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Effect of Prestain on the Release Rate of Copper, Chromium, and Arsenic From Western Hemlock

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Abstract

To enhance appearance, stains are often sprayed onto western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) lumber prior to treatment with chromated copper arsenate (CCA-C). Recently, concerns have increased that prestaining may affect the rate of leaching of CCA-C components from the treated wood and that leaching data generated with prestained material may not reflect the rate of release from nonstained wood. A secondary concern is that copper naphthenate field treatments applied to wood exposed during construction may contribute to the amount of copper released from CCA-C-treated structures. This paper describes a study in which the release of copper, chromium, and arsenic was compared with end-matched nonstained and prestained CCA-C treated specimens exposed to artificial rainfall. The effect of copper naphthenate end coating on release of copper was also evaluated. The application of prestain prior to CCA-C treatment reduced the release rate of arsenic from the treated wood by approximately 28%. Most of the decrease in leaching appeared to occur early in the test, during the time when arsenic release was greatest. The prestain also appeared to slightly decrease the release of copper and chromium, but these differences were not statistically significant. The application of a copper-naphthenate end coating did significantly increase the amount of copper detected in the leachate. Results from this study indicate that release rate data generated from nonstained CCA-C-treated wood may overestimate the release of arsenic from wood that has been prestained. In addition, results suggest that the application of a prestain may be a valuable tool in minimizing the release of arsenic from CCA-C-treated wood.

Keywords: prestain, western hemlock, chromated copper arsenate, CCA-C, leaching

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Effect of Prestain on the Release Rate of Copper, Chromium, and Arsenic From Western Hemlock

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Introduction

The use of wood treated with chromated copper arsenate (CCA-C) has increased rapidly during the past two decades, primarily because of expanded use in residential applications such as deck construction (AWPI 1996). However, some consumers dislike the greenish color of the treated wood. Accordingly, CCA-C producers and wood treaters have developed methods to color the wood to enhance its appearance. One method is to spray the wood with a "prestain" prior to treatment. This practice is sometimes used during production of treated Southern Pine, but has become particularly common on the West Coast, where much of the CCA-C treatment is applied to western hemlock (*Tsuga heterophylla* (Raf.) Sarg.)[1]

Recently, there has been concern about the use of prestaining and how it may affect the rate of leaching of CCA-C components from the treated wood. In addition, researchers have questioned whether leaching data generated with prestained material reflects the rate of release from nonstained wood (Lebow and others [in press]). One study indicated that the use of an iron-oxide-based prestain may actually decrease the subsequent release of copper from CCA-C treated wood (Envirochem Special Projects, Inc. 1992). That study was designed to address concerns about the loss of CCA-C from wood stored in the treating plant yard and to monitor the runoff from single packets of prestained and nonstained CCA-C treated lumber. Although the lack of replication and the configuration of the test made comparisons between treatments somewhat difficult, it did appear that the prestained lumber released significantly less copper than did the nonstained lumber. However, this trend was not noted for chromium or arsenic (Envirochem Special Projects, Inc. 1992).

[1]Western hemlock is produced as part of the Hem–Fir species mix, of which western hemlock is typically the largest component.

The effect of prestaining on the rate of CCA-C leaching needs additional investigation to ensure that suitable release rate data are being used to assess the potential environmental impacts of treated wood. In addition, if prestaining can lessen the rate of release of CCA-C components (as suggested by the Envirochem Special Projects, Inc. (1992) study), then the use of this technique to minimize leaching warrants further investigation.

This paper describes a study in which the release of copper, chromium, and arsenic was compared for end-matched nonstained and prestained CCA-C treated specimens exposed to artificial rainfall. This study reports on the effects of only one type of prestain. The findings are not necessarily applicable to prestains produced by other manufacturers.

Materials and Methods

Lumber

Ten Select Structural, western hemlock boards, standard 38 by 140 mm (nominal 2 by 6 in.) and 2.4 m (8 ft) in length, were obtained from a mill in western Washington. No attempt was made to select for sapwood or a specific grain orientation. Each board was conditioned to uniform moisture content in a room maintained at 23°C (74°F) and 65% relative humidity (equilibrium moisture content approximately 12%). Then, each board was cut into five specimens: two specimens were 610 mm (24 in.) in length and three specimens were 406 mm (16 in.) in length (Table 1). Both ends of each section were end sealed with two coats of a neoprene rubber sealant.

