Proceedings, American Wood Preservers' Association. 97:15-23

PROCEEDINGS

Ninety-Seventh Annual Meeting

of the

AMERICAN WOOD-PRESERVERS' ASSOCIATION

1030

Minneapolis Marriott City Center
Minneapolis, Minnesota
May 20-23, 2000

VOLUME 97

AMERICAN WOOD-PRESERVERS' ASSOCIATION
P.O. BOX 5690 GRANBURY, TEXAS 76049

FIELD PERFORMANCE OF COPPER NAPHTHENATE-TREATED HARDWOODS[1]

H. M. Barnes, T. L. Amburgey, M. H. Freeman, and J. A. Brient

Abstract: Copper naphthenate (CuNap) is a proven, commercially produced and industry utilized preservative for many wooden commodities including poles, fence posts, lumber, timber and wood shakes/shingles. Historically, most wood preservatives are tested using the sapwood of softwood species like pine (*Pinus* spp.) and or Douglas-fir (*Pseudotsuga menziesii*). Although the railroads of the world have commercially utilized hardwoods for the material that bears the load of the gauge, not many preservative evaluations are performed on hardwood species. This paper examines the historical tests of copper naphthenate performance in North American hardwood species previously established by the TVA (Tennessee Valley Authority) and the AREA (American Railroad Engineering Association). This efficacy review includes previously unpublished data of copper naphthenate-treated hardwoods compared to P2 creosote in a high hazard test site. The recent results from the timber bridge-testing program where CuNap is being evaluated in seven hardwood species plus southern pine. The test data presented in this paper supports the potential commercial uses of copper naphthenate to treat hardwoods and provide adequate to excellent service life for those treated members.
Keywords: Copper naphthenate, preservative, efficacy, hardwoods, performance, crossties

Introduction

The use of copper naphthenate (CuNap) as an industrial biocide has been well established since the turn of the century (Freeman 1992, 2000). CuNap is basically the reaction product of a copper compound with naphthenic acids. The naphthenic acids are typically alicyclic acids and are broadly classified as acids of the formula $C_nH_{2n-z}O_2$. Chemically speaking, these compounds are known as cupric cyclopentane carboxylates or cyclohexane carboxylates. The physical and chemical characteristics of CuNap and naphthenic acids have been described in detail (Brient *et al.* 1995). Hartford (1973) discussed their use in wood preservation. A review of the literature cites many applications for use, including field boxes, beehives, benches, flats, fence posts, water tanks, canvas, burlap, ropes, nets, greenhouses, utility poles, crossarms, and wooden structures in ground contact and above ground contact (Thomson 1991). Work presented in this paper will show that CuNap is an excellent preservative for hardwoods and may well be the next preservative for the use of hardwood crosstie material.

Trade names for copper naphthenate in commercial use include Perm-E8, Cop-R-Nap, CuNap8, Cunapsol, and Cuprinol. Of these, the most common name is Cuprinol, dating back to the Danish of over a century ago, meaning, "copper in oil" (Freeman 1992, 2000). Copper naphthenate began its strong leap into the wood preservation business with the need to extend the useful volume of creosote available in the postwar effort. Due to a modification of operating practices of the steel mills, creosote, whose main source is the coking of coal and of petroleum products, was in short supply. The American Wood Preservers' Association (AWPA) began a search for combination biocides that could be added to creosote to effectively extend its service life. It was determined that copper naphthenate was a likely extender for creosote and did not offer some of the proposed problems that addition of pentachlorophenol (penta) as a phenolic acid would pose in treating plant corrosion.

---

[1] The authors are, respectively, Professor and Professor, Forest Products Laboratory, Mississippi State University,
Wood Scientist, Memphis, TN, and Manager, Naphthenic Acid Technology, Merichem, Houston, TX.
Published as Journal Article No. FP-213, Forest & Wildlife Research Center, Mississippi State University, Mississippi State, MS 39762, USA.

Minich and Goll (1948) provided a broad background of the technical aspects of copper naphthenate as a wood preserving chemical including solubility in organic solvents, relative vapor pressure, electrical conductivity properties, compatibility with commercially available oils, permanence, ease of application, safety in handling, and the effectiveness against wood decay fungi. A specification was proposed to add copper naphthenate to the AWPA Book of Standards.

