

# WOOD MODIFIED BY INORGANIC SALTS: MECHANISM AND PROPERTIES. I. WEATHERING RATE, WATER REPELLENCY, AND DIMENSIONAL STABILITY OF WOOD MODIFIED WITH CHROMIUM (III) NITRATE VERSUS CHROMIC ACID<sup>1</sup>

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(Received October 1983)

## ABSTRACT

Chromic acid treatment of wood improves surface characteristics. A simple dip or brush application of 5% aqueous chromic acid to a wood surface stops extractive staining, improves dimensional stability, retards weathering of unfinished wood, and prolongs the life of finishes. A better understanding of how chromic acid effects these improvements may facilitate the development of even better treatments. The improvements may be due to a combination of factors: oxidation of wood by hexavalent chromium compounds, formation of coordination complexes with trivalent chromium, and the presence of insoluble chromium compounds at the surface. Most trivalent chromium compounds do not become fixed in wood (i.e., do not form water-insoluble wood-chemical complexes). However, chromium (III) nitrate treatment of western redcedar (*Thuja plicata*), southern pine (*Pinus* sp.), and ponderosa pine (*Pinus ponderosa*) produced modified wood with properties similar to chromic acid-treated wood. Evaluation of the chromium (III) nitrate- and chromic acid-modified wood by leaching, Xenon arc-accelerated weathering, and swellometer experiments clearly demonstrated similar fixation, erosion, and water-repellent properties.

Based on the results from chromium (III) nitrate-treated wood, fixation through coordination of trivalent chromium with wood hydroxyls and formation of insoluble chromium appear to be the critical factors in improving the performance of the treated wood. Thus, the oxidation of the wood surface by hexavalent chromium appears to be less important and may not be required for improving properties.

*Keywords:* Weathering, water repellency, dimensional stability, chromic acid, inorganic salts, chromium nitrate, modified wood.

## INTRODUCTION

Researchers at the Forest Products Laboratory (Feist 1979; Feist and Ellis 1978; Williams and Feist 1983) and Pizzi (1980, 1981, 1982) have investigated the mechanism by which chromic acid and other hexavalent chromium salts stabilize the surface of wood, thereby greatly reducing weathering while preserving the natural grain and figure of finished wood (Black and Mraz 1974; Feist 1979; Feist and Mraz 1980). A dip or brush application of 4.8% chromic acid decreases the erosion rate of unfinished wood to one-third or one-fourth that of untreated wood.

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The chromic acid-modified wood also exhibits greatly improved water repellency, better mildew resistance, and reduced extractives staining. If used as a pretreatment under clear and lightly pigmented finishes, it improves the performance of the finishes. UV transparent films over chromic acid-treated wood prepared by Black and Mraz (1974) are still intact after 15 years of exterior southern exposure in Madison, Wisconsin.

Treatments with hexavalent chromium compounds have not been commercialized because of their toxicity and the green color the trivalent chromium imparts to wood. However, a better understanding of the mechanism by which these compounds improve wood performance may lead to the development of comparable or better treatments.

In this paper we will report further on the chromium mechanism, particularly the role of hexavalent chromium oxidation in the modification of wood surfaces. The objective of the study was to determine if trivalent chromium compounds that fix to wood such as chromium (III) nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), chromium (III) sulfate hydrate ( $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ), and chromium (III) acetate hydrate ( $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot x\text{H}_2\text{O}$ ) would form a wood-chromium complex similar to chromic acid and thus give similar improved performance in weathering and finishing. If so, then the fixation of chromium salts (not oxidation) would be the critical factor in improving the performance of the treated wood.

In a previous investigation, we found that chromic acid caused chemical changes in the surface of wood (Williams and Feist 1984). Chromic acid oxidation resulted in a partial decarboxylation of the surface leaving a surface more hydrophobic than before treatment. This decarboxylation partially explains the improved water repellency but not the other improvements found for treated wood surfaces. The fixation of chromium salts in the wood must also affect the properties. This fixation results from the formation of insoluble complex salts that coordinate with free hydroxyls in the carbohydrates and lignin (Bravar et al. 1973; Duncalf and Dunn 1964; Van Nice and Farlee 1976; Williams and Feist 1983). In addition to the hexavalent chromium salts, several trivalent chromium salts have been used to either fix dyes to cotton fabric or as crosslinking agents in leather tanning (Udy 1956). Fatty acid-chromium (III) chloride complexes have been used to improve dimensional stability of wood (Poller and Reichelt 1981).

Because the properties that these trivalent chromium compounds impart to the substrate are independent of oxidation, the performance of wood treated with trivalent chromium compounds might give insight into the mechanism of hexavalent chromium compounds. Similar results with trivalent and hexavalent chromium compounds should establish that oxidation of the wood is not an important consideration.

In this study, we first screened several trivalent chromium compounds to determine if fixation occurred, then documented the fixation with more extensive leaching experiments. Because of possible contamination of wood by nitrogen dioxide during chromium (III) nitrate fixation, several experiments were done to evaluate the effect of nitrogen dioxide and nitric acid on fixation of trivalent chromium compounds. Finally, the best trivalent chromium compound (chromium (III) nitrate) was compared with chromic acid in weathering performance, water repellency, and dimensional stability of the treated wood.

