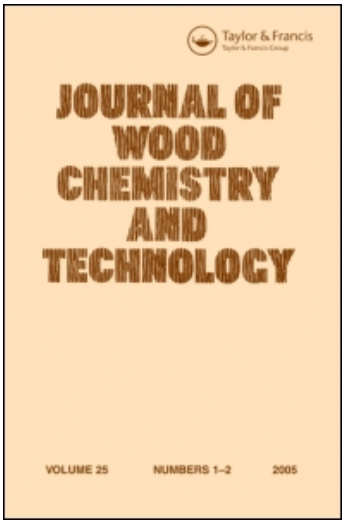

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FIXATION OF CHROMIUM IN WOOD FROM DICHROMATE AND CHROMATE SALT SOLUTIONS

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ABSTRACT

It has been reported that treatment of wood surfaces with aqueous solutions of chromium trioxide imparts some beneficial properties like weather resistance and some degree of water repellency. The work presented here aims at finding alternative ways of fixing chromium in wood with the avoidance of the very acidic and strong oxidant conditions of chromic acid solutions. This is because these solutions may affect the strength of wood, and are known to have a very high human toxicity. In this study, chromium has been fixed into wood from hexavalent chromium solutions at pH's of ~1.5 (CrO_3 aq.), ~3.8-3.9 ($K_2Cr_2O_7$ aq.) and ~9.5-10.3 (K_2CrO_4 aq.). For the CrO_3-solutions the effects of temperature and reaction time on the fixation of chromium were investigated. For the dichromate and chromate solutions, fixation experiments were carried out with Cr-concentration and reaction times as variables. It is shown that a 3%-fixation level of chromium in small wood specimens can be attained from dichromate and chromate solutions without significant mechanical damage to wood. On the other hand, even diluted CrO_3-solutions (0.01 M) impart serious strength reductions in wood at temperatures of 90° C and higher when reacted for 8 hours, and the chromium content of wood resulting from such treatment is of the order of only 1%.

INTRODUCTION

Chromium has been used in formulations for wood treatment for a long time (Gunn, 1926)[1]. The impregnation of wood with CCA (chromium-copper-arsenic) chemicals is the most common inorganic treatment process for preservation purposes. One example of a commercial formulation of CCA is a paste containing CuO (14.8%), CrO_3 (26.6%), As_2O_5 (34.0%) and H_2O (24.6%). Although the chemical fixation mechanisms are still not clearly known, a detailed study suggests that chromium plays mainly the role of a co-precipitant for copper and arsenic[2]. Some degree of water repellency is also exhibited by wood treated with chromium-containing preservatives[3,4].

The expanding use of waterborne preservatives has created an awareness of the enduring aesthetic properties imparted by some treatments. The fungicidal properties of copper, and water repellency of chromium and its ability to protect wood surfaces against ultra-violet radiation, provide an effective natural finish. Currently there is active research in progress aimed at protecting wood surfaces against weathering with chromium-containing solutions. Photographic[5] and image analysis[6] evidence illustrate the deleterious effects of UV-light on wood surfaces, and the protective effect imparted by treatment with chromium(VI) trioxide solutions. Chromium protects wood surfaces against accelerated weathering[7] or natural weathering conditions[8], and greatly increase the life of transparent and semi-transparent finishes[9], and oil- or latex-based paints[10].

Aqueous CrO_3-solutions are also very acidic and oxidant, and they may affect the mechanical properties of wood. These effects become more important as the dimensions of wood specimens decrease. For instance, toughness of small clear specimens of pine was reduced by CCA treatment[11], while ammoniacal copper arsenate (ACA) did not produce that effect[12]. The magnitude of these effects depends both on the CCA retention and the temperature of the subsequent drying process[13]. Heating CCA treated timber to temperatures of 65° C led to long-term

(beyond 60 days) decreases in the modulus of rupture (MOR) and in the work to maximum load (WML)[14].

Another area of concern with the use of formulations based on Cr(VI) for wood treatment is their influence on human health. Chromium(VI) compounds such as chromate and dichromate salts, and particularly chromium(VI) oxide, act as irritants of the skin and mucous membranes[15]. In addition, there is some evidence that Cr(VI) compounds have carcinogenic and mutagenic effects on humans[16].

