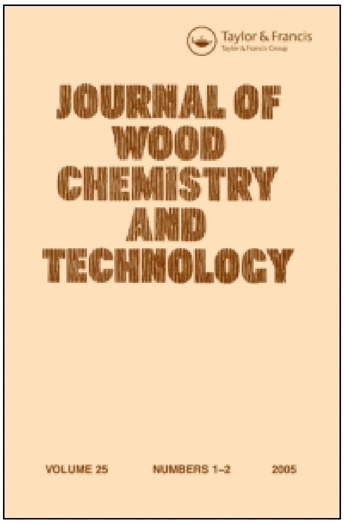

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SPECTROSCOPIC ANALYSIS OF SOUTHERN PINE TREATED WITH CHROMATED COPPER ARSENATE. II. DIFFUSE REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY (DRIFT)

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ABSTRACT

Although chromated copper arsenate (CCA) is one of the most important treatment methods for the prevention of decay in wood, the nature of wood/CCA reactions are 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 diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). Evaluation of DRIFT data indicated that the preservative components reacted with the aromatic and carbonyl groups in wood.

INTRODUCTION

One of the most important preservative treatments for the prevention of decay in lumber is chromated copper arsenate (CCA). Between 33% and 41% of all the southern pine lumber produced annually is treated with CCA to prevent decay.[1-2] Although the advantages of CCA treated lumber (such as superior decay resistance, minimal environmental leaching, and relatively low cost) are known,[3-5] the influence of CCA treatment on the mechanical properties of wood are not yet clear.[6-7] Because any differences in mechanical properties may be a result of chemical changes that occur during treatment, a fundamental understanding of the wood/CCA reactions could lead to treatments that do not have a negative impact on mechanical properties. Studies led by Dahlgren[8-13] and Pizzi[14-17] investigated the kinetics of CCA fixation and suggested possible metal complexes, but the nature of wood/CCA bonding was not determined.

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. These methods do not require an extraction or isolation step, and should, therefore, be more representative of the actual condition of the wood. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) is one of these techniques, and Schultz et al.[18-19] and Schultz and Glasser[20] have demonstrated that DRIFT can be applied to wood, cellulose, and lignin. Consequently, the functional groups in treated and untreated wood could be evaluated without altering the nature of the sample during preparation, such that the reactions between preservative components and the constituents of wood might be detected. This paper, the second in a series, presents results from the DRIFT analysis of treated and untreated wood, and provides supporting evidence for the nature of wood/CCA complexes. In the first paper of this series,[21] it was found that the components of the treating solutions reacted with non-oxygenated carbon atoms (predominately found in the aromatic ring of lignin) of wood, probably through some type of chromate ester. Future papers will present additional chemical data and will correlate the chemical information with matched mechanical data.

EXPERIMENTAL

The experimental design for this project consisted of six treatments, each at two levels and two sets of controls, one water-treated and one untreated (Table 1). Target retentions for single (Cr) and double (Cr/Cu and Cr/As) component treating solutions were based on individual component 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

TABLE 1.

Treatment Retentions.

Treatment	Retention Kg/m^3 (pcf) Low Target	Low Actual	High Target	High 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	-- --	-- --	-- --	-- --

the amount of that element in CCA type C at the same target retention level. Thus, when only one or two components were contained in the treating solution, the target retention was less than the target retention of the three component CCA solutions. The various treating formulations were employed in an attempt to better understand the reactions between the preservative components and the constituents of wood.

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 treated. To reduce variability, the sample material for the chemical analyses 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 and conditioned for three months in a controlled environment maintained at 23.3°C (74°F) and 65% relative humidity. After conditioning, 12.7 cm (5 inches) was cut off one end of each specimen for chemical analysis. Sample blocks were cut from this 12.7 cm (5 inch) specimen for chemical analysis. Except for samples analyzed for preservative retention (which included the entire cross section), all chemically analyzed material originated from within the "bulk" of the original sample (which excluded the original sample surfaces). Specimens for DRIFT analysis were prepared from sample blocks, measuring 1.0 cm (0.4 inch) radially, 1.0 cm (0.4 inch) tangentially, and 2.0 cm (0.8 inch) longitudinally, by cutting a clean, smooth transverse surface using a sliding microtome. The specimen for analysis was then sawn off the sample block at 0.2 cm (0.08 inch) below the microtome prepared surface.

