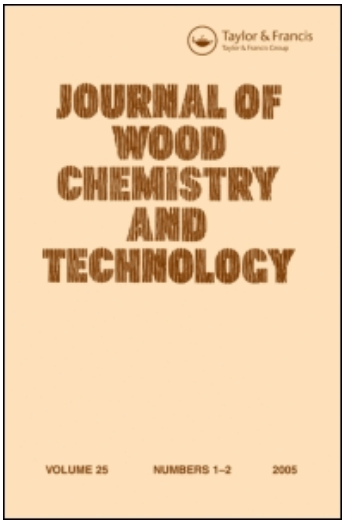

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Spectroscopic Analysis of Southern Pine Treated with Chromater Copper Arsenate. I. X-Ray Photoelectron Spectroscopy (XPS)-[17]

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SPECTROSCOPIC ANALYSIS OF SOUTHERN PINE TREATED WITH CHROMATED COPPER ARSENATE. I. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)[1/]

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ABSTRACT

The amount of southern pine lumber treated with chromated copper arsenate annually is considerable, yet the association of this preservative with the wood structure is not clear. The current study was undertaken to elucidate the nature of chemical reactions occurring between the components of the treating solution and the constituents of wood. Small, clear Southern pine samples were treated with six different preservative solutions (Cr; Cr/Cu; Cr/As; CCA-A; CCA-B; CCA-C), at 6.4 and 40 Kg/m^3 (0.4 and 2.5 pcf) retentions, and compared to water treated and untreated controls. Samples were dried following treatment and analyzed by X-ray photoelectron spectroscopy (XPS). Evaluation of XPS data indicated that the preservative components reacted with wood, through aromatic and possibly alkene substitution, while oxidation of hydroxyl groups was not detected. The proposed

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wood/CCA bonding also offers an explanation for differences in hardwood and softwood durability following treatment.

INTRODUCTION

The use of waterborne preservatives in the United States represents a large and increasing treatment method for the prevention of decay in lumber and plywood. One such preservative, chromated copper arsenate (CCA), is used to treat about one-third of the lumber produced in the Southern United States.[1] More recent statistics indicate that as much as 41% of the southern pine lumber produced annually might be treated.[2] While the benefits of treating with CCA preservatives have been demonstrated,[3-5] the chemical reactions between the constituents of wood and the components of CCA are not well understood. Furthermore, it has been indicated that changes in mechanical properties may occur in treated wood. Winandy et al.[6] and Bendtsen et al.[7] noted that the literature regarding the effect of different formulations of waterborne preservatives on the mechanical properties of wood was inconsistent and often conflicting. Because differences in mechanical behavior are undoubtedly a function of the treatment conditions, a fundamental understanding of wood/CCA reactions may lead to improved control or modification of the treating solutions to avoid the particular interactions which are deleterious toward strength.

While numerous methods have been used for the quantitative determination of CCA retained in wood during treatment and the chemical analysis of the wood following treatment, past research

has done little to explain the nature of chemical bonding between the components of the treating solution and the constituents of wood. Two in-depth studies of CCA fixation were led by Dahlgren [8-13] and Pizzi.[14-17] These studies investigated the kinetics of fixation and suggested possible metal complexes, but not the nature of the wood/metal bonding. Pizzi[14-17] concluded that most of the CCA formed insoluble complexes with lignin and unstable complexes with cellulose. In other studies, fixation of CCA varied with solution strength, post treatment drying conditions, and species.[18,19] It was also suggested that the fixation mechanism varies between hardwoods and softwoods.[20-23] Although exact reactions between the components of CCA and the constituents of wood are unknown, studies consistently suggest that the chromium component of the preservative is required for most of the fixation mechanisms.[14-17,24-26] From the chromic acid oxidation of organic compounds, it can be generalized that:

1. Chromic acid oxidation of primary and secondary alcohols yields aldehydes and ketones, respectively.[27-30]
2. Chromic acid oxidizes aldehydes and ketones to carboxylic acids.[27-30]
3. While ethers are relatively stable against chromic acid oxidation, esters can be formed.[27,30]
4. Alkene oxidation by chromic acid results in cleavage of the carbon-carbon bond and formation of two carbonyls.[27,30,31]
5. During chromic acid oxidation, an intermediate chromate ester is formed.[27,29]

6. The rate limiting step in chromic acid oxidation is the decomposition of the intermediate chromate ester.[28]

Studies of the treatment of wood surfaces with chromium trioxide show that the chromium forms soluble complexes with cellulose, and insoluble complexes with lignin.[32-35] Because both cellulose and lignin contain hydroxyl groups, it is probable that they are both oxidized to some extent. The formation of insoluble lignin-chromium complexes suggests that additional reactions are occurring between the lignin and chromium, other than simple oxidation.[34,35]

From the findings discussed above, it appears that the main reaction of cellulose with CCA is the reduction of chromium. Many of the hydroxyl groups present in cellulose would, therefore, be expected to be oxidized to carbonyl groups. Further, while lignin might be oxidized, it appears to supply most of the metal bonding sites.[17,34] To arrive at these conclusions, previous studies have required at least one of the following assumptions:

1. During quantitative isolation of the chemical constituents of wood, the preservative chemicals associated with each fraction are also extracted intact.
2. Model compounds react with the treating chemicals in the same manner as with solid wood.