Prestain

The prestain applied was a commercial water-soluble acrylic polymer, with an iron-oxide-based rust color (Osmose, Inc., Buffalo, NY). The prestain was brushed onto one 406-mm- (16-in.-) and one 610-mm- (24-in.-) long specimen cut from each board 18 h prior to preservative treatment.

Table 1—Study design and average CCA-C retention levels

Specimen length (mm)	Number of replicates	Prestain applied?	Specimen use	Uptake retention (kg/m^3)	Assay retention (kg/m^3)				Copper naphthenate end coating
					CuO	CrO_3	As_2O_5	CCA-C	
610	5	No	Leaching	6.6	—	—	—	—	No
610	5	No	Leaching	6.1	—	—	—	—	Yes
610	5	Yes	Leaching	6.3	—	—	—	—	No
610	5	Yes	Leaching	5.8	—	—	—	—	Yes
406	10	No	Retention assay	6.9	1.6	4.8	2.9	9.3	No
406	10	Yes	Retention assay	6.0	1.4	4.3	2.6	8.3	No

Preservative Treatment

One 406-mm- (16-in.-) long specimen cut from each board that had not been prestained was weighed, pressure treated with water using a full-cell treatment process, then weighed again. The vacuum was maintained at 85 kPa (25 inHg) for 30 min; the pressure was maintained at 1.03 MPa (150 lb/in^2) for 2 h. These specimens were then discarded. The uptake of water during this preliminary treatment was used to calculate the solution concentration needed to achieve a CCA-C target retention of 6.4 to 9.6 kg/m^3 (0.4 to 0.6 lb/ft^3). An oxide-based CCA-C solution (active ratio of 17.4% CuO, 46.9% CrO_3, 35.7% As_2O_5) was prepared accordingly. The remaining specimens were weighed and treated in a single charge using the same treatment conditions that were used for the water treatment. Following treatment, the specimens were weighed again to determine the amount of solution uptake (Table 1). Then, each specimen was placed into a plastic bag and stored for 10 days at 23°C (74°F). After storage, the specimens were removed from the bags and stickered to air dry in a room maintained at 23°C (74°F) and 65% relative humidity.

Analysis of Preservative Retention

The 406-mm (16-in.) specimens cut from each board, one nonstained and one prestained, were analyzed for concentration of CCA-C components. Preservative retention was determined in the outer (bark side) wide face of each piece. Assay samples were removed from the boards by drilling holes to a depth of 15 mm (0.6 in.) from the sample surface using a 6-mm- (0.25-in.-) diameter bit. The shavings were analyzed as specified in AWPA A11-83 (AWPA 1998). In short, the wood was dried, ground, then digested in a mixture of hydrogen peroxide and nitric acid. The resulting solution was analyzed for preservative components by atomic absorption spectroscopy. The average CCA-C retention in the nonstained specimens was 9.3 kg/m^3 (0.58 lb/ft^3), and that of the prestained specimens was 8.3 kg/m^3 (0.52 lb/ft^3). Although slight, this difference was statistically significant, as discussed in Lebow and Halverson (1999).

Copper Naphthenate End Coating

The neoprene rubber sealant was cut off one end of each of the 610-mm- (24-in.-) long specimens. One day prior to leaching, two coats of a commercial copper naphthenate preservative solution were brushed onto the exposed end-grain of five nonstained and five prestained specimens. This commonly used field treatment contains 22.3% copper naphthenate (2% copper) and small amounts of paraffin and hydrocarbon resins that are dissolved in mineral spirits. The amount of the solution added to each specimen varied between 2 and 4 g.

