Pressure Treatment with a Water-based Chlorothalonil Formulation

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ABSTRACT

This study evaluated the ability of a waterborne chlorothalonil (CTL) formulation to penetrate into Southern Pine lumber during pressure treatment. Treatments with a conventional amine copper formulation were conducted for comparative purposes. End-matched specimens cut from southern pine lumber were treated using either a full cell or modified full cell (low weight) treatment schedule. Uptake (by weight gain) of preservative by the specimens was not statistically different for the CTL and amine copper formulations. For both CTL and amine copper treatments, the proportion of active ingredient was significantly greater in the outer (0 - 5 mm) assay zone than in the 10 - 15 mm or 20 - 25 mm assay zones. The difference between proportions of active ingredients in the 10 - 15 and 20 - 25 mm assay zones was not statistically different. The proportion of copper in the outer 0 - 5 mm assay zone was significantly greater than the proportion of CTL in this assay zone, meaning that copper had a steeper retention gradient. There was no statistical difference between the proportions of CTL and copper in the two inner assay zones. The gradients for the full cell and low weight schedules were not statistically different. These findings indicate that the CTL in the water-based CTL formulation penetrated the wood at least as well as the copper in the amine copper formulation, and that this CTL formulation has potential for use in pressure-treatment applications.

Keywords: Chlorothalonil, water-based, pressure treatment, Southern Pine

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INTRODUCTION

Application of chlorothalonil (tetrachloroisophthalonitrile or CTL) to wood protection has primarily been as a surface treatment to prevent growth of mold or sapstain, although a solvent-based CTL preservative was standardized as a potential pressure treatment preservative in1993 (AWPA, 1993). The oil-based formulation has potential disadvantages, including cost, odor and surface cleanliness, which are barriers for use in some applications. These drawbacks can be overcome with the use of a water-based CTL formulation such as those currently being used as additives for paints, caulks and adhesives. However, CTL has low water solubility, and the water-based formulations are dispersions and suspensions. Before these water-based formulations can be accepted for pressure treatment applications the ability of the active ingredients to penetrate the wood during pressure treatment and the efficacy of the water-based formulations in preventing biodegradation must be evaluated. In this study we conducted an evaluation of the ability of a water-based formulation to penetrate into Southern Pine lumber during pressure treatment. Treatments with an amine copper formulation were conducted for comparative purposes.

MATERIALS AND METHODS

***Specimen Preparation*:** Four (n= 4) end-matched Southern Pine sapwood specimens (38 mm by 89 mm by 203 mm) were cut from each of the 9 longer parent boards and labeled as A, B, C or D. The Southern Pine species group was selected for this trial because it represents the majority of treated wood produced in the United States. Specimens were selected to exclude stain fungi, knots, pitch pockets and other defects that might be expected to affect treatment. The specimens were conditioned to uniform weight in a room maintained at 23 C and 65% relative humidity. They were then end-sealed with a neoprene rubber coating (Republic Powdered Metals and Coatings, Beachwood, Ohio) to prevent end-grain penetration.

***Treatment Parameters*:** Two treatment schedules were evaluated. The traditional full cell treatment was used for many years by the pressure treating industry and is still used by mosty researchers when preparing samples for field exposure. The long initial vacuum and pressure period of the full cell process typically produces the deepest and most uniform penetration with water-based preservatives. However, the full cell process also produces a heavier (wetter) proeduct and for many years most Southern Pine treaters have been using a modified (low weight) full cell treatment that uses a lower initial vacuum, shorter pressure period, and a long final vbacuum. Accordingly, a "low weight" schedule was also evaluated in this study (Table 1).

***Treatment Formulations*:** At this time the concentration of w3ater-based CTL that is needed to protect wood from biodegradation has not been established, but a review of the reportsd (Laks and Woods, 1992; Schultz, et al., 2006; Woods et al, 1993; Woods and Bell, 1990) on solvent-based CTL indicates that the effective retention for protecting wood in ground is in the range of 3.2 - 6.4 kg/m^3 (0.2 - 0.4 lb/ft^3). Slightly lower retentions would be expected to be effective in protecting wood exposed above ground. For the purposes of this study we assumed a target CTL retention of 4.8 kg/m^3 (0.3 lb/ft^3), and prepared a formulation of 1% CTL. To allow comparison to the CTL gradient, we also conduicted treatments with an amine copper solution that was prepared to obtain a copper concentration of 0.67% (as CuO).