While these assumptions may be reasonable and correct, it seems necessary to find nondestructive techniques for analyzing wood which will not only test the validity of these destructive

methods, but also provide information about the nature of wood/CCA bonding.

In the current study, several nondestructive, solid-state, spectroscopic techniques were utilized to elucidate the nature of wood/CCA complexes in situ, in an attempt to understand the influence of CCA treatment on the mechanical properties of Southern pine lumber. These methods are not predicated on an extraction or isolation step, and may, therefore, be more representative of the actual condition of the wood. One of these techniques, X-ray photoelectron spectroscopy (XPS), often referred to as electron spectroscopy for chemical analysis (ESCA), has been developed for the surface analysis of solids. Since its development, a great deal of research has employed XPS in the evaluation of polymers including cellulose, lignin, wood, pulp, and paper.[33,35-44] These studies range from simple material characterization to evaluation of wood oxidation by weathering, periodate, and nitric acid treatments. Application of XPS to CCA-treated wood should give an indication of the extent of oxidation that occurs in wood upon treatment, and with which constituents of wood the preservative components react. This paper, the first in a series, presents results from the XPS analysis of treated and untreated wood, and gives evidence for the nature of wood/CCA complexes. Future papers will include additional chemical analysis data which will ultimately be related to mechanical testing data.

TABLE 1. Treatment Retentions.

Treatment	Retention kg/m^3 (pcf)			
	Low		High	
	Target	Actual	Target	Actual
CCA type A	6.4 (0.4)	6.2 (0.39)	40 (2.5)	42 (2.63)
CCA type B	6.4 (0.4)	4.8 (0.30)	40 (2.5)	24 (1.52)
CCA type C	6.4 (0.4)	5.6 (0.35)	40 (2.5)	39 (2.42)
Chromium	3.0 (0.19)	2.7 (0.17)	19 (1.19)	23 (1.41)
Chromium + Copper	4.2 (0.26)	3.8 (0.24)	26 (1.65)	25 (1.53)
Chromium + Arsenic	5.3 (0.33)	4.8 (0.30)	33 (2.04)	38 (2.36)
Controls -Water	-- --	-- --	-- --	-- --
-Untreated	-- --	-- --	-- --	-- --

EXPERIMENTAL

The experimental design for this project consisted of six treatments, each at two levels, and two sets of controls, one untreated and one water treated (Table 1). Target retentions for single and double component treating solutions were based on individual element retentions of a comparable CCA type C solution, not on total combined retention. In this way, the amount of any particular preservative element in the single and double component formulations was comparable to the amount of that component in CCA type C at the same target retention level. Thus, when only one or two components were contained in the treating solution, the actual retention was less than the combined target retention of the three component CCA solution.

Sample Preparation

For this experiment, only clear Southern pine sapwood, measuring 2.54 cm x 6.35 cm x 76.2 cm (1.0 inch x 2.5 inches x 30 inches), was used. To reduce variability, the sample material for

all chemical analysis was cut from a single southern pine flitch. Prior to treating, the samples were conditioned to an equilibrium moisture content of 12% by storing for two months in an environment chamber maintained at 23.3°C (74°F) and 65% relative humidity. Treating was performed at the United States Department of Agriculture Forest Service, Forest Products Laboratory in Madison, Wisconsin, in an experimental pressure cylinder at ambient temperature with an initial vacuum of 74 kPa (22 inches of mercury) maintained for 15 minutes, followed by 60 minutes of pressure at 1034 kPa (150 psig). Following treatment, samples were stickered, stored and dried for three months in a controlled environment maintained at 23.3°C (74°F) and 65% relative humidity. After drying, 12.7 cm (5 inches) was cut off one end of the specimen for chemical analysis. Sample blocks were cut from within this specimen such that all chemically analyzed material originated from the "bulk" rather than the surface of the original sample.

Sample Analysis

Analysis by X-ray photoelectron spectroscopy was performed in the Department of Chemical Engineering at Auburn University, using a Leybold-Heraeus LHS-10 spectrometer fitted with a water-cooled aluminum anode and hemispherical optics. The water-cooled aluminum anode maintained the sample at less than 30°C (86°F) during analysis. The spectrometer was operated at 200 watts, using Al $K\alpha_{1-2}$ radiation (1487 eV) and a detector pass energy of 20 eV. XPS analysis was performed with minimal sample

preparation to determine if the surface chemistry of the wood was altered by treatment. Specimen surfaces for XPS analysis were prepared by cutting a clean, smooth transverse surface on sample blocks using a sliding microtome. The specimen was then sawn off at 0.2 cm below the prepared surface. The specimens were then separated into earlywood and latewood portions, using a clean, single edge razor blade. Six to eight individual strips, containing only one portion of the annual growth rings (either earlywood or latewood), were then glued side-by-side to the surface of an aluminum boat using a low vapor pressure resin such that only the prepared transverse surfaces were analyzed. Although the sampling depth via XPS is less than 0.01 micron,[45] because the surfaces analyzed by XPS were taken from within the "bulk" of the sample rather than the original sample surface, the spectra should effectively represent the whole sample.