The oxidative power and toxicity of a Cr(VI)-solution increases as the pH is reduced. The reason why the CrO_3 chemical is incorporated in some preservative formulations and CrO_3-solutions have been applied in wood protection studies is probably due to their high reactivity at ambient temperatures.

Chromium(VI) species are soluble over all ranges of pH. In this study we have examined alternative methods for chromium fixation in wood from Cr(VI)-solutions, with avoidance of the very acidic and oxidant properties characteristic of CrO_3 aqueous solutions. Such systems would avoid the deterioration of wood, particularly if it is used in a fragmented form, and minimise effects on human health.

RESULTS AND DISCUSSION

Chromium Levels in Wood

Washing of unreacted chromium from wood wafers just after reaction was considered to be very important. In this way, the formation of insoluble inorganic salt deposits on wood surfaces is prevented. It is known that preservative treated wood presents problems in gluing and in resin curing when boards are made[17,18]. Chemical and physical interference from preservative deposits may contribute to some extent to those difficulties.

Tables 1 to 3 show the results from the assessment of reacted wood wafers for chromium content and dry weight increase when the temperature, or the initial Cr(VI)-concentration, and reaction time were varied.

With CrO_3 solutions of 0.01 M concentration, taking into account the whole trend over the period from 1 to 8 hours, it seems that a variation in temperature of 10° C in the range 70 - 100° C has a small effect on chromium levels fixed in wood (Table 1), and beyond 6 hours the effect of reaction time is less pronounced. However, there is an evident increase on chromium levels with reaction time. Generally, the chromium content of wafers is relatively low, reaching a maximum of only about 1.3%.

Higher levels of chromium in wood would certainly be achieved if more concentrated solutions were used. Concentrations were kept low in order to avoid reduction in strength properties. Even after reacting for 8 hours at 100° C, the pH of the solution was 2.7. Therefore, knowing that the pH tends to increase when wood is reacted in CrO_3 aq. solutions, it can be inferred that, with CrO_3 aq., acidic conditions (pH between about 1.5 and about 2.7) always apply.

Reaction time and Cr-concentration variables were investigated with $K_2Cr_2O_7$ and K_2CrO_4 solutions (Tables 2 and 3). The effects of these variables were not to marked for dilute solutions. Chromium fixation levels only start to be important, and increase with time, for Cr-concentrations of 0.05 M or higher.

Furthermore, changes in Cr-concentration can have an important effect on chromium fixation levels. This was observed mainly with 0.1 M and 0.5 M $K_2Cr_2O_7$ or 0.5 M and 1 M K_2CrO_4. A sharp increase in Cr-levels in wood was observed when going from the lower concentration to the higher. The maximum chromium level fixed in wood wafers treated with $K_2Cr_2O_7$ solutions was 6.5%, with a concentration of 0.5 M and a reaction time of 8 hours, while for K_2CrO_4 solutions, the maximum was 3.3% at 1 M concentration and 8 h reaction time.

A key factor when treating wood with Cr(VI)-solutions is the pH. The solutions are more reactive, i.e. more oxidant, when the pH is low. Furthermore, the reduction of hexavalent chromium gives trivalent chromium in a labile form.

TABLE 1: Effect of 0.01 M CrO_3 Treatment on Dry Weight Increase and Chromium Content of Wood Wafers.

Reaction Conditions[1]	Reaction Time (h)	Weight Increase Average[2] (% $^w/_w$)	Weight Increase Std. Deviation	Chromium Content Average[3] (% $^w/_w$)	Chromium Content Std. Deviation
H_2O	1	0.3	0.1	-	-
	2	0.1	0.2	-	-
	4	0.0	0.1	-	-
	6	-0.1	0.1	-	-
	8	0.0	0.2	-	-
CrO_3	1	-0.3	0.2	0.11	0.03
0.01 M	2	0.9	0.3	0.35	0.05
70 °C	4	1.2	0.5	0.61	0.05
	6	0.5	0.3	0.86	0.06
	8	1.1	0.4	0.70	0.03
CrO_3	1	-0.2	0.7	0.13	0.00
0.01 M	2	0.2	0.6	0.41	0.10
80 °C	4	0.9	0.6	0.69	0.11
	6	0.9	0.5	1.01	0.07
	8	1.6	0.4	1.05	0.11
CrO_3	1	-0.3	0.4	0.24	0.06
0.01 M	2	0.1	0.5	0.37	0.08
90 °C	4	0.6	0.6	0.57	0.00
	6	0.6	0.2	0.86	0.04
	8	2.0	0.5	1.27	0.00
CrO_3	1	0.1	0.2	0.33	0.09
0.01 M	2	0.7	0.1	0.52	0.00
100 °C	4	0.6	0.4	0.89	0.15
	6	0.9	0.1	1.08	0.14
	8	1.1	0.2	1.16	0.07

