Update On Copper Naphthenate Tie Research

Jim Brient
Merichem Co.

David A. Webb
David A. Webb, Inc.

Presented at the American Wood-Preservers' 2002 Annual Meeting
Memphis, TN April 23, 2002

The North American railroad industry has been served since its earliest days by the wood crosstie. These ties have been the very foundation on which the rail and track structure have been placed. The performance of this wood component with its dependability and service life has been exemplary. However it has been the application of preservatives, particularly creosote, to the wood crosstie that has given the significant durability and service life enhancement.

Due to a shortage of creosote during the mid-part of the 20th century, there was a focus on extending the availability of the preservative through the use of additive materials. Heavy petroleum was used as an extender, which made more material available but with a somewhat reduced effectiveness. However, other active preservative products were also used as creosote extenders, including copper naphthenate.

Copper naphthenate is produced by the reaction of various copper compounds with naphthenic acid, which is the naturally occurring acidic component of petroleum. The term naphthenic acid, as commonly used in the petroleum industry, refers collectively to the carboxylic acid components found in petroleum (Brient *et al.*, 1995). Naphthenic acids are generally classified as monobasic carboxylic acids, composed predominantly of cycloaliphatic acids containing single or multiply fused rings, as shown in Figure 1. The naphthene moiety consists of alkylated cylcopentane and cyclohexane derivatives. Naphthenic acid is recovered commercially from kerosene, jet fuel, and diesel fractions during petroleum refining. Standard P8 of the American Wood Preservers' Association specifies the grades of naphthenic acid applicable to production of copper naphthenate, and by definition excludes the use of synthetic and other non-naphthenic acids in copper naphthenate.

US EPA classifies copper naphthenate as a registered, non-restricted use pesticide under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), meaning no certified pesticide applicator's license is required for its use. Under FIFRA, copper naphthenate is not listed as an acute toxicity category I chemical, and has no significant sub-chronic, chronic, or delayed toxic effects. Like naphthenic acid, copper naphthenate is not a carcinogen, mutagen, or reproductive/developmental toxicant.

Copper naphthenate is classified as a non-hazardous waste under the Resource Conservation and Recovery Act (RCRA). Copper naphthenate wood preservation wastes are neither "listed" nor "characteristic" hazardous wastes under RCRA guidelines. Copper and copper naphthenate are also not subject to the Toxicity Characteristic. No reportable quantity (RQ) for copper naphthenate spills is required under Comprehensive Environmental Reporting, Compensation and Liability Act (CERCLA, or "Superfund") regulations. Releases must be cleaned up but do not have to be reported under CERCLA.

Copper naphthenate has been used since the late 1800's in wood poles, timber, shingles, and lumber. It has also been used in preserving cordage and textiles. Copper naphthenate was first widely used in the US to extend creosote during World War II. Minich and Goll (1948) summarized the physical properties of copper naphthenate, including water and solvent solubility, vapor pressure, and electrical properties. Copper naphthenate was moved to AWPA Standard P8 in 1949. AWPA retention standards for poles (Standard C4) include 0.06, 0.08, and 0.13 pcf (as copper) in southern pine and 0.075, 0.095, and 0.150 pcf (as copper) for the outer assay zone of coastal Douglas fir, depending on the AWPA hazard zone. Land or freshwater piles under AWPA Standard C3 have retention standards of 0.100 and 0.140 pcf (as copper) for southern pine and Douglas fir, respectively. There are currently no standards for copper naphthenate treatment of oak and other hardwoods under AWPA Standard C6 for crossties and switch ties.

Copper naphthenate is currently used in pressure and non-pressure treatment of wood. Pressure treatment markets include utility poles, cross arms, bridge timbers, lumber, posts, and glue-lam beams. Greater than 2 million cubic feet of wood were pressure treated with copper naphthenate in 1997, representing about 70,000 poles. Non-pressure treatments include remedial treatment of poles, shingles, pallets, millwork, and ammo boxes. In addition to heavy-duty applications such as pressure treatment of utility poles, copper naphthenate is sold over-the-counter for consumer use.

