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### Oxidation of Wood Components During Chromated Copper Arsenate (CCA-C) Fixation

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## OXIDATION OF WOOD COMPONENTS DURING CHROMATED COPPER ARSENATE (CCA-C) FIXATION

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### ABSTRACT

Pre-extracted radial sections of southern yellow pine sapwood were treated with CCA-C and analyzed by x-ray photoelectron spectroscopy (xps). The ratio of C1 (carbon bonded only to carbon and/or hydrogen) to C2 (carbon bonded to one oxygen with a single bond) was used to determine the progress of oxidation of wood components during CCA fixation. This ratio increased after treating times of 10 minutes and 60 minutes and decreased after 180 minutes soaking suggesting that oxidation of C2 predominates on initial contact with CCA solution but oxidation of C1 (lignin) becomes more important with extended exposure to the treating solution. Oxidation of C2 to C3 (carbon bonded to two oxygens or a carbonyl group) was demonstrated by *in situ* trapping of C3 with ethylene glycol as it was formed. Further oxidation of C3 to C4 (carboxylic carbon) was not observed in the xps spectra, consistent with the findings of others. The hypothesis that rapid decarboxylation results in loss of C4 as evolved CO<sub>2</sub> is supported by the observation that the C4 component of untreated wood was reduced by more than 90 % after 10 minutes of CCA soaking followed by high temperature fixation and by the observation of CO<sub>2</sub> evolution during early stages of accelerated fixation. The Cr(2p) spectra of Cr<sup>VI</sup> and Cr<sup>III</sup> were established at 580.2 and 577.8 eV respectively. Accelerated fixation of CCA-C treated specimens resulted in a very high degree of reduction of Cr<sup>VI</sup> to Cr<sup>III</sup>. XPS Cu (2p<sub>3/2</sub>) peaks were established at 935.1 for CCA-C, 935.3 for Cu(OH)<sub>2</sub>, and 933.7 for CuO. Cu (2p<sub>3/2</sub>) peaks in CCA-treated wood were shown at 932.9 with no satellite peaks for the 10-60 minutes soaking in CCA series, and at 933.9 and 936.4 with satellite at 941-948 for the 3 hours soaking time. The latter are attributed

to complexed copper oxide and hydroxide forms of  $\text{Cu}^{\text{II}}$ . Peaks attributed to  $\text{Cu}^{\text{II}}$  hydroxides were shown to diminish in leached samples.

## INTRODUCTION

Water based chromated copper arsenate (CCA) has become the most important wood preservative in use in North America. It is used in most exterior wood applications from utility poles to construction of residential decks and fences. The complex "fixation" mechanisms responsible for the good resistance of CCA to leaching in soil and water contact are still not well understood. However, the most dominant and easily monitored reaction during fixation is the reduction of hexavalent chromium ( $\text{Cr}^{\text{VI}}$ ) in the treating solution to its trivalent state ( $\text{Cr}^{\text{III}}$ ) through oxidation of wood components.

Early studies by Dahlgren and co-workers<sup>1,2</sup> helped define the major chemical reactions that occur among the CCA components during the fixation reactions. More recent work has focussed more on the impacts of the treatment on the chemistry of the wood. X-Ray photoelectron spectroscopy (xps) has proven a valuable and relatively non-destructive technique for studying surface reactions of CCA treated wood. A significant decrease of C1 in the carbon spectrum of CCA treated southern pine, fixed at room temperature was observed<sup>3</sup> suggesting that carbons on the aromatic rings of lignin were oxidized. A decrease of C2 expected with the oxidation of hydroxyl groups was not observed and it was concluded that this reaction did not occur under the test conditions. Others<sup>4</sup> showed a substantial decrease in the C2 component of the C1s peak but very little change in the C3 (carbon bonded to two oxygens or a carbonyl group) in rapidly fixed ponderosa pine and Douglas-fir. The oxidation of C2 (hydroxyl) is expected to yield a corresponding increase in C3 as carbonyl compounds. The lack of change in C3 content was attributed to the oxidation of hydroxyl groups followed by further oxidation of the C3 formed to C4 (carboxylic carbon:  $-\text{O}-\text{C}=\text{O}$ ) followed by decarboxylation<sup>5</sup>. It is not clear if these different observations result from fundamental differences between low temperature

and high temperature fixation, or from interference by extractives at the wood surface (Ostmeyer *et al*<sup>3</sup> did not pre-extract their samples).