Copper naphthenate in the AWPA Standard P8 (2000) has the following specifications:

- The acid used in the manufacture of copper naphthenate shall be naphthenic acid of the group of alicyclic carboxylic acids occurring in petroleum and shall have an acid number of not less than 180 and not more than 250 on an oil-free basis (see 1999 AWPA *Proceedings*, p. 133 for a gas chromatographic method for determining conformity with this and following requirement).
- All of the copper present in the concentrate shall be combined as copper naphthenate.
- The copper naphthenate concentrate used to prepare wood preserving solutions shall contain not less than 6 percent, nor more than 8 percent, copper in the form of copper naphthenate.
- The copper naphthenate concentrate shall not contain more than 0.5 percent water.
- The foregoing tests shall be made in accordance with the standard methods of the AWPA Standards A5.
- Solvents used to prepare solutions of copper naphthenate shall comply with the standards of AWPA Standard P9.
- The copper naphthenate concentrate shall not contain more than 2 percent (relative) of the total copper in the concentrate as determined by Standard A14.

The values in the current AWPA Standards (2000) vary slightly from the original proposal prepared by Minich and Goll (1948).

Studies with Softwoods

The performance of CuNap in softwood species has been widely reported. In a recent study (Nicholas and Freeman 2000) the performance of CuNap- and penta-treated pine stakes in ground contact was compared at two test sites in Mississippi corresponding to a high hazard zone (AWPA zone 4) and a severe hazard zone (AWPA zone 5). After ten years exposure, the efficacy of CuNap at a retention level of 0.80 kg/m^3 Cu was equivalent or slightly better than penta at a retention level of 0.64 kg/m^3.

Barnes and Freeman (2000) reported no deleterious effects of pre- or post-treatment steaming on the performance of CuNap-treated pole sections after 12 years of in-ground exposure. A survey of CuNap-treated poles showed that southern pine and Douglas-fir poles in service across all hazard zones in the US demonstrated excellent serviceability (Barnes *et al.* 2000). McIntyre (2000), in analyzing tests conducted with oilborne preservative systems, concluded that CuNap was an effective preservative equivalent to creosote or penta at comparable retentions. Grace *et al.* (1993) showed CuNap to be effective against *Coptotermes formosanus* with less than 2% weight loss for pine treated to 0.64 kg/m^3 (as Cu).

Laboratory Studies with Hardwoods

Historically, hardwoods have not been used for many efficacy tests with the exception of some white rot tests and some limited efficacy tests of lesser-used species.. In a laboratory soil-block study on northern red oak (*Quercus rubra*), Kamdem *et al.* (1995a) found that at 1.28 kg/m^3 (as Cu) of an oilborne CuNap preservative, weight loss of northern red oak exposed to brown rot (*Gloeophyllum trabeum*) or white rot (*Pleurotus ostreatus* or *Trametes versicolor*) fungi was $\leq 3\%$. A higher elemental Cu retention of 1.6 kg/m^3 was needed to protect red oak against the Cu-tolerant brown rot *Poria placenta*.

Monoculture tests by Kamdem *et al.* (1996) showed that 3.2 ± 0.5 kg/m^3 or 4.2 ± 0.5 kg/m^3 of a waterborne CuNap system was needed to protect northern red oak (*Quercus rubra*) or red maple (*Acer rubrum*), respectively. Results from AWPA standard leaching tests indicated that the treated samples retained 85 to 95% of the copper initially absorbed depending on the initial retention. In agar plate tests, Smith *et al.*

(1996) showed that the oilborne formulation was more effective than the waterborne formulation at equivalent copper loading.

