IRG/WP 00-30246

THE INTERNATIONAL RESEARCH GROUP ON WOOD PRESERVATION

Section 3 Wood Protecting Chemicals

Copper Naphthenate-Treated Southern Pine Pole Stubs in Field Exposure
Part II: Chemical Characterization of Full Size Pole Stubs 12 Years After Treatment

By

H.M. Barnes
Mississippi State University, Starkville, MS, USA

D. Pascal Kamdem
Michigan State University, East Lansing, MI, USA

M.H. Freeman
Memphis, TN, USA

Paper prepared for the 31st Annual Meeting
Kona, Hawaii, USA
14-19 May 2000

IRG Secretariat
KTH
SE-100 44 Stockholm
Sweden

Copper Naphthenate-Treated Southern Pine Pole Stubs in Field Exposure
Part II: Chemical Characterization of Full Size Pole Stubs 12 Years After Treatment[1]

By

H.M. Barnes, D. Pascal Kamdem, and M.H. Freeman[2]

ABSTRACT

This study examines the influence of pre-treatment and post-treatment steaming on the character and physio-chemical nature of copper naphthenate in hydrocarbon solvent treated pine in larger, pole diameter, pole stub-length samples. This work is the continuation of two projects that began almost a decade ago. Previous reports indicated that certain morphological changes might occur in small laboratory steamed samples of copper naphthenate treated southern pine. Toluene-methanol extraction, UV-Vis spectroscopy, X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM) were used to investigate the nature and properties of the copper naphthenate present in the wood after 12 years of exposure. The formation of solid cuprous oxide occurred regardless of pre- or post-steaming conditioning.

Keywords: XPS, XRD, ESEM-EDXA, copper naphthenate, steam, southern pine, post-treatment steaming, fixation

INTRODUCTION

Copper naphthenate (CN) has been used as a wood preservative in the USA for more than 50 years for a variety of commodities (Hartford 1973, McIntyre 2000, Nicholas and Freeman 2000). Archer *et al.* (1990) showed that CN toxic thresholds may vary with the type of solvent and the quality of carboxylic acid used to make the copper carboxylate salt of the relative conjugate acid. Several recent studies have reported efficacy for control of a wide range of decay fungi and termites for both softwood and hardwood (Kamdem *et al.* 1995, Freeman 1994, De Groot *et al.* 1988).

---

[1] Approved as Journal Article FP-173 of the Forest & Wildlife Research Center, Mississippi State University.

[2] The authors are, respectively, Professor, Forest Products Laboratory, Mississippi State University, Mississippi State, MS; Associate Professor, Michigan State University, Department of Forestry, East Lansing, MI, USA and Wood Scientist, Memphis, TN, USA.

Unlike several waterborne preservatives, copper loss from oilborne CN-treated wood is relatively low (Freeman 1994). Generally, water insoluble copper sources are used in its preparation unless the copper naphthenate is produced by double decomposition process (Brient 1992), and the organic components, naphthenic acid and diesel oil, have limited water solubility unless contaminated with other materials. CN is known chemically as a group of cupric cyclopentane carboxylates or cyclohexane carboxylates. Recent changes to the AWPA Standards have clarified the specifications for sources of naturally occurring naphthenic acid may be used to manufacture copper naphthenate, and still conform to AWPA P-8 specifications (Anderson 1998, Freeman 1998).

The color of freshly CN-treated wood is green and the odor of naphthenic acid is evident. Findings indicate that post-treatment steaming freshly treated wood at 240°F(115°C) will reduce both the green color and the odor resulting in a clean dry surface (DeGroot *et al.* 1988). The duration of post-treatment steaming may vary from one to 3 hours depending upon initial steaming and the size/species of the treated-wood commodity.

Steam/vacuum treatment can remove up to 80kg/m^3 (5 pcf) of water from poles. Barnes and Hein (1988) also reported that the ratio of copper to naphthenic acid remaining in the treating solution after treatment was lower than in the initial treating solution. They suggested that the post-treatment steam conditioning promotes the fixation of copper in wood resulting in the build up of naphthenic acid in the treating solution. This may also be explained by selective absorption of copper during treating. Fixation is also enhanced by a patented post-treatment elevated temperature bath (Hein and Kelso 1987).