Copper naphthenate-treated wood is not conductive; resistance of copper naphthenate-treated southern pine at 315 kΩ is greater than the 275 kΩ of untreated southern pine. Southern pine treated with chromated copper arsenic (salt formulation) is much more conductive at 35 kΩ. Since copper naphthenate is insoluble in water, leaching of preservative from treated wood is minimal.

For the past several decades there has been an active effort by both the preservative manufacturers and the wood treating industry to develop new preservatives for the wood crosstie. Copper naphthenate has been evaluated in lab and field stake test studies as a preservative for oak and other hardwood species. Soil block studies (Kamdem, *et al.*,1995) found that 0.08 pcf (as Cu metal) was the minimum retention necessary for protection against *G. trabeum*, *P. ostreatus*, and *T. versicolor*, while 0.10 pcf Cu was required for copper-tolerant fungi such as *P. placenta*. A follow-up study (Kamdem, *et al.* 1999) showed that oak was readily treatable with copper naphthenate, with no adverse effects on bending strength of the treated wood.

McIntyre (2000) recently summarized test data originally reported in 1975 by the American Railway Engineering Association (AREA) Committee 3 - Ties and Wood Preservation. AREA recommended minimum retentions for copper naphthenate (as Cu) and creosote of 0.10 and 8.0 pcf, respectively. Retentions of 50% & 100% of the AREA recommendations for copper naphthenate, creosote and 60:40 creosote:coal tar gave comparable decay ratings over 15 years in oak stakes exposed in Florida, as shown in Figures 2 and 3. A stake test study was also recently reported on various hardwood species treated with copper naphthenate or creosote (Barnes *et al.*, 2001). Those data showed that copper naphthenate (Mooney Chemical's T500) compares favorably with creosote or creosote - coal tar systems after 7.5 years in test in Mississippi and Florida, as shown in Figures 4 and 5. That study reported 4.0 pcf creosote retention is roughly equivalent to 0.10 pcf (Cu as metal) copper naphthenate in red oak.

At the fall 2000 RTA convention, railroads challenged the industry to improve tie performance against biological degradation in Southern, wet, and certain high decay hazard areas. This brings into focus the subject of this paper, which is an inspection of copper naphthenate and borate preservatives used in the treatment of oak crossties. This crosstie test was installed on the old Conrail system, now Norfolk-Southern, near Lewistown, Pennsylvania. Along with the railroad company, the original participants were the Burke-Parsons-Bowlby Corporation (BPB), Spencer, WV; Mooney Chemical Company, Cleveland, OH; and U. S. Borax, Los Angeles, CA.

Mooney Chemical Company developed a copper naphthenate formulation known as M-Guard™ T500 specifically for the wood tie industry using a heavy #6 fuel oil carrier and containing a water repellant. This particular formulation contained 10% copper naphthenate (~0.9% as Cu) having a density of 7.0 lb/gal, 240°F flash point, 65°F pour point, and 72 cP viscosity at 80°F. This product was prepared from Merichem Company's naphthenic acid but is not currently being produced commercially by Mooney (now OM Group).

Methods And Materials

A total of 923 oak crossties were treated for the test by BPB at their wood treating plant in Spencer, WV during February of 1988. Two tank trucks were used as the work tank during the treatment process. Pour point of the M-Guard™ T500 copper naphthenate treating solution was higher than that for creosote and caused some difficulty in transferring the liquid treating solution through the lines during the treating cycle due to the sub-freezing ambient temperature. Stream tracing the transfer lines and an adjustment in the diluting solvent would solve the pour point problem. Charge data from treating with copper naphthenate are summarized in Table I; the ties were treated to a retention of 0.031-0.046 pcf (as Cu). Copper naphthenate is not currently listed in AWPA Standard C6 for crossties or other commodities using oak or mixed hardwoods. The minimum retention for southern pine poles under AWPA C4 is 0.06 pcf as Cu, greater than the retention used in this crosstie test.