[1] The pH of the CrO_3 solutions 0.01 M was approximately 1.5.
[2] Average of 6 replicates.
[3] Average of 2 replicates.

That is why, in some circumstances, it is easier to have Cr(III) complexed with a given ligand if the reduction of Cr(VI) to Cr(III) occurs concurrently with the fixation reaction, rather than trying to induce Cr(III)-ligand replacement[19]. Cr(III)-complexes are well known for their chemical inertness. The oxidation power, or the availability of Cr(III) generated, explains the differences in chromium levels

TABLE 2: Effect of $K_2Cr_2O_7$ Treatments at 100 °C on Dry Weight Increase and Chromium Content of Wood Wafers.

Reaction Conditions[1]	Reaction Time (h)	Weight Increase Average[2] (% $^w/_w$)	Weight Increase Std. Deviation	Chromium Content Average[3] (% $^w/_w$)	Chromium Content Std. Deviation
H_2O	1	-1.2	0.2	-	-
	2	-1.4	0.5	-	-
	4	-1.5	0.1	-	-
	6	-1.6	0.5	-	-
	8	-1.5	0.3	-	-
$K_2Cr_2O_7$ 0.01 M	1	-1.1	0.2	0.02	-
	2	-1.8	0.2	0.12	0.02
	4	-1.8	0.1	0.20	0.01
	6	-2.1	0.2	0.32	0.02
	8	-1.6	0.1	0.18	-
$K_2Cr_2O_7$ 0.05 M	1	-1.4	0.1	0.36	0.04
	2	-1.2	0.2	0.67	0.09
	4	-0.7	0.3	1.09	0.06
	6	-0.3	0.2	1.37	0.00
	8	-0.1	0.2	1.40	0.10
$K_2Cr_2O_7$ 0.1 M	1	0.4	0.2	0.65	0.05
	2	0.5	0.2	1.12	0.01
	4	1.1	0.2	1.62	0.10
	6	1.1	0.3	2.42	0.35
	8	2.1	0.3	2.66	0.13
$K_2Cr_2O_7$ 0.5 M	1	2.4	0.5	2.23	0.05
	2	3.3	0.3	3.41	0.03
	4	4.2	0.4	5.18	0.14
	6	6.2	0.5	5.32	0.10
	8	9.6	0.9	6.49	0.28

[1] The pH of the $K_2Cr_2O_7$ solutions was 3.8-3.9, regardless the concentration.
[2] Average of 6 replicates.
[3] Average of 2 replicates; when the standard deviation is not included, it is only one sample.

obtained with the solutions of CrO_3, $K_2Cr_2O_7$ or K_2CrO_4 in similar conditions of initial Cr-concentration and temperature. For example, with an initial concentration of 0.01 M and a temperature of 100° C, the levels of chromium fixed in wood after 6 hours were respectively 1.08%, 0.32% and 0.27% respectively for CrO_3, $K_2Cr_2O_7$ or K_2CrO_4. The initial pH's of the solutions were respectively about 1.5, 3.8 and 9.5.

TABLE 3: Effect of K_2CrO_4 Treatments at 100 °C on Dry Weight Increase and Chromium Content of Wood Wafers.