Leaching

All twenty of the 610-mm- (24-in.-) long specimens were leached simultaneously in a weathering chamber, using sprinklers to generate artificial rainfall (Fig. 1). The specimens were placed individually in plastic trays that were 762 mm (30 in.) long and 127 mm (5 in.) deep. The width of each tray was 152 mm (6 in.) at the top, narrowing to 102 mm (4 in.) at the bottom. This taper allowed the specimens, placed with the wide outer (bark side) face up, to sit approximately 25 mm (1 in.) above the bottom of the tray. The trays were placed at a 45-degree angle, allowing run off from the boards to collect at the bottom and drain into 19-L (5-gal) jugs by way of plastic tubing.

The eight full-cone sprinkler nozzles were also oriented at a 45-degree angle, so that the direction of spray was perpendicular to the wide face of the specimens. Deionized water was forced through the nozzles at 414 kPa (60 lb/in^2), resulting in a flow rate of approximately 0.30 L/min

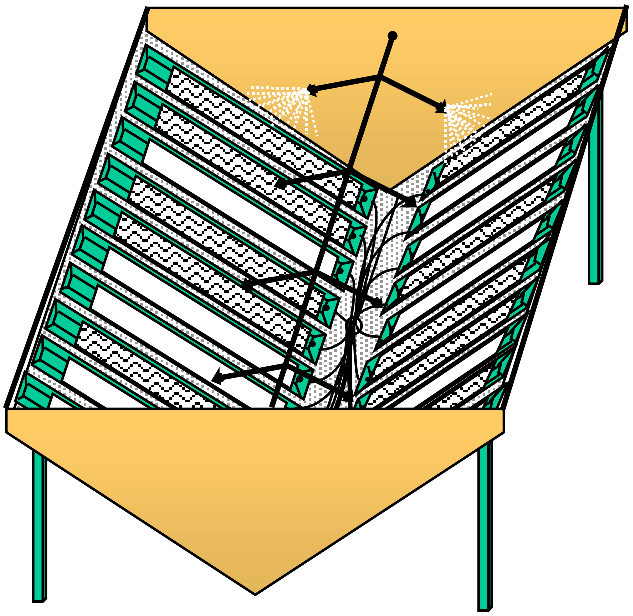

Figure 1—Design of weathering chamber and placement of specimens. Chamber cover is not shown.

(0.075 gal/min) from each nozzle. Spray distribution was not uniform across all specimens; rate of rainfall varied from an average low of 0.20 mm/min (0.008 in./min) to an average high of 1.4 mm/min (0.054 in./min). To compensate, the specimens from each treatment group were assigned to trays in a manner that minimized rainfall differences between pairs of end-matched specimens.

The weekly pattern of artificial rainfall used in this study was intended to create alternating periods of wetting and drying within the specimens. For 3 consecutive days each week, the sprinklers were run for 24 min each day. This 24 min was distributed over 3 h, using alternating cycles in which the sprinklers were on 8 min and off 52 min. With the cover closed on the chamber, this spray pattern caused the boards to remain wet for 3 days each week, while delivering between 15 mm (0.6 in.) and 99 mm (3.9 in.) of rainfall to each tray during the 72 min of rainfall per week. The specimens were then allowed to dry during the remaining 4 days of each week.

The specimens were exposed to rainfall for 17 weeks, or a total of 259 to 1,684 mm (10.2 to 66.3 in.) of rainfall. The run-off water was collected for analysis at 1, 2, 3, 4, 6, 8, 11, 14, and 17 weeks. The run-off water was weighed, acidified to between pH 1 and 2 using nitric acid, thoroughly agitated, then sub-sampled for analysis of preservative components. Concentration levels of copper, chromium, and arsenic in the water were determined by atomic absorption analysis, using either furnace or flame atomization, as appropriate.

Table 2—Summary of the significance level of factors included in the analysis of covariance

	Significance level		
Factor	Copper	Chromium	Arsenic
Total rainfall	0.0022[a]	0.0269[a]	0.0006[a]
Prestaining	0.5837	0.1709	0.0144[a]
End coating	0.0330[a]	0.3073	0.0994
Prestain/end-coat interaction	0.9363	0.3970	0.8098

[a]Significant at the 95% confidence level.