There is also some disagreement concerning the hexavalent chromium status in CCA treated wood after fixation. Chromium reduction during aqueous chromic acid treatment of wood and cellulose could be followed by the chemical shift of the Cr(2p) binding energy in the xps spectra<sup>5</sup>. Cr<sup>VI</sup> reduction to Cr<sup>III</sup> was nearly complete after 3 weeks of drying at ambient temperature<sup>6</sup>. However, others<sup>3,7</sup> suggest that some of the chromium may persist as Cr<sup>VI</sup> on fixed treated wood.

The objective of this paper was to further investigate the above questions about the oxidation process under accelerated fixation conditions.

### MATERIALS AND METHODS

200 μm thick sections were cut with a microtome from the radial surface of water saturated southern yellow pine sapwood blocks. The sections were subjected to one of the pretreatment and treatment cycles shown in Table 1. Extracted samples were serially extracted in a Soxhlet apparatus with 1:2 ethanol:toluene (8h), ethanol (8h) and distilled water (2h). This is expected to remove most of the high in C1 terpene extractives present in southern pine sapwood<sup>8</sup>. Specimens were stored in a refrigerator until time of CCA treatment and freeze dried prior to xps analysis.

Some sections were pretreated with ethylene glycol (EG, 10 minute soak) before CCA treatment. The ethylene glycol treatment was used in an attempt to trap C3 carbonyls, if formed by oxidation of hydroxyl groups. Under acidic conditions, ethylene glycol reacts with carbonyl functionalities forming the corresponding acetals and ketals (Equation 1).

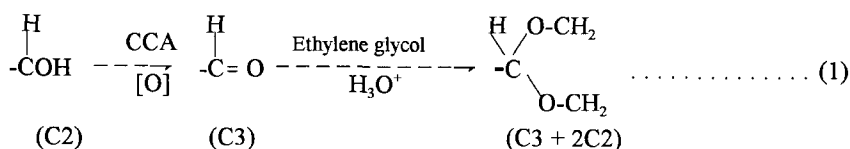


TABLE 1.  
Summary of Pretreatment and Treatment Conditions

Designation	Details of treatment
UX/UT	Unextracted and untreated
X/UT	Extracted and untreated
X/CCA-10	Extracted and treated for 10 minutes
X/CCA-60	Extracted and treated for 60 minutes
X/CCA-180	Extracted and treated for 180 minutes
X/CCA-10/L	Extracted, treated for 10 minutes and leached
X/CCA-180/L	Extracted, treated for 180 minutes and leached
X/EG/CCA-10/L	Extracted, pre-treated with ethylene glycol, treated with CCA for 10 minutes and leached

Formation of acetals and ketals prevents further reaction of the C3 and gives rise to an increase in the C2 and C3 components of the xps C1s peak. Provided all of the unreacted ethylene glycol (also C2) is washed out, an increase in C2 and C3 accompanied by a decrease in O/C confirms transient C3 formation during the fixation process.

Sections treated with CCA were soaked in 3 % CCA-C for 10 minutes, 60 minutes or 180 minutes. Fixation was accomplished by storing bagged samples in an environmental chamber set at 63°C and 95 % RH for 17 hours. One treated series (with and without EG pretreatment) was leached in stirred water at 65°C for 10 minutes. Care was taken with all samples to avoid surface contamination during handling prior to xps analysis.

To determine if CO<sub>2</sub> is evolved during high temperature fixation of CCA, six 25 mm cubes of CCA treated southern yellow pine were heated to approximately 70°C in a glass flask connected by glass tubing to a container of a 0.02 N barium hydroxide solution. The resulting precipitate was collected, dried and analyzed by infrared spectroscopy. Control flasks containing either distilled water treated pine blocks or free CCA solution were heated in the presence of the barium hydroxide solution.