Biological performance of CN-treated pole stock was not well documented until recently (Barnes and Freeman 2000, Barnes *et al.* 2000, Engdahl and Baileys 1992). These studies show that properly conditioned and treated pole stock had extremely low (1%) failure rates. Southern pine stakes treated with copper naphthenate solution in a light aromatic solvent were post-treatment steamed for an hour at a maximum temperature of 126°C (259°F) followed by a one hour vacuum (Gutzmer and Crawford 1995). The service life difference between non-post-treatment steamed and post-treatment steamed stake samples did not appear to be significant. Both post-treatment steamed and non-post-treatment steamed in light aromatic solvent similar to lacolene, failed after about 12 years exposure in Mississippi. It was noted, however, that both penta and copper naphthenate post-steamed samples in this study did perform 8 -14 % better than non-post-treatment steamed samples, but this was not a statistically significant difference.

This study evaluates the physio-chemical effect for initial conditioning post-treatment steaming, and post-treatment fixation of CN-treated southern pine after exposure. The data will be compared to the results found with small, laboratory treated samples of CN-treated wood (Kamdem *et al.* 1997, 1998a, 1998b).

MATERIALS AND METHODS

Preparation and Exposure of Southern Pine Pole Stubs

In 1987, pole sections treated with CN were placed horizontally in an above-ground storage environment as well as vertically in ground contact in a high decay, high termite hazard area (AWPA Hazard Zone 4) near Starkville, MS (Barnes and Hein 1988). Data and conditions of these pole stubs have not been reported since their installation over 12 years ago. Many of the pole stubs in this test were exposed to steaming conditions, either pre-steamed for conditioning purposes, post-steamed for aesthetic reasons, or a combination of these two steaming conditions. Other variables in these pole stub tests included initial conditioning method (air-dried or steam-conditioned), varying solution temperature conditions, and use of a final fixation/expansion bath. Details of the treating and conditioning processes and procedures can be found in the literature (Barnes and Hein 1988). A summary of the treatment details is given in Table 1.

Table 1. Processing variables and materials used

Variable	Description
Initial conditioning	Steam-conditioned, Air-dried
Treatment cycle	Rueping: 30 psig initial air; 150 psig maximum pressure; Final vacuum >24 in Hg; Treating temperature varied (ambient to 200°F)
Preservative	8% (as Cu) copper naphthenate (CN) concentrate
Solution	0.8% (as Cu) CN in No. 2 fuel oil meeting AWPA specifications for P9 type A solvent except for penta solvency
Final conditioning	None + vacuum; Steam flash +vacuum; Fixation (expansion) bath +vacuum

Selected trees of loblolly pine (*Pinus taeda* L.) were cut, bucked into 8-ft pole stubs, immediately debarked and cut into matched 4-ft sections for use in this study. Average pole stub diameter was eight inches.

After cooling overnight following the initial treatments in 1987, each of the 4-ft pole stubs was bored to the pith on third points around the circumference of the stub at the mid-point and 1-ft from the end. Borings were segmented into the following zones for analysis: 0.0-0.5, 0.5-2.0, 2.0-3.0, and 3.0-4.0 inches from the surface. Similar zonal segments from all stubs in a charge were combined for copper analysis by X-ray fluorescence spectroscopy (AWPA Standard A9-95). The data were cross-checked by atomic absorption spectrometry (AAS) (AWPA Standard A11-96) using wet ashing procedures (AWPA Standard A7). In December 1987, half of the treated pole stubs were placed 18 inches into the ground while the remainder were placed horizontally on treated 4x4s in above-ground exposure. In 1999, selected pole stubs representing the extremes in the treated population were bored and reassayed using AA spectroscopy. For pole stubs placed in ground contact, four borings were taken at quarter-points mid-way between the ground line and the stub top and four additional borings were taken mid-way between the ground line and the butt end of the stub. For stubs exposed above-ground, four borings were taken at approximately mid-length. One boring from each position was reserved for future testing while the three from each location were separated into the 0-0.5 in, 0.5-2.0 in, and 2.0-3.0-in zones for assay. The three cores for each zone and location were combined for assay. The fourth core section, taken by hand boring, was maintained for further assay and characterization by ESEM, XRD, and /or extraction-chelation with chromophoric reagents.