Creosote ties were treated to 7.8 pcf retention, slightly above the AWPA C6 required retention of 7.0 pcf. Satisfactory and comparable penetration and retention of both the copper naphthenate and creosote preservatives were achieved in mixed red and white oak ties. Borings taken during treatment show >3 inches of penetration in red oak ties. Poorer penetration was seen in white oak ties, as expected.

Within the test track layout in Lewistown, shown in Figure 6, Sections 1, 2, 6 and 7 contain the copper naphthenate and creosote oak crossties that were conditioned by either air seasoning or Boulton drying methods (Table II). Boulton seasoning involves heating the green ties in a solution of the preservative under vacuum to remove water much faster than obtained with air seasoning.

Three sections of ties were also dipped with borates followed by air seasoning prior to further treatment with preservatives. Two groups of the borate dipped crossties were treated with secondary treatments of copper naphthenate and creosote. One small test group of crossties (10 ties) was borate dipped only with no secondary preservative treatment. Sections 3, 4 and 5 in the test track contain the borate dip treated crossties. Timbor™ (U. S. Borax, Inc.) solution (32% concentration) was used to pre-treat green ties, using specific gravity tests and air agitation to insure proper solution strength and mixture of solution. While maintaining temperature between 135-150° F., two ties were dipped for two minutes. Dipped ties were then bundled together in plastic for 90 days to reduce moisture loss and aid in the diffusion of the borate into the wood.

As previously indicated, the location of the test track is in Lewistown, PA on the old Conrail system (now Norfolk-Southern). Specifically the test site is located on #2 track of the Harrisburg to Pittsburgh mainline between milepost 165.2 and 165.5, with a slight grade of 0.46%. This line was rated at ~34 MGT at the time of installation but has now increased to ~55 MGT. Part of the test section consists of a 6°49' curve, mostly in sections 2-6 (Figure 6) containing the copper naphthenate and borate-treated ties. Installation of the test crossties took place August 22nd and 23rd in 1988.

Inspection Of The Test Crossties

The last inspection of these test ties occurred in 1990. Since that inspection the railroad has changed ownership from Conrail to Norfolk Southern, and Mooney

Chemical Company (now OM Group) no longer produces copper naphthenate for use in the pressure treated wood preservation industry.

Within the past several years Merichem Company, the world's largest producer of naphthenic acid, has started producing and actively promoting copper naphthenate for the pressure treated wood preservation industry. Merichem received permission from OMG to obtain and reference many of Mooney's research tests that involved treated wood products, including the test site for crossties at Lewistown, PA.

Even though it had been approximately ten years since the Lewistown site was last inspected, it was determined that some valuable information could be obtained by conducting another inspection, particularly in light of the railroads' recent requests to RTA for alternatives to creosote. During the later part of June, 2001 a team of four individuals conducted an inspection of the crossties at the Lewistown site. Those involved with inspection were Jim Brient of Merichem Company; Harry Bressler and Jim August of Burke-Parsons-Bowlby, and Dave Webb, consultant and representing the Railway Tie Association and its Research and Development Committee.

The inspection consisted of the following procedures:

- Note and record number of crossties remaining in the test for each type of treatment. It was observed that many of the original metal tags were still place on the test ties.
- Physically measure the checks and splits in the ties. The RTA Tie Gauge (Figure 7) was used to measure the depth and width of the checks and splits; while a tape measure was used to measure the length. This information was recorded in a notebook for each tie. Following the inspection, the average volume (as cubic inches) for the void space was calculated from these field measurements and recorded.
- Measurements were taken and recorded for plate cutting.
- Each tie was given a rating according to its performance and observed by the number of checks, splits and their severity. This was a visual observation following the guidelines for evaluating wood preservatives in a soil bed in American Wood-Preservers' Association Standard E14-94, with the subjective rating scheme as follows:

Ten (10)	Sound; No indication of degrade.
Nine (9)	Slight degrade with some checks & splits.
Seven (7)	Moderate degrade; more severe checking.
Four (4)	Significant degrade; severe checking.
Zero (0)	Failure; severe plate cutting & checking. No longer a serviceable tie.