Statistical Analysis

This study considered the effects of four treatments on leaching. The four treatments were arranged as a 2 X 2 factorial experiment with the factors being prestain (yes and no) and copper naphthenate end coating (yes and no). The effects of these treatments on the total amounts of copper, chromium, and arsenic released during the 1, 2, 3, 4, 6, 8, 11, 14, and 17 weeks of collection were evaluated. Because the amount of rainfall was not the same for every treatment, there was concern that the amount of rainfall might have affected the release rate, even when calculated on a per mm (in.) of rainfall basis. It was determined that a linear relationship existed between total rainfall and total leaching, and that this relationship was unaffected by the use of prestain or the copper naphthenate end coating. Accordingly, total rainfall was used as a factor in an analysis of covariance to assess the effect of prestaining and copper naphthenate end coating on release rates.

Results and Discussion

The effect of the use of prestain and the copper naphthenate end coating on the total amount of copper, chromium, and arsenic released in the collected run off was evaluated using an analysis of covariance (Table 2). This analysis revealed a significant relationship ($\alpha = 0.0144$) between the use of prestain and the amount of arsenic released. However, application of prestain did not significantly affect the total amount of chromium or copper released. The application of the copper naphthenate end coating did significantly affect ($\alpha = 0.033$) the amount of copper collected in the run off but not the amounts of chromium or arsenic detected. Interaction between prestaining and end coating was not significant for copper, chromium, or arsenic, meaning that it is valid to consider either of these factors independently of the other, and that treatment group means can be calculated (Table 3). The use of analysis of covariance allowed us to adjust these treatment group means to what a common amount of rainfall should have produced (Table 3).

Table 3—Average total amounts of rainfall and the amount of copper, chromium, and arsenic released during weeks 1, 2, 3, 4, 6, 8, 11, 14, and 17 of leaching

Type of treatment	Rainfall (mm)	Copper (mg) Un-adjusted	Copper (mg) Ad-justed[a]	Chromium (mg) Un-adjusted	Chromium (mg) Ad-justed[a]	Arsenic (mg) Un-adjusted	Arsenic (mg) Ad-justed[a]
Prestain applied?							
No	489	8.69	9.15	2.06	2.15	5.42	5.70[b]
Yes	570	8.93	8.48	1.76	1.67	4.40	4.12[b]
Copper-napthenate end coated?							
No	554	7.84	7.57[b]	2.15	2.09	5.58	5.41
Yes	505	9.78	10.05[b]	1.68	1.73	4.24	4.41

[a]Averages adjusted to a common amount of rainfall.
[b]Pairs of means found to be significantly different at $\alpha = 0.05$.

The results of this study disagree with those of Envirochem Special Projects, Inc. (1992), who indicated that staining reduced the release of copper but did not lessen the release of chromium or arsenic. It is possible that the difference in method of testing (bundles compared with single boards) and the additional variable (fixation condition) used by Envirochem Special Projects, Inc., masked the effects noted in our study. It is also possible that the slight difference in average CCA-C retention between the prestained (average of 8.3 kg/m^3) and nonstained boards (average of 9.3 kg/m^3) contributed to the trends noted in our study, but it is unlikely that this retention difference accounted for the sizable difference in arsenic release. In fact, previous studies have indicated that the rate of arsenic release actually decreases with increasing CCA-C retention (Lebow 1996).

When compared on a weekly basis, it appears that the prestain caused the greatest reduction in arsenic release during the first 8 weeks of exposure (Fig. 2). The prestain appeared to lessen the initial wave of release of poorly fixed or readily accessible arsenic that occurred in the nonstained wood.

The mechanism of the decrease in arsenic release from the prestained wood is unclear. Previous work reported that water-repellent coatings brushed onto treated wood can slow losses of preservative components in rainwater (Cooper and Ung 1997). In the case of coatings applied after treatment, it is likely that the release of CCA-C components is slowed because the movement of water into and out of the wood is retarded and a barrier is formed between the preservative components and the water. However, this mechanism does not necessarily explain the decreased arsenic release in the prestained specimens. Because the prestain is applied before treatment, it would not necessarily make the CCA-C components less available to rainwater. This would be especially true of preservative on the outer surface of the wood. It is possible that arsenic that does not react with chromium during treatment, or that is released during leaching, is subsequently stabilized by reactions with the iron oxide in the stain pigment. Iron oxides are known to adsorb arsenic from soil solutions. In soils with a high level of iron, nearly all the arsenic present is associated with this metal (Fordham and Norrish 1974, O'Neill 1990, Walsch and Keeney 1975).