AAS Analysis

AAS was used to analyze the elemental copper content of the laboratory treated and non-steamed, or post-steamed copper naphthenate treated samples. AAS was also used to analyze the copper content of the 12-year old field stubs. AAS was performed in accordance with AWPA standard A11-93 (AWPA, 1999).

ESEM-EDXA

Environmental scanning electron microscopy (ESEM) coupled with energy dispersive X-rays (EDXA) analysis was performed on an ESEM model 2020 with an accelerating voltage of 20 kV at 77°F (25 °C) and a vacuum level of 2.0 to 3.5 torr. The EDXA detector was equipped with an Oxford Atmospheric thin window capable of detecting elements with atomic number greater than 6 and less than 99. The acquisition time for each spectrum was set at approximately 500 seconds with 1600 to 2500 counts per seconds.

XRD Analysis

X-ray diffraction (XRD) analysis was carried out on a Rigaku Rotaflex model CN-4148B2 X-ray diffractometer using Cu-$K_{\text{á}}$ radiation (ë=1.5418 Δ) at 45 kV and 100 mA. The diffraction angle (2Θ) was measured from 5° to 65° at speed of 2°/minute. XRD pattern of Cu_2O was obtained by running the standard compounds without further preparation. Special care was given to the preparation of wood samples for X-ray analysis. Wood samples were razor cut to about 300 µm thickness slices and mounted on a glass sample holder with a double-sided tape.

UV-Vis Analysis

A specific reaction between cuprous ion (Cu^+) and 2,2'-biquinoline in glacial acetic acid was used to identify and quantify cuprous oxide (Cu_2O) in treated wood. At 540 nm wavelength, the absorbance of Cu^+ -[2,2'-biquinoline] complex is proportional to the amount of Cu^+ present in a solution. A Beckman DU 640 B spectrophotometer with a 10-mm light path silica cuvet (Model: S-10C) from Sigma was used to avoid interference with 2,2'-biquinoline solution. All UV-vis scans were performed at a rate of 600 nm/min. Cu^+-2,2'-biquinoline complex was prepared by dissolving Cu_2O in 2,2'-biquinoline reagent (0.004mol/l). Standard solutions of cuprous $^+$-2,2'-biquinoline were made by dissolving cuprous oxide in -2,2'-biquinoline with copper content varying from 0 to 100 ppm. These standard solutions were used to build the calibration curve. The total amount of copper was determined by AAS. 2,2'-biquinoline reagent was scanned as a blank. The calibration curve was obtained by plotting the maximum UV-VIS absorbance at 540 nm against the copper concentration in the Cu^+-2,2'-biquinoline solutions as determined by AAS analysis.

About 25 ml of 2,2'-biquinoline reagent was used to extract about 0.1 g wood sawdust by ultrasonic extraction for 5 minutes at room temperature using ultrasonator Model: ULTRA sonik 57X from Cole-Parmer Instrument Co. samples were purged with nitrogen to prevent air oxidization. After centrifuge, the supernatant solution clear of solid particles was used for UV-VIS analysis.

RESULTS AND DISCUSSION

In previous work (Kamdem *et al.* 1997, 1998a, 1998b), using EDXA analysis on the post-steamed lab produced samples, the ratio of Cu to O indicated the presence of Cu_2O in the samples. Further, XRD analyses proved the presence of the actual crystalline structure of Cu_2O acid was used to semi-quantify the level of the Cu_2O found in the post-treatment steamed samples. Analytical results are shown in Table 2. The X-ray diffraction patterns of lab produced post-treatment steamed samples are compared to CuO and Cu_2O standards in Figure 1.

