

ULTRAVIOLET SPECTROPHOTOMETRY AND FOURIER TRANSFORM INFRARED SPECTROSCOPY CHARACTERIZATION OF COPPER NAPHTHENATE

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ABSTRACT

Ultraviolet-Visible (UV-VIS) spectrophotometry and Fourier Transform Infrared (FTIR) spectroscopy were used to characterize copper naphthenate (Cu-N) complex in treating solution and in Cu-N treated wood. At wavelength 680 ± 2 nm, the absorption was proportional to the amount of Cu-N present in solution. FTIR was used to confirm the presence of the carboxylate group in the Cu-N complex and the carboxylic acid in the non-complexed naphthenic acid (NA). Toluene was used to extract Cu-N from treated wood for UV-vis quantitative analysis. This method can be applicable to the determination of Cu-N in solution and in treated wood with detection limits ranging from 4 to 80 ppm.

Keywords: FTIR, UV-vis, copper naphthenate, naphthenic acid.

INTRODUCTION

Today in the United States treated wood is an important material in construction. When exposed outdoors, wood can be destroyed by decay fungi and insects. The protection of wood is achieved by treatment with an appropriate wood preservative. One of the objectives of the American Wood-Preservers' Association (AWPA) is to ensure the quality of the chemical preservatives.

The AWPA defines a number of criteria that a chemical formulation must meet in order to be an accepted wood preservative. For Cu-N, the AWPA standard P8-98: 2.3 (AWPA 1998) states, "all of the copper present in the concentrate (Cu-N) shall be combined as copper naphthenate." It is reported that the presence of water and wood carbohydrates in Cu-N

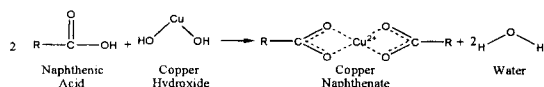
treating solution enhances the formation of emulsions and copper oxides (Freeman 1992; Kamdem et al. 1998). It has also been documented that Cu-N-treated utility poles sometimes fail prematurely, and remedial treatments are necessary to extend the useful service life (Forsyth and Morrell 1993). The early failure has been tentatively attributed to either the quality of Cu-N formulations or the poor treatment with inadequate retention or penetration (Kamdem et al. 1998). However, Cu-N is reported to be an attractive good wood preservative because of its low mammalian toxicity (U.S. Army 1987). Field decay tests have shown Cu-N treated lumber to have a predicted service life of 38–43 years (De Groot et al. 1988; Gjovik and Gutzmer 1991). Low toxicity and successful decay resistance justify the study of the preservative. The quantification of Cu-N complex in wood and in treating

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solution would facilitate the quality control of Cu-N treatment.

The objective of this work is to characterize the Cu-N complex qualitatively and quantitatively in treating solution and treated wood and develop an analytical method to determine Cu-N concentration. If successful, this method will allow direct determination of Cu-N rather than estimate the concentration of elemental copper as suggested in standard A5 in the AWWPA Book of Standards (AWPA 1998) or the naphthenic acid (NA) composition. The determination of the amount of Cu in Cu-N solution or treated wood is not sufficient to understand and predict the performance of Cu-N. Each species and form of Cu may have a different degree of solubility and bioavailability, thus varying wood protection level. It would be beneficial to quantify Cu-N complex rather than individual Cu or NA in treating solution and in treated wood.

In order to study Cu-N, it is important to understand its formation. Numerous analytical methods have been used to study the reaction of Cu-N (Craciun and Kamdem 1997). Cu-N is formed when copper, for instance copper hydroxide $\text{Cu}(\text{OH})_2$ or copper oxide, and NA are combined. NA is obtained from crude oil and may contain C5-C35 carboxylic acids (Dzidic et al. 1988). The carboxylic acid groups from NA react with copper to form the Cu-N complex as represented in the following reaction:



FTIR spectroscopy can be successfully used to follow the carboxylic acid in NA and the carboxylate of Cu-N (Craciun and Kamdem 1997). Also the chemistry of various metal carboxylates has also been examined using UV-vis (Ingle and Crouch 1988; Mehrota and Bohra 1983).