Sample Analysis

Diffuse reflectance Fourier transform infrared spectroscopic (DRIFT) analysis was performed during February 1986 at the Anglo-American Clays subsidiary of ECC America Inc., in

Sandersville, Georgia, using a Perkin-Elmer 1710 FTIR equipped with a Harrick Scientific diffuse reflectance attachment. All spectra were the result of 250 scans being signal averaged, with a resolution of 2 cm^{-1}. A single spectrum was obtained for each treatment. The specimens were placed directly into the diffuse reflectance sample holder, such that the infrared beam impinged on the microtomed transverse surface. It should be noted that DRIFT is considered to be a "bulk" analysis technique, with a sampling depth for wood greater than 1.0 micron.[22]

RESULTS AND DISCUSSION

Peak assignments for DRIFT spectra were made according to those of Liang and Marchessault,[23] Higgins et al.,[24] Marchessault,[25] Szymanski,[26] Sarkanen et al.,[27] Marton and Sparks,[28] and Pretsch et al[29] (Figure 1). While DRIFT (reflectance) spectra are not identical to transmission (absorbance) spectra obtained via a KBr disk, it was found that the regions of interest are consistent between the two methods. It should be noted that the spectra could be smoothed to reduce noise, however, this smoothing masked changes between the treatments. The spectra were therefore, analyzed without smoothing. For between sample comparisons, the peak areas of interest were taken as their ratio against the carbon-hydrogen (C-H) stretching peak area (3020 - 2775 cm^{-1}), to reduce the influence of sample heterogeneity due to variations in signal

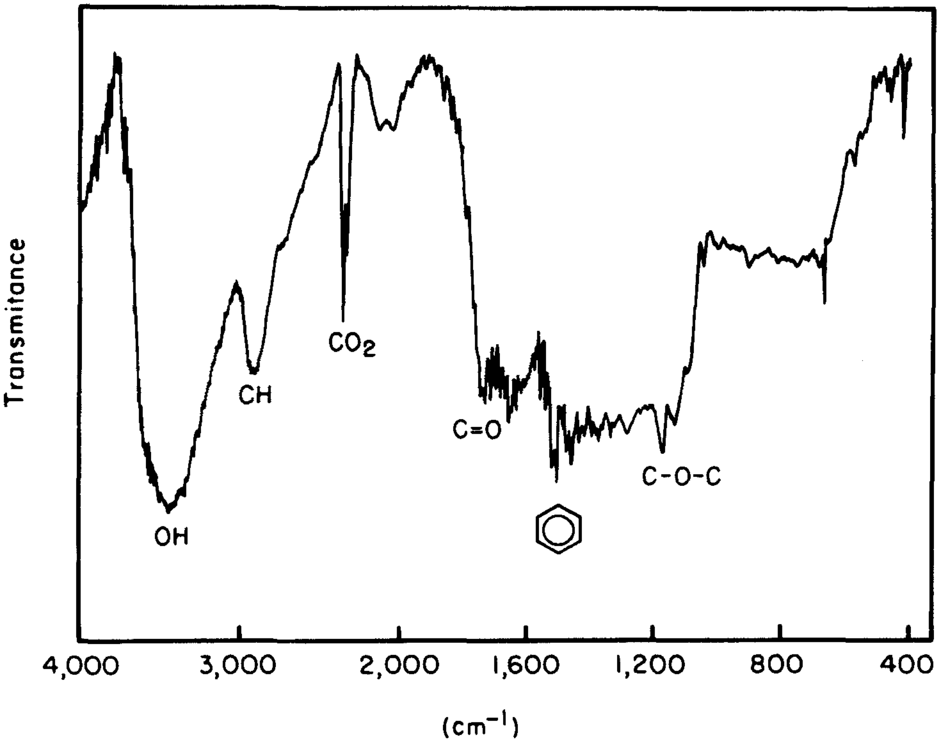

FIGURE 1. Major Peak assignments for DRIFT Spectra (CO_2 peak is from the air not the sample).