Table 2. Analytical results from treatment and post-steaming of small southern pine samples under laboratory conditions (Kamdem *et al.* 1998a)

Sample Description (19 mm SYP Cubes)	**Total Copper (AAS)**	**Cu from Cu_2O (XRD)**	**Estimated % Conversion of Cu in CN to Cu_2O (by XRD)**
Treating solution strength, (% w/w Cu)	pcf (kg/m^3)	pcf (kg/m^3)	
0.0 % (diesel only)	0.0 (0.0)	0.0 (0.0)	0
0.5 %	0.11 (1.76)	0.054 (0.86)	50
1.0 %	0.19 (3.04)	0.077 (1.23)	40
2.0 %	0.23 (3.68)	0.035 (0.56)	15

ESEM-EDXA (Pole Size Stubs After 12 Years Exposure)

ESEM images of CN treated southern pine, non-post-treatment steamed, fixed, and post-treatment steamed show solid deposits on the cell walls. Examples are shown in Figure 2. Thus, post-treatment steaming, fixation bath, and even outdoor exposure resulted in formation of solid deposits in CN treated wood. Closer examination by EDXA confirmed that the solids observed on CN treated poles exposed outdoors, were rich in copper, carbon and oxygen. Additionally, solid deposits were also rich in Ca, Si, Al, and Fe. Unlike the solids found in the laboratory steamed small samples, which were relatively rich in Cu and oxygen with a high Cu to oxygen ratio, the outdoor exposed samples had many more deposits in addition to the ones rich in both Cu and O.

XRD (Pole Size Stubs After 12 Years Exposure)

The XRD patterns contain two peaks at 2Θ =36.50°and 42.20° as illustrated on the XRD patterns (Figure 3). These two peaks were earlier assigned to cuprous oxide. Their intensity in terms of count per second was lower than that observed from laboratory treated and conditioned wood. This may be due to the interference with other crystals in wood as revealed by the presence of significant quantities of Fe, Al, Si and Ca by the EDXA.

Qualitative Analysis

The pressure treatment with copper-naphthenate wood preservatives did not change or affect cellulose crystal lattice structure. Figure 3 shows the XRD patterns of 12-year old stub samples. Included in these samples are all the treatment variable extremes from Table 1. No significant modification in XRD patterns was noticeable after post-treatment steaming of untreated wood. XRD patterns for all CN-treated pole stubs contain the characteristic peaks at 2Θ values of 36.5º and 42.1º, suggesting the presence of Cu_2O. These crystals were absent in the non-post-treatment steamed laboratory samples (Fig. 1C and 1D). These crystals could arise from four possible sources: Cu_2O in the original treating solution, treatment of hot wood, post-treatment steaming, or field exposure.

Analytical data are shown in Table 3. These data suggest post-steaming has no significant influence on copper reduction. In fact, post-steaming slightly reduced conversion. For example, air-dried, post-steamed samples (T18B) averaged about 10% conversion compared to T19B (no post-steaming) which averaged about 16% conversion.

The fixation process increases conversion compared as illustrated by the results for sample T17A vs. T19B for fixed and non-fixed air-dried material. A similar trend is evident for the steam-conditioned stock. The highest degree of conversion is obtained when steam-conditioned poles are treated at 140º F and given a final fixation bath. In general, the degree of conversion is greatest near the pole surface.

SUMMARY AND CONCLUSIONS

Conversion of Cu^{++} to Cu^{+} in CN-treated southern pine was demonstrated. Conversion of the cupric copper to cuprous form ranged from 9 to 32 % (w/w) in large scale tests of stubs exposed for after 12 years in ground contact depending on assay zone depth and post-pre-treatment conditioning methods. Neither pre-treatment steam-conditioned or post-treatment steaming increased the occurrence of cuprous copper. Post-treatment fixation at elevated temperature increased the relative occurrence of Cu^{+}. This study, coupled with the work by Barnes and Freeman (2000), indicates that regardless of the conversion of some small fractional amount of cupric copper found in copper naphthenate to cuprous oxide after 12 years of exposure, the pole stubs continued to perform satisfactorily with no colonization by decay fungi and subterranean termites.

LITERATURE CITED

American Wood-Preservers' Association (AWPA). 1999. Book of Standards. Granbury, TX.

Anderson, T.A. 1998. Annual report of sub-committee P-5: Chemical analysis of preservatives. Proc., American Wood-Preservers Association. 94: 77-80.

Archer K., J. V. W. and M. Hedley. 1990. The comparative performance of copper naphthenate formulations in laboratory decay tests. Proc., American Wood-Preservers' Association. 86: 78-95.