Table 1. Treatment schedules evaluated

Treatment Schedule	Replicate Charges	Initial Vacuum		Pressure		Final Vacuum		Formulation
		Minutes	kPa	Minutes	kPa	Minutes	kPa	
FPL Full cell	3	30	-85	60	1241	-	-	CTL
Low Weight	3	10	-51	20	1241	30	-85	CTL
FPL Full cell	3	30	-85	60	1241	-	-	Amine CuO
Low Weight	3	10	-51	20	1241	30	-85	Amine CuO

Specimen assignment and replicate charges Three replicate (n = 3) charges of each treatment schedule/preservative formulation were conducted (a total of 4 x 3 = 12 charges). Each charge contained 3 specimens. End-matched specimens from each parent board were assigned to the 4 schedule/formation combinations. Each specimen was weighed before and after treatment to determine uptake of preservative. (Table 2).

Assaying for preservative retention and penetration Following treatment, two cross-sectional wafers were cut from each specimen. Penetration of water/preservative was observed on the cross-sectional face of these wafers, and the wafers were then sectioned to obtain assay zones correspoinding to 0-5, 10-15, and 20-25 mm from the wood surface. The corresponding assay zones from each cross-section and from each side of each cross section were combined to obtain one composite sample for each specimen. The sectioned samples were allowed to air-dry at ambient temperature, and then milled and homogenized for chemical analysis. Milled samples treated with CTL were extracted and analyzed by GC following the procedures provided an American Wood Preservers Association Standard A20, Part 2, Chlorothalonil Assay by Gas Chromatography (AWPA Bood of Standards, 2001). The extraction was conducted at the FPL, and the GC analysis was conducted at a cooperating university laboratory. Samples treated with the amine copper solution were digested and analyzed for copper by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the FPL.

Data Analysis For each specimen, the percent of active in each assay zone (relatively to the sum in all 3 assay zones) was calculated. A statistical analysis was conducted to determine if the gradient of actives was significantly different for copper and CTL, and to determine if the gradient was statistically different based on treatment conditions. Comparisons between assay gradients were based on a spit-plot design with treatment/schedule as the whole plot factor and assay zone as the split plot factor. The analysis also considered that nesting occurs with boards, that assay zone is a factor repeated across space within a block, and that percent active is a constrained variable. Analysis was also conducted to determine if preservative formulation or treatment schedule significantly affected uptake of retention of preservative.

RESULTS AND DISCUSSION

No abnormalities were observed during the pressure treatments. Excessive sludging or precipitation was not observed during treatment with the CTL formulation for either the full cell or low weight treatments.

Preservative Uptake The uptake of preservative liquid (as determined by weight gain) was similar for the CTL and amine copper formulations (Table 2). Uptake with the CTL formulation was slightly greater than the amine copper for the low weight schedule, while uptake of the amine copper solution was slightly greater than the CTL with the full cell schedule. However, these differences were not statistically significant (p-value for interaction=0.1849) (Table 3). As expected, the forumation uptake was greater for full cell (683.0 kg/m^3) than low weight treatments (493.8 kg/m^3), and this difference was highly statistically significant (p-value<0.0001, Table 3).

Visual Penetration The cross-sections cut after treatment were observed for penetration of the treatment formulation. The cross-sections, cut from the specimens treated with amine copper were sprayed with Chrome Azurol S copper indicator to readily observe copper penetration. All but one specimen (from one of the low weight treatments) was fully penetrated. The exceptional specimen was approximately 77% penetrated (an average of 17 mm penetration when measured from the two narrow faces and an average of 12 mm penetration when measured from the two wide faces). All of the CTL treated specimens appeared to be fully penetrated, regardless of treatment schedule. However, because CTL is colorless we could not visually determine whether the penetration observed was the CTL actives or simply water. That question was addressed by comparing the amounts of CTL in the three assay zones.