energy and baseline errors. Peak baselines were drawn from the point of transmittance on one side of the peak to the point of transmittance on the other side of the peak. Past studies have often used the aromatic peak centered at 1510 cm^{-1} as an internal standard.[26] Since the aromatic peak at 1510 cm^{-1} was to be analyzed in this study, the C-H peak was chosen as the internal standard because of its between sample stability. It should be noted that when the peaks of interest were taken as their ratio against the oxygen-hydrogen (O-H) stretching peak (3700 - 3020 cm^{-1}), which was used as an internal standard by St-Germain and Gray[30], the same general results were obtained as when the C-H peak was used.

DRIFT analysis of earlywood specimens gave consistent results, but the latewood results were inconsistent, with a low-signal-to noise ratio. This was because the higher density latewood portion of the sample resulted in extensive specular reflectance. While latewood spectra could have been obtained by grinding the sample and diluting in potassium bromide (KBr), the reason the neat DRIFT technique was used in this study was to analyze the wood in the solid state without altering its chemical structure. Because the reaction of KBr with the treating chemicals and treated wood are unknown, mixing KBr with the wood samples might result in uncertainty in interpretation and was unacceptable. Therefore, DRIFT analysis was restricted to the earlywood samples. While the earlywood DRIFT spectra could have been smoothed to yield very clear spectra with a high signal-to-noise ratio, it was found in this study that the smoothing procedure masked treatment effects. For this reason, the original unsmoothed spectra were evaluated.

Aromatic Peak

In general, the aromatic region (1549 - 1483 cm^{-1}) of the spectra is larger for the controls than for the CCA treatments,

TABLE 2.

DRIFT Peak Ratios.

Treatment	CH:Aromatic Low Ret.	CH:Aromatic High Ret.	CH:Carbonyl Low Ret.	CH:Carbonyl High Ret.
CCA type A	4.0	5.8	4.5	5.5
CCA type B	6.3	6.5	5.4	5.9
CCA type C	6.1	12.1	5.9	8.1
Chromium	4.3	3.5	4.2	4.0
Chromium + Copper	3.6	2.8	4.2	3.7
Chromium + Arsenic	3.6	3.8	4.0	4.1
	CH:Aromatic		CH:Carbonyl	
Controls -Water	4.4		4.6	
-Untreated	3.7		3.9	

with CCA-C having the smallest aromatic peak (Table 2 and Figure 2). The single and double component treating solutions indicate no differences in aromatic content relative to the controls, suggesting that the single and double component treatments cannot be used as model systems to understand the CCA treatments. CH:aromatic ratio was 3.7 for the untreated control and 12.1 for high retention CCA-C treated wood. With almost a 70% reduction in the aromatic peak, this suggests that some of the preservative components in CCA treatments react with the lignin constituents of the wood. It is also interesting that for each of the three CCA formulations the high retentions resulted in greater reductions in the aromatic peak than the comparable low retentions, indicating that both formulation and retention are important. Further, it should be noted that the water treated control has a smaller