RESULTS AND DISCUSSION

Spectra Characterization and Deconvolution

In X-ray photoelectron spectroscopy, an increase in the degree of oxidation increases the binding energy of photoelectrons by approximately 1.5 electron volts (eV) per oxidation state.[45] The carbon 1s (C 1s) peak in the XPS spectra of wood is composed of three main components,[39,41] as shown in Figure 1. The C1 component of the C 1s peak is comprised of carbon atoms bound only to other carbon atoms and hydrogen atoms (non-oxidized carbon).[39] This component arises predominately from the lignin constituent of

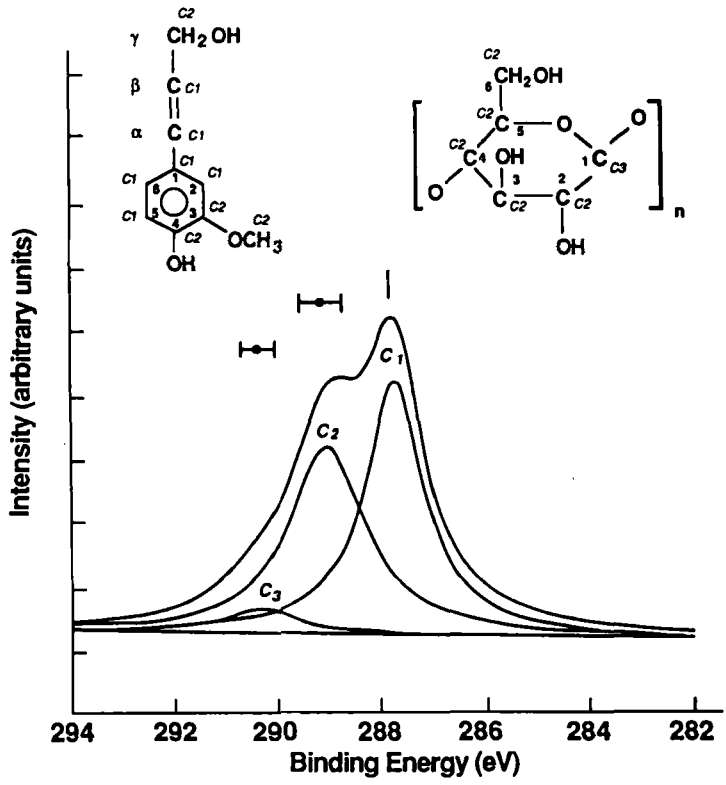

Figure 1. Schematic Representation of C 1s Peak Deconvolution Procedure. Experimental Data Obtained from Untreated Southern Pine Latewood.

wood (see Figure 1). The C2 component of the C 1s peak is composed of carbon atoms bound to a single non-carbonyl oxygen atom in addition to other carbon and hydrogen atoms (oxidation state of one).[39] As shown in Figure 1, the C2 component can arise from both the carbohydrate and lignin constituents of wood. The C3 component of the C 1s peak represents carbon atoms bound to other carbon and hydrogen atoms, plus either: 1) one carbonyl

oxygen atom, or 2) two non-carbonyl oxygen atoms (both 1 and 2 result in an oxidation state of two).[39] By evaluating the electronic environment of the different carbon atoms comprising the three components of the C 1s peak, it is apparent that the variability within each component is tremendous. This variability results in component peak broadening (i.e., carbon atom 5 of glucose will cause a different shift than carbon atom 3 of the coniferyl alcohol unit, thereby broadening the C2 component of the C 1s peak). Due to the natural variability of wood (i.e., earlywood/latewood differences), the validity of constant peak widths and separations becomes questionable. Further, when wood is chemically modified via some process, the idea of constant peak widths and separations is disputable, because new chemical species are formed. However, some rationale must be used to deconvolute the C 1s peak, such that the data can be interpreted.

In this study, the following assumptions were made with regard to spectral deconvolution:

1. The binding energy separation between the C1 component of the C 1s peak and the center of the oxygen 1s (O 1s) peak should remain relatively stable (245 eV ± 1.0 eV).
2. Separation of the C1 and C2, and C2 and C3 components should remain relatively stable (1.5 eV ± 0.5 eV).
3. All three components should be present to some extent in all treatments.
4. Peak full width at half maximum (FWHM) for the individual components should remain relatively stable (C1 FWHM=1.85

eV ± 0.6 eV; C2 FWHM=1.85 eV ± 0.5 eV; C3 FWHM=1.55 eV ± 0.6 eV).

Using these assumptions and a Gaussian deconvolution program, peak locations, separations, and widths were varied until the convolution of the three components gave the best fit to the data. Peak locations, separations, and widths may vary slightly from one spectrometer to another, and these variations should be allowed for in future studies.

The separation of the C 1s component peaks from the O 1s peak are presented for all samples in Figure 2, along with variations in peak widths. The three components are reasonably well resolved, with only one minor point of overlap in peak location. However, when the separation of the C2 and C3 components from the C1 component is plotted as in Figure 1, the three component peaks are shown to be well resolved. As such, the criteria used for deconvolution allow for meaningful C 1s peak interpretation.