Penetration Evaluated by Assay The proportion of preservative actives detected in the 0-5, 10-1 5 and 20-25 mm assay zones are shown in Table 2 and Figure 1. For all treatments, the concentration of actives in the outer (0 - 5 mm) assay zone was slightly greater than that in the inner assay zones. This pattern is typical for many wood preservative treatments. As can be see in Figure 1, the gradient for CTL concentration across the three assay zones appears to be slightly flatter than that of copper from the amine copper formulation, indicating that the CTL active penetrated at least as well as the copper.

A statistical analysis was conducted to determine if the proportion of active ingredient in each assay zone differed for copper and CTL, and to determine if this relationship was affected by treatment schedule. Table 4 summarizes part of the analysis of assay zone. The analysis indicates a significant interaction between preservative and zone (p-value=0.0013). Differences in zone were expected and are apparent in the analysis, although their interpretation alone is hindered by the interaction with preservative. The model used in the analysis considered two zones (0-5 and 10-15), while the third zone (20-25) is a linear function of the first two and estimates and comparisons between and within all zones are constructed based on the constrained model. The model also attempted to account for correlations between zones with an unstructured covariance matrix (using proc mixed in SAS Version 9.1). The comparisons of interest are listed in Table 5, with both a comparison-wise p-value and Bonferroni-adjusted p-value (adjustment for multiple, dependent comparisons). The comparisons show that for the outer assay zone, the copper formulation had a higher percent active penetration (adj. p-value=0.0288), while for each of the inner two zones the copper formulation and CTL were not significantly different from each other (adj. p-values of 0.6435 and 0.9612, respectively). For both CTL and amine copper, the proportion of preservative in the outer 0 - 5 mm is significantly greater than that in the 10 - 15 mm assay zone (adj. p-values of 0.0414 and <0.0009, respectively); while the differences between the 10 - 15 and 20 - 25 mm assay zones are not statistically significant for either preservative (adj. p-values of 1).

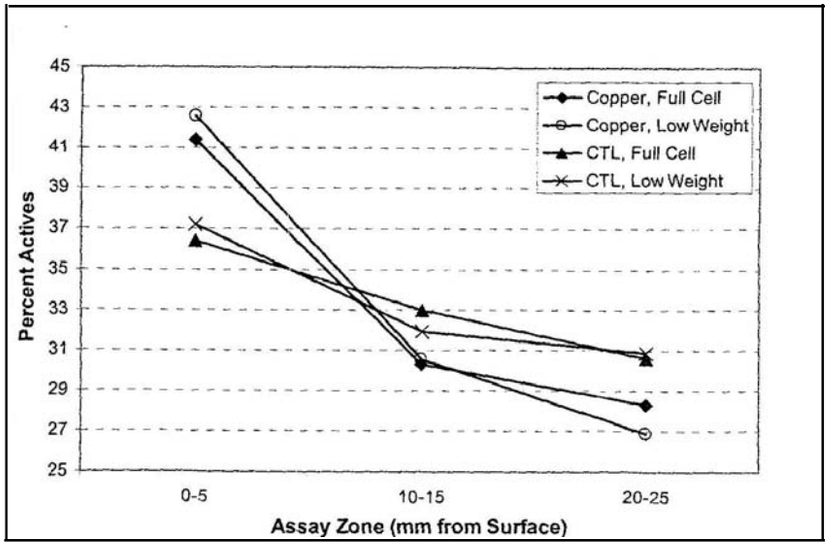

Figure 1. Proportion of copper or CTL detected in each of the three assay zones.

Table 2. Summary of treatment results for amine copper and chlorothalonil charges.