One sample was treated with CCA for 10 minutes, blotted dry, mounted and transferred immediately to the cooled, high vacuum chamber of the spectrometer. Using an Al monochromatic source, the Cr(2p) spectra were obtained. High temperature fixed samples from the above study were also analyzed for comparison.

Both the earlywood and latewood surfaces were evaluated by xps because of the significant differences between these spectra observed by others<sup>3</sup> for unextracted southern pine.

The xps spectra were obtain on a Leybold MAX 200 XPS system. Unmonochromatized Mg K x-ray radiation was used as the primary excitation source. The source was run at 15 kV and 20 mA. Features in the resultant spectra due to excitation from the weaker x-ray satellite lines which are also present in the unmonochromatic source were subtracted using an algorithm supplied with the instrument and based upon a program<sup>9</sup>. Atomic percentages of the elements present were derived from spectra run in a low resolution mode (pass energy = 192 eV) which were normalized to unit transmission of the electron spectrometer by means of a routine provided by the manufacturer<sup>10</sup>.

The sensitivity factors used (Cu 2p<sub>3/2</sub> = 3.0, Cr 2p = 3.6, O 1s = 0.34 and As 3d = 0.82) were empirically derived by the equipment manufacturer for the normalized spectra.

To obtain further information on the nature of the surface, the spectral regions of interest were run also in a high-resolution mode with the unmonochromatic source (pass energy = 48 eV) and in some cases with a monochromatic Al K source (pass energy = 36 eV). While no differential charging was apparent with the unmonochromatic source, it was necessary to charge compensate when using the monochromatic source. This was achieved by using thermal electrons from a heated tungsten filament attached to the sample holder. The energy scale of the spectrometer was calibrated to the Ag 3d<sub>5/2</sub> and Cu 2p<sub>3/2</sub> peaks at 368.3 eV and 932.7 eV respectively<sup>11</sup> and the binding energy scale was then shifted to place the main hydrocarbon C 1s feature (carbons bonded only to carbons and hydrogens, C1) at 285.0 eV. Large-area analysis was performed (4x7 mm) to minimize exposure of the

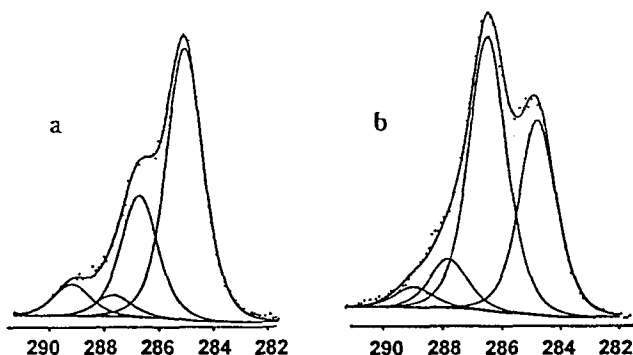


Figure 1: XPS C1s Spectra of Southern Yellow Pine.  
(a) Unextracted Latewood (b) Extracted Latewood

samples to x-ray while obtaining sufficient signal-to-noise for the spectral features. Peak areas and curve deconvolution were obtained by use of routines provided with the instrument.

## **RESULTS AND DISCUSSION**

### Earlywood vs Latewood - Effect of Extractives:

The xps results for both earlywood and latewood southern pine were similar. Table 2 summarises the changes in O/C, C1/C2 ratios as well as differences in the C3 and C4 components brought about by pre-extraction. As has been noted<sup>4</sup>, extractives have a significant effect on the xps spectra of the wood surface. The presence of extractives results in significantly lower C1/C2 ratios (Figure 1), presumably as a result of migration of C1 rich extractives such as terpenes to the surface during drying of the samples<sup>4</sup>. This tends to mask the wood oxidation effects. Thus, to facilitate interpretation of the spectra, it is important to remove the C1 rich extractives from the samples or to prepare samples in a manner that avoids the migration of extractives to

the surface during preparation. However, it should be recognised that in practice, wood is not extracted prior to treatment and the oxidation effects of the CCA solution on the wood surface may be different when these extractives are present.