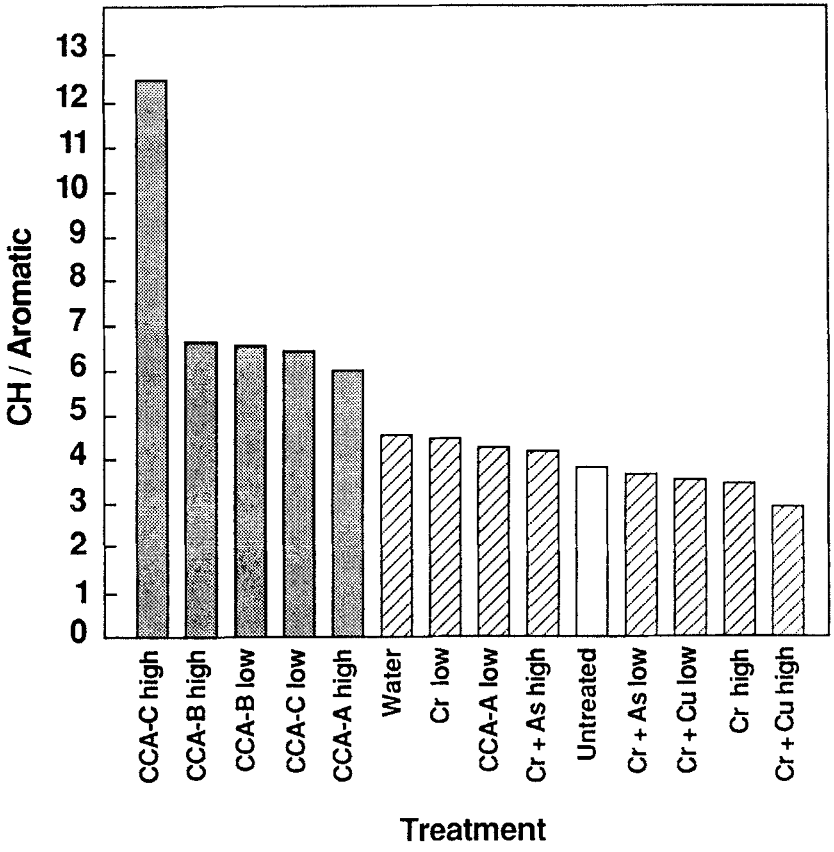

FIGURE 2. CH:Aromatic Peak Ratios from DRIFT Spectra for Earlywood Samples.

aromatic peak than the untreated control, suggesting that water treatment alone may cause changes in the lignin constituent of wood.

The aromatic ring of lignin contains non-oxygenated carbon atoms, and X-ray photoelectron spectroscopy indicated that some of

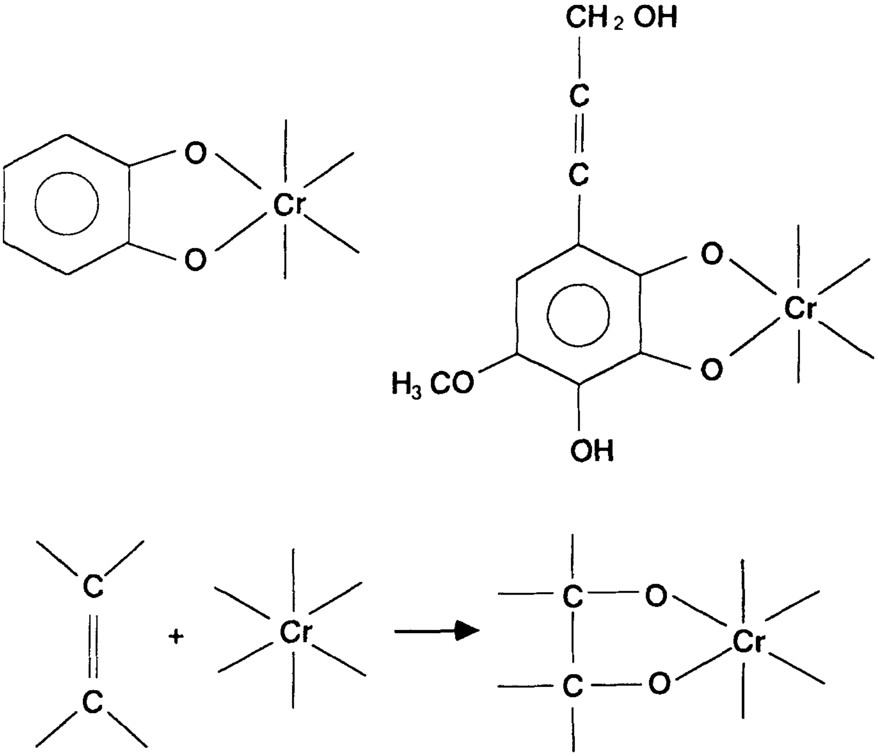

FIGURE 3. Proposed Wood Chromate Esters.