MATERIALS AND METHODS

Chemicals

Cu-N with the commercial name Perm-E8 from ISK Biosciences, containing 2% copper

TABLE 1. Copper-containing compounds, solvent, and corresponding wavelength at maximum absorption.

Chemical name	Solvent	λ max (nm)
Copper naphthenate	hexane	680
Copper naphthenate	toluene	680
Copper naphthenate	diesel	680
Copper-8-quinolate	water	472
Copper-8-quinolate	hexane	488
Copper ethanolamine	water	642
Copper hydroxide	water w/EDTA	740
Copper (II) nitrate	water	816
Copper (II) acetate	water	775
Cupric sulfate	water	827
Copper formate	water	782
Copper gluconate	water	804
Copper (II) carbonate	W, H, T and D*	insoluble
Copper (I) oxide	W, H, T and D*	insoluble
Copper (II) oxide	W, H, T and D*	insoluble
Copper oxalate	W, H, T and D*	insoluble
Copper citrate	W, H, T and D*	insoluble

* W: water, H: hexane, T: toluene, and D: diesel.

metal, and Cu-N with a commercial name M GARD S520 from OMG Chemical, containing 8% copper metal, were used after dilution in hexane, toluene, or diesel fuel. Cu-N formulations from two sources were used in this study to validate the analytical method since the two formulations are manufactured differently and used commercially. The hypothesis of the method developed in this paper was based on the quantification of copper carboxylate interaction taking place in each formulation. These solvents and water were used to solubilize Cu-N and other copper containing compounds as listed in Table 1.

UV-vis spectrophotometry

To scan all Cu containing solutions from 200 nm to 800 nm, a Beckman DU 640 B spectrophotometer with a 10-mm light path cuvet from Sigma was used. All UV-vis scans were performed at a speed of 600 nm/min.

FTIR spectroscopy

A Nicolet Protégé 460 FTIR spectrometer with a horizontal attenuated total reflectance (HATR) accessory from Spectratech was used to scan various solutions from 4000 cm^{-1} to

650 cm^{-1} . FTIR spectra were collected using 32 scans and a resolution of 4 cm^{-1} .

Dilution and analysis of spiked Cu-N solutions

A 1:5 v/v NA to hexane solution, a 1:2 v/v dilution of Perm E8, and M Gard S520 in hexane were prepared. The diluted Perm E8 solution was spiked with the NA solution, $\text{Cu}(\text{OH})_2$ and then with both the $\text{Cu}(\text{OH})_2$ and NA solution. The FTIR spectra of these resulting solutions were taken. Dilutions to equalize the original amount of Perm E8 present in each solution were made, and the absorption of the diluted solutions at the wavelength of peak absorption of Cu-N was taken.

Atomic absorption spectrometry

The concentration of Cu in the Cu-N solution was determined using a Perkin Elmer 3110 atomic absorption spectrometer (AAS). The Cu-N was prepared for this analysis by dilution to an approximate concentration of 5 ppm in a 90% ethanol and about 10% water.

Solid sample extraction

A total of five Cu-N treated southern yellow pine cubes measuring 0.25 by 0.25 by 0.25 in. and an average Cu retention of 0.62 pcf (pound per cubic foot) were soxhlet-extracted with 300 mL aliquots of toluene. The toluene was changed every 18 h until there was no color change as determined by scanning all visible wavelengths by UV-vis. During the soxhlet extraction, six changes of toluene were needed until there was no color change. The extracted toluene solutions were analyzed by AAS for Cu content, and the absorption at the wavelength of peak absorption of Cu-N was read by UV-vis.