## EXPERIMENTAL

*Materials*

Specimens for erosion and leaching experiments were cut from vertical-grain heartwood of western redcedar (WRC) (*Thuja plicata* Donn ex D. Don). Strips were cut from three different boards with growth rates of 24, 38, and 43 rings/in. Strips 1 in. (radial)  $\times$   $\frac{5}{16}$  in. (tangential) were abrasive planed with 100-grit paper to  $\frac{1}{4}$  in. (tangential), then cut to 1-in. specimens and end-matched controls. Specimens from southern pine (SP) sapwood (*Pinus* sp.) having growth rates of 4, 6, and 9 rings/in. were prepared similarly. Specimens from ponderosa pine (PP) sapwood (*Pinus ponderosa*) for leaching experiments measured 1 (tangential)  $\times$  1 (radial)  $\times$   $\frac{1}{4}$  (longitudinal) in., all cut from the same board. The PP sapwood swellometer specimens measured 10 (tangential)  $\times$   $1\frac{1}{2}$  (radial)  $\times$   $\frac{1}{4}$  (longitudinal) in., and five pairs of longitudinally matched specimens and controls were cut from five different boards. Growth rates varied from 5 to 30 rings/in. Filter paper (FP) used in the leaching experiment was Whatman No. 1 FP (lot 410318).

Chromium (VI) trioxide (Mallinckrodt, analytical reagent) was oven-dried (105 C) overnight prior to dissolving in distilled water to give chromic acid. Chromium (III) nitrate nonahydrate (Matheson Coleman and Bell, reagent grade), hydrated chromium (III) sulfate, and chromium (III) acetate (Mallinckrodt, analytical reagent) were used as received and dissolved in distilled water.

*Methods*

*Preliminary leaching experiment.*—Single 1-  $\times$  1-  $\times$   $\frac{1}{4}$ -in. specimens of WRC were submerged in 5 wt % aqueous solutions of chromium (III) nitrate, chromium (III) sulfate, and chromium (III) acetate for 6 days. After removal, specimens were air-dried overnight and heated (2 h, 135 C). Following immersion of the treated specimens in 25 ml of distilled water for 4 days, soluble chromium was determined by atomic absorption analysis of the solution.

*Nitric acid treatment.*—The same type substrate and a similar procedure as used above were used to evaluate the nitric acid activation of wood with the following exceptions. Specimens were immersed in trivalent chromium solutions and nitric acid solutions for 3 min. Only chromium (III) sulfate and chromium (III) acetate were used in conjunction with nitric acid. Specimens were heated (135 C) 20–30 min following nitric acid treatment and approximately 2 h following treatment with trivalent chromium. Specimens were leached in 25 ml distilled water for 2½ h.

For the nitric acid treatment, specimens were immersed in either 5 or 25 wt % nitric acid and air-dried overnight or for 15 min prior to heat treatment. Following the treatment, specimens were immersed in solutions of trivalent chromium compound for 3 min, air-dried for 15 min, heated, and leached.

In a second experiment, the 5 wt % chromium (III) sulfate and chromium (III) acetate solutions were modified to contain 10 wt % nitric acid. The specimens were heated and leached as in the first experiment.

A third set of specimens was dip treated in trivalent chromium solution, air-dried and heated 2 h (135 C) in nitrogen dioxide vapor. The nitrogen dioxide was prepared by decomposing a few grams of chromium nitrate in a covered beaker containing the specimens. The concentration of nitrogen dioxide in the beaker was sufficient to easily observe visually.

TABLE 1. Treatment conditions for WRC, SP, PP, and FP specimens used in the leaching experiment.

Treatment designation	Chemical <sup>a</sup>	Immersion time	Time heated <sup>b</sup>
		..... Min .....	
I	Chromium (III) nitrate	3	25
II	Chromium (III) nitrate	3	40
III	Chromium (III) nitrate	10	25
IV	Chromium (III) nitrate	10	40
V	Chromium (VI) trioxide	3	25

<sup>a</sup> Chromium ion concentration for both chromium (III) nitrate and chromium (VI) trioxide was 2.5%.

<sup>b</sup> Oven temperature, 135 C.

*Leaching experiments.*—After oven-drying at 105 C to constant weight (12 h), triplicate specimens were dip treated in 19.2 wt % aqueous chromium (III) nitrate nonahydrate or 4.8 wt % chromium (VI) trioxide solution (chromic acid), air-dried overnight, and heat treated (Table 1). Each solution contained 2.5 wt % chromium. Specimens were reweighed at oven-dry condition before treatment, and before and after leaching. Each specimen was submerged in successive 25-ml portions of distilled water for 16, 24, and 96 h (total time, 136 h). The chromium leached at each stage was determined by atomic absorption analysis of the solutions.

*Weathering.*—In the first experiment, a set of WRC and a set of SP specimens were edge-sealed with aluminum flake-pigmented varnish and dried, dip treated for 3 min in aqueous 19.2 wt %  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or 4.8 wt %  $\text{CrO}_3$  solutions (each solution contained 2.5 wt % Cr ion), air-dried overnight, and heated (40 min at 135 C, then 15 min at 105 C). Chemical pickup was determined from difference in oven-dry weight before and after treatment. The specimens were weathered in a Xenon arc weatherometer and evaluated by measuring springwood erosion (Feist 1979; Feist and Mraz 1978).

In the second experiment, the WRC specimens from the leaching experiment were weathered and evaluated by the same procedure as used in the first experiment.

In the third and fourth experiments, WRC specimens received measured amounts of treating solution over a constant area. The rate was 0.1 ml/in.<sup>2</sup> (0.016 ml/cm<sup>2</sup>). The treating solution was 2.5 wt % chromium ion (19.2 wt %  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or 4.8 wt %  $\text{CrO}_3$ ). Following air-drying (1 h), specimens were heated at 135 C for 10 min. Erosion rates were measured by comparing springwood erosion against summerwood erosion (Black and Mraz 1974). In the fourth experiment, one set of chromium (III) nitrate-treated specimens was not heated but was conditioned for 1 week at 80 F, 65% relative humidity (RH). Another set was brushed with 5 wt %  $\text{H}_2\text{O}_2$  and air-dried 1 h prior to heating. The daily accelerated weathering schedule was the same (20 h light followed by 4 h distilled water spray without light) in all four experiments. Weathering time is based on light exposure only (Feist 1979).