#### Effect of CCA Treatment:

It was hypothesized that oxidation of C2 hydroxyl groups leads ultimately to loss of C4 by decarboxylation<sup>4,5</sup>. To confirm this, it is necessary to monitor the reduction in C4 component and/or the evolution of CO<sub>2</sub> as a result of the interaction of CCA with wood. Thus, the C1s curve in the xps spectra was fitted for all 4 components (C1, C2, C3 and C4). This resulted in a better "full width at maximum height" and overall peak synthesis. The chemical shifts of C2, C3 and C4 were similar to those reported for wood materials<sup>12</sup> and are appropriate for the type of bonding observed (1.5 eV, 3 eV and 4.0 eV for C2, C3 and C4 respectively).

Analysis of the C4 component of the C1s spectra of untreated and CCA treated specimens showed a large reduction (more than 90 %) in C4 carbon content with CCA treatment (Table 2). This supports the hypothesis that decarboxylation occurs.

When fresh treated blocks were subjected to accelerated fixation conditions in the presence of a barium hydroxide solution, gas was evolved from the samples. It was confirmed that the gas was CO<sub>2</sub> by the formation of insoluble barium carbonate in the solution. No precipitate formed with the control samples (CCA solution only and distilled water treated pine blocks).

#### Ethylene Glycol Pretreatment:

Samples treated with ethylene glycol before CCA treatment had a lower C1/C2 and O/C ratios and increased C3 components (Table 2). Those differences were evident in the unleached sections as well as in the sections that were washed with hot water after the CCA fixation step to remove unreacted ethylene glycol and water soluble oxidation products of ethylene glycol (Table 2 and Figure 2). This suggests that C2 conversion to C3 carbonyls occurs during the fixation process.



TABLE 2.  
XPS Spectra Observations for Southern Pine Sections

Specimen	Relative peak areas Ratios of peaks					
	C1	C2	C3	C4	C1/C2	O/C
UX/UT - earlywood	58.0	31.7	8.2	2.1	1.83	0.30
UX/UT - latewood	60.7	27.3	4.8	7.1	2.22	0.28
X/UT - earlywood	31.9	38.4	20.3	9.4	0.83	0.48
X/UT - latewood	33.2	40.9	16.7	9.2	0.81	0.48
X/CCA-10 ew	41.2	48.6	9.3	0.9	0.85	0.57
X/CCA-10 lw	42.3	49.0	8.3	0.3	0.86	0.65
X/CCA-60 ew	41.7	46.7	10.2	1.3	0.89	0.53
X/CCA-60 lw	43.3	45.5	9.9	1.3	0.95	0.52
X/CCA-180 ew	30.6	56.4	10.7	2.3	0.54	0.69
X/CCA-180 lw	30.8	59.5	6.6	3.1	0.52	0.67
X/EG/CCA-10 ew	36.9	50.5	10.9	1.8	0.73	0.52
X/EG/CCA-10 lw	35.2	54.1	9.4	1.3	0.65	0.49
X/CCA-10/L ew	46.1	43.7	8.6	1.7	1.05	0.53
X/CCA-10/L lw	41.4	46.2	9.7	2.6	0.90	0.52
X/EG/CCA-10/L ew	38.1	47.7	11.5	2.7	0.80	0.47
X/EG/CCA-10/L lw	37.5	49.4	11.0	2.2	0.76	0.48

#### Effect of CCA Soaking Time:

Sections soaked in CCA solution for longer periods (60 and 180 minutes) were exposed to high acid chromate ion concentration (favoured by low pH) for the entire soaking period. In practice, only the wood surfaces would be subject to these conditions. On removal from the solution and exposure to the high temperature fixation conditions, Cr<sup>VI</sup>, acid chromate and hydrogen ion contents drop rapidly. Oxidation of C2 is known to be kinetically dependent on the acid chromate

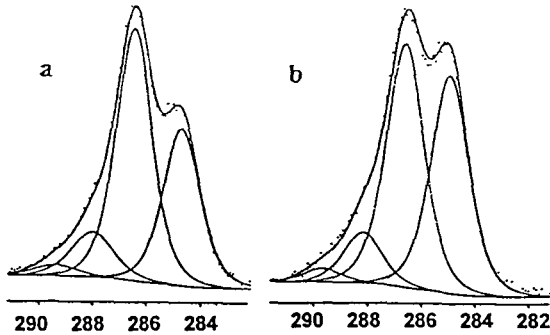


Figure 2: XPS C1s Spectra of CCA Treated Southern Pine Latewood.  
 (a) Specimens Pretreated with Ethylene Glycol (EG) and Leached  
 (b) Specimens not Pretreated with EG but leached

concentration while C1 oxidation depends on total Cr<sup>VI</sup> concentration<sup>13</sup>. Both reactions can occur during soaking in CCA but perhaps at different rates.

