COPPER IN DOUGLAS-FIR AND ASSOCIATED DIELECTRIC CHANGES[1]

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ABSTRACT

The dielectric constant, loss tangent, and AC resistivity of 60 Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) heartwood specimens were determined at 100 Hz, 1 kHz, 50 kHz, and 100 kHz before and after treatment with copper sulphate solutions. The copper retentions, based on oven-dry weight before treatment, ranged from 1 to 7%.

Of the three electrical properties, AC resistivity changed most as a result of treatment. This change, a factor of 7, occurred at 100 Hz and with specimens at an estimated 20% moisture content. A statistical analysis showed even changes of this magnitude are insufficient to form a basis for a nondestructive method for estimating copper retention in wood.

Additional keywords: *Pseudotsuga menziesii*, dielectric constant, loss tangent, AC resistivity, wood preservation.

INTRODUCTION

Because of the heavy demands on preservative treated wood products and their steadily increasing costs, new methods for quality control must be considered and their feasibility investigated. Ideally, these methods or variations thereof could be used in the mill and on the product in service.

A useful tool for the wood preservation industry would be a method by which chemical retention could be determined quickly and nondestructively both immediately after treatment and also after years of service. Preliminary work indicated the dielectric parameters at the lower frequencies were strongly affected by salt content. The authors thought these changes perhaps could be used for estimating the salt content. This study, therefore, is aimed at measuring the dielectric parameters of copper sulphate treated and untreated wood and then to see whether a dielectric method could be developed to estimate nondestructively the copper retention.

The dielectric properties considered in this investigation are dielectric constant (K), loss tangent (D) and alternating current resistivity (R_{AC}). These properties vary, among other physical parameters, with density, frequency, and moisture. Because little work has been done at low frequencies and because moisture contents below 20% are usually the more important for wood in use, this investigation was limited to frequencies between 100 Hz and 100 kHz and moisture contents below 20%.

MATERIALS AND PROCEDURES

Sixty specimens of edge-grain Douglas-fir heartwood, 0.2 cm thick by 10 cm square

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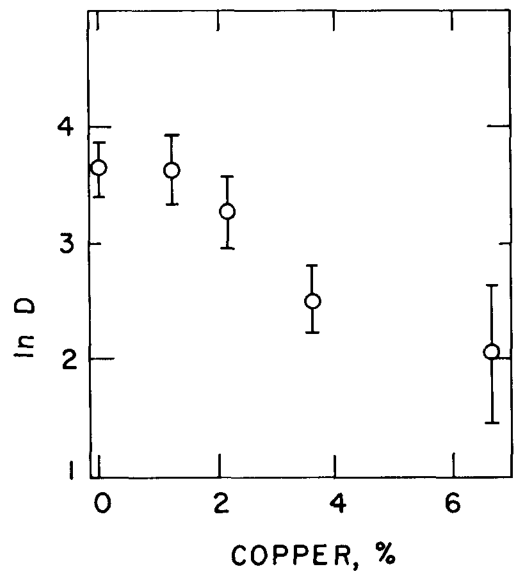

FIG. 1. Effect of copper retention on loss tangent (D) at 100 Hz for Douglas-fir heartwood at 20% MC. 0 represents the average value of D and the bars represent the extent of the 95% confidence interval around lnD.

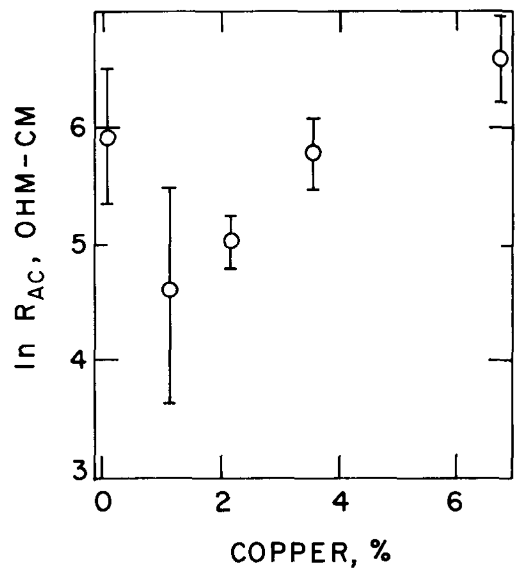

FIG. 2. Effect of copper retention on AC resistivity at 100 Hz of Douglas-fir heartwood at 20% MC. 0 represents the average value of $\ln R_{AC}$ and the bars represent the extent of the 95% confidence interval around $\ln R_{AC}$.