RESULTS AND DISCUSSION

UV-vis spectrophotometry

Figure 1 is the UV-vis spectra of hexane, toluene, diesel fuel, and Cu-N diluted in hexane. The peak absorption specific to Cu-N di-

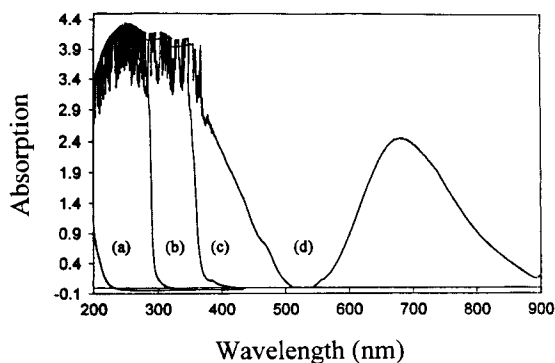


FIG. 1. The UV-vis spectra of (a) hexane, (b) toluene, (c) diesel, and (d) 1:5 Cu-N in hexane.

luted in hexane, toluene, or diesel was obtained at 680 ± 2 nm (Fig. 1d and Table 1). The same peak was obtained for both Perm-E8 from ISK Biosciences and M GARD S520 from OMG Chemical. No differences were detected between the two formulations of Cu-N, suggesting that indeed the UV-vis method characterizes the carboxylate copper complex. Interference of hexane, toluene, and diesel was negligible on the UV-vis specific peak. Peaks in the UV region due to the organic solvents appear at 230 nm for hexane (Fig. 1a), 320 nm for toluene (Fig. 1b), and at 410 nm for diesel (Fig. 1c).

Several other Cu-based compounds were dissolved and then scanned by UV-vis (Table 1). None of the soluble compounds had a peak of absorption at 680 nm. No further attempt was made to scan UV-vis data from the insoluble copper compounds.

FTIR spectroscopy

Hexane was used as the solvent for FTIR spectra analysis. No bands due to hexane conflict with bands at 1708 cm^{-1} , 1605 cm^{-1} and 1593 cm^{-1} (Fig. 2a). The FTIR spectrum of the NA solution has a band at 1708 cm^{-1} (Fig. 2b) attributed to the carbonyl stretch from the carboxylic acid. Mixing $\text{Cu}(\text{OH})_2$ and NA results in the decrease of intensity of the band at 1708 cm^{-1} and a new band at 1605 cm^{-1} (Fig 2c). The decrease in intensity of the band at 1708 cm^{-1} is due to the reduction of free

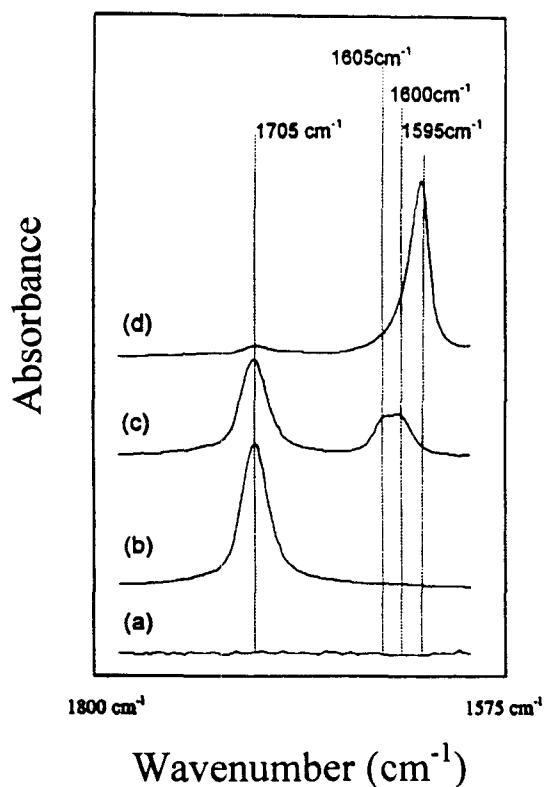


FIG. 2. The FTIR spectra of (a) hexane, (b) naphthenic acid, (c) naphthenic acid with copper hydroxide, and (d) copper naphthenate.

carboxylic acid from the NA. The proportion of $\text{Cu}(\text{OH})_2$ and NA favors copper-carboxylate interaction of Cu-N. The new band at 1605 cm^{-1} is due to the carbonyl stretch in the Cu-N complex. The FTIR spectrum of Cu-N exhibits a band at 1593 cm^{-1} from the carbonyl stretch of the Cu-N complex (Fig. 2d). The band due to the carbonyl stretch in the Cu-N complex is different from the corresponding band in Fig. 2c. This shift in wave number from 1605 cm^{-1} to 1593 cm^{-1} may be due to different ratios of free NA and Cu-N in the solutions. While NA is present in excess with Cu-N, the FTIR band due to the carboxylate in Cu-N appears closer to 1605 cm^{-1} with higher concentrations of NA. Fig. 2 demonstrates how the formation of Cu-N can be monitored by FTIR.

