THE CHEMISTRY OF COPPER BASED WOOD PRESERVATIVES

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Summary

The reaction of micronized copper carbonate with wood components was studied with electron paramagnetic resonance (EPR) spectroscopy. The structure of the copper-wood complexes was referenced to previous published research confirming the presence of octahedral copper complexes with six Cu-O bonds. The spectra of sawdust treated with basic copper carbonate revealed that within two hours mobile copper could be detected confirming the rapid reaction between the protic acid groups in wood with the basic copper carbonate particles. In the second phase of the research the EPR information was combined with X-ray fluorescence analysis (XRF) to allow quantification of the EPR information. Through the use of copper sulphate treated sawdust the agreement between the EPR and XRF analyses was found to be very high. This allowed the XRF data for micronized copper treated wood to be quantified. The maximum mobile copper content in Micronized copper quat (MCQ) treated southern pine sawdust was found to be about 2000 ppm.

1. Introduction

For several decades the preferred preservative for protection of wood used in a residential setting was chromated copper arsenate (CCA). Indeed it was the evolution of the residential CCA-treated wood market in the mid 1970's that created the platform for the growth of the industry in subsequent decades. The fixation of CCA in treated wood became an important research focus the results of which stimulated the development of post treatment steam fixation chambers. While the main reaction leading to fixation was the reduction of hexavalent chromium, the formation of metal lignin complexes was also important. Copper was primarily "fixed" by ion exchange and increasing the solution concentration – lowering the solution pH – slowed the copper fixation.

In 2003 the wood treating industry agreed to withdraw the use of CCA-treated wood from the residential end-use, replacing it with alkaline copper preservatives. Ammoniacal copper preservatives had been used for many decades, for industrial uses. They had not been considered for the residential market because of the uneven and stronger colour of the treated wood. One of the causes of this was the fixation chemistry which was driven by the loss of the ammonia from the wood surface. This resulted in the formation of stable copper-ammonia-wood complexes. However, the loss of ammonia from the wood surface also resulted in copper compounds being precipitated on the wood surface. There was also some concern over the enhanced corrosiveness of the ammoniacal copper treated wood.

With the introduction of the alkaline copper preservatives based on monoethanolamine as the solvent, the fixation mechanism is driven not by loss of solvent, but by the change in the solution pH. The initial alkaline solution reacts with the acidic wood substrate lowering the solution pH. This changes the copper species present in the solution, as shown below.

$$[Cu(MH)_2]^{2+} \Leftrightarrow [Cu(MH)(M)]^{+} \Leftrightarrow [Cu(M)_2]$$

pH 5-7 7-10 >10

Research has confirmed that copper-amine-wood complexes are formed when the alkaline copper preservatives react with wood. While increasing the temperature can accelerate the rate of the copper insolubilization the fixation is driven by the ion exchange of the copper with replaceable protons in the wood, particularly those on the phenolic and carboxylic acid functional groups.

In a recent innovation, a new approach has been to impregnate wood with a aqueous solution containing small particles of basic copper carbonate suspended with the co-biocide. As with the alkaline copper preservatives, the two most commonly used formulations contain copper carbonate formulated with either a quaternary ammonium compound (MCQ) or a triazole, such as tebuconazole (MCA). Since the chemistry of these new systems remains not well understood, it is important to investigate how the copper in these “micronized” formulations is able to solubilise and react with - and thereby protect - the wood. Previous research has concluded that the solubility of basic copper carbonate is less than 50 ppm at a pH of between 5 and 6 (Scaife, 1975). Nevertheless recent papers on i) the corrosiveness of MCQ and MCA treated wood (Kofoed and Ruddick, 2010); and ii) loss of copper from MCQ copper treated wood (Stirling and Morris, 2010), support the hypothesis that significant mobile copper forms in micronized treated wood. This paper describes some of the recent research in this ongoing study to investigate the chemistry of micronized copper treated wood.