*Water repellency.*—PP sapwood specimens for measuring water repellency, or moisture-excluding effectiveness (MEE), were prepared by either dip or pressure treating. Swellometer test and calculation methods have previously been reported (Feist 1979).

Specimens were oven-dried, immersed 30 s or 3 min in either 4.8 wt % chro-

TABLE 2. Chromium leached in preliminary leaching experiments and nitric acid treatment experiments.

Number	Treatment <sup>a</sup>	Substrate	Chromium leached Mg
1	Chromium (III) acetate	WRC	5.48
2	Chromium (III) sulfate	WRC	2.52
3	Chromium (III) nitrate	WRC	0.12
4	Chromium (III) nitrate	FP	0.17
5	Chromium (III) acetate	WRC <sup>b</sup>	3.42
6	Chromium (III) sulfate	WRC <sup>b</sup>	1.77
7	Chromium (III) nitrate	WRC	0.12
8	Chromium (III) acetate	WRC <sup>c</sup>	3.25
9	Chromium (III) sulfate	WRC <sup>c</sup>	2.36
10	Chromium (III) nitrate	WRC	0.08
11	Chromium (III) acetate 10% nitric acid	WRC	2.86
12	Chromium (III) sulfate 10% nitric acid	WRC	1.97
13	Chromium (III) nitrate	WRC	0.02
14	Chromium (III) acetate post treated, NO <sub>2</sub>	WRC	4.28
15	Chromium (III) sulfate post treated, NO <sub>2</sub>	WRC	1.92
16	Chromium (III) nitrate	WRC	0.02

<sup>a</sup> All chromium solutions were 5% by weight of salt.

<sup>b</sup> Acidified with 5% HNO<sub>3</sub>. Stored overnight at room temperature, then heated 30 min.

<sup>c</sup> Acidified with 25% HNO<sub>3</sub>. Stored overnight at room temperature, then heated 30 min.

mium (VI) trioxide or 19.2 wt % chromium (III) nitrate solution, air-dried overnight, heated 40 min (135 C), then 15 min (105 C), and conditioned for up to 10 weeks (80 F, 65% RH). MEE was calculated from the tangential swelling of the treated versus untreated matched controls (Feist 1979). Pickup of chemical was determined from oven-dry weights or weights at the same equilibrium moisture content (EMC) before and after treatment.

Several sets of PP specimens were pressure treated with chromic acid. Hexavalent chromium ion concentrations were 0.5, 1.0, 1.5, 2.5, and 5.0%. Specimens were brought to EMC at 80 F, 65% RH and treated as follows:

1. 24.5-in. vacuum (18.4 kPa pressure) (30 min, room temperature).
2. 150 lb/in.<sup>2</sup> (1,034 kPa) pressure (30 min, room temperature). Following reconditioning to EMC (80 F, 65% RH), MEE was determined (Feist 1979).

*Instrumentation.*—Chromium analysis was performed using a Perkin Elmer 500 Atomic Absorption Spectrophotometer.

## RESULTS AND DISCUSSION

### *Chromium (III) nitrate fixes to wood*

A preliminary leaching experiment using chromium (III) sulfate, acetate, or nitrate showed that chromium (III) nitrate fixed to wood and paper (Table 2, Nos. 1–4). The preliminary data indicated significantly better fixing with chromium (III) nitrate than with the other salts. Visually, chromium (III) sulfate- and chromium (III) acetate-treated specimens showed little water repellency, and the water became colored from soluble trivalent chromium almost immediately after im-

mersing the specimens. The chromium (III) nitrate-treated wood showed good water repellency and no noticeable color in the water during the first hours of leaching. The probable explanation for the difference between the chromium (III) nitrate and the other trivalent chromium salts, which did not fix, is that chromium (III) nitrate nonahydrate decomposes at 100 C (Udy 1956). This temperature is well below the temperature used in this work to condition the treated wood and thus fix the salt. The decomposition of the nitrate likely resulted in the trivalent chromium coordinating to the hydroxyls in wood and paper and the formation of insoluble chromium (III) oxide. The resulting fixation of trivalent chromium was accomplished *only* by heating either wood or paper for at least 10 min at 135 C. Sixteen hours of exposure to UV light did not fix the chromium (III) nitrate on treated but unheated wood as it did on chromic (VI) acid-treated wood. Because the small amount of chromium nitrate absorbed on the wood did not permit monitoring the changes during heating, approximately 0.5 g of chromium nitrate was placed in a beaker and observed during heating. At 135 C, crystalline  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  melts, then loses water of hydration leaving a solid residue. Continued heating at 135 C decomposes this solid, yielding nitrogen dioxide and a water-insoluble chromium compound.

*Nitric acid has no effect*

Because the objective of the experiment was to compare the performance of a nonoxidizing trivalent chromium compound with the strongly oxidizing chromic acid, the production of  $\text{NO}_2$  by chromium (III) nitrate complicated the experiment. Although  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  contains no hexavalent chromium oxidant, the  $\text{NO}_2$  released may have oxidized the wood to form a reactive surface species that enhanced coordination with trivalent chromium. Nitric acid (Johns et al. 1978; Rammon et al. 1982) and gaseous nitrogen dioxide (Brink et al. 1977) treatments of wood have been used to activate wood surfaces for nonconventional bonding, but the interaction of the activated surface with Cr has not been reported. To investigate the impact of this activation, chromium (III) sulfate and chromium (III) acetate were evaluated in conjunction with nitric acid-treated wood and the leaching results compared with chromium (III) nitrate treatment.