Contact with CCA solution resulted in an increase in the C1/C2 ratio from 0.81-0.83 in the untreated wood to 0.85-0.86 for samples soaked for 10 minutes. This suggests preferential oxidation of C2 relative to C1 oxidation. This ratio increased further to 0.89-0.95 for samples exposed for 60 minutes; however, it then dropped to 0.52-0.54 for the 180 minute exposure (Table 2, Figure 3). This suggests that after initial preferential oxidation of C2, C1 carbons continue to be oxidized, while oxidation of carbons bearing hydroxyl groups (C2) slows relative to the C1 oxidation. The reduction in C1 content combined with the formation of stable C2 carbons result in a substantial decrease in C1/C2. The O/C ratios decrease after the 60 minutes soaking treatment presumably as a result of disproportional loss of O by decarboxylation of oxidized C2's. After 180 minutes soak treatment, the O/C ratio increased due to stable C2 formation from oxidation of C1's.

The C1 component of the C1s peak, in extractive-free wood, results mainly from the lignin component of wood. About one half of the lignin carbons are C1, mainly components of the aromatic ring. The drop in C1/C2 ratio for long exposure to CCA

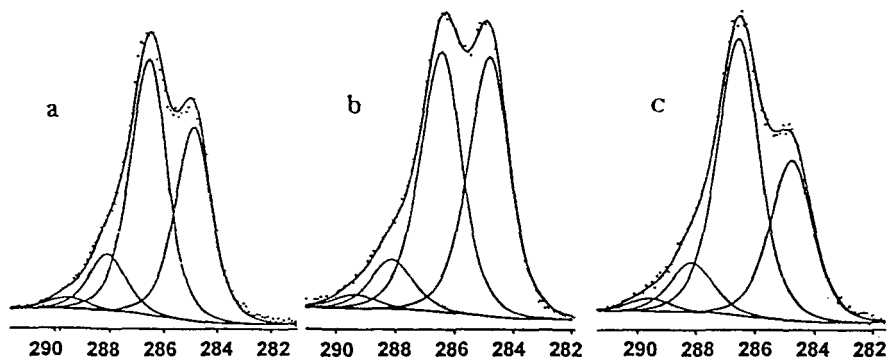


Figure 3: XPS C1s Spectra for CCA Treated Southern Pine Earlywood.

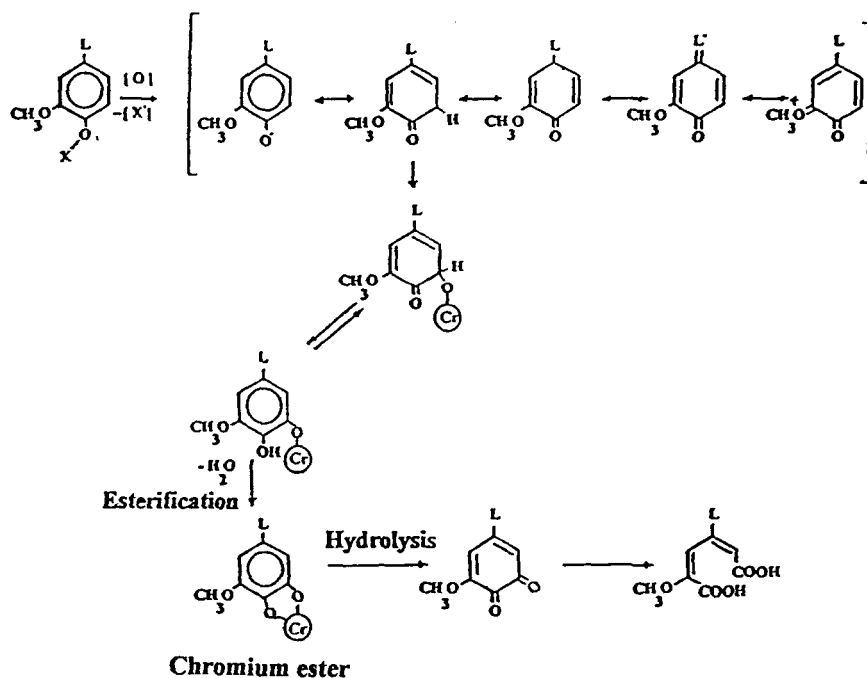
- (a) 10 Minutes Duration of Soak
- (b) 60 Minutes Duration of Soak
- (c) 180 Minutes Duration of Soak