(the longitudinal-radial plane formed the 10 cm square face), were prepared and divided randomly into five groups. All the samples were conditioned at conditions for 0, 7, and 15% EMC. The dielectric measurements were made when EMC was attained. Each group then was saturated with distilled water or various aqueous solutions containing 1, 5, 10, or 20% copper sulphate. The treated specimens were reconditioned to equilibrium at the previous conditions for EMC of 0, 7, and 15% for untreated wood, and dielectric measurements were repeated. Each specimen was reduced to ash and its retention of copper was determined.

Electrical measurements consisted of sandwiching each specimen between two brass electrodes 0.5 cm thick by 9.75 cm square and clamping the sandwich in a teflon-insulated jig. The loss tangent and capacitance were measured on a capacitance bridge at 100 Hz, 1 kHz, 50 kHz, and 100 kHz. All series capacitance values were converted to equivalent parallel values according to:

$$Cp = \frac{Cs}{1 + D^2} \qquad (1)$$

where Cp is the equivalent parallel capacitance (farads), Cs is the series capacitance (farads) and D is the loss tangent. The dielectric constant was calculated from Cp in the standard manner for a thin parallel-plate capacitor as:

$$K = \frac{(11.3\ Cp\ d \times 10^{12})}{A} \qquad (2)$$

where Cp is the capacitance, A is the area of the plates (cm^2) and d is the distance between the plates (cm). R_{AC} was calculated according to definition (Skaar 1949) as:

$$R_{AC} = \frac{(18 \times 10^{11})}{fKD} \text{ ohm cm} \qquad (3)$$

where f is frequency (Hz) of the impinging electrical field.

Copper retention was determined gravimetrically and photometrically. Gravimetrically, the chemical pickup was considered as the difference in oven-dry weight before and after chemical treatment. Photometric determinations consisted of dissolving the

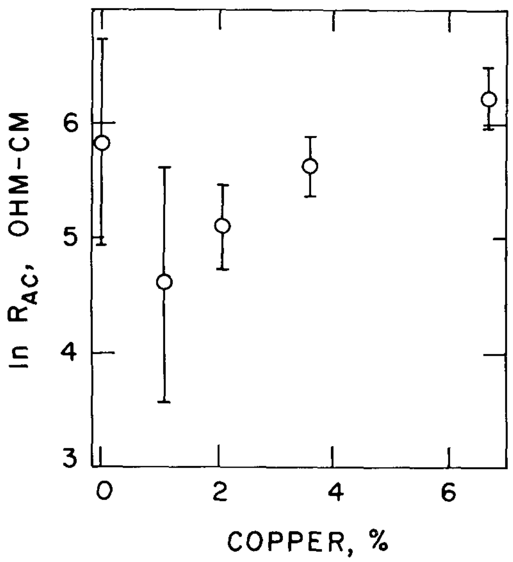

FIG. 3. Effect of copper retention on AC resistivity at 1 kHz of Douglas-fir heartwood at 20% MC. 0 represents the values of $\ln R_{AC}$ and the bars represent the extent of the 95% confidence interval around $\ln R_{AC}$.

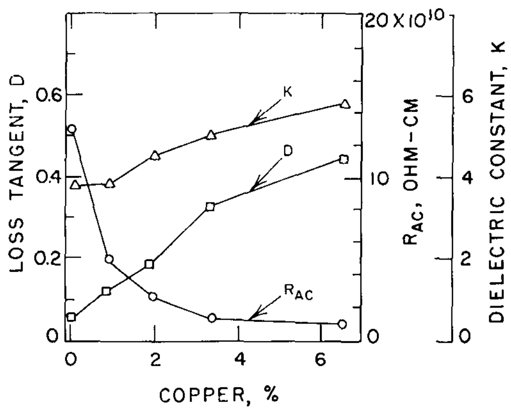

FIG. 4. The dielectric constant (K), loss tangent (D), and AC resistivity (R_{AC}) at 100 Hz for Douglas-fir heartwood at 7% MC and various copper retentions. Copper retention is based on oven-dry untreated wood.

ashed remains in a concentrated mixture of nitric and sulphuric acid and through use of Beer's law (Ewing 1969).