2. Methodology

A challenge facing researchers studying the micronized copper systems is how to examine the mobile copper component in the presence of the immobile basic copper carbonate. In the current research, electron paramagnetic resonance (EPR) also known as electron spin resonance (ESR) was chosen. This technique has been used previously to examine the chromium and copper species formed in wood during preservation (Yamamoto and Ruddick, 1992; Hughes et. al., 1994).

EPR is based on the phenomenon in which every electron has a magnetic moment and a spin quantum number and the atom has an odd number of electrons. In the presence of an external magnetic field the electron can align itself parallel (m_s = -1/2 low energy) or anti-parallel (m_s = +1/2 high energy) to the magnetic field.

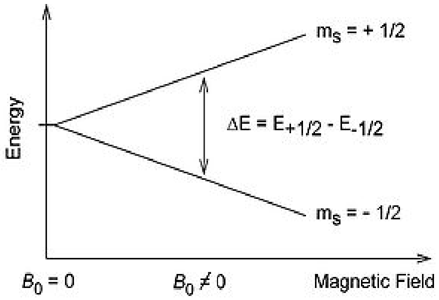

Figure 1. Splitting of the energy for electron aligning parallel and anti-parallel to the applied magnetic field

An unpaired electron can move between the two energy levels by absorbing electromagnetic radiation. In practice it is usual to keep the photon frequency constant and vary the magnetic field. Without interaction of the electron with neighbouring nuclear spins the EPR spectra would be comprised of a single line. The spacing of the EPR lines indicates the degree of interaction with the adjoining nuclei and so can be related to molecular structure. EPR results are reported in terms of “g” and “A” tensors which yield information about the molecular environment of the unpaired electron. EPR can be employed to define the geometric relationship of iso-structural copper complexes.

In the current study, treated sawdust samples were placed in an EPR tube and ESR spectra recorded. For each sample multiple scans are used to generate the spectrum which is then fitted by computer simulation. Three replicate spectra were analyzed and the values shown are the average of these replicate samples. All spectra were measured at 77 °K.

The samples were typically generated by stirring 0.4 g of sawdust (southern pine sapwood, 40 mesh) with 100 ml of the appropriate solution, for 10 minutes at room temperature. The solution was then filtered and the treated sawdust collected. It was then either stored in sealed petri dishes for monitoring of reactions in wet sawdust or dried for generation of EPR spectra of dry sawdust. Drying of the sawdust was typically done at 45 °C for 6 hours.

3. Results and Discussion

EPR has been previously used to study the copper and chromium species formed in treated wood (Hughes, et al., 1994; Humar et al., 2002; Ruddick, 1996; Yamamoto and Ruddick, 1992; Zhang and Kamdem, 2000.) Data shown in Table 1 have been reported previously by Ruddick, (1996). It confirms the presence of the nitrogen in the coordination sphere of the copper when complexed in wood, (Peisach and Blumberg, 1974). The large $A_{//}$ of 190 observed for the copper ethylenediamine complex with four Cu-N bonds, can be compared with the smaller $A_{//}$ of 16 for the copper ammine wood complex with only two Cu-N bonds. Both are larger than the $A_{//}$ value of about 130 for copper sulphate treated wood. The EPR spectra of copper compounds with well defined structures are useful in confirming the spectral parameters for typical copper complexes (Xie et al., 1995; Ruddick, Xie and Herring. 2001)

Table 1. EPR spectral data from the literature (Ruddick, 1996)

Treatment	$g_{//}$	$A_{//}$	$g_{\perp}$
$CuSO_4$ in water*	2.388	150	2.080
$CuSO_4$ in wood**	2.372	132	2.082
$CuCO_3/NH_4OH$*	2.282	177	2.069
$CuCO_3/NH_4OH$ in	2.272	166	2.068
$[Cu(en)_2]SO_4$ in water*	2.204	190	2.064

* Measured at temperature 77K; ** Measured at room temperature

In the current study the spectra generated from copper sulphate treated wood were examined. The objective was to determine the reactions that take place and examine the affects of concentration and time on the spectral parameters of the copper-wood species formed. The results are shown in Tables 2 and 3.