Sample stability during XPS analysis

A question was raised concerning XPS spectra being real or a result of sample degradation while in the analysis chamber. In a recent study by Fowler et al.,[46] soft magnesium X-rays were not found to induce significant changes in cellulose nitrates over usual XPS analysis times. In contrast, Fowler et al.[46] found that titanium X-rays reduced the surface of cellulose nitrates with time. Because soft aluminum X-rays were used in this study, sample degradation was not expected to occur. In an effort to support this belief, a latewood sample treated with CCA-C at 5.6

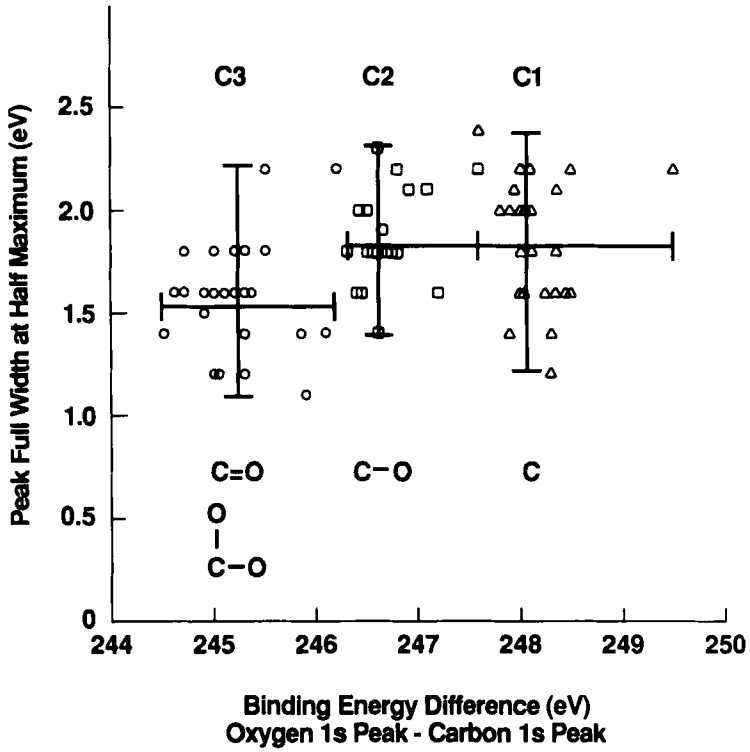

Figure 2. Separation of C 1s Components from O 1s Peak (O 1s - C 1s)

Kg/m^3 (0.35 pcf) was prepared and analyzed after various periods of time in the analysis chamber. During this test the sample was not moved between analyses, so that the same portion of the sample was always being analyzed. Because all of the initial C 1s spectra were acquired after the sample had been exposed to the X-ray source for about one hour, the behavior of the sample during the first two hours of exposure was of the most interest. For this reason, during the first two hours of analysis, the X-ray

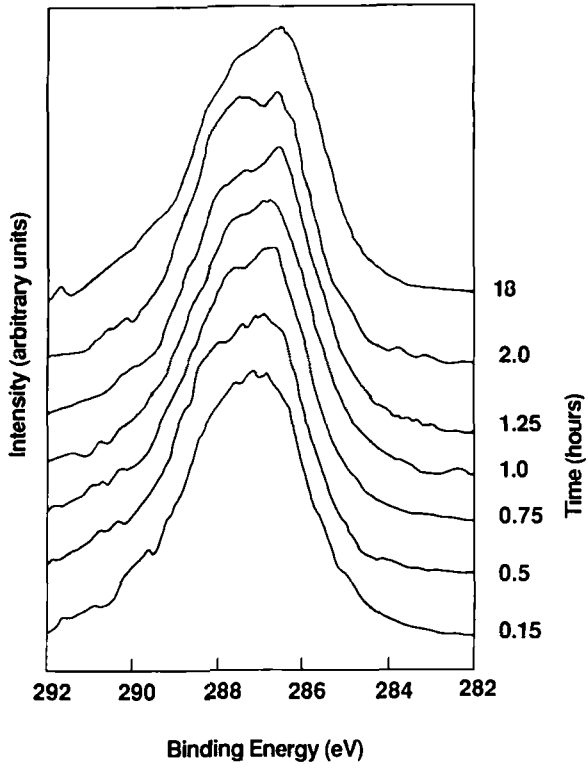

Figure 3. Variation in XPS C 1s Spectra as a Result of Different Lengths of X-ray Exposure

source was never turned off, and several C 1s spectra were obtained. After the sample had been analyzed at the end of two hours, the X-ray source was turned off, but the sample was left in the analysis chamber for an additional 16 hours. After 16 hours the X-ray source was turned back on and a C 1s spectra was again obtained from the sample. The C 1s spectra did not change markedly with increased analysis time (Figure 3). If there was a change in the C 1s spectra with time, it was in the form of