Wood was pretreated with nitric acid, post-treated with  $\text{NO}_2$  vapor, or treated with acidified treating solution. For the pretreatment using nitric acid, specimens were immersed in 5 or 25 wt % nitric acid and either air-dried overnight or oven-dried at 135 C prior to trivalent chromium treatment (Table 2, Nos. 5–10). The acidified treating solutions were adjusted to 10 wt % nitric acid and specimens prepared as above (Table 2, Nos. 11–13). The post-treatment using  $\text{NO}_2$  was done in an 135 C oven (Table 2, Nos. 14–16). From the leaching data, nitric acid and  $\text{NO}_2$  had little effect on chromium (III) sulfate or acetate fixation. In all cases, the chromium (III) nitrate leached less than one-tenth of the amount of the other two trivalent chromium salts. The initial assumption that the fixation is due to the change in ligands through loss of  $\text{NO}_2$  or the formation of insoluble Cr compounds and not chemical change of the wood seems valid.

*Woods modified with chromium (III) nitrate and chromic acid have similar properties*

The results with chromium (III) nitrate indicated that additional experiments would be worthwhile. Thus, leaching experiments were expanded to include chro-

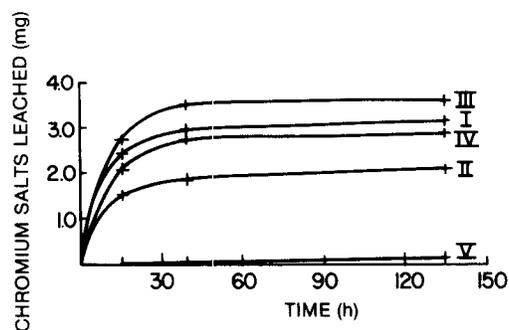


FIG. 1. Chromium salts leached from trivalent- and hexavalent chromium-treated WRC (average of three replicates). I;  $\text{Cr}(\text{NO}_3)_3$ , 3-min dip, 25-min heat. II;  $\text{Cr}(\text{NO}_3)_3$ , 3-min dip, 40-min heat. III;  $\text{Cr}(\text{NO}_3)_3$ , 10-min dip, 25-min heat. IV; 10-min dip, 40-min heat. V;  $\text{CrO}_3$ , 3-min dip, 25-min heat.

mium (III) nitrate treatment of WRC, SP, PP, and FP, using several different treating conditions (Table 1). For the remainder of the paper, the shorthand notation Cr(III) will refer only to chromium (III) nitrate and Cr(VI) to chromic acid ( $\text{CrO}_3$  in water).

The average amount of chromium salts leached from the three replicates of WRC shows that the four Cr(III)-treated woods lost 2.0–3.5 mg of chromium whereas the Cr(VI)-treated WRC lost only 0.035 mg after 135 h (Fig. 1). Although chromium leached significantly more from the Cr(III)-treated wood than from the Cr(VI)-treated WRC, the Cr(III) loss essentially leveled out after 40 h. Comparison of total leached chromium after treatment with weight gain for the treatment shows less than 10% loss of available chromium (Table 3, Col. 3). The nominal pickup of Cr(III) was 30–60 mg, yet the losses were less than 3.8 mg (Table 3, col. 2). The table contains only part of the WRC leaching data. Leaching data on SP, PP, FP, and part of the WRC are not included because the results

TABLE 3. Chromium pickup in WRC following treatment with Cr(III) and Cr(VI), losses with leaching and Soxhlet extraction, and surface analysis.

Description	Pickup <sup>a</sup>	Weight	Cr	Residual	Weight	Cr
		Cr				
		Mg	%	Mg	Mg	%
Cr(III)-treated WRC	50	3.4	6.8	20	160	1.46 ± 0.16
dipped 10 min	60	3.7	6.2	20	140	1.48 ± 0.11
heated 25 min	40	3.8	9.5	10	150	1.72 ± 0.09
Cr(III)-treated WRC	30	3.0	10	10	170	1.02 ± 0.18
dipped 10 min	50	3.0	6.0	20	140	1.20 ± 0.40
heated 40 min	50	2.9	5.8	20	150	1.60 ± 0.04
Cr(VI)-treated WRC	50	0.03	0.06	30	120	4.98 ± 0.83
dipped 3 min	50	0.04	0.08	30	100	5.72 ± 0.61
heated 40 min	60	0.04	0.07	30	80	4.20 ± 0.36

<sup>a</sup> Specimens weighed to ± 5 mg.

<sup>b</sup> Calculated from chromium analysis of the solution.

<sup>c</sup> Average of two samples from each specimen.