Similar, but smaller, reductions were noted in the early stages of copper (Fig. 3) and chromium (Fig. 4) release from the prestained specimens. For arsenic and chromium, the average rate of release from the nonstained boards remained slightly greater than from the prestained boards during the latter stages of the study, but the copper release rates for the two groups became very similar after 11 weeks of exposure.

The effect of the copper naphthenate end coating was consistent, causing additional copper release for both prestained and nonstained specimens at each time point (Fig. 3). It appears that the copper naphthenate end coating contributed to release of copper at a much greater rate than did the CCA-C treatment. Based on the uptake and assay retention levels shown in Table 1, we calculated that the elemental copper derived from CCA-C in each treated specimen was approximately 3 to 4 g. This amount of copper resulted in the release of approximately 7.5 mg of copper in the specimens that did not receive a copper naphthenate end coating (Table 3). In contrast, the amount of copper applied to each specimen by way of the copper naphthenate end coating was between 0.04 and 0.08 g. This much smaller amount of copper appears to be responsible for the 2- to 2.5-mg increase in copper release that was noted for the end-coated specimens.

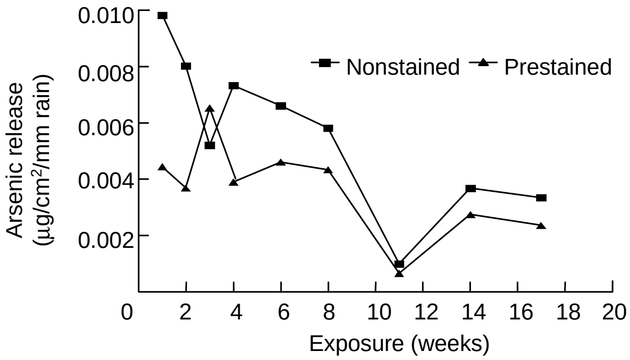

Figure 2—Release rate of arsenic from nonstained and prestained specimens during 17 weeks of exposure to artificial rainfall.

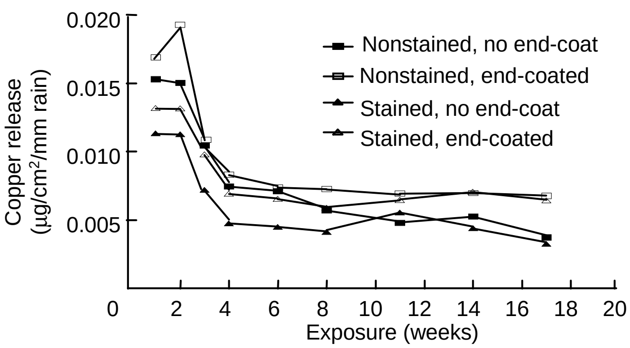

Figure 3—Effect of prestaining and copper naphthenate end coating on the release rate of copper during 17 weeks of exposure to artificial rainfall.

A comparison of the amount of copper released from each source with that originally applied to the wood indicates that copper naphthenate end coating is releasing copper at a rate approximately 20 times greater than the CCA-C treated wood. Some of this difference is probably due to the way the two forms of copper "fix" in the wood. However, keep in mind that the end coating is all applied to the wood surface, thus readily available for leaching, while the majority of the copper from the CCA-C pressure treatment is fixed much more deeply within the wood.

Thus, based on movement of water alone, it is expected that release of copper from the CCA-C treatment would be much more gradual and protracted. It is likely that the effect of the end coating will eventually lessen, because the available pool of copper in the end coating is much more limited than that within the wood. Even with the higher release from copper naphthenate, the overall proportion of copper released from the field treatment in a treated structure is likely to be small unless a large number of field cuts are made. For example, this study suggests that it may not be good practice to intentionally purchase decking boards two or three times the length needed, cut them to length on site, and apply copper naphthenate to one or two ends of each board.