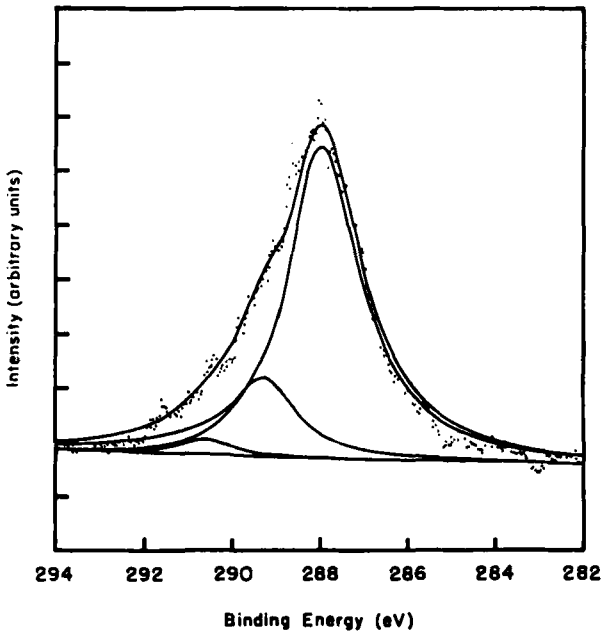

Figure 4. XPS Spectrum of Untreated Southern Pine Latewood

reduction. Therefore, if X-ray or vacuum induced damage had occurred in any of the initial analyses, it would have been in the form of reduction and would have masked part of the oxidation seen in this study.

Spectral variation with treatment

Earlywood and latewood samples resulted in quite different C 1s spectra. An example of this difference is illustrated in the untreated latewood (Figure 4) and untreated earlywood (Figure 5) spectra. The C1 component was greater in the earlywood spectrum than in the latewood spectrum. This was expected because the C1 component of the C 1s band represents part of the lignin and

TABLE 2. C1:C2 Ratios from XPS Spectra.

	C1:C2 Ratio			
	Earlywood		Latewood	
Treatment	Low Ret.	High Ret.	Low Ret.	High Ret.
CCA type A	0.66	0.39	0.49	0.48
CCA type B	0.34	0.43	0.78	0.23
CCA type C	0.30	0.37	0.47	0.29
Chromium	1.22	0.70	0.84	0.67
Chromium + Copper	2.05	1.99	0.37	0.36
Chromium + Arsenic	1.17	0.75	0.88	0.47
	Earlywood		Latewood	
Controls -Water	3.09		1.03	
-Untreated	4.37		1.08	

extractive constituents of wood, which are present in higher percentages in earlywood than latewood.[47]

For the earlywood specimens, the C1 component of the C 1s band decreases substantially from the controls to the CCA treatments, with a concomitant increase in the C2 component, indicating that the preservatives are reacting with the lignin constituent of wood. The C1:C2 ratio was 4.4 for the untreated control and 0.3 for low retention CCA-C treated wood (Table 2). The most prominent feature of the XPS data was the stepwise shift from the C1 to the C2 component with various treatments. This shift can be seen in Figures 5, 6, 7, and 8. The graphical representation of the results in Figure 9 tends to indicate the synergistic nature of CCA preservatives.

The close grouping of different levels of the various treatments indicates that the retention level was somewhat less critical than the formulation of the treating solution, with respect to chemical reactions between preservative components and

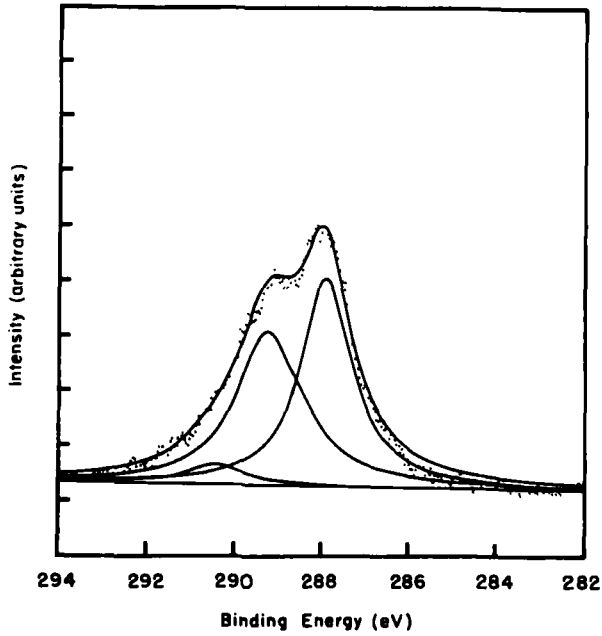

Figure 5. XPS Spectrum of Untreated Southern Pine Earlywood

the constituents of wood. The interaction of the treating chemicals also becomes evident by noting that the high retention chromium treatment falls between the two and three component treatments, with the CCA systems indicating the greatest oxidation. Because the high retention chromium treatment resulted in greater oxidation of the wood than did the two component treatments, it appears that the presence of all three of the preservative components are required for true wood/CCA reactions to occur. As such, single and dual component treatments should not be used to model wood/CCA reactions.