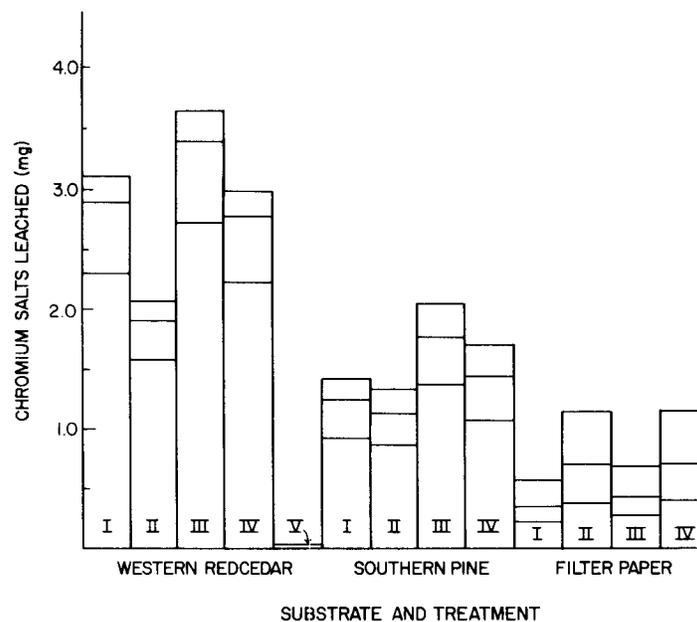


FIG. 2. Chromium leached from WRC, SP, and FP. The Roman numerals designate the treatment (Table 1), and the divisions on each bar indicate the chromium leached at 16, 40, and 136 h. Plots of the data for SP and FP would be similar to Fig. 1.

were similar. Following leaching, the residual weight gain for Cr(III)-treated WRC was still 10–30 mg (col. 4). The discrepancy between the amount of chromium leached (as found by analysis of the leachant, col. 2) and the residual weight gain of the specimens (weight difference between pickup, col. 1, and residual pickup, col. 4) is probably due to loss of water-soluble wood substances. Disregarding chromium, the WRC specimens lost approximately 150 mg (col. 5) of water-soluble substances during 6 days of Soxhlet extraction.

After 5 days of leaching and 6 days of Soxhlet extraction, WRC specimens still contained chromium from the Cr(III) treatment. Two small slices were removed from the surface of several specimens of Cr(III)- and Cr(VI)-treated WRC and the percent chromium was determined (Table 3, col. 6). These percentages should not be rigorously compared since the thickness of each specimen would affect the results. Note, however, that all specimens contain chromium, but the Cr(VI)-treated specimens show approximately three times more chromium.

SP absorbed slightly more (40–100 mg) Cr(III) than WRC (50–70 mg), yet less chromium was leached (Fig. 2). The relative position of the various treatments (I–IV) remains the same for the two species—for example, treatment II (3-min dip, 40-min heat) gave the minimum. The two vertical grain wood species (WRC and SP) retained slightly more Cr(III) with longer heating time. The trend with FP differed from WRC and SP (Fig. 2). Contrary to the performance with WRC and SP, the retention decreased with heating. This difference may have something to do with extractives and lignin. Reaction of Cr(III) with lignin may account for the slightly greater fixation of chromium with wood specimens upon heating. The trend showing increased retention from WRC to SP to FP also indicates that

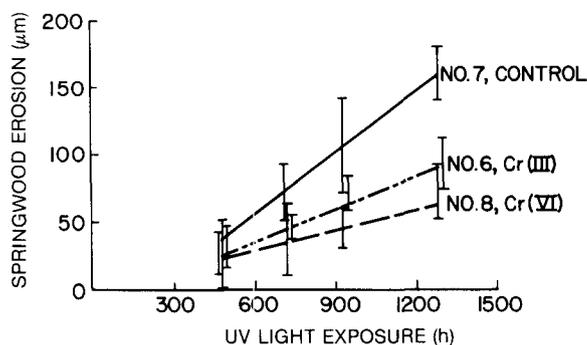


FIG. 3. Springwood erosion of chromium-treated SP and control. No. 7 (—) untreated control. No. 6 (---) Cr(III) treatment. No. 8 (- - -) Cr(VI) treatment. Brackets show the spread in the five observations at the four times. Chromium ion concentration of the treating solutions were 2.5%.

extractives may inhibit retention since the extractive contents of these materials decrease in this order.

Leaching data on treated FP show little dependence on treatment time as the specimens were completely saturated almost immediately after immersion (Fig. 2). Although the measurement of weight gain during treatment does not indicate much difference between 3- and 10-min dips, the slight differences in retention of WRC and SP at 3 and 10 min probably reflect slightly more absorption and therefore slightly higher leaching for those specimens dipped 10 min. The chromium loss for PP is not shown on the bar graph in Fig. 2 because the cross-section specimens absorbed and leached two to three times more chromium; PP gained 120–190 mg, whereas SP gained 40–100 mg. They leached 7–9 mg and 1.5–2 mg, respectively. PP had the same trends for the four Cr(III) treatments:

Treatment I	8.2 mg leached
Treatment II	7.6 mg leached
Treatment III	9.2 mg leached
Treatment IV	8.8 mg leached

The leaching experiments show 80–90% fixation with Cr(III) treatment of wood and FP but substantially less than that found for Cr(VI) treatment. The most important observation from the leaching experiments is that the total amount of Cr(III) leached is low compared with original pickup.

*Weathering rates similar.*—In four separate Xenon arc-accelerated weathering experiments, Cr(III) treatment significantly reduced WRC springwood erosion compared with untreated controls, and in one of these studies the Cr(III)-treated WRC eroded at the same rate as Cr(VI)-treated specimens. Erosion rates of 0.04–0.16  $\mu\text{m}/\text{h}$  have previously been reported for Cr(VI)-treated WRC (Feist 1979). The erosion rate of Cr(VI)-treated wood depends on chromium concentration, pH, species, growth rate, and even the piece of wood. Matched controls are essential, and the results from treated specimens can only be compared with controls in the same experiment.

The first weathering experiment consisted of WRC and SP vertical-grain specimens dip treated in Cr(III) or Cr(VI) and their end-matched untreated controls. Chromium ion concentrations were 1.25% and 2.50% for Cr(III) and 2.50% for

TABLE 4. Springwood erosion rate and statistical data for chromium-treated WRC and SP specimens based on linear best fit of the data.