Field Studies with Hardwoods

In a study partially funded by the US Timber Bridge Initiative, the pressure treatment of keruing, maple (heartwood and sapwood), yellow birch, and southern pine is being investigated (Crawford *et al.* 2000). The most recent progress report indicates wood treated with CuNap in oil at retentions as low as 0.26 kg/m^3 is performing satisfactorily at a South Mississippi site (AWPA zone 5). Some attack at the low level was noted after four years of exposure. The stakes were treated full cell with toluene dilutions of CuNap in diesel using the following treatment solution strengths: 0.04%, 0.08%, 0.30 % and 1.2 % copper (as metal). Based on the average uptake of treating solution, the approximate retentions were 0.26, 0.51, 1.92, and 7.7 kg/m^3 copper (as metal). At all except the lowest solution strengths, ratings were perfect with no termite attack or decay after four years exposure. Untreated controls after four years were completely destroyed or rated at a level of 1 on a scale of 0 to 10, with 10 being perfect with no attack.

Smith *et al.* (1996) evaluated the treatability of red maple with oilborne and waterborne CuNap systems. Variability between oilborne and waterborne systems was minimal. Kamdem and others (1995b, 1999) investigated the treatability and effect of pressure on CuNap absorption in red maple, sugar maple, beech, and red oak. For applied pressures of 1.03 MPa or higher, the authors found no difference in the preservative gradient for a given species. Absorption followed the trend beech < red oak < sugar maple < red maple.

Kresyzewski (1977) compared preservative-treated crossties in service in Canadian railways for more than 40 years. Checking, splitting, plate or rail cutting, and decay were the main defects noted. In most of the species in this test, the performance of CuNap compares favorably with that of creosote. Yellow birch ties treated with CuNap had an average service life of 25 years in secondary track. Creosoted aspen/poplar ties had an average life of 23 years in low speed main track. Red oak in this study was mechanically superior to other hardwood species evaluated with service life exceeding 25 years minimum.

DeGroot and Stroukoff (1986) evaluated five oilborne and nine waterborne preservatives with 5% penta in petroleum solvent for protecting nailed pine boxes, wire-bound gum (*Nyssa sylvatica* and *Liquidambar styraciflua*) boxes and wire bound plywood boxes. Boxes were exposed above ground for 36 months in a jungle and in an open field in Panama and for 47 months in a partially shaded field in South Mississippi. Oil- and water-based formulations of CuNap performed better than penta in the jungle. All treatments protected pine and plywood boxes, and both oil-borne and water-borne CuNap were effective on gum boxes in Mississippi. Results for the open-field site in Panama were intermediate between those from the jungle and those from Mississippi.

The US Forest Products Lab maintains test plots on the Mississippi Gulf Coast (AWPA zone 5) and other sites that contain CuNap-treated stakes of various species treated with different treatment methods (Gutzmer and Crawford 1995). Red oak stakes treated with CuNap in high boiling point aromatic oil ranging in retention from 2.2 – 5.1 kg/m^3 have yet to fail after 30 years in ground contact. Only one similarly treated stake (1.2 kg/m^3) exposed in Florida (AWPA zone 5) had failed. Performance in both plots for CuNap-treated stakes (Cu as metal) was equivalent to that for creosote at $\geq$ 96 kg/m^3. In analyzing these data, DeGroot *et al.* (1988) noted that at comparable retentions, red oak stakes performed substantially better than pine stakes in Florida.

Laks *et al.* (1997) compared seven hardwood species and southern pine treated with eleven different wood preservative systems, including oilborne CuNap. In this study there was good correlation between soil bed and field stake results. The more highly developed preservative systems and those in an AWPA P9 Type A oil carrier, like oilborne CuNap, tended to perform better (Laks *et al.* 1997). Updated information shows that CuNap is performing well in all species tested, with only one species, cottonwood, having limited performance after 54 months of testing in Hawaii. Dose response curves from this study by species for CuNap and creosote can be seen in Figures 1 and 2.

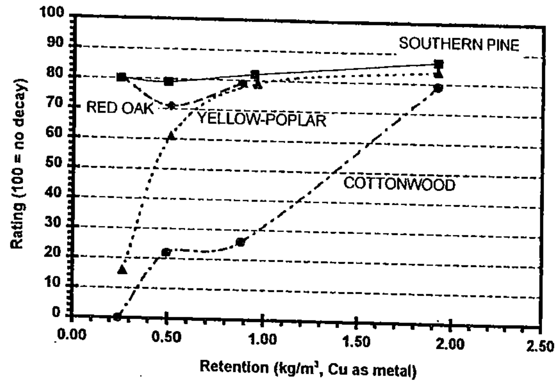


Figure 1. Dose-response curves for four hardwood species treated with copper naphthenate after 54 months exposure in Hawaii.