solution suggests more extensive reaction with lignin under these conditions. This condition of long exposure of wood to acidic solution with a high  $\text{Cr}^{\text{VI}}$  concentration may simulate low temperature fixation better than high temperature fixation conditions. This would confirm the observations of reduced C1 component in ambient temperature fixed wood<sup>3</sup>. This also supports observations<sup>14,15</sup> that the chemistry involved and the end products of CCA/wood interactions are affected by fixation temperature.

Hypotheses have been advanced on the nature of the Cr-Lignin complex by others<sup>3,7</sup>. The existence of a complex in which some of the  $\text{CrO}_4$  oxygens are covalently bonded to the aromatic nuclei of phenyl propane units has been suggested. We propose an alternative structure for this compound and mechanism of formation (Scheme 1).

#### XPS Analysis of Chromium Reduction in Wood:

In the spectra for the sample measured immediately after treatment, (Figure 4) two well resolved Cr(2p) peaks are seen indicating that the reduction of  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$  had



Scheme 1: Formation and Hydrolysis of Chromium Esters

already begun.  $\text{Cr}^{\text{VI}}$  and  $\text{Cr}^{\text{III}}$  peaks were at 580.2 eV and 577.8 eV respectively. These values compare well with the reported  $\text{Cr}(2p)$  binding energy of  $\text{Cr}^{\text{VI}}$  in  $\text{CrO}_3$  of 580.0 eV and that of  $\text{Cr}^{\text{III}}$  in  $\text{Cr}_2\text{O}_3$  of 577.4 eV<sup>13</sup>. Peak fitting for samples exposed to accelerated fixation conditions only allowed for one peak, corresponding to trivalent chromium at 577.8 eV, although a small shoulder at the  $\text{Cr}^{\text{III}}$  location may be seen (Figure 4 b) indicating a high degree of reduction of hexavalent chromium during accelerated fixation. The presence of other higher oxidation states of chromium in the spectra such as  $\text{Cr}^{\text{V}}$  cannot be ruled out<sup>17</sup>.

#### XPS Analysis of Copper Fixation in CCA-Treated Wood:

Shorter CCA soaking times (10-60 minutes) spectra showed only one  $\text{Cu}(2p_{3/2})$

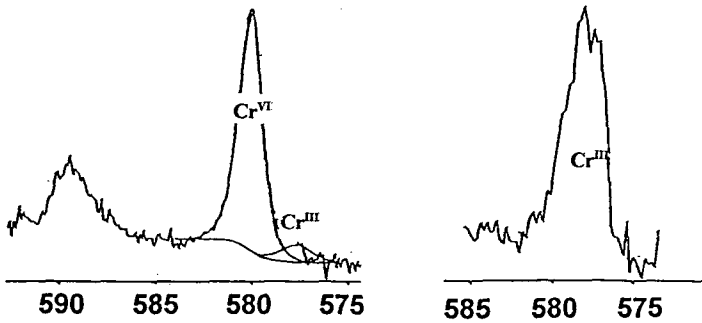


Figure 4: XPS Cr(2p) Spectra.