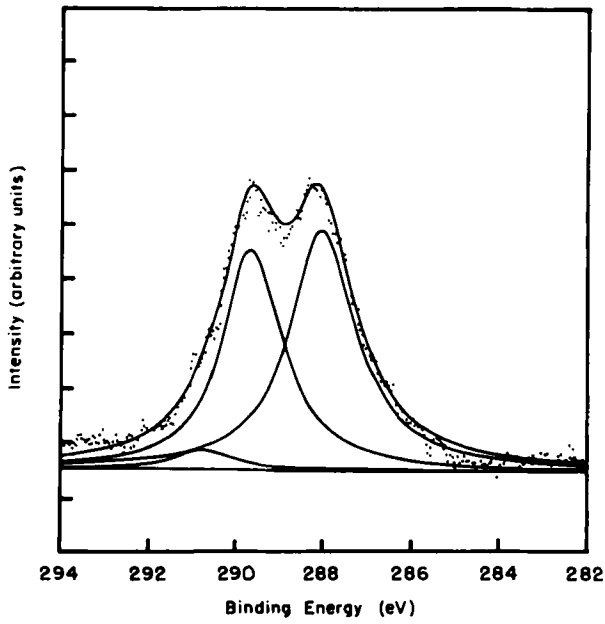

Figure 6. XPS Spectrum of the Earlywood Portion of Southern Pine Treated with Chromium at 0.4 pcf

Further, no differences were detected between the CCA formulations, because they all resulted in approximately the same degree of oxidation.

For the latewood portion of the samples, the same general trend of increasing lignin oxidation with treatments was found (Figure 10). Higher preservative retentions in the latewood always resulted in lower C1:C2 ratios than low retentions of the same treatment. The magnitude of change in oxidation was less for the latewood portion than the earlywood portion, with the former having a C1:C2 ratio of 1.1 for the untreated control and

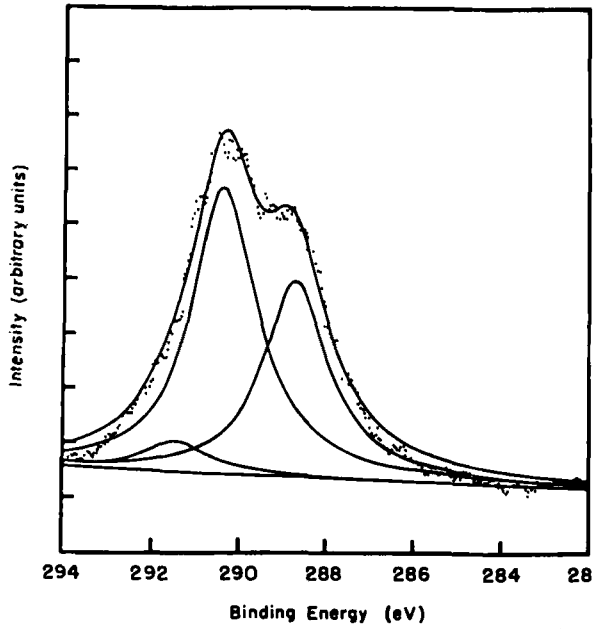

Figure 7. XPS Spectrum of the Earlywood Portion of Southern Pine Treated with Chromium at 2.5 pcf

0.23 for CCA-B treated wood (Table 2). This change in magnitude could be due in part to the lower initial lignin and extractive contents of latewood samples with respect to the earlywood samples.[44] However, differences in lignin and extractive contents between earlywood and latewood alone cannot explain the fourfold increase in the C1:C2 ratio of untreated controls from 1.08 for latewood to 4.37 for earlywood. This result suggests that a more fundamental difference could exist in the chemical nature of cell wall constituents between earlywood and latewood.

Perhaps more important than the information revealed by XPS, was what the data did not indicate. As indicated earlier, it was

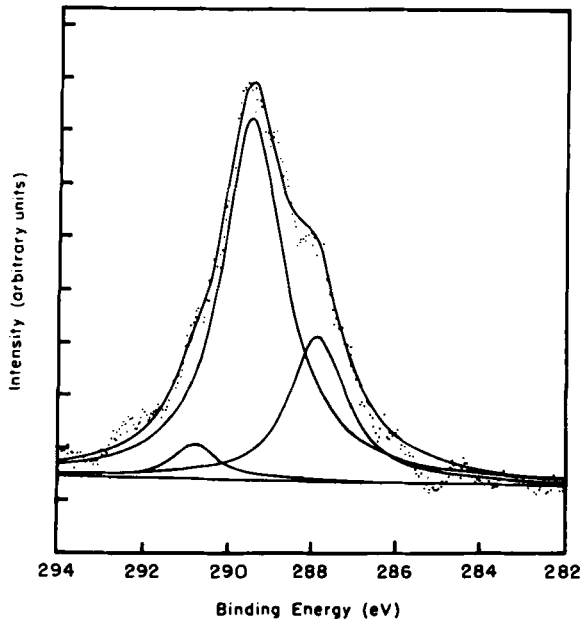

Figure 8. XPS Spectrum of the Earlywood Portion of Southern Pine Treated with CCA-C at 2.5 pcf

expected that chromium would oxidize hydroxyl groups in the wood to carbonyl groups. This would result in an increase in the C3 component of the C 1s peak and a concomitant decrease in the C2 component. Throughout this study, the C3 component remained relatively minor in all of the samples while the C2 component increased with treatments. Accordingly, the expected oxidation of hydroxyl groups to carbonyl groups by chromium was not observed.