With four individuals performing the inspection, it was possible to work in teams of two, both grading the ties with one recording and the other taking measurements on each crosstie. The inspection of all nine hundred and twenty-three (923) ties was completed in approximately one and a half days.

Results of the Inspection

The tabular results of the inspection are given in Table III and shown in Figure 8. The average rating of all ties in the test was 8.66, with ± one standard deviation ranging from 9.59 to 7.73. Except for the borate dip-only ties, all combinations of preservative and seasoning regimens fell within one standard deviation of the mean rating for all ties, indicating there was no significant difference in performance after 13 years in those preservatives and treating schemes. The small (10) number of borate-dip only ties makes suspect any conclusions drawn about the performance of that treatment relative to the other treatments.

It was determined part way through the inspection of the Section No. 2 (copper naphthenate air seasoned ties) that a number of new ties had been installed. Discussions with Norfolk Southern track personnel indicated that new creosote treated crossties were randomly inserted in the test track in July of 1998. In Section 7 (Boulton seasoned creosote) no crossties had been replaced. However, only sixty-seven (67) ties were graded and considered part of the test due to the presence of a grease box (for rail/wheel lubrication) located at the end of the test section, which influenced the results. Thirty-three (33) ties were completely covered with grease and thus not graded.

In Section 6, which consisted of four hundred and two (402) crossties, each tie was given a rating; however, only ever fourth crosstie was measured for the length, depth and width of the checks and splits using the RTA gauge. Originally there had been ten (10) crossties in the test given the borate dip treatment, and two of these had been replaced. There were too few ties to reach any conclusion about this treatment.

Ties given a borate dip pretreatment followed by secondary treatment with copper naphthenate or creosote had the greatest void volume due to splits and checks after 13 years of exposure (Table III). On the other hand, ties treated with a borate dip only had the lowest average void volume results, although they had the most "weathered" appearance in terms of rounded-off edges, as seen when comparing Figures 9-11. This appears to confirm the statement by Webb (1991) that a certain degree of weather protection is provided by a creosote and/or oil type treatment that is not provided by waterborne preservatives.

There was not a significant amount of plate-cutting on any the test ties, less than the thickness of the tie plate. In fact, after initially taking some measurements in Sections 1 and 2, it was decided to not continue taking them. Where plate-cutting did occur it was simply noted in the field notebook. No significant differences were seen in the extent of plate cutting between the various preservative treatments. Several ties were noted to have both clip- and spike-type fasteners.

Summary of the Results

The crossties at time of inspection had been in test for thirteen (13) years. The following summary of the results were made from the inspection of the test ties:

- As a general observation the crossties remaining in the test are supporting the track system and giving satisfactory performance.
- There did not appear to be a significant difference between the performance of the creosote and copper naphthenate (CuN) treatments.
- In addition, similar performance was noted between the air seasoned and Boulton seasoned crossties.
- With regard to the ties in Sections 3 and 5, borate dipped followed by a secondary copper naphthenate and creosote treatment, respectively, both groups of ties showed the highest level of "checks & splits" as measured by average void volume but otherwise performed adequately.
- Too few ties, only ten (10) originally, were in the test to make any judgment on the performance of crossties that were borate dipped with no other treatment.

References Cited

Barnes, H. M.; Amburgey, T.L.; Freeman, M.H.; Brient, J.A. 2001. Performance Of Copper Naphthenate-Treated Hardwoods, International Research Group – Wood Preservation, 32nd Annual Meeting, Nara, Japan, 20-25 May 2000. Document No. IRG/WP/01-30269.

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

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

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.

McIntyre, C. R. 2001. Summary Report on Copper Naphthenate Performance in AREA Stake Tests. RTA Wood Preservative Technology/ Methodology Task Force Meeting, Perdido Beach, AL.

Minich, A.; Goll, M. 1948. The technical aspects of copper naphthenate as a wood preserving chemical. In: *Proc. American Wood Preservers' Assoc.* 44:82-81.