Reaction Conditions	Reaction Time (h)	Weight Increase Average[1] (% $^w/_w$)	Weight Increase Std. Deviation	Chromium Content Average[2] (% $^w/_w$)	Chromium Content Std. Deviation
H_2O	1	-1.2	0.4	-	-
	2	-1.4	0.5	-	-
	4	-1.5	0.1	-	-
	6	-1.6	0.5	-	-
	8	-1.5	0.3	-	-
K_2CrO_4 0.01 M (pH 9.5)	1	-1.2	0.4	0.00	0.02
	2	-1.3	0.2	0.07	0.01
	4	-1.5	0.1	0.16	-
	6	-1.6	0.1	0.27	0.00
	8	-1.4	0.5	0.39	0.01
K_2CrO_4 0.05 M (pH 9.5)	1	-1.4	0.2	0.24	0.01
	2	-1.3	0.3	0.40	0.06
	4	-1.4	0.2	0.55	0.12
	6	-1.4	0.3	0.93	0.01
	8	-1.3	0.2	1.18	0.05
K_2CrO_4 0.1 M (pH 10.1)	1	-1.4	0.1	0.45	0.01
	2	-1.3	0.4	0.56	0.14
	4	-1.1	0.1	1.16	0.02
	6	-1.2	0.1	1.33	0.07
	8	-1.3	0.2	1.60	0.00
K_2CrO_4 0.5 M (pH 10.3)	1	-1.6	0.1	1.11	0.05
	2	-0.4	0.1	1.41	0.11
	4	0.3	0.2	2.06	0.01
	6	0.4	0.2	2.34	0.05
	8	0.6	0.3	2.66	0.08
K_2CrO_4 1 M (pH 10.3)	1	-0.8	0.1	1.35	0.20
	2	0.5	0.2	1.98	0.02
	4	0.9	0.4	2.51	0.01
	6	2.0	0.3	2.82	0.02
	8	2.2	0.3	3.28	0.01

[1] Average of 6 replicates.

[2] Average of 2 replicates; when the standard deviation is not included, it is only one sample.

The weight increase parameter reflects some degree of chromium uptake only for levels of chromium of about 1% and higher. Hence, this factor cannot be used to predict if fixation of chromium has occurred when the Cr-levels are too low. Furthermore, a given reaction medium can lead to a weight loss of wood, thus masking any weight gain from chromium fixation. Tangential dimension increase is even less sensitive. In all cases with the Cr(VI)-solutions investigated, width increase (average values of the order of 1.0%) did not show any variation that cannot be ascribed to wood variability. The effects of the Cr-fixation processes on wood mechanical properties are discussed later.

No improvements in thickness swelling or water absorption properties were recorded as a result of the treatments. Results show that the levels of these parameters measured with reacted wafers were not very different from those measured with the controls, i.e. wafers soaked in boiling water (10-12% thickness swelling and 70-110% water absorption). No treated sample gave a rate of thickness swelling different enough from controls that could be ascribed to effects other than the natural variability of wood.

Although very reasonable chromium levels were obtained (up to 6.5% by weight) no water resistance was imparted. Some degree of water repellency imparted to wood after CCA or CrO_3 aq. treatments have been often reported previously[3,4]. However, the lack of such effect in wood samples obtained in this work may be explained by differences in chromium fixation procedures.

In reported research experiments, wood has been treated with CCA or CrO_3 aq. solutions, respectively for preservation or weathering resistance, in a way very similar to that applied for introduction of preservatives in commercial practice. That is, wood is immersed in the solution for some time, with or without vacuum/pressure, and then is allowed to dry. With this procedure, inorganic salts are very likely to deposit on wood surfaces because of excess reagent and very slow chemical reactions may occur involving these moist deposits, before any leaching is carried out. Microscopic evidence for the occurrence of salt deposits has been presented[20, 21]. Also, the formation of such precipitates seems not to be

undesirable, but perhaps crucial for an effective CCA-treatment of wood. One explanation for the fixation of CCA in wood is based on the formation of insoluble inorganic precipitates that contain the active elements[2]. It seems that the water repellency effect reported may be due to the deposition of hydrophobic salts on wood surfaces, rather than because of a chemical reaction with the wood. The fact that CCA-treated wood loses almost all the water repellency property after Soxhlet extraction is worthy of mention [22].