While these findings indicate no changes in the carbohydrate constituents of wood, it can not be concluded that reactions

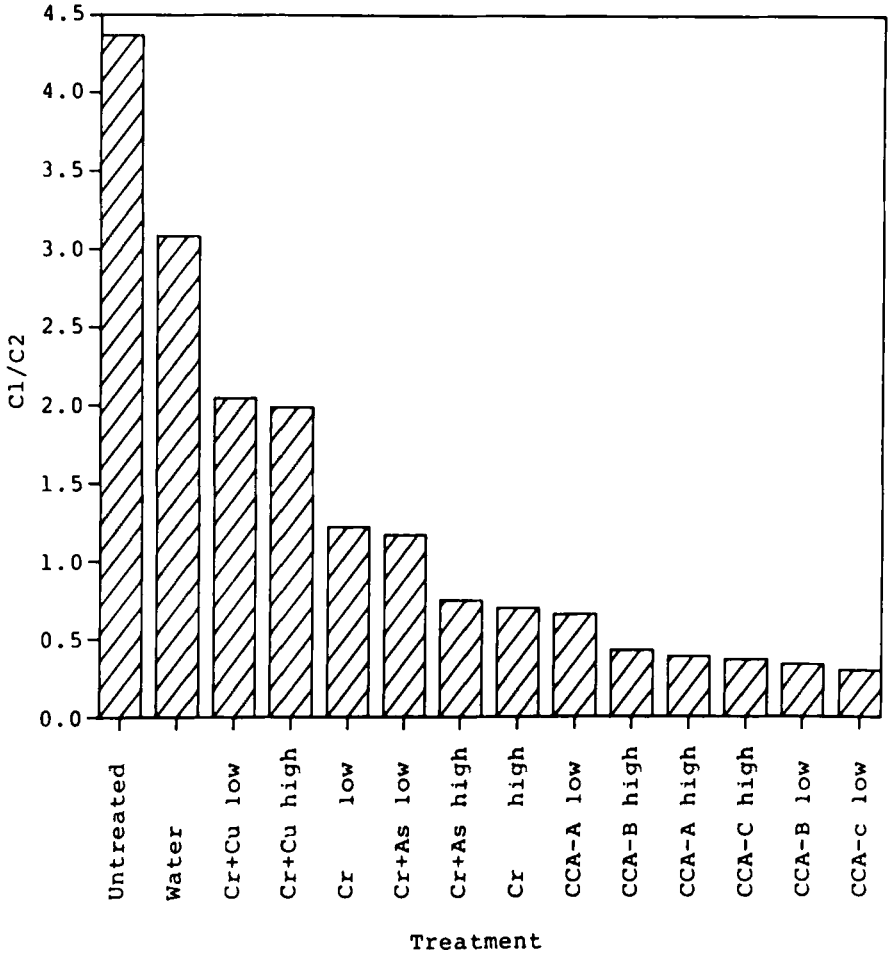

Figure 9. C1:C2 Ratios of XPS Peaks for the Earlywood Portion of Southern Pine

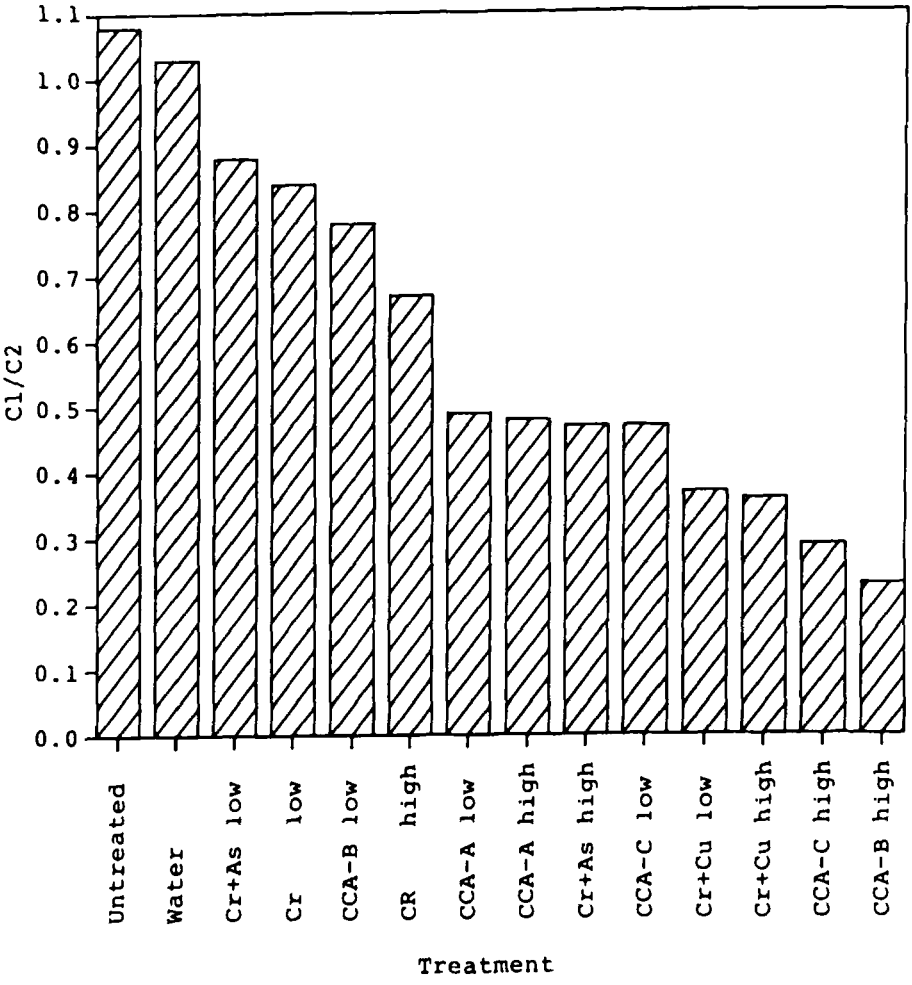

Figure 10. C1:C2 Ratios of XPS Peaks for the Latewood Portion of Southern Pine

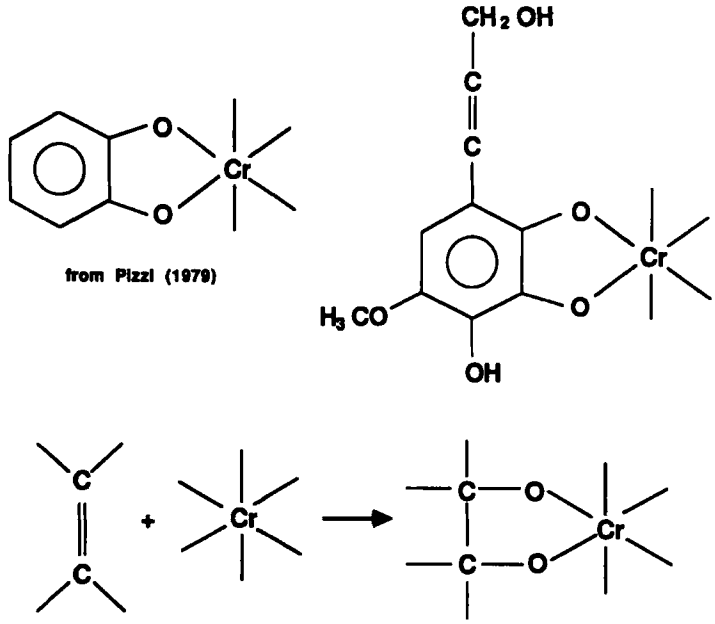

Figure 11. Possible Wood Chromate Esters

between the components of the treating solution and carbohydrates do not occur. For example, if CuO_2 reacts with the hydroxyl groups of cellulose such that C-O-Cu bonds are formed, the C 1s peak will not be significantly effected, because the carbon atom is still bound to a single non-carbonyl oxygen atom. However, if non-substituted carbon atoms in an aromatic ring (such as carbons 2, 5, and 6 in a coniferyl alcohol unit) reacted with chromic acid, such that chromate esters were formed similar to those indicated in Figure 11 by Pizzi,[34] the observed shift from C1 to C2 would be expected.

If the nature of wood/CCA bonding is through the proposed lignin complex, then it would also offer an explanation for differences in hardwood and softwood durability following treatment. Because hardwood lignins contain syringyl structures, it is possible that the second methoxyl group limits the formation of "stable" wood/chromate complexes. This theory is supported by two facts. First, it is known that in some hardwoods, fibers contain predominantly syringyl type lignin, while vessels and rays contain more guaiacyl type lignin.[48] Second, it has been found that hardwood fibers retain markedly lower concentrations of preservative elements.[49] Since the proposed wood/CCA complex cannot form with syringyl structures, and poorly treated hardwood fibers contain predominantly syringyl lignin, then the proposed wood/CCA complex also provides an explanation for durability problems in CCA-treated hardwood.