Webb, D. A. 1991. Wood Preservative Treatments for Crossties and Potential Future Treatments. *Crossties*, December 1990/January 1991.

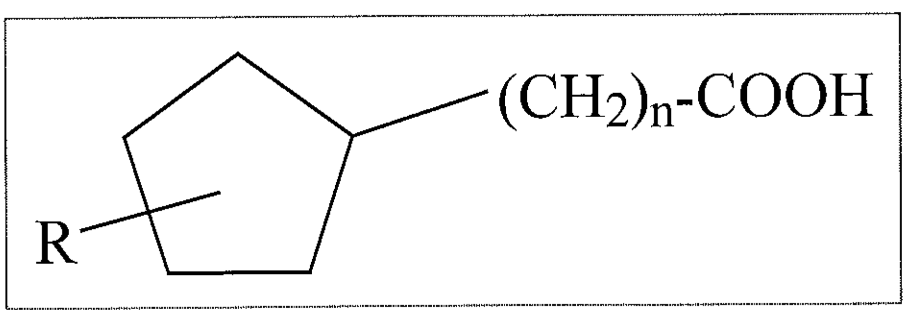


Figure 1. Typical Structure of Naphthenic Acid (R = alkyl)

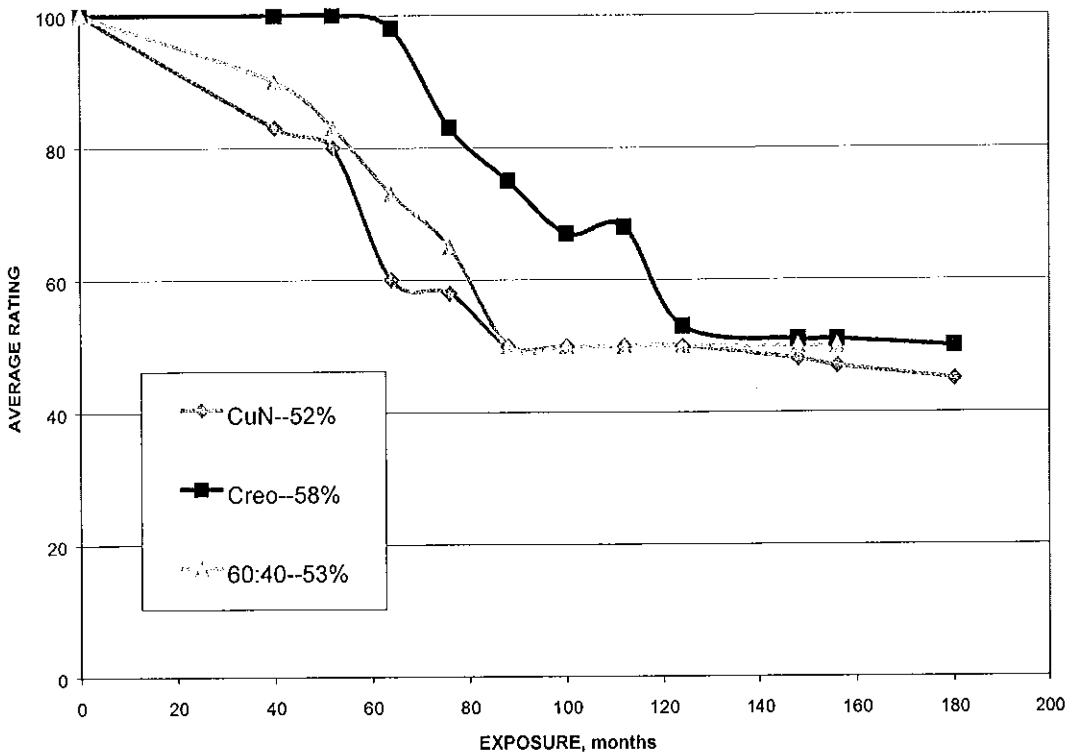


Figure 2. Red Oak Data from Florida - 50% of AREA retention