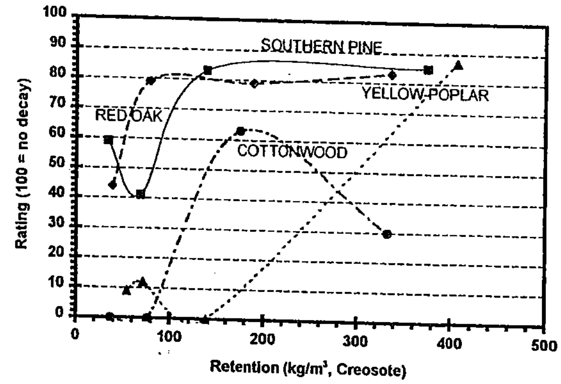


Figure 2. Dose-response curves for four hardwood species treated with creosote after 54 months exposure in Hawaii.

In a test established by the Tennessee Valley Authority, Schell (1952) reported that fence post size specimens were dip treated with a 0.50% (Cu as metal) solution to an average net retention of 0.03 pcf Cu (as metal) or roughly 1/2 of the AWPA recommended retention for softwood fence posts. TVA (Anon. 1964) evaluated these fence posts over a 17+ year period. The results of the last inspection reported are shown in Table 1.

In an unpublished report, McIntyre (2001) analyzed the results of a field stake test at the Austin Carey Forest near Gainesville, Florida (AWPA zone 5) initiated by the American Railway Engineering Association (AREA) in 1957 (AREA 1975). After 15 years of exposure, the test was terminated. The test specimens were nominal 2 x 4 x 18-in. stakes of red oak, coastal Douglas-fir, or southern yellow pine. Three nominal retentions were used for this study: the AREA-recommended (100%) level, half the AREA-recommended (50%) level, and twice the AREA-recommended (200%) level. The AREA 100% retention recommended level for CuNap was 1.6 kg/m^3 (Cu as metal) and 160 kg/m^3 of creosote or 60:40 creosote coal tar (CCT) solution. The creosote and CCT solution generally conformed to the current AWPA (2000) Standards P1/P13 or P2, respectively. Untreated stakes of appropriate species were installed periodically, and these stakes would generally last 2-3 years before failure occurred.

Table 1. Results of 17+ year field performance of fence posts cold soaked in a 0.50% (Cu as metal) copper naphthenate solution (average retention = 0.03 pcf Cu as metal).

Species	Untreated		CuN-treated		
	No.	Service life (yrs)	No.	Estimated Service life (yrs)	Fail,%
Southern Pine	123	1.9	494	***16-17***	23
Willow	25	2.4	50	***12-13***	52
Hybrid Poplar	25	2.4	-	-	-
River birch	25	2.6	49	***11***	84
Sycamore	25	2.6	49	***12-13***	55
Black oak	25	2.8		***15-16***	
Yellow-poplar	23	2.8	50	***17+***	12
Blackgum	25	3.4	50	***14-15***	34
Sourwood	50	3.6	50	***17+***	16
Red maple	25	4	50	***11-14***	56
Hickory	25	4.7	50	***12-15***	18
Chestnut oak	25	4.8	50	***18+***	6
White oak	17	***11***	50	***14+***	18
Sassafras	25	***11***	50	***16+***	20
Black locust	25	***15***	25	***20+***	0
E. Redcedar	23	***18***	25	***20+***	4

Estimated service life in ***bold italics***; data from Anon. (1964).

Generally, the actual retentions were reasonably close to the targets except for the highest retention red oak stakes. In this case, a retention of only 146% (vs. 200%) was achieved with CuNap. As shown in Figure 3, the 50% and 100% retentions of CuNap, creosote (P1/P13), and CCT gave decay ratings that were essentially identical. However, the lower pickup at the "200%" retention resulted in a slight departure of the CuNap ratings from those of creosote and CCT, but this was to be expected since the CuNap-treated stakes had considerably less preservative actives. It should be noted that even though the CuNap stakes had only three-fourths of the relative retention, the CuNap parallels the performance of creosote and matches the 60:40 CCT in red oak stakes.