Moisture content in each sample was calculated from the oven-dry weight before and after treating.

A statistical analysis was performed to determine which combination of dielectric variables, frequency, and moisture content showed the highest sensitivity to copper sulphate treatment, and to determine whether that combination was sufficiently sensitive to discriminate between different amounts of copper sulphate in wood. In this analysis, wood density, moisture content, and frequency of the applied electric field were treated as independent variables, and the electrical properties were dependent variables.

RESULTS

Copper retention in treated wood ranged from about 1 to 7%, compared to 1.6% copper chrome arsenate (CCA) salt found in commercial use (James 1966). The largest dielectric changes attributable to copper sulphate treatment occurred at the highest moisture level (ranging from 15 to 20%) and lowest frequency (100 Hz).

Chemical treatment and moisture in wood are interacting variables. A first step in statistically separating these variables consisted of finding an acceptable regression model. The following model:

$$\ln(Y) = B_0 + B_1(MC) + E \qquad (4)$$

was tested. Here, Y is the dependent variable such as R_{AC}, K, or D; B_0 is the Y intercept; B_1 is the slope of the regression line; and E is an error term. The model's validity was established by an analysis of the regression residuals (Draper and Smith 1966). By this analysis, Eq. 4 may be a valid model when residuals of the regression show a normal distribution and are uncorrelated with MC. The behavior of the residuals met the criteria. Further analysis showed that density when considered after moisture content was not a statistically significant variable. If, however, density was considered before moisture content, then density became significant and accounted for about 30% of the variability in Y. Density being significant in one instance and not in another indicates density and moisture content are not statistically independent. As density of wood varies with moisture content, these results are consistent. Therefore, provided mois-

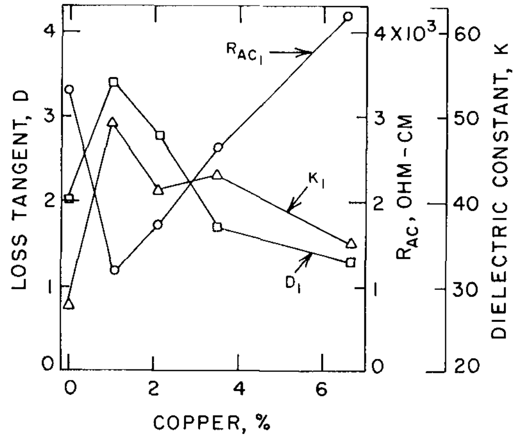

FIG. 5. The dielectric constant (K), loss tangent (D), and AC resistivity (R_{AC}) at 100 Hz of Douglas-fir heartwood at 15% MC and various copper retentions.

ture content changes, Eq. 4 is statistically valid and physically reasonable.

With Eq. 4 as a model, regressions of lnY then provided estimates and 95% confidence intervals of three variables for estimated moisture contents of 0, 5, and 15%, interpolated for 10% and extrapolated to 20% for all five specimen groups before and after chemical treatment. These estimates of lnY and 95% confidence intervals were plotted against moisture content. When the confidence intervals of these least squares lines do not overlap, lnY discriminates between treatments. The advantage of this analysis is that discrimination sensitivity can be seen physically on plots as the distance between confidence intervals. The greater this distance, the greater is the sensitivity.

The highest moisture level offered the best separation of confidence interval and therefore sensitivity for all dielectric variables. Loss tangent at 100 Hz and R_{AC} at 100 and 1 kHz when observed at 20% MC were dielectric variables showing large change because of treatment. These results at 20% MC are plotted in Figs. 1 through 3. In Fig. 1, copper retention changes the average value of lnD by 1.6 at 20% MC and 100 Hz, or D changes by a factor of almost 5. Similarly from Figs. 2 and 3, copper retention can be seen to cause changes in R_{AC} at 100 Hz and R_{AC} at 1 kHz by factors as high as 7 and 5, respectively.