It is also possible for the α and β carbon atoms of the lignin monomer side chain to contribute to the C1 component of the C 1s peak. This is especially true when they are joined via a double bond. Double bonds are also known to be attacked by chromic acid (Figure 11).[27,30,31] Thus, if there are more α-β double bonds in earlywood lignin than in latewood lignin, this would help explain the large difference in the C1:C2 ratio between untreated earlywood and latewood.

SUMMARY AND CONCLUSIONS

1. The surface of wood is not significantly altered during XPS analysis provided soft x-rays are used and the sample is kept cool.

2. Criteria were established for meaningful carbon 1s peak deconvolution.
3. Earlywood and latewood samples yield different XPS spectra.
4. XPS data show that the number of carbon atoms not bound to an oxygen atom (predominantly originating from the lignin fraction of wood) decreased dramatically when samples were treated.
5. The carbonyl content did not change substantially from the untreated to the treated samples.
6. XPS results demonstrate that a synergistic relationship exists between the components of the treating solution, and how they react with southern pine lumber.
7. Because all three of the CCA preservative components appear to be required for true wood/CCA reactions to occur, single and dual component treatments should not be used as CCA model systems.
8. XPS data suggest that the preservative components react with lignin via aromatic, and possibly alkene, substitution. The nature of this substitution is expected to be through the formation of chromate esters.
9. Considering this proposed formation of chromate esters, differences in the structure of hardwood and softwood lignins could explain why hardwoods are often not effectively treated with CCA.

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