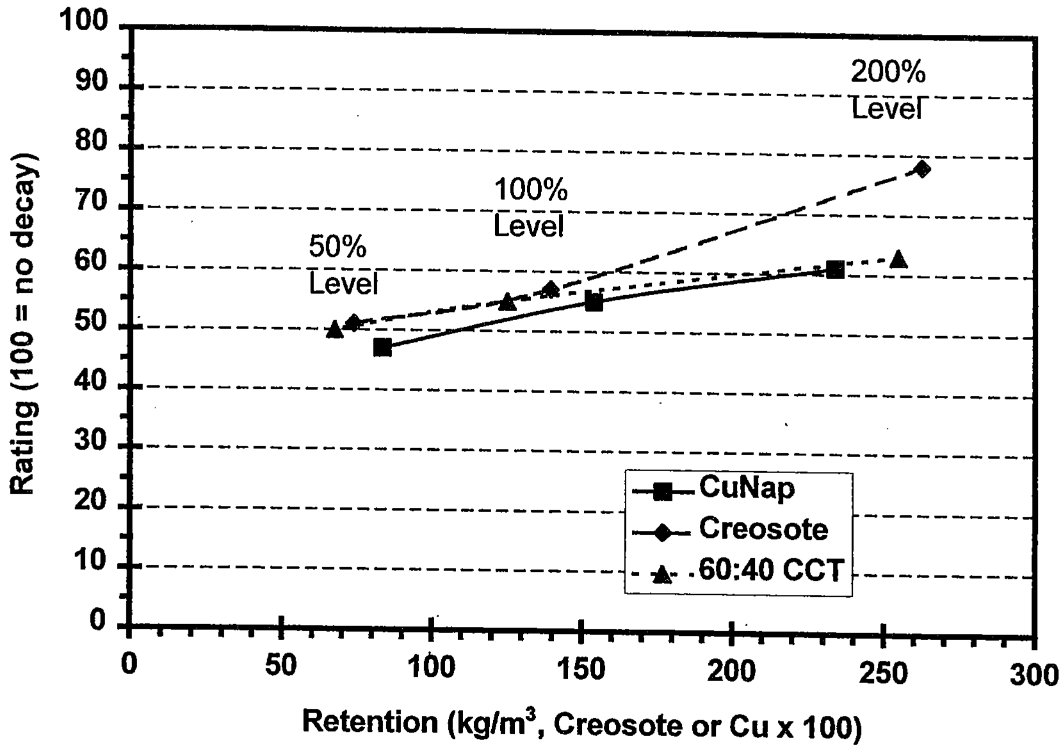


Figure 3. Dose-response curves for red oak stakes after 15 years of exposure [Note: the Cu retention has been multiplied by 100 for comparison purposes only].

The following sections of this paper will outline the results from an ongoing study being conducted at Mississippi State University to evaluate the performance of CuNap in hardwoods.

Materials and Methods

Test stakes, nominally 19- x 19-x 1118-mm, were cut from dried red oak (*Quercus spp.*), sweetgum (*Liquidambar styraciflua*), or southern pine (*Pinus spp.*) and segregated into uniform density distributions by species according to AWPA Standard E7 (2000). Ten replicate stakes/species were treated using a conventional full-cell process with solutions of creosote or CuNap. The creosote conformed to AWPA Standard P2. The CuNap was a nominal 8% (Cu as metal) concentrate formulated in #6 fuel oil.

The desired creosote retentions were achieved by using toluene dilution. A similar method was used with CuNap concentrate except that a 75:25 (toluene: P9 type A oil) solvent mix was used to dilute the CuNap concentrate. This resulted in a residual oil content in the CuNap-treated stakes of approximately 96-120 kg/m^3. After treatment, a 100-mm section was removed from both ends and saved for reference. The remaining piece was cut into 457-mm matched halves. One matched half was placed in the MSU Dorman Lake test plot (AWPA zone 4) and the other at the Austin Carey Forest, FL (AWPA zone 5) in 1992. Untreated controls were used as reference stakes. The stakes were evaluated annually for decay and termites according to the AWPA (2000) rating scale in Standard E7.