Table 2. Concentration effect on ESR spectra

Treatment	g-factors			Hyperfine Splitting/Gauss			Line width (in Gauss) and shape (L/G), frequency
	g_z	g_y	G_x	A_z	A_y	A_x	
2%, unleached	2.411	2.090	2.082	123	29	4	55; 100;30 L/G = 1, 9.4173GHz
1%, unleached	2.411	2.088	2.081	123	15	4	56; 90; 30 L/G = 1, 9.4234GHz
0.5%, unleached	2.410	2.088	2.078	123	7	4	47; 90;30 L/G = 1, 9.4238GHz
0.2%, unleached	2.404	2.089	2.080	130	17	2	54; 84; 30 L/G =1, 9.4230GHz
0.1%, unleached	2.409	2.083	2.079	125	4	6	52; 90; 30 L/G = 1, 9.4156GHz
$CuSO_4 \cdot 5H_2O$ reference	2.256		2.083	10		9	67; 67; 25 L/G = 0, 9.4201GHz

They confirm that within the range of concentrations studied, there was no affect of concentration on the copper species being formed in the treated wood. They also show that for copper sulphate treated wood, the spectral parameters did not change, when samples were examined one month after treatment. Leaching too did not cause any significant change in the EPR parameters from copper sulphate treated wood.

Table 3. Effect of time after treatment on the EPR spectra

Treatment	g-factors			Hyperfine Splitting/Gauss			Line width (in Gauss) and shape (L/G), frequency
	g_z	g_y	g_x	A_z	A_y	A_x	
0.2%, unleached Day 0	2.404	2.089	2.080	130	17	4	54; 84; 30 L/G =1, 9.4230GHz
0.2%, unleached Day 1	2.409	2.089	2.081	130	24	4	55; 77; 30 L/G =1, 9.4189GHz
0.2%, unleached 2 months	2.382	2.092	2.076	130	30	4	69; 120; 30 L/G = 1, 9.4172GHz
0.2%, leached Day 1	2.409	2.084	2.080	120	24	4	65; 80; 30 L/G =1, 9.4165GHz
0.2%, leached 2 months	2.382	2.092	2.076	130	30	4	69; 100; 30 L/G =1, 9.4200

When a sample of basic copper carbonate is examined, no EPR spectrum is observed. This is because basic copper carbonate is antiferromagnetic. However, copper carbonate treated wood showed the typical EPR spectrum for soluble copper compounds (Figure 2).

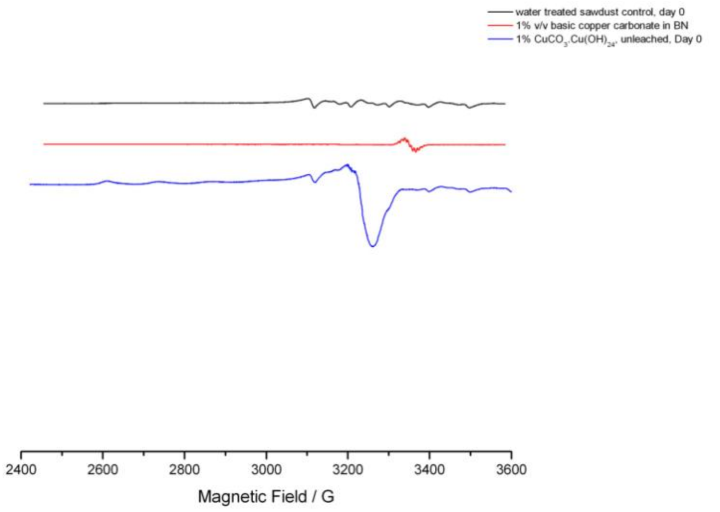

Figure 2. EPR spectrum of untreated southern pine sawdust, basic copper carbonate, and copper carbonate treated wood at 77 °K