Barnes, H.M., and R. W. Hein. 1988. Treatment of steam-conditioned pine poles with copper naphthenate in hydrocarbon solvent. Record Annual Convention British Wood Preservers Association. p. 3-33.

Barnes, H. M.; Freeman, M.H.; Brient, J.A.; Kerr, C.N., Jr. 2000. Serviceability of copper naphthenate-treated poles. International Research Group on Wood Preservation. Document No. IRG/WP (In Press).

Barnes, H.M. and Freeman, M.H. 2000. The performance of copper naphthenate treated wooden pole stubs after 12 years of field exposure. 5th Annual International Conference on Wood Poles and Piles, Colorado State Univeristy and EDM, Ft. Collins, CO. (In Press).

Brient, J.A. 1992. "Naphthenic Acid", in The Kirk-Othmer Encyclopedia of Chemical Technology, V.o. 4.0 Edited by Jacqueline I Kroschwitz. (Last Edition-December 1998)

Wiley-Interscience, New York. ISBN: 0471527041or *Kirk-Othmer Encyclopedia of Chemical Technology* [online]. 3rd ed. New York : John Wiley, 1984 [cited 3 January 1999]. Available from: DIALOG Information Services, Palo Alto, CA.

De Groot, R. C., C. L. Link, J. B. Huffman, 1988. Field trials of copper naphthenate treated wood. Proc., American Wood-Preservers' Association. 84: 186-200.

Engdahl, Eric K.; Baileys, Randall T.1992. A report on southern pine utility poles treated with copper naphthenate. Proc., American Wood-Preservers' Association 88: 268-88.

Freeman, M. H., 1994. Copper Naphthenate: An effective wood pole and cross arm preservative. Proc., 1st Southern Pole Conference. Forest Products Society, Madison, Wisconsin, pp. 68-77.

Freeman, M.H. 1998. Report of Sub-Committee P-3; Organo and organometallic wood preservatives and systems. Proc., American Wood-Preservers' Association. 94: 70-73.

Gutzmer D. I. and D. M. Crawford. 1995. Comparison of wood preservatives in stake Tests - 1995 Progress report. Res. Note FPL-RN-02. U.S. Department of Agriculture, Forest Service, Forest Product Laboratory, Madison, WI, 124 pp.

Hartford, W. H., 1973. Chemical and physical properties of wood preservatives. In: Deterioration and its prevention by preservative treatment (Nicholas, D. D., ed.) Syracuse University Press NY.

Hein, R.W.; Kelso, W.C. 1987. U.S. Patent 4, 649, 065. Process for preserving wood.

Kamdem, D. P., K. Gruber, M. Freeman, 1995. Laboratory evaluation of copper naphthenate as wood preservative for northern red oak. Forest Prod. J. 45(9): 72-76.

Kamdem, D. Pascal; Freeman, Michael H.; McIntyre, Craig R.; Woods, Thomas. 1998a. Copper naphthenate treated southern yellow pine (SYP): Effect of post-treatment steaming. Proc., American Wood-Preservers' Association. 94: 15-29.

Kamdem D. P. J. Zhang, and M. Freeman. 1998b. The Effect of post-treatment post treatment steaming on copper naphthenate treated southern pine. Wood & Fiber Sci. 30(2): 210-217.

Kamdem, P.D., Freeman, M.H., and Jun Zhang. 1997. The effect of post-steaming on copper naphthenate treated southern pine wood. International Research Group on Wood Preservation, Document No. IRG/WP/97-40086.

Kamdem D. P. and C. R. McIntyre. 1998. Chemical investigation of 23 year old CDDC treated southern pine. Wood & Fiber Sci. 30(1): 64-71

McIntyre, C.R. 2000. The history of copper naphthenate. 5th Annual International Conference on Wood Poles and Piles, Colorado State University and EDM, Ft. Collins, CO. (In Press).

Nicholas, D.D. and Freeman, M.H. 2000. A comparison of pentachlorophenol and copper naphthenate in field stake tests. 5th Annual International Conference on Wood Poles and Piles, Colorado State University and EDM, Ft. Collins, CO. (In Press).