Results and Discussion

Typical depreciation curves for the Dorman Lake site are shown in Figure 4 for sweetgum and Figure 5 for red oak.

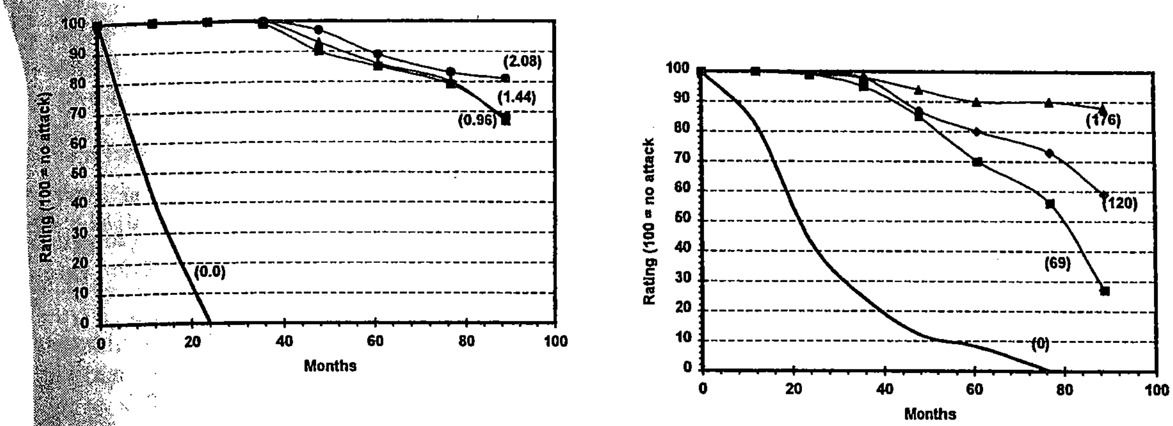


Figure 4. Depreciation curves for copper naphthenate- (left) and creosote-treated sweetgum exposed in the Dorman Lake test plot (AWPA zone 4) [retentions in kg/m^3 shown in parentheses].

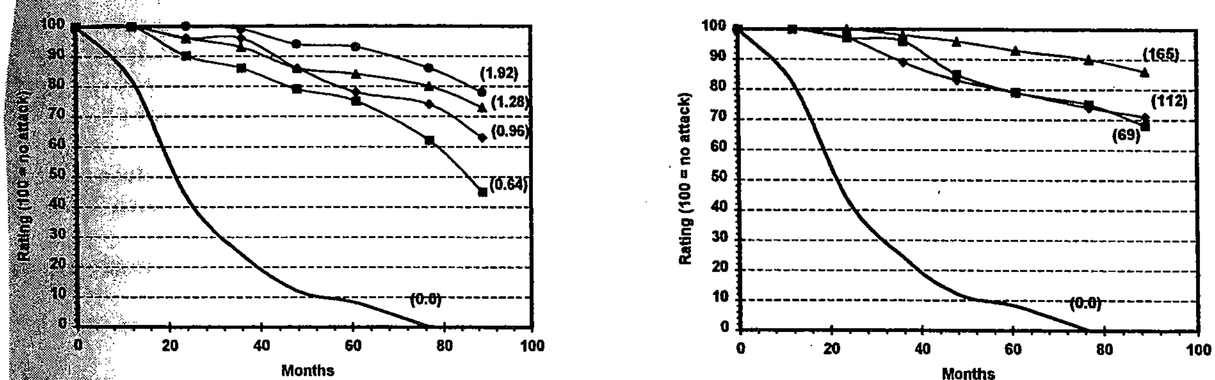
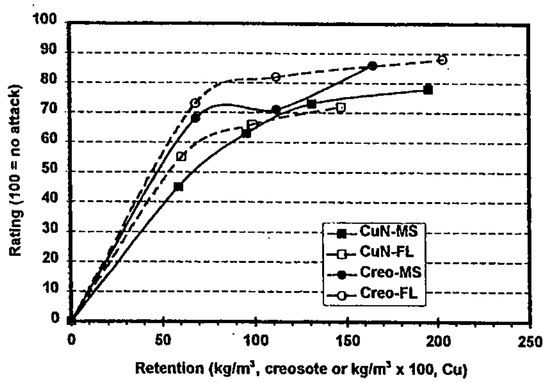


Figure 5. Depreciation curves for copper naphthenate- (left) and creosote-treated red oak exposed in the Dorman Lake test plot (AWPA zone 4) [retentions in kg/m^3 shown in parentheses].