Number	Treatment	Species	Spring-wood erosion rate (slope)	y intercept	R <sup>2</sup>	Standard deviation
%						
A. DIP TREAT						
1	1.25% Cr(III)	WRC	0.16	-53	83	24
2	Control	WRC	0.22	-77	94	18
3	2.5% Cr(III)	WRC	0.13	-43	65	31
4	Control	WRC	0.23	-73	86	31
5	2.5% Cr(VI)	WRC	0.02	20	7	28
6	2.5% Cr(III)	SP	0.08	-13	86	10
7	Control	SP	0.15	-34	85	21
8 <sup>b</sup>	2.5% Cr(VI)	SP	0.05	-2	53	16
B. DIP TREAT, LEACHED (see Table 1)						
10	I (Cr(III))	WRC	0.19	-60	88	21
11	Control	WRC	0.30	-97	94	23
12	II (Cr(III))	WRC	0.17	-40	61	42
13	III (Cr(III))	WRC	0.14	-24	72	27
14	Control	WRC	0.26	-83	84	35
15	IV (Cr(III))	WRC	0.14	-40	95	10
16	V (Cr(VI))	WRC	0.05	-14	32	23
17	Control	WRC	0.26	-94	86	35
C. CONTROLLED VOLUME/SURFACE APPLICATION						
18	Control	WRC	0.24	-82	88	67
19	Cr(III)	WRC	0.20	-108	72	89
20	Cr(VI)	WRC	0.17	-91	59	106
21	Control	WRC	0.31	-122	98	23
22	Control	WRC	0.32	-160	97	33
23	Cr(VI)	WRC	0.20	-141	84	48
24	Cr(III) no heat	WRC	0.31	-181	86	71
25	Cr(III) heated	WRC	0.20	-112	87	43
26	Cr(III), heated, H <sub>2</sub> O <sub>2</sub>	WRC	0.22	-141	86	50

<sup>a</sup> The standard deviation of y about the regression line.

<sup>b</sup> No number 9 was tested.

Cr(VI). Five replicate specimens of each treatment and control were measured at three places on the specimens, giving fifteen observations at each time. The three erosion measurements for each specimen were averaged and the five averages plotted versus time of UV light exposure. Plots for SP treated with 2.5% Cr(III) or Cr(VI) are shown (Fig. 3). Statistical analysis of erosion data indicated a linear relationship, and the least squares fit gave the erosion rate or slope in  $\mu\text{m}$  erosion/h (Table 4A). The selection of the five specimens from three different boards led to data representing the usual variation in wood. This natural variability in wood caused the high standard deviation about the line based on the regression (Table 4A). Even with this variation, little overlap between treated and control specimens was observed at the later stages of weathering (i.e., Fig. 3). Comparison of slope between treated specimens and controls measures the retardation or the effectiveness of the treatment. The lower the slope, the better resistance to weathering.

The % variation explained ( $R^2$ ) show reasonable values for all treatments except the Cr(VI) treatment of WRC. The low erosion values and the difficulty in eval-

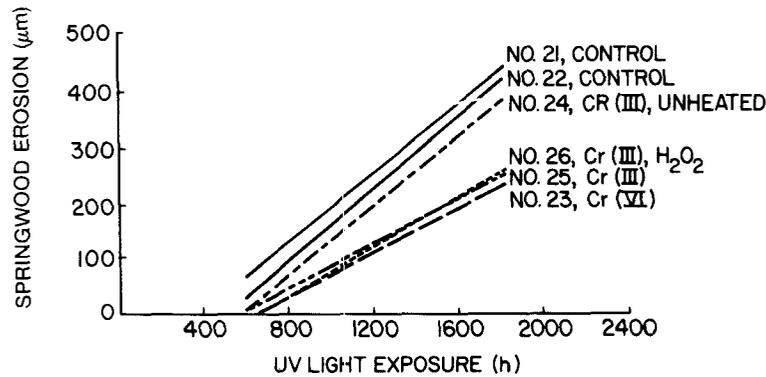


FIG. 4. Springwood erosion of chromium-treated WRC and controls. No. 21 and No. 22 (—) untreated controls. No. 23 (— —) Cr(VI) treatments. No. 24 (— - —) Cr(III) treatment, unheated. No. 25 (- - - -) Cr(III) treatment, heated. No. 26 (- · - ·) Cr(III) treatment, H<sub>2</sub>O<sub>2</sub> treatment, heated.

uating early stages of erosion led to the high variation in these specimens. For both the WRC and SP, Cr(III) treatment showed significant improvement over the untreated controls. The value for Cr(VI) treatment is extremely low and may be due to rather high pickup of chromium caused by dipping as compared to application of measured amounts. The dip-treated specimens absorbed approximately 17 mg chromium salts/in.<sup>2</sup>, whereas the controlled application of 0.1 ml of 4.8% chromic acid gives only 4.8 mg/in.<sup>2</sup>. Dip-treated specimens in this experiment were edge-sealed. The values for SP are more comparable for Cr(III) and Cr(VI) (0.08 and 0.05 compared with 0.15 for the control) (Table 4A). The negative intercepts for the least squares fit indicate some period of inhibition, but the differences are difficult to interpret because the initial stages of erosion are not linear.

