southern pine sapwood, were treated by a full-cell process with two levels of each biocide with and without BHT and/or TOR co-added. These samples were installed at the Saucier, MS and Viance's Hilo, HI test plots in February 2007.

No decay in any of the samples treated with a biocide was observed at the first year's inspection at both Saucier and Hilo, but the untreated controls and samples treated with only the additives had some decay. The authors hope that decay will be observed shortly in some of the biocide-treated samples so that the effect by co-adding the BHT antioxidant and/or the TOR metal complexing compounds can be determined. Furthermore, some depletion samples were pulled at the first year and the results, which should be available shortly, indicate if BHT and/or TOR reduces biodegradation of the organic biocides.

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Table 1. Average decay and termite ratings for field stakes treated with chlorothalonil (CTN) and the antioxidant BHT, and exposed for 105 months at Dorman Lake, MS, and 108 months at Saucier, MS.

Treatment (wt. %)		Average Retention (kgm^{-3})	Dorman Lake		Saucier	
CTN	BHT		Decay	Termite	Decay	Termite
0 (Control)	0 (Control)	---	0	0	0	0
0	4.0	19.4	2.9	4.8	2.4	0.4
0.15	0.0	0.74	3.0	3.1	1.6	0.6
0.15	2.0	0.72/9.5	6.7	7.0	5.6	4.1
0.15	4.0	0.70/18.8	6.4	6.4	5.9	3.9
0.30	0.0	1.47	5.7	7.1	3.5	2.7
0.30	2.0	1.54/10.1	7.9	8.7	8.0	7.3
0.30	4.0	1.41/18.8	8.0	8.1	6.0	5.1
0.50	0.0	2.42	8.3	8.6	2.7	5.3
0.50	2.0	2.41/9.6	9.9	9.9	9.0	8.6
0.50	4.0	2.43/19.5	8.1	9.9	9.3	8.4

Table 2. Average ratings for mini lap-joint samples exposed for six years at Hilo, HI. Samples with co-added wax, as a water repellent, are indicted by WR in the biocide treatment, with the samples treated using a full-cell process. 0.07% DDAC and 0.19% Barlox gave a retention of about 0.48 and 1.44 kg/m^3, 0.4% BHT about 2.3 kg/m^3, 0.2% Phen (phenanthroline) about 0.9 kg/m^3, and 1% water repellent (paraffin wax) about 4.6 kg/m^3.

% Barlox + DDAC	% Propyl Gallate	% BHT	% Phen	Average Ratings at Six Years
	0.5			0.5
	1.0			3.9
		0.4		0
			0.2	3.6
0.07 + 0.19				0
0.07 + 0.19	0.5			1.0
0.07 + 0.19	1.0			0.9
0.07 + 0.19 + WR	1.0			8.2
0.07 + 0.19		0.4		1.0
0.07 + 0.19 + WR		0.4	0.2	9.2
0.14 + 0.37				1.2
0.14 + 0.37	0.5			2.7
0.14 + 0.37	1.0			7.4
0.14 + 0.37 + WR	1.0			8.1
0.14 + 0.37		0.4		2.0
0.14 + 0.37 + WR		0.4	0.2	9.5
0.21 + 0.56				3.9
0.21 + 0.56	0.5			3.6
0.21 + 0.56	1.0			4.5
0.21 + 0.56 + WR	1.0			7.7
0.21 + 0.56		0.4		7.4
0.21 + 0.56 + WR		0.4	0.2	9.4
1.12 kg/m^3 CCA				10

Table 3. Average ratings of mini lap-joint samples treated with propiconazole/1% wax by a full-cell process and exposed in Hilo,HI. The retention with 0.05% propiconazole was about 270 grams/m^3 and about 540 grams/m^3 with 0.1% propiconazole.

% Propiconazole	**% Propyl Gallate**	**Decay Ratings, 4 Years**	**Decay Ratings, 5 Years**
0.05	0	9.9	9.1
0.05	0.5	10	10
0.05	1.0	10	9.7
0.1	0	9.9	9.0
0.1	0.5	10	9.9
0.1	1.0	10	9.4
0.2	0	10	10
0.2	0.5	10	9.7
0.2	1.0	10	9.9
Controls, wax only		6.9	3.8