With sweetgum (Figure 4), the performance of CuNap-treated stakes ranging from 0.96-2.08 kg/m^3 (as Cu) fell between that for creosote treatments at 120 and 176 kg/m^3. For red oak (Figure 5), CuNap-treated stakes at retentions of 0.96-1.92 kg/m^3 performed similarly to those treated with creosote ranging from 69-165 kg/m^3. Similar results were found in the Florida test plot. Dose-response curves after 7.5 years in ground contact are shown in Figure 6 for red oak and gum. Based on a rating of 70, 60-70 kg/m^3 of creosote is roughly equivalent to 1.7 to 1.9 kg/m^3 (Cu as metal) in red oak. There was more variability in the gum stakes with roughly 75 kg/m^3 of creosote equivalent to 1.4 kg/m^3 (as Cu) in the Florida plot and 140 kg/m^3 creosote equivalent to 2.6 kg/m^3 (as Cu) in the Mississippi plot. The dose-response curves for CuNap were remarkably similar for both plots. Interestingly, both the CuNap and creosote curves indicated that the Mississippi site was a more severe site than was the Florida site. This is unexpected since the Florida site is in zone 5 and the Mississippi site is in zone 4.



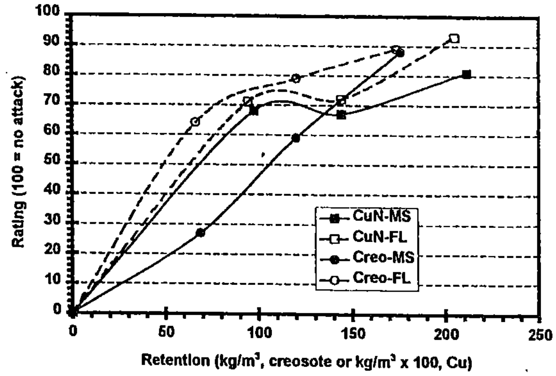


Figure 6. Dose-response curves for red oak (left) and sweetgum (right) after 7.5 years in ground contact in Mississippi and Florida. [Note: Cu retentions have been multiplied by 100 for ease of graphing and comparison].

Summary and Conclusions

The data for CuNap compare favorably with data for creosote or creosote coal-tar systems. The field data presented in this paper should represent an exposure condition more severe than that found in track with well-maintained ballast. Therefore, the data reviewed and the new data presented in this paper indicate an excellent potential for the use of CuNap as a crosstie (sleeper) preservative.

Literature Cited

American Railway Engineering Association. 1975. Report of Committee 3 – Ties and Wood Preservation. 75:1ff.

Anon. 1964. Twelve-year Service Tests on Treated Posts, Tennessee Valley Authority, Norris, TN, 6 pp.

AWPA. 2000. Book of Standards. American Wood-Preservers' Association, Granbury, TX.

Barnes, H.M.; Freeman, M.H. 2000. The performance of copper naphthenate-treated wooden pole stubs after 12 years of field exposure. *In*: Proceedings, International Conference on Utility Line Structures, March 2000, Ft. Collins, CO, p. 207-226.

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, Doc. No. IRG/WP 00-30214, 10 pp.

Brient, J.A.; Wessner,P.J.; Doyle, M.N. 1995. Naphthenic Acids. *In*: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley and Sons, New York, NY. 16:1017-1029.

Crawford, D.; Woodward, B.; DeGroot, R. 2000. Unpublished Report -- Progress Report from Wood in Transportation Structures. USDA Forest Service, Forest Products Laboratory, Madison, WI.

DeGroot, R.C.; Link, C. L.; Huffman, J. B. 1988. Field trials of copper naphthenate-treated wood. Proc., American Wood-Preservers Assoc. 84:186-200.