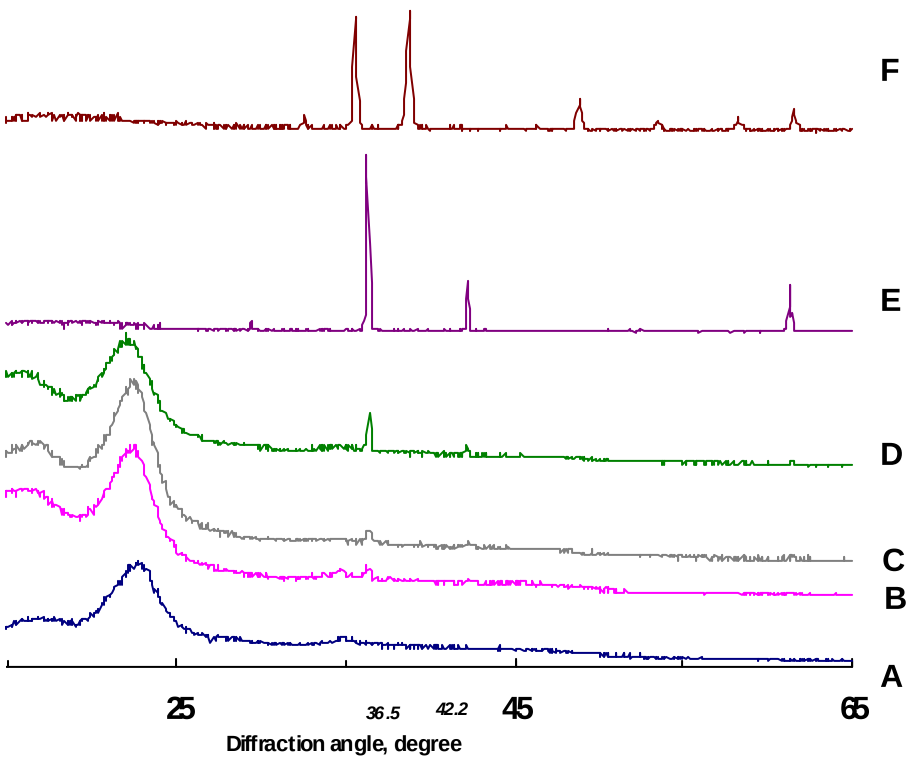

Figure 1. XRD of southern pine: (A) Small samples that were laboratory treated with CN and non-post-treatment steamed; (B) Small samples that were laboratory treated with CN and post-treatment steamed; (C) Physical mixture of wood meal and Cu_2O; (D) Small samples that were CN treated post steamed and spiked with 0.2% Cu_2O; (E) Pure Cu_2O; (F) Pure CuO.