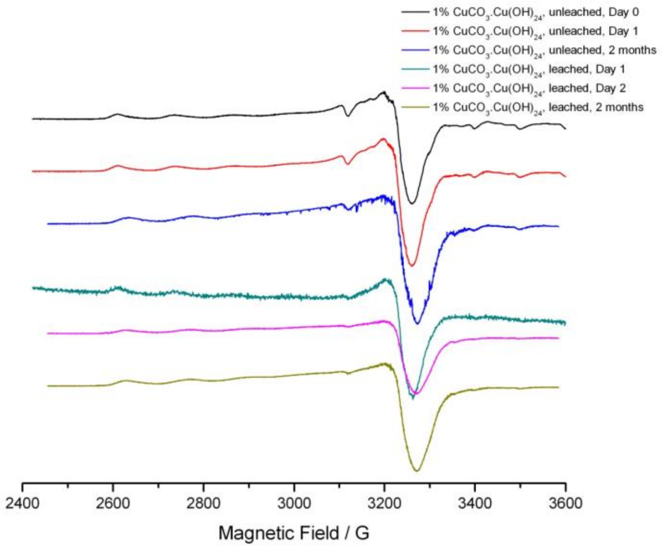

Figure 3. EPR spectra of copper carbonate treated wood immediately, and 2 months, after treatment

From the spectra of basic copper carbonate treated sawdust at varying times after treatment it is clear that basic copper carbonate reacts quickly with wood to form mobile species (Figure 3). The spectra collected immediately after treatment (approximately 2 hours) clearly show the presence of the mobile copper which appeared to increase for approximately three days after treatment. Comparison of the EPR spectra of copper carbonate treated sawdust, with those from micronized copper treated wood (MCQ and MCA) showed that all were very similar to copper sulphate treated wood and all were quite different from alkaline copper quat (ACQ) treated wood (Figure 4).

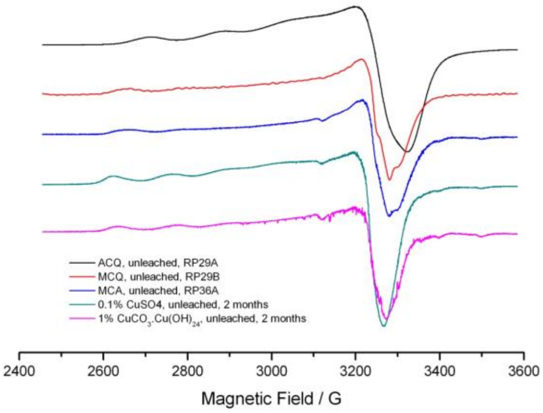

Figure 4. EPR spectra of alkaline copper quat (ACQ), micronized copper quat (MCQ), micronized copper azole (MCA), $CuSO_4$ and basic copper carbonate treated wood.

The $A_{//}$ values for ACQ were as expected much larger (179) than the corresponding $A_{//}$ values for MCQ (139), MCA (139), copper sulphate (145) or basic copper carbonate (130). The similarity of the $A_{//}$ for the four aqueous treatments confirmed the formation of similar hydrated copper complexes in the treated wood.

While the first objective, to confirm the rapid formation of mobile copper had been realized, an equally important objective remained. This was to determine whether it is possible to quantify the amount of mobile copper formed in copper carbonate treated wood. The use of EPR to provide quantitative measurements has not been reported before. Previous reports have suggested that the amount of mobile copper could vary from less than 50 ppm to values, ten or twenty times greater. (McIntyre et. al, 2009; Jin, Walcheski and Preston, 2008 and 2010; Scaife, 1957). In order to measure the amount of mobile copper it was necessary to develop quantitative techniques for the EPR spectra. The details of this are discussed in a separate paper, but a few of the observations are highlighted here. It was possible to correlate the EPR spectral data with the Cu concentration in the treating solution, (Figure 5).