the components of the treating solutions reacted with the non-oxygenated carbon atoms in wood.[21] Therefore, the decrease in aromatic content observed here supports previous findings from the analysis of CCA treated southern pine by X-ray photoelectron spectroscopy,[21] that CCA forms bonds with lignin. Because infrared bands are sensitive to variations in substitution,[26] the wood/CCA bonding proposed by Ostmeyer et al.[21] (see Figure 3) may explain the decrease in the aromatic peak detected via DRIFT. It must be noted that the decrease in the aromatic peak evaluated here does not infer that the aromatic ring is being destroyed, but only that the bonding about the aromatic ring is changing.

It is important to note that five of the six CH:Aromatic ratios for the CCA treatments are all grouped together, and those for the two controls and all of the single and double component treatments are also grouped together. Of the six CCA treatments, four had CH:aromatic ratios between 5.8 and 6.5. The CH:aromatic ratio for high retention CCA-C was 12.1, indicating that it reacted with the lignin to a greater extent than the other formulations. Conversely, the low retention CCA-A treatment had a CH:aromatic ratio of only 4.0, indicating that this formulation did not react with lignin to the extent of the other CCA formulations. The single and double component treatments indicate little or no difference in aromatic content as compared to the untreated control. This then, demonstrates the synergistic nature of CCA formulations, and indicates that all three of the preservative components are required to evaluate CCA/wood reactions. This is in good agreement with X-ray photoelectron spectroscopy results.[21]

Carbonyl Peak

The carbonyl (C=O) stretching region (1767 - 1690 cm-1) of the spectra indicates the same trend as found in the aromatic region, such that treatment with CCA decreases carbonyl content