DeGroot, R. C.; Stroukoff, M. 1986. Efficacy of alternative preservatives used in dip treatments for wood boxes. Forest Products Laboratory, USDA Forest Service, Research Paper, FPL-RP-481, Madison, WI, 21 pp.

Freeman, M.H. 1992. Copper Naphthenate: An Effective Wood Pole and Crossarm Preservative. *In*: Proceedings, First Southeastern Pole Conference (H. M. Barnes, T. L. Amburgey, eds.), Mississippi State University, Starkville, MS, Proceedings No. 7314. Forest Products Society, Madison, WI, pp. 68-77.

Freeman, M.H. 2000. An Update on the Performance and Efficacy of Copper Naphthenate. 2000 Northeast Pole Conference, Binghamton, NY. Sponsored by AWPA, NYSEG and Oregon State University, 27 pp.

Grace, J.K.; Yamamoto, R.T.; Laks, P.E. 1993. Evaluation of the termite resistance of wood pressure treated with copper naphthenate. Forest Products Journal (11/12): 72-76.

Gutzmer, D. I.; Crawford, D.M. 1995. Comparison of wood preservatives in stake tests: 1995 progress report. USDA FS FPL, Res. Note FPL-RN-02, Madison, WI, 124 pp.

Hartford, W.H. 1973. Chemical and physical properties of wood preservatives. *In*: Wood Deterioration and its Prevention by Preservative Treatment (D.D. Nicholas, ed.), Syracuse University Press, Syracuse, NY.

Kamdem, D.P.; Fair, R.; Freeman, M. 1996. Efficacy of water-borne emulsion of copper naphthenate as preservative for northern red oak (*Quercus rubra*) and soft maple (*Acer rubrum*). Holz als Roh- und Werkstoff 54(3):183-187.

Kamdem, D.P.; Gruber, K.; Freeman, M. 1995a. Laboratory evaluation of the decay resistance of red oak (*Quercus rubra*) pressure treated with copper naphthenate. Forest Products Journal 45(9): 74-76.

Kamdem, D.P.; Freeman, M.; Murdoch, L., Chow, P. 1995b. Pressure treatment of hardwoods. *In:* Proceedings, Wood Preservation in the 90's and Beyond, Proceedings No. 7308, Forest Products Society, Madison, WI, pp. 89-94.

Kamdem, D.P.; Chow, P. 1999. The effect of pressure on the retention and bending properties of copper naphthenate and CCA type C treated hardwoods. Wood & Fiber Science 31(2):128-135.

Kresyzewski, J. 1977. Performance of preserved railway ties. Eastern Forest Products Laboratory, Report No. OPX183E., Ottawa, ONT., Canada.

Laks, P.; Gutting, K.W.; DeGroot, R.C. 1997. Field Performance of Wood Preservatives in Secondary Wood Species. Doc. No. IRG/WP 97-30152 (Data updated by personal communication with P. Laks, 2000).

McIntyre, C.R. 2001. Summary Report On Copper Naphthenate Performance In AREA Stake Tests. Unpublished Report to Merichem Chemicals and Refinery Services. RTA Research and Development Program, Jan. 2001, Perdido Beach, AL.

McIntyre, C.R. 2000. Copper naphthenate performance: a new way to look at old data. International Research Group on Wood Preservation, Doc. No. IRG/WP 00-30215, 14 pp.

Minich, A.; Goll, M. 1948. The technical aspects of copper naphthenate as a wood preserving chemical. Proc., American Wood-Preservers' Assoc. 44:72-81.

Nicholas, D.D.; Freeman, M.H. 2000. A comparison of pentachlorophenol and copper naphthenate in long term field stake tests. *In*: Proceedings, International Conference on Utility Line Structures, March 2000, Ft. Collins, CO.

Schnell, R. L. 1952. Treatability of shortleaf pine by the cold soaking method. Forest Products Journal 2(2):80.

Smith, W.B.; Abdullah, N.; Herdman, D.; DeGroot, R.C. 1996. Preservative treatment of red maple. Forest Products Journal 46(3): 35-41.

Thomson, W.T. 1991. Agricultural Chemicals: Book IV – Fungicides. Thomson Publications, Fresno, CA