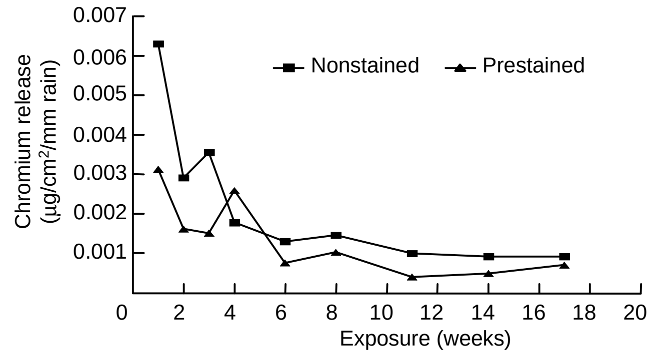

Figure 4—Release rate of chromium from nonstained and prestained specimens during 17 weeks of exposure to artificial rainfall.

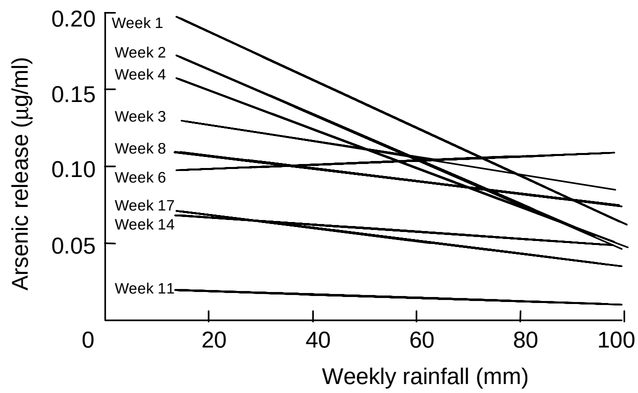

Figure 5—Effect of the amount of rainfall on the release rate of arsenic for each week that leachate was collected, as shown by fitting a straight line to the data points. Data for prestained and nonstained specimens were combined.

Total rainfall delivered to a specimen was also shown to significantly ($\alpha = 0.05$) affect the total leaching of all three CCA-C components (Table 2). Although the specimens were placed to minimize differences in rainfall between end-matched specimens, on average the prestained specimens received more rainfall than did their nonstained counterparts (Table 3). Using the regression relationship between total rainfall and total release, the average total amounts of copper, chromium, and arsenic released have been adjusted to a common, average amount of rainfall (Table 3). This adjustment slightly increased the difference in release between the prestained and nonstained specimens.

Although an increase in the total rainfall increased the total leaching, the rate of release of arsenic tended to decrease as the rate of rainfall increased (Fig. 5). Similar trends were noted for copper and chromium. This effect was most noticeable during the initial stages of leaching when the release rate was greatest. Other researchers have noted that the release of CCA components is greater when wood is exposed to slow, steady rainfall than when wood is exposed to heavy showers

(Evans 1987, Cockroft and Laidlaw 1978). It is probable that at higher rates of rainfall a greater proportion of the rainfall simply runs off the sample without diffusing into the wood.

Conclusions

The application of one type of commercial prestain prior to CCA-C treatment significantly reduced the release rate of arsenic from the treated wood. Most of the decrease in leaching appeared to occur early in the test, during the time when arsenic release was greatest. The prestain also appeared to slightly decrease the release of copper and chromium, but these differences were not statistically significant. The application of a copper naphthenate end coating to one end of the specimens significantly increased the release of copper from those specimens, and this effect remained constant over time.

This study indicates that release rate data generated with nonstained CCA-C treated wood may overestimate the release of arsenic from wood that has been prestained. It also suggests that the application of prestain may be a valuable tool in lessening the release of arsenic from CCA-C treated wood. These findings are not necessarily applicable to other types of commercially available prestains. Additional evaluation of the mechanism in which prestaining reduces arsenic leaching is warranted.

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