The spectra of Cu-N and Cu-N spiked with

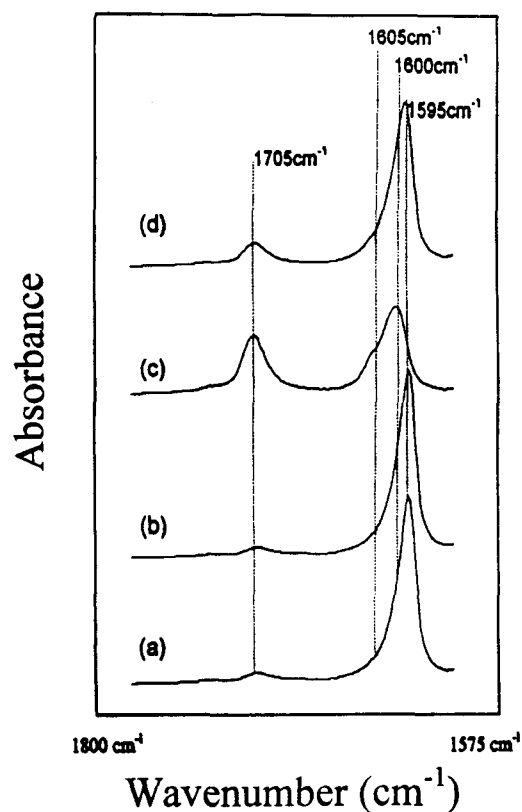


FIG. 3. The FTIR spectra of (a) copper naphthenate, (b) copper naphthenate with copper hydroxide, (c) copper naphthenate with naphthenic acid, and (d) copper naphthenate with naphthenic acid and copper hydroxide.

$\text{Cu}(\text{OH})_2$ appear in Fig. 3a and 3b, respectively. Both spectra have a band at 1593 cm^{-1} due to the carbonyl stretch in Cu-N. The addition of $\text{Cu}(\text{OH})_2$ did not affect the intensity of the band at 1593 cm^{-1} because no free carboxylic acid from NA was available to form a complex through carboxylation. Figure 3c represents the FTIR spectrum of Cu-N solution spiked with NA. Two bands were observed—one at 1708 cm^{-1} from the carboxylic acid and another at 1605 cm^{-1} from the carboxylate in the Cu-N complex. The band specific to Cu-N appears at 1605 cm^{-1} rather than 1593 cm^{-1} . As observed in Fig. 2, this may be due to the ratio of NA to Cu-N. Figure 3d represents the FTIR spectrum of the Cu-N spiked with NA and $\text{Cu}(\text{OH})_2$. The band at

1708 cm^{-1} (Fig. 3d) is less intense and the band at 1593 cm^{-1} more intense than the corresponding bands of the sample spiked with only NA (Fig. 3c). The addition of $\text{Cu}(\text{OH})_2$ favors the formation of the carboxylate (1593 cm^{-1}) with the carboxylate acid of NA (1708 cm^{-1}).

Analysis of spiked Cu-N samples

Cu-N spiked with NA and/or $\text{Cu}(\text{OH})_2$ were UV-vis scanned. The value of the absorption at 680 nm of the Cu-N solution, $\text{Cu}(\text{OH})_2$ spiked, and NA spiked Cu-N solutions was 0.50. The addition of NA or $\text{Cu}(\text{OH})_2$ to Cu-N does not increase the absorption at 680 nm. However, when spiked with both NA and $\text{Cu}(\text{OH})_2$, the value of absorption increased from 0.50 to 0.67. The increase in absorption is due to the formation of copper-carboxylate interaction with the addition of $\text{Cu}(\text{OH})_2$ and NA. The coinciding increase of the FTIR band intensity at 1593 cm^{-1} and UV-vis absorption at 680 nm confirm that the absorption at 680 nm is due to the copper carboxylate complex in Cu-N.