The procedure undertaken here to avoid salt deposition consisted of a thorough washing of the reacted wood wafers with water immediately after reaction. Insoluble deposits, if any, would only result from the reaction itself, and not from the evaporation of reacting solution. For example, after reacting wood with K_2CrO_4 1 M, a large amount of chromium is leached, and the yellow colour of chromate is noticed even after several hours of soaking in running water.

Effects on Wood Strength

Table 4 shows the results of the assessment of the effects of chromium fixation reactions on wood strength, expressed as the ratio between samples and controls of the average maximum tensile strength divided by the specimen cross sectional area.

Fixation of chromium from hexavalent chromium solutions leads to some degradation. Strength loss seems to become important where high Cr uptake is observed, and then to become more marked with increase in Cr content.

CrO_3 aq., even at 0.01 M, caused some strength loss after reacting for 8 hours at 100° C. The level of chromium in wood was found to be only 1.2%. With dichromate only the 0.5 M-concentration gave strong deleterious effects. After 8 hours the level of chromium in wood was 6.5%. With chromate no damaging effects were found, even at 1 M-concentration and an 8-hour reaction period. Therefore, if fixation of chromium in wood is the primary objective, then it can be

TABLE 4: Strength Ratio[1] Between Reacted and Unreacted Thin Wood Strips as a Function of the Reaction Conditions in Cr(VI)-Solutions.

Reaction Conditions	Average[2] Strength Ratio (%)	Standard Deviation
CrO_3, 0.01 M, 8h, 70° C	100.7	6.6
80° C	100.1	7.9
90° C	90.0	2.6
100° C	84.6	1.8
$K_2Cr_2O_7$, 100° C, 8h, 0.01 M	98.8	1.3
0.05 M	95.0	2.0
0.1 M	91.7	3.5
0.5 M	75.0	1.4
K_2CrO_4, 100 °C, 8h, 0.01 M	98.4	0.1
0.05 M	97.4	1.4
0.1 M	104.6	17.0
0.5 M	104.4	3.3
1 M	95.1	5.5

[1] Ratio of (Average maximum tensile strength of treated strips divided by their sectional area) / (Average maximum tensile strength of controls divided by their sectional area)

[2] Average of 2 sets of 15 to 20 paired samples and controls.

seen that an alkaline solution of chromate can be used, causing minimal loss of wood stength. Moreover, this solution is safer to handle than those of acidic pH. Washing of wood from unreacted chromium would ensure a wood surface free of salt deposits. This would prevent the corrosion of fasteners and perhaps problems in gluing with commom resins.

CONCLUSION

Chromium can be fixed in wood from hexavalent chromium solutions in reasonable amounts without seriously reducing its strength so long as strong acidity is avoided. The reaction of wood with dichromate or chromate salt

aqueous solutions at 100 °C leads to the fixation of wood at levels that depend both on reaction time and chromium concentration. These salts give respectively slightly acidic and alkaline aqueous solutions. Reaction of small wood specimens in potassium chromate solutions of 1 M-concentration for 8 hours gives chromium levels of the order of 3% without apparent damage to wood strength. About the same level can be obtained with 0.1 M potassium dichromate solutions. Chromium levels of the order of 7% were achieved with 0.5 M-potassium dichromate solutions, but at the same time the tensile strength of wood was reduced.

MATERIALS AND METHODS

Fixation of Chromium in Wood

Wood samples were cut from sapwood of maritime pine (*Pinus pinaster*) from Portugal (20 x 20 x 5 mm, respectively for the tangential, radial and longitudinal directions). This geometry allowed easy penetration of reacting chemicals, and assessment of the dimensional changes due to the reaction and the subsequent exposure to water.

Wood specimens were Soxhlet-extracted with toluene-ethanol (2:1 $^{v}/_{v}$) for 8 h. They were then washed with hot ethanol to remove the toluene, extracted with ethanol for 6 h, soaked in boiling water for 1 h, and finally washed with boiling water[23]. This procedure was used to remove extractives and the solvents used in their removal. Drying was performed at 70° C, first at atmospheric pressure, then under vacuum.