- (a) Fresh CCA Treated Southern Pine
- (b) Fixed CCA Treated Southern Pine

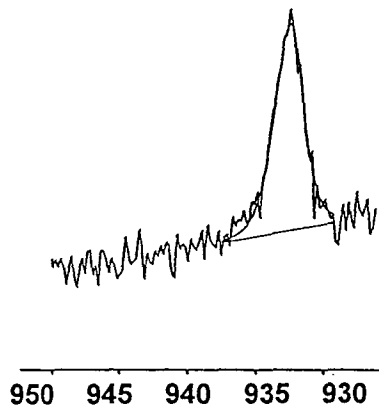


Figure 5: XPS Cu 2p<sub>3/2</sub> Spectrum of One Hour Soaking in CCA Indicating Cu<sup>I</sup> Formation.

peak at 932.9 indicating reduction of Cu<sup>II</sup> to Cu<sup>I</sup> (Figure 5). This is also evidenced by the complete absence of the shake-up satellite peaks which are characteristic of Cu<sup>II</sup> compounds. The reduction of Cu<sup>II</sup> to Cu<sup>I</sup> as a result of exposure to x-ray photoelectrons was ruled out in progressive time exposure to x-ray photoelectron study of CuO, Cu(OH)<sub>2</sub>, and copper acetate. Copper hydroxide was dehydrated,

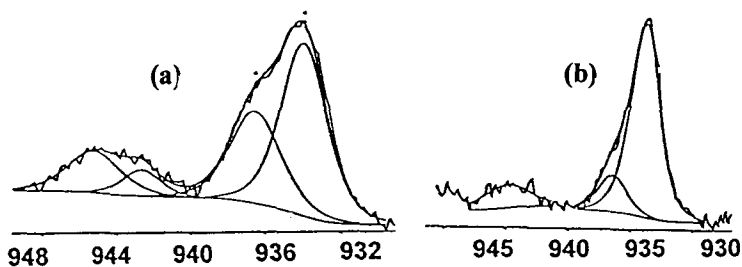


Figure 6: XPS Cu 2p<sub>3/2</sub> Spectra of Three Hours Soaking in CCA.  
(a) Unleached (b) Leached

under the high vacuum conditions of xps, to CuO during 10 hours exposure but reduction to Cu<sup>I</sup> was not observed. Longer CCA soaking time (3 hours) resulted in oxidation of the originally formed Cu<sup>I</sup> compounds to Cu<sup>II</sup> compounds with binding energies at 933.9 (CuO.wood) and 936.4 (CuOH.wood), Figure 6. The mechanisms involved are not yet clear. It is likely, however, that the reduction of Cu<sup>II</sup> to Cu<sup>I</sup> is affected by organic free radicals formed during the oxidation of wood.

#### Effect of Leaching:

Regardless of soaking time, all leached samples (10 minutes extraction with water at 60 °C) showed reduction in C2 content and increase in C4 content in their xps C1s spectra. Spectra of leached samples also exhibited higher O/C. An explanation of this is that compounds such as the proposed chromium esters are being hydrolysed and subsequently converted to stable unsaturated carboxylic acids. A possible mechanism to one example is presented in Scheme 1.

When the xps spectra were compared for leached and unleached samples, it was evident that loss of all CCA elements occurred in leached samples. Comparison of Cu(2p<sub>3/2</sub>) peaks also indicated that copper fixed as copper hydroxides was more susceptible to leaching than copper fixed in the form of oxides (Figure 6).

## CONCLUSIONS

CCA oxidation of wood carbons bearing hydroxyl groups occurs readily under high temperature fixation conditions leading to production of the corresponding carbonyl compounds. These are rapidly converted to the corresponding carboxylic acids, which are quickly lost by decarboxylation and the evolution of CO<sub>2</sub> gas.

Prolonged contact of wood components with CCA treating solution appears to result in more extensive oxidation of the lignin constituent of wood. This suggests indirectly that fixation temperature may affect the fixation chemistry as well as the rate of fixation. More work is needed to clarify these effects.

At high temperatures, rapid fixation of CCA treated southern pine results in a high degree of reduction of hexavalent chromium to the more stable and less toxic trivalent chromium. Copper, on the other hand, appeared to undergo reduction to Cu<sup>I</sup> then oxidation to give mixture of Cu<sup>II</sup> oxides and hydroxides depending on the extent of exposure to CCA treating solution. This again indicates that fixation temperature may affect the chemical nature of fixation products.

## ACKNOWLEDGEMENTS

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