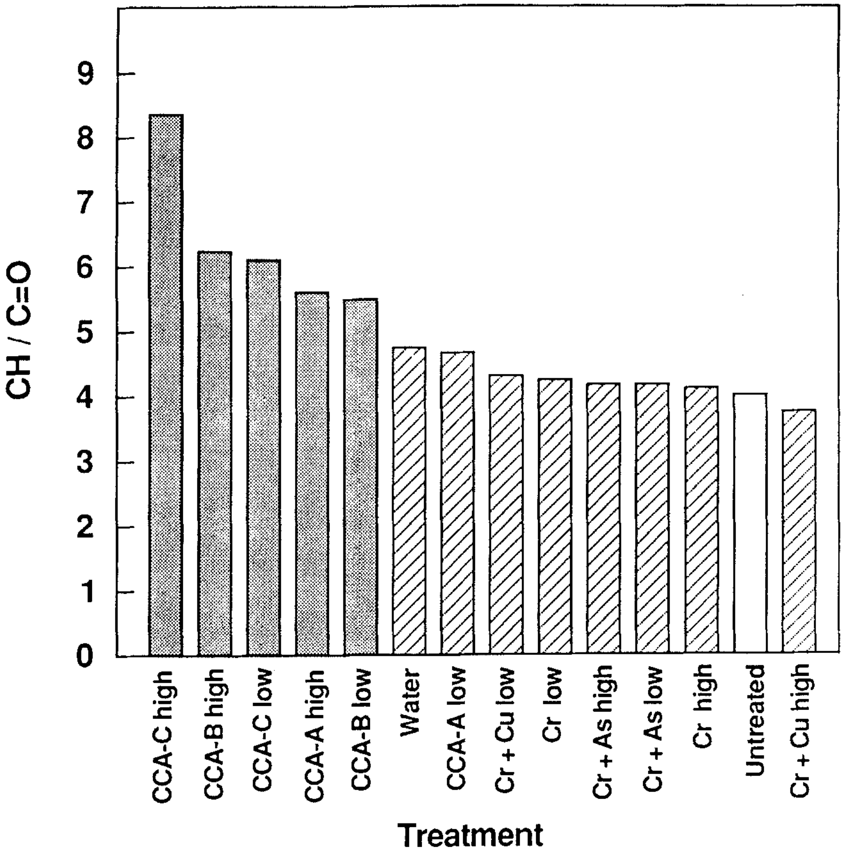

FIGURE 4. CH:Carbonyl Peak Ratios from DRIFT Spectra.

(Table 2 and Figure 4). As was the case with the aromatic region, most of the CCA treatments were grouped together, and the two controls and all of the single and double component treatments were grouped together. The CH:carbonyl ratio was 3.9 for the untreated control and 8.1 for high retention CCA-C treated wood which had the highest CH:carbonyl ratio. Four of the six CCA treatments had CH:carbonyl ratios between 5.4 and 5.9, with low retention CCA-A having a CH:carbonyl ratio of only 4.5. This again indicates that the most and least reactive CCA formulations are high retention CCA-C and low retention CCA-A, respectively. As was the case with the aromatic peak, increasing retentions for the CCA formulations resulted in greater reductions in carbonyl content. Water treatment also appears to result in a decrease in carbonyl content as compared to untreated controls.

It is surprising, however, that none of the treatments indicated a marked increase in carbonyl functionality over the untreated control. Based on classical organic chemistry, it might be expected that the large number of alcoholic -OH groups present, particularly in cellulose, would be oxidized to carbonyl compounds (aldehydes, acids, and ketones),[31-35] and suggests that the reactions between the constituents of wood and the components of CCA preservatives are quite complex. It has been reported, however, that the rate-limiting step in chromic acid oxidation of alcohols and aldehydes is the decomposition of the intermediate chromate ester to form the carbonyl.[32] It is possible, therefore, that the wood/chromate intermediates, formed by alcohol and aldehyde oxidations, do not decompose to form carbonyls, but rather remain as stable complexes. This would explain why the carbonyl peak decreased with treatment rather than increased. Thus, it appears that wood/CCA complexes also form at carbonyl functionalities in wood.

There was no evidence in the infrared spectra indicating a reaction of carbohydrates with the components of the treating solution. However, this does not mean that the carbohydrates could not have reacted with the treating solutions. Due to the complexity and width of the C-O band of the infrared spectra, peak shifts resulting from some wood/preservative bonds may not have been detectable. For example, if cellulose reacted with CuO, the resulting C-O vibration from a C-O-Cu bond might not be discernable from other C-O vibrations such as C-O-C and C-O-H bonds. The C-O band also overlaps the aromatic C-H in-plane deformation band.[36] Therefore, due to questionable interpretation and reliability, the C-O band was not evaluated.

SUMMARY AND CONCLUSIONS

DRIFT analysis of earlywood samples resulted in consistent spectra that were similar to transmission (absorbance) spectra. Latewood samples, however, resulted in inconsistent spectra, with a low signal-to-noise ratio, that could not be analyzed. As such, only the earlywood results were discussed.

Treatment of southern pine with CCA preservatives resulted in a decrease in both the aromatic and carbonyl peaks of the infrared spectra. This supports the results obtained using X-ray photoelectron spectroscopy[21] and suggests that the components of the various treating solutions studied form bonds with the aromatic ring of lignin and the carbonyl groups present in wood.

Of the CCA formulations, it appears that CCA-C and CCA-A may be slightly more and less reactive with the wood, respectively. While the CCA treatments resulted in decreased aromatic and carbonyl functional groups, none of the single or double component treatments had a marked effect on the aromatic or carbonyl groups as compared to water-treated or untreated controls. It appears that all three of the CCA components are required in the treating solution for wood/CCA reactions to occur.

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