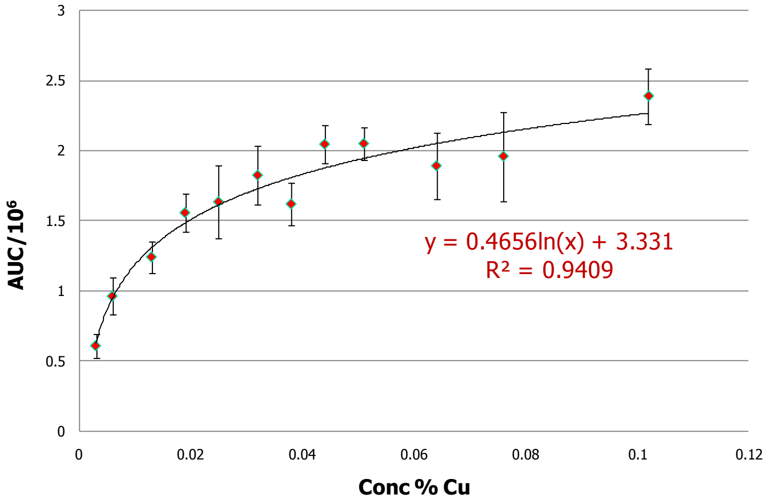

Figure 5. EPR spectral area of treated sawdust plotted against copper concentration % in the treating solution

Plotting the EPR spectral area and the total copper (% as CuO) in copper sulphate treated wood against the concentration of copper in the treating solution revealed a good correlation between the two curves (Figure 6). A direct plot of the EPR spectral area against the percent copper in the copper sulphate treated wood produced a linear relationship over the concentration range examined with an R^2 of 0.956. It was then possible to use this correlation to determine the mobile copper content in micronized copper treated wood.

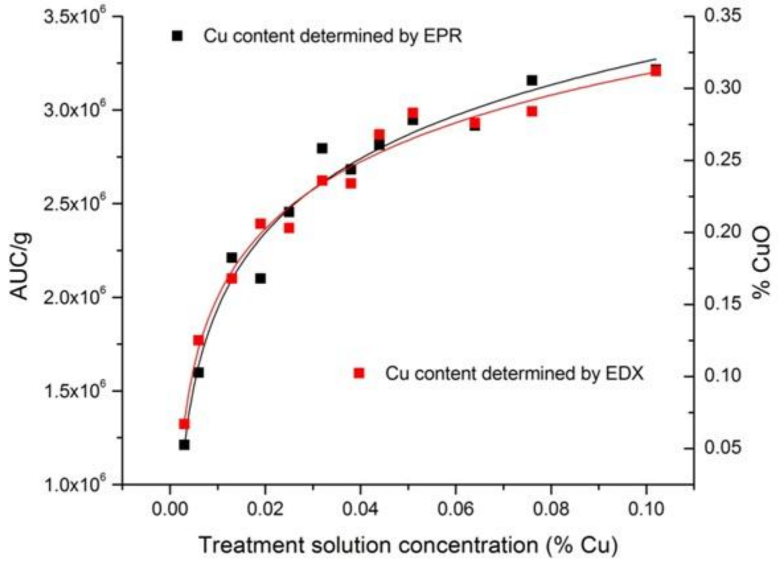

Figure 6. EPR spectral area and x-ray analysis of treated sawdust plotted against copper concentration (%) in the treating solution

Depending on the initial copper concentration in the treating solution, the amount of mobile copper ranged from about 0.1 % (1000 ppm) to approximately 0.23 % (2,300 ppm). These observations confirm the importance of the carboxylic functionality in wood in providing an acidic environment (pH approximately 3.8) to mobilize the copper from the micronized copper carbonate. This interpretation is supported by the observations of Lee and Cooper (2010) who reported the two inflection points in the graph of cation exchange capacity between pH 3 to 5 and pH 7 to 11 due to reaction of the sodium ions with the carboxylic acid and phenolic protons respectively.

4. Conclusions

EPR is able to distinguish the mobile copper formed during reaction of basic copper carbonate with wood, from the unreacted copper carbonate.

The EPR spectra revealed that mobile copper is produced in less than 2 hours after treatment.

The amount of mobile copper continued to increase for almost three days after treatment before reaching a maximum concentration.

The amount of mobile copper produced depended on the treating solution concentration, but reached concentrations in excess of 0.2 % or 2,000 ppm.

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