Quantification of Cu-N

The UV-vis absorption at 680 nm was used to develop a quantitative method to estimate the amount of copper complex in solution. The original Cu-N solution diluted in ethanol was AAS analyzed and the concentration was determined to be 2%. This Cu-N was diluted in all three solvents (hexane, toluene, and diesel) to yield concentrations ranging from 0 ppm to 500 ppm. The absorption of each diluted sample was read at 680 nm. The concentration of Cu-N in each solution was plotted against the corresponding UV-vis absorption at 680 nm. A linear regression with an R^2 value of 0.99 was constructed from data obtained with all three solvents. The regression line obtained from dilution of Cu-N in diesel is shown in Fig. 4. This regression line relies on the assumption that all Cu present in the initial Cu-N solution was complexed with carboxylic acid as evidenced by the FTIR.

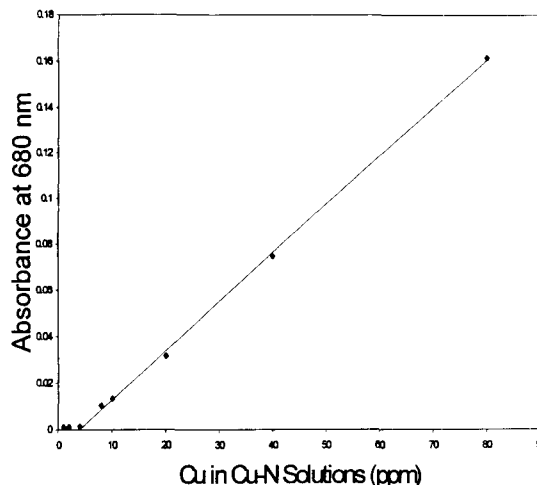


FIG. 4. The regression line for copper naphthenate diluted in diesel. The linear portion of the curve is from 4 ppm to 80 ppm. The R^2 value for the best fit line through these points is 0.9993. Similar regression lines can be made by diluting copper naphthenate in hexane or toluene.

Cu-N treated wood was extracted with toluene, and the extract was analyzed by UV-vis at 680 nm. After the appropriate dilution, the concentration of Cu-N in the extract was determined by fitting the absorption at 680 nm to the calibration curve varying from 4 to 80 ppm (Fig. 4). The value of the concentration of Cu-N extracted from cubes was 4635 ppm, similar to the value of 4610 ppm determined by AAS. This 0.55% difference was attributed to experimental error with extraction, dilution, and absorption reading.

This study shows that UV-vis can be used to identify and determine the copper-carboxylate complex in solution. The use of AAS to analyze CU for the estimation of Cu-N is still a valid method although it assumes that all copper is present as copper carboxylate complex.

CONCLUSIONS

UV-vis and FTIR techniques monitored the formation of Cu-N from the mixture of $\text{Cu}(\text{OH})_2$ and NA. Cu-N exhibits a peak specific to the Cu-carboxylate interaction at 680

nm with UV-vis and a band at $1600\text{ cm}^{-1} \pm 10\text{ cm}^{-1}$ using FTIR.

The UV-vis specific peak at 680 nm was used to quantify Cu-N in treatment solution and in the extract from soxhlet-extracted Cu-N treated wood. This method is valid in the range of 4 to 80 ppm using hexane, toluene, or diesel as solvent. The availability of the three solvents allows different applications of the method. Hexane may be better in FTIR and UV studies of Cu-N treated wood because there are fewer peaks from the solvent. Toluene seems better for use with solid wood soxhlet extraction, and diesel fuel is best suited for treatment solution because it is typically used as a solvent in treatment solution.

A similar method could be used to quantify other metal complex-based wood preservatives.

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