The reactions with wood were performed using aqueous solutions of CrO_3, $K_2Cr_2O_7$ and K_2CrO_4. These solutions were characterised by being respectively acidic (pH ~1.5), slightly acidic (pH 3.8-3.9) and alkaline (pH 9.5-10.3). Generally, for each experiment 3 wafers were used with 50 ml of solution. An

exception was the CrO_3 aq. treatment where 125 ml were applied, because if only 50 ml were used in this case, chromium would be exhausted from solution before the end of time given for reaction . Each experiment was performed twice, and the reaction data were averaged.

A temperature of about 100° C (reflux) was used in all experiments with $K_2Cr_2O_7$ and K_2CrO_4 solutions. The variables assessed were initial Cr-concentration and reaction time. Concentration of chromium was varied from 0.01 M to 1 M, and the reaction times considered were 0, 1, 2, 4, 6 and 8 h. Because of its strong oxidation capacity, the temperature of CrO_3 aq. was varied from 70 to 100° C, and the initial Cr-concentration was kept constant at 0.01 M for all experiments. Reaction times were as above.

After reaction, wood wafers were leached of excess reagent by soaking in running water for 24 h. After that they were air-dried and then oven-dried at 70° C, first at atmospheric pressure and then under vacuum.

Dried, modified wood specimens were measured for changes in dimensions in the tangential direction and weight as a consequence of the reaction with Cr(VI)-species. Tangential width and weight increases were calculated as the percentage increase in width or weight after reaction, based on values before reaction. In a process for chemical modification of wood, as it is the aim in this work, a high chemical uptake within cell wall is accompanied by an irreversible thickness swelling because of the bulking effect in cell walls. On the other hand, shrinkage usually indicates serious degradation of cell wall polymers.

To assess any improvement of water resistance exhibited by the modified wood wafers, water repellency, dimensional stability and water absorption were measured for all wood samples.

Water repellency was assessed by measuring the initial thickness swelling during soaking in water. The experimental apparatus consisted of a small platform where the wood wafer was placed with the tangential direction oriented in the vertical plane. A transducer was held above the wood sample also in the vertical position, with the core touching the upper side of the wafer. The transducer was

connected to an amplifier that was itself connected to a chart recorder. Such assembly enabled to measure continuously the rapid thickness swelling that takes place during immersion of the wood wafers in water. To avoid disturbance of the transducer, the small platform was fixed and a small water container was raised to soak the wood. For most samples, about 80-90% of the ultimate thickness swelling was achieved in 5 to 10 minutes.

After the water repellency tests, wafers were kept in water for 24 h. Then, the final width in the tangential direction and specimen weight were registered as the ultimate thickness swelling and water absorption values. Before these measurements, superficial water was removed by blotting with tissue paper.

After testing, wood wafers were dried and were ground to flour with a hammer mill. Chromium content was determined by X-ray fluorescence analysis.

Tests for the Effect of the Chromium Fixation Process on the Strength Properties of Wood

Changes in wood strength as a consequence of reaction with Cr(VI)-solutions were assessed with thin wood strips. The comparison of the ratio of the ultimate tension strength of reacted compared to unreacted wood strips, gives an indication of the extent that strength properties are affected.

Wood strips (10 mm-wide, 80 mm-long and 150 μm-thick) were cut from the radial plane of pine (*Pinus pinaster*) wood blocks. To minimise the effect of variability between strips, one was assigned to the control group and the subsequent one was assigned to the sample group, as they were being cut. In this way every sample strip had a matched control.

Each sample consisted of 15 to 20 wood strips. Reactions were carried out for an 8-hour period in 0.01 M CrO_3 aq. solutions at 70 - 100° C, or in $K_2Cr_2O_7$ and K_2CrO_4 solutions, where the range of concentration was from 0.01 M to 0.5 M and to 1 M, respectively, and temperature was always 100 °C. Control wood strips were subjected to just hot-water at the given temperatures and times

Drying of the wood strips was performed at room temperature in moving air. To prevent curling, the strips were held at their ends between two glass plates. Before testing, wood strips were conditioned in an atmosphere of 20° C and 65% RH.

The wood strips were tested in tension in a universal testing machine. Thickness was measured at three points along its length, and then averaged. Samples were then fixed in the test machine with a 20 mm-gap, and tested at a head speed of 1 mm/min. Maximum tensile strength at failure was recorded.

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