Preservative		Average Formulation Uptake (kg/m³)	Average Retn. by Assay[1] (kg/m³)	Average Percent of Actives in Each Assay Zone 0-5mm	10-15mm	20-25mm
Amine Copper			CuO			
Full Cell	Charge 1	689.4	3.66	39%	31%	30%
Full Cell	Charge 2	662.0	3.38	45	29	25
Full Cell	Charge 3	733.5	4.01	40	31	29
Full Cell	**Average**	**694.9**	**3.69**	**41**	**30**	**28**
Low Weight	Charge 1	488.0	3.19	37	31	31
Low Weight	Charge 2	458.2	2.44	50	29	21
Low Weight	Charge 3	499.4	3.26	40	31	29
Low Weight	**Average**	**481.9**	**2.96**	**43**	**31**	**27**
Chlorothalonil			CTL			
Full Cell	Charge 1	664.7	5.04	37	30	34
Full Cell	Charge 2	653.8	4.34	37	34	29
Full Cell	Charge 3	694.4	5.21	36	36	29
Full Cell	**Average**	**671.0**	**4.86**	**36**	**33**	**31**
Low Weight	Charge 1	460.1	4.07	37	31	32
Low Weight	Charge 2	514.7	4.12	36	30	34
Low Weight	Charge 3	542.4	4.74	39	34	27
Low Weight	**Average**	**505.7**	**4.31**	**37**	**32**	**31**

[1] Combined average across all three assay zones.

Table 3. Analysis of formulation uptake, with a p-value of <0.05 considered significant.

Tests of Fixed Effects				
Effect	Numerator Degrees of Freedom	Denominator Degrees of Freedom	F Value[a]	p-value
Preservative	1	6	0.00	0.9977
Chargetype	1	6	140.49	<.0001
Preserv*Chargetype[b]	1	6	2.24	0.1849

[a]Higher values indicate the effect is important in explaining variation.
[b]Evaluates interactions between effects.

Table 4. Analysis of assay zone, with a p-value of <0.05 considered significant. (Note: The analysis table considers two zones while third zone is a linear function of the first two).

Tests of Fixed Effects				
Effect	Numerator Degrees of Freedom	Denominator Degrees of Freedom	F Value[a]	p-value
Preserv	1	8.86	3.22	0.1068
Chargetype	1	8.86	0.10	0.7539
Preserv*Chargetype[b]	1	8.86	0.22	0.6481
zone	1	32	61.32	<.0001
Preserv*zone[b]	1	32	12.41	0.0013
Chargetype*zone[b]	1	32	0.46	0.5022
Preserv*Charget*zone[b]	1	32	0.05	0.8259

Table 5. Statistical comparisons of percent actives by assay zone, and gradient of actives across zones.

Comparison	Difference	Error	Degrees of Freedom	t Value[a]	p-value	Bonferroni-adjusted[b] p-value
Zone 0-5:AmCu vs CTL	5.17	1.6158	30	3.20	0.0032	0.0288
Zone 10-15:AmCu vs CTL	-2.00	1.0148	12.6	-1.97	0.0715	0.6435
Zone 20-25:AmCu vs CTL	-3.18	1.7710	8.86	-1.79	0.1068	0.96 12
AmCu: 0-5 vs 10-15	11.56	1.4396	32	8.03	<.0001	<.0009
AmCu: 10-15 vs 20-25	2.86	2.1105	4.04	1.36	0.2462	1.0000
CTL: 0-5 vs 10-15	4.39	1.4396	32	3.05	0.0046	0.0414
CTL: 10-15 vs 20-25	1.68	2.1 105	4.04	0.80	0.4702	1.0000
AmCu vs CTL: 1st gradient	7.17	2.0359	32	3.52	0.0013	0.01 17
AmCu vs CTL: 2nd gradient	1.18	2.3919	6.04	0.49	0.6389	1.0000

[a]Higher values indicate a difference between the designated group means.
[b]Adjusted for multiple dependent comparisons.

CONCLUSIONS

This study compared the ability of a water-based CTL formulation and an amine copper formulation to penetrate Southern Pine sapwood during pressure treatment. There was no significant difference in formulation uptake (weight gain) between CTL and the amine copper treatment using either a full cell or low weight treatment schedule. The amine copper treatments resulted in a significantly higher proportion of active ingredient in the outer (0 - 5 mm) assay zone than did the CTL treatment, meaning that copper had a steeper retention gradient. These findings indicate that the CTL in the CTL formulation penetrates the wood at least as well as the copper in the amine copper formulation. The results indicate that this water-based CTL has potential for use in pressure-treatment applications, although further research is needed to confirm this finding.

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