Despite these apparently large changes, in Fig. 2 for example, the confidence interval representing specimens with no copper overlaps those of specimens with 1.03, 3.5, and 6.6% copper retention and is just separated from specimens with 2.1% copper. In Figs. 1 through 3, the vertical distance between confidence intervals, when it exists, is small and therefore we have poor sensitivity. Even though large changes exist in the means of the dielectric properties, for practical purposes, the dielectric methods presented here cannot be used to readily separate specimens containing various amounts of copper.

As copper retention increases, R_{AC} should decrease. Figures 2 and 3 are consistent with this expectation below copper retention of 1.03%. At higher retentions, R_{AC} increases. This increase in R_{AC} seems contrary to the concept that number of potential charge carriers increases as concentration of inorganic salt increases and therefore electrical resistivity should decrease.

We theorize that moisture in the wood-salt aggregate can be divided into moisture associated with wood and that associated with salt as water of hydration. Experimentally, we found the water of hydration adds little to the dielectric properties. As treated wood was oven-dried, we assume copper sulphate in wood lost between three and four moles of water. On being exposed to humidity, this salt competes with wood for available water. Because water in wood above 5 to 6% moisture content (multilayer sorption) is not as tightly held as water that composes the monolayer (0 to 6%), wood below 5 to 6% moisture content may, compared to partially anhydrous copper sulphate, preferentially adsorb water. Two model reactions are considered, one the takeup of moisture by wood and two, the takeup of moisture by the salt, i.e.

Wood (oven-dry) + H_2O $\rightarrow$ Wood (H_2O) Reaction 1

$CuSO_4(3H_2O) + 2H_2O \rightarrow CuSO_4(5H_2O)$
Reaction 2.

For reactions one and two to proceed to completion, water needs to diffuse through the salt as well as wood. All else being equal, the salt, being both on the inside and outside of the cell wall, should have the greatest opportunity to take up water. Further, if the kinetics in reactions 1 and 2 are such that both reactions go easily to completion, the change in Gibbs free energy may offer an estimate of the tendency to proceed spontaneously.

Under isothermal conditions, ΔG° for reaction 1, according to Kelsey (1956), is −2.43 and Stamm (1934) is −2.88 kcal per mole of water adsorbed onto oven-dry wood. The ΔG° of wood at 7 and 15% moisture content adsorbing water, drops to about −0.36 and −0.036 kcal/mole (Stamm 1934). The handbook value for the change in Gibbs free energy for reaction 2 is −7.43[1] kcal per mole of water taken up. Therefore, from a strictly thermodynamical point of view, both reactions are expected to proceed spontaneously, but reaction 2 would have a greater tendency to proceed.

Water available for sorption in wood beyond the monolayer, having ΔG even less negative than that for the monolayer, could be even more likely to be taken up by the $CuSO_4(3H_2O)$ as water of hydration. As a result, the actual moisture content of wood as moisture increases beyond 7% could be substantially less than the calculated or apparent moisture content. The greater the amount of salt in wood, the lower the moisture content of the wood substances. The lower the moisture content the higher the resistivity, all else equal. Therefore, AC resistivity apparently may increase as degree of treatment increases beyond a critical level.

This critical level is the level of treatment at which the increase in charge carriers is offset by a decrease in water associated with wood, and the net result is an increase in resistance rather than the expected decrease. This critical level will vary with moisture content. At lower moisture contents, for example 7% as in Fig. 4, R_{AC} decreases with treatment and no critical retention is evident. As the moisture content increases to 15% (Fig. 5), however, R_{AC} decreases with retentions up to 1.03%. Beyond this critical level R_{AC} increases. We believe the amount of water associated with wood at higher moisture levels diminishes as copper retention increases. Therefore, at high salt concentrations the expected decrease in R_{AC} because of increase in salt (charge carriers) could be cancelled by loss of mobile water, with the net result of an unexpected increase in R_{AC}.

[1] In this experiment, reaction 2 could just as well have been with $CuSo_4(H_2O)$. Here, ΔG° would be −11.6 kcal/mole. Therefore, reaction 2, as shown in text, gives a minimum value for $|\Delta G|$.

CONCLUSIONS

The AC resistivity of Douglas-fir heartwood at 20% moisture content when measured at 100 Hz is the combination of dielectric property and frequency that shows the greatest response to changes in copper sulphate concentration. Even these changes in AC resistivity, however, are insufficient to serve as a quantitative basis for nondestructively segregating heartwood samples with copper retentions ranging from 0 to 7%.

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