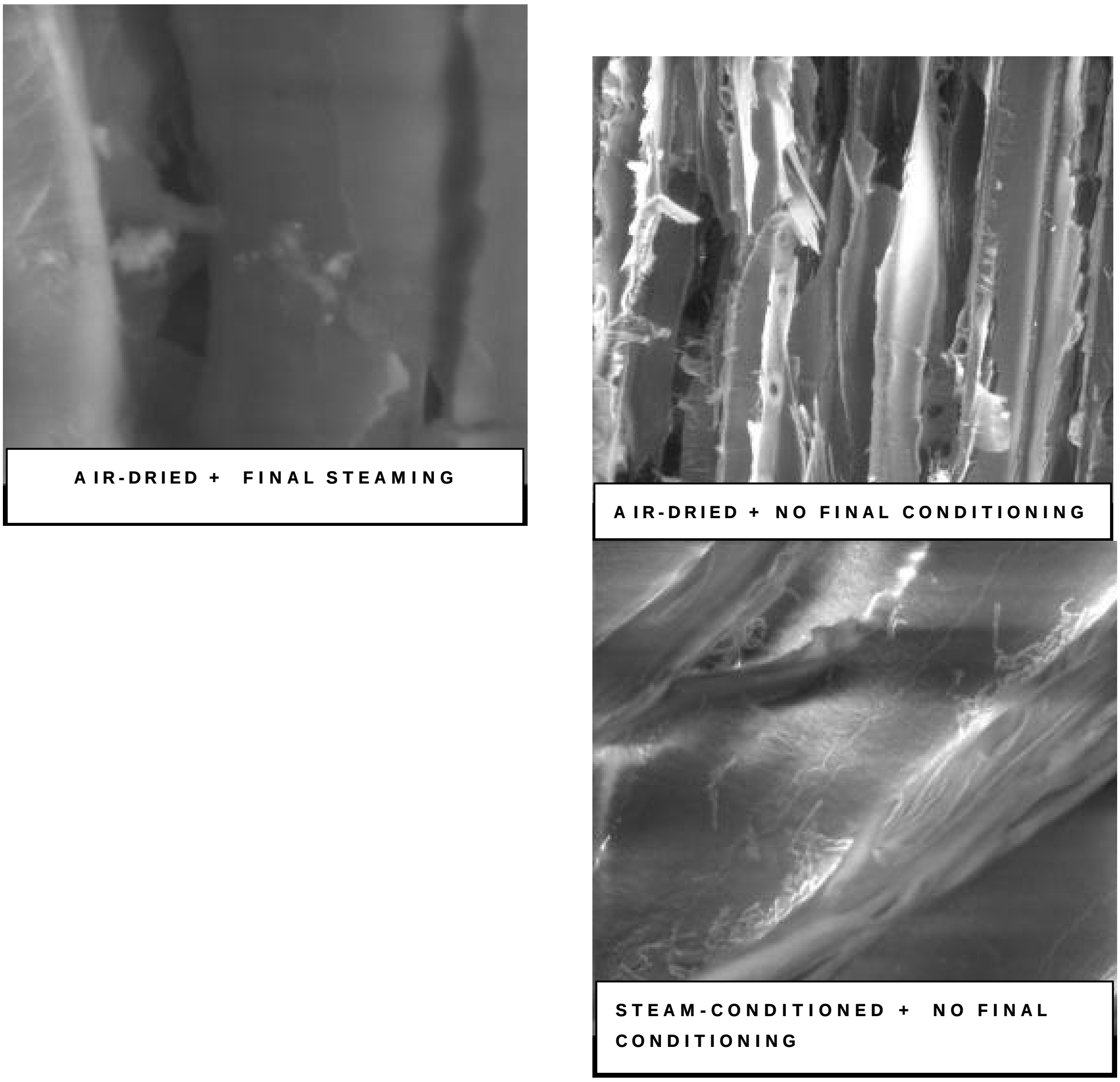

Figure 2. Typical ESEM images of southern pine pole stubs after 12 years of exposure.