The WRC specimens used for the leaching experiment were also subjected to accelerated weathering (Table 4B). Although the leached specimens contained less chromium compared with those unleached (Table 4A), the erosion values are similar. The similarity in results may be due to the slow leaching of unfixed chromium from the surface of the originally unleached specimens during the

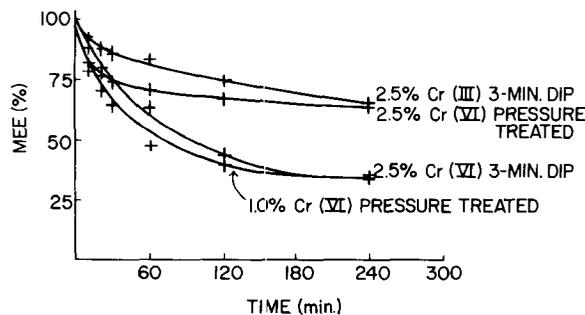


FIG. 5. MEE of 2.5% Cr(III) and Cr(VI) dip-treated and 2.5% Cr(VI) pressure-treated PP cross sections (% indicates chromium ion concentrations).

TABLE 5. Treatment conditions and water repellency of chromium-treated ponderosa pine cross sections.

Number	Treating chemical	Treatment		Regression equation <sup>a</sup>			Moisture-excluding effectiveness, percent after		Percent solids pickup
		Concentration	Treating time	Intercept	Slope	R <sup>2</sup>	30 min	240 min	
		% <sup>b</sup>							
1	Cr(III)	1.25	3-min dip	76.7	-1.12	48	44	26	3.9 ± 0.4
2	Cr(III)	2.5	3-min dip	90.8	-0.22	55	84	67	8.1 ± 2.0
3	Cr(VI)	2.5	3-min dip	93	-0.86	76	67	23	5.2 ± 0.8
4	Cr(VI)	2.5	30-sec dip	90	-1.56	82	45	22	—
5	Cr(III)	2.5	30-sec dip	—	—	<sup>c</sup>	33	32	—
6	Cr(III)	2.5	30-sec dip	—	—	<sup>c</sup>	34	18	—
7	Cr(VI)	5.0	1-h pressure	88.0	-0.11	35	85	81	42.8 ± 4.9
8	Cr(VI)	2.5	1-h pressure <sup>d</sup>	84.0	-0.28	25	76	64	25.0 ± 2.0
9	Cr(VI)	1.5	1-h pressure	85.1	-0.37	66	76	53	14.0 ± 2.0
10	Cr(VI)	1.0	1-h pressure	86.7	-0.73	84	65	36	8.4 ± 1.3
11	Cr(VI)	0.5	1-h pressure	72.2	-1.08	44	40	24	5.2 ± 0.8

<sup>a</sup> Based on data from 10, 20, and 30 min. The slope indicates the rate of water absorption as the decrease in MEE per minute.

<sup>b</sup> % chromium ion concentration, Cr(III) ions are chromium (III) nitrate and Cr(VI) ions are chromic acid.

<sup>c</sup> Regression not done because the specimens were only 30% effective after 10 min and showed no change after that time. Essentially an almost vertical slope from 0–10 min or no moisture-excluding effectiveness.

<sup>d</sup> Pressure treatment at 150 lb/in.<sup>2</sup> (1,034 kPa).

weatherometer water spray and/or because of insignificant concentration difference between leached and unleached specimens. Specimens dipped longer (treatments III and IV) eroded slightly slower, but the different heat treatments (25 min versus 140 min) had no effect. In light of the significantly lower amounts of chromium in the Cr(III)-treated specimens compared with the Cr(VI)-treated specimens (Table 3, col. 6), the erosion performance is quite good. The concentration of chromium in the Cr(VI)-treated specimens was three times that of the Cr(III)-treated specimens, and the erosion rates differ by approximately three times. Erosion rates seem to be strictly a function of the amount of chromium fixed at the wood surface and independent of the original amount.

To avoid the possibility of unequal absorption of chemical during dip treatment, a constant volume of solution was applied to a fixed surface area. In these two experiments (Table 4C), equal amounts of solution were pipetted onto the surface. Cr(III)- and Cr(VI)-treated WRC eroded at the same rate for one of the experiments (Table 4C, Nos. 23 and 25, Fig. 4) and at similar rates for the other experiment (Table 4C, Nos. 19 and 20). In No. 24 (Table 4C, Fig. 4), the Cr(III) was not heated prior to weathering, and the poor performance results from the rapid leaching of the unfixed chromium.

*Fixed chromium key to performance.*—As with Cr(VI)-treated wood, fixation of the chromium salt is critical. If the chromium, whether initially Cr(III) or Cr(VI), is not coordinated (complexed) to the wood, it quickly leaches and the wood erodes at the same rate as the controls. The surface oxidation of Cr(III)-treated specimens with H<sub>2</sub>O<sub>2</sub> produced little additional improvement in control of erosion (Fig. 4, No. 26). The presence of fixed chromium is the key to UV stability of the wood surface. Chemical changes in wood do not appear to be important except as they might relate to the ultimate fixation.

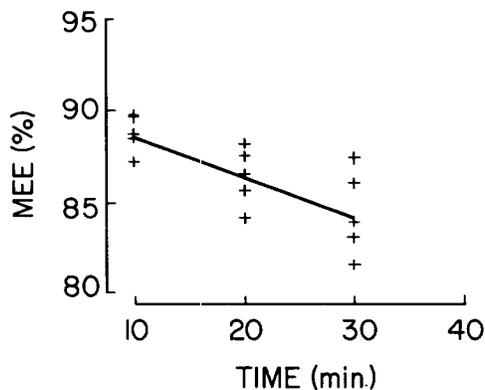


FIG. 6. MEE for the 5 specimens of 2.5% Cr(III) dip-treated PP and the line based on regression of the 15 data points (% indicates chromium ion concentration).

*Water repellency similar.*—In addition to slowing wood surface erosion, Cr(VI) treatment improves liquid water repellency (Feist 1979). The water repellency or percent moisture-excluding effectiveness (MEE, found by comparing the swelling of treated specimens against untreated controls) was better for PP cross sections dipped in solution having 2.5% chromium (III) ion than for specimens dipped in solution having 2.5% chromium (VI) ion concentration (Fig. 5). These results should be compared in light of the amount of chromium absorbed by the specimens. The percent weight gain of solids for the specimens shown in Fig. 5 are:

3-min dip, 2.5% Cr(III)	$8.1 \pm 2.0\%$
3-min dip, 2.5% Cr(VI)	$5.2 \pm 0.8\%$
pressure treated, 2.5% Cr(VI)	$25.0 \pm 2.0\%$
pressure treated, 1.0% Cr(VI)	$8.4 \pm 1.3\%$

The performance of Cr(III) at 8.1 wt % gain is similar to that obtained at 25 wt % gain of Cr(VI). The high pickup from the pressure treatment with Cr(VI) may be due to lumen filling and may not accurately reflect cell-wall modification. Pickup from dip treatment with Cr(VI) was only 5.2%, and the performance was poorer than the Cr(III)-treated specimens. Cr(VI) dip treatment produced MEE similar to the pressure treatment with Cr(VI) solution having 1% chromium (VI) ion concentration. The proportion of cell-wall modification compared with lumen filling was not determined in this work. However, based on the weight gains with treatment, the Cr(III) dip-treated specimens performed better than either the dip-treated Cr(VI) or the specimens pressure treated to similar retentions. The Cr(III) may penetrate the cell wall better than Cr(VI) or may interact with cell-wall components differently than Cr(VI). If fixation of Cr(III) involved more coordination with cellulose hydroxyls than fixation of Cr(VI), better MEE would result.

The initial change in percent MEE was close to linear and the values for the five replicates were plotted at 10, 20, and 30 min. The slope of the line following least squares fit of this portion of the curve gives a measure of the initial rate of water absorption. A typical plot is shown for Cr(III) dip-treated PP cross sections (Fig. 6), and the slopes and % variation explained ( $R^2$ ) for all Cr(III)- and Cr(VI)-

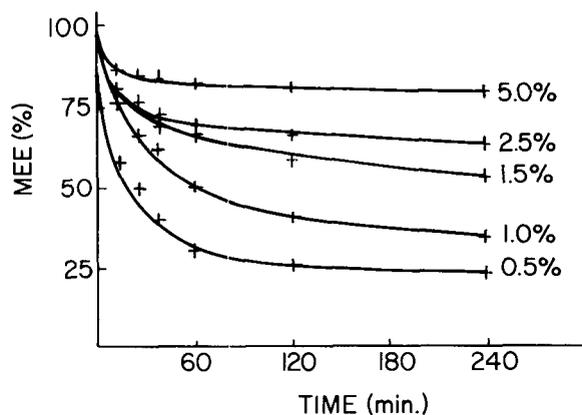


FIG. 7. MEE of Cr(VI) pressure-treated PP cross sections. The percent shown in the figure is the chromium (VI) ion concentration of the treating solution.

treated specimens are listed (Table 5). The average percent MEE for several concentrations of Cr(VI)-treated PP cross sections shows the concentration depends on the final MEE (Fig. 7). The percent MEE at 30 min allows comparison with the National Woodwork Manufacturers Association swellometer test, NWMA-M-2-69 (NWMA 1969), and the values at 240 min approach the minimum as shown in Figs. 5 and 7. The slopes in the range of 10–30 min indicate that the 30-s dip in Cr(III) solution is not effective; however, a 3-min dip produced specimens with MEE equal to Cr(VI) pressure treatment (Table 5, No. 2 vs. No. 8). As previously shown (Fig. 5), the water repellency for Cr(III)-treated specimens was better than the Cr(VI)-treated specimens. Slopes were  $-0.22$  for Cr(III) versus  $-0.73$  for Cr(VI) having chromium retentions of 8% (Table 5, No. 2 vs. No. 10).

*Chromium (III) and increases in dimensional stability.*—Chromium not only affects the rate of water absorption but also the final MEE value—the more chromium, the slower the rate and the higher the final MEE (Fig. 7). Sufficient penetration of chromium salts into wood, such as is possible with  $\frac{1}{4}$ -in.-thick cross sections, improves bulk properties, particularly dimensional stability. Although chromium treatment can affect the rate of moisture absorption either through surface cellulose modification (Williams and Feist 1984) or changes in surface-wetting characteristics, the equilibrium values, as shown by the final values in the MEE curves, can only be affected by changes in the bulk properties of the wood. This cell-wall modification is also indicated by the 1–2% increase in tangential length during chromium treatment. The chromium complexes with hydroxyls, thus preventing swelling.

#### CONCLUSIONS

A trivalent chromium compound capable of fixing to wood can produce the same weathering protection and water repellency as hexavalent chromium compounds. The critical factor is the ability of the chromium to fix or become un-leachable, not the oxidative chemistry of the hexavalent chromium ion on wood. Chromium (VI) trioxide fixes by the formation of insoluble compounds or complexes and the coordination of chromium to the hydroxyls in wood. If these

hydroxyls are unavailable for hydrogen bonding with water, the wood has greater water repellency and dimensional stability. Other than this coordination, chemical changes in wood brought about by hexavalent chromium compounds have little to do with improved weathering performance and water repellency. Chromium (III) nitrate hydrate fixes to wood as it decomposes during heating. The fixation probably involves coordination of chromium (III) ions to the hydroxyls in wood and the formation of water-insoluble chromium (III) oxide and leads to the same property improvements as chromic acid treatment.

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