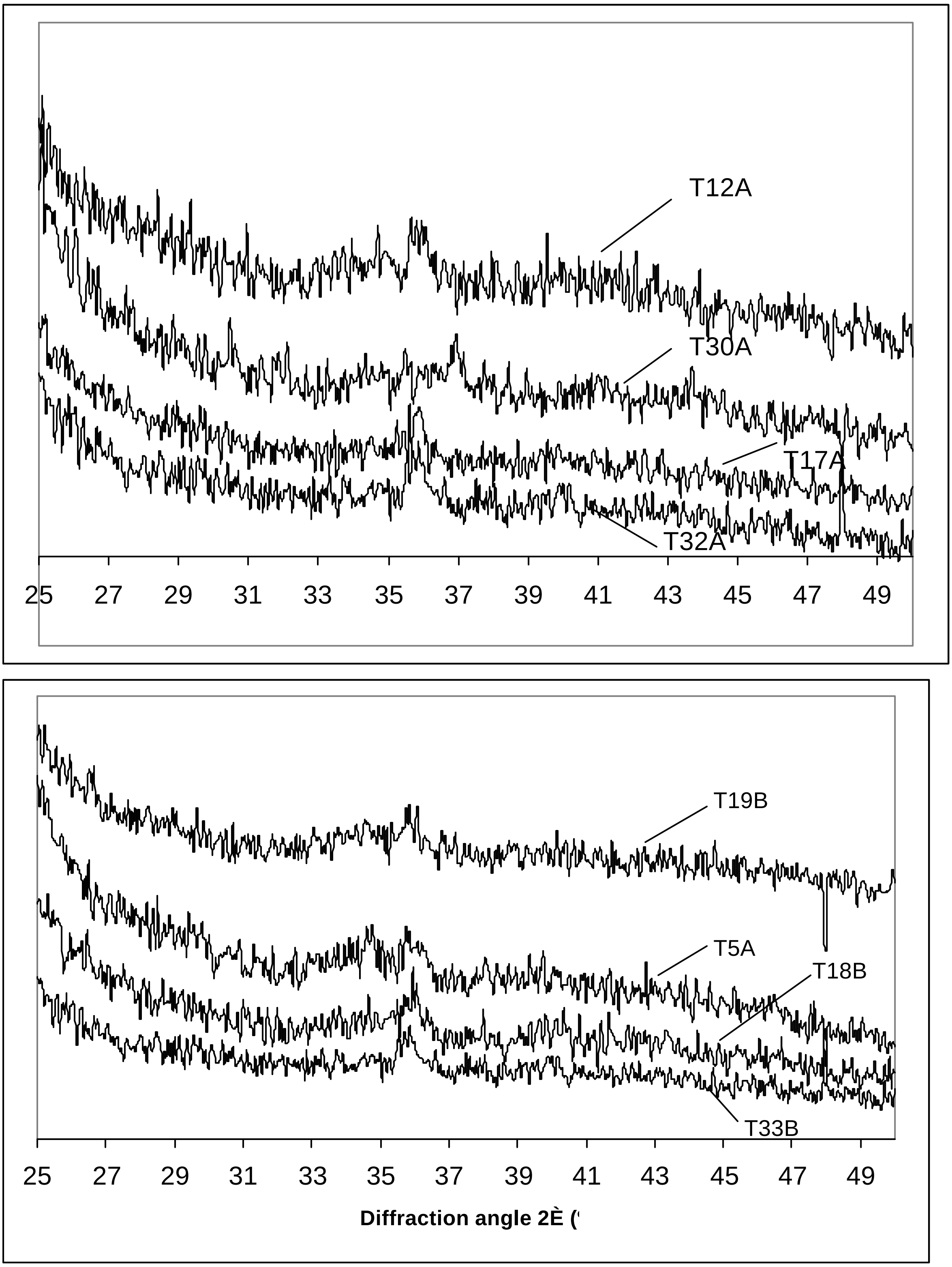

Figure 3. XRD of southern pine pole stubs after 12 years exposure.

Table 3. Analytical results from treatment and post-treatment conditioning of southern pine pole stubs after 12 years of exposure

Sample ID #	Treatment Temperature	Pre- Treatment Conditioning Method	Post Treatment Conditioning	Assay Zone (Median Depth from Pole Surface)	Total Copper Assay by AAS (pcf) by QFS	Total Copper Assay by AAS (w/w %) by MSU	Cu_2O Dete in samp (by use of biquin (w/w %
T17A	AMBIENT	Air Dried	FIXED	0.25 inches	0.032	NA	0.033
				1.25 inches	0.055	0.114	0.036
				2.5 Inches	0.058	0.166	0.015
T18B	180 F	Air Dried	STEAMED	0.25 inches	0.056		0.031
				1.25 inches	0.066	0.182	0.017
				2.5 Inches	0.041	0.127	0.013
T19B	AMBIENT	Air Dried	NONE	0.25 inches	0.048		0.024
				1.25 inches	0.064	0.153	0.018
				2.5 Inches	0.038	0.083	0.017
T5A	AMBIENT	Steam Conditioned	NONE	0.25 inches	0.074		0.037
				1.25 inches	0.081	0.146	0.028
				2.5 Inches	0.035	0.119	0.011
T30A	200 F	Steam Conditioned	NONE	0.25 inches	0.032		0.038
				1.25 inches	0.067	0.139	0.026
				2.5 Inches	0.044	0.083	0.007
T33B	180 F	Steam Conditioned	STEAMED	0.25 inches	0.046		0.038
				1.25 inches	0.115	0.279	0.036
				2.5 Inches	0.132	0.156	0.026
T12A	140 F	Steam Conditioned	FIXED	0.25 inches	0.053		0.069
				1.25 inches	0.080	0.260	0.050
				2.5 Inches	0.046	0.149	0.048
T32A	AMBIENT	Steam Conditioned	FIXED	0.25 inches	0.045		0.039
				1.25 inches	0.054	0.125	0.029
				2.5 Inches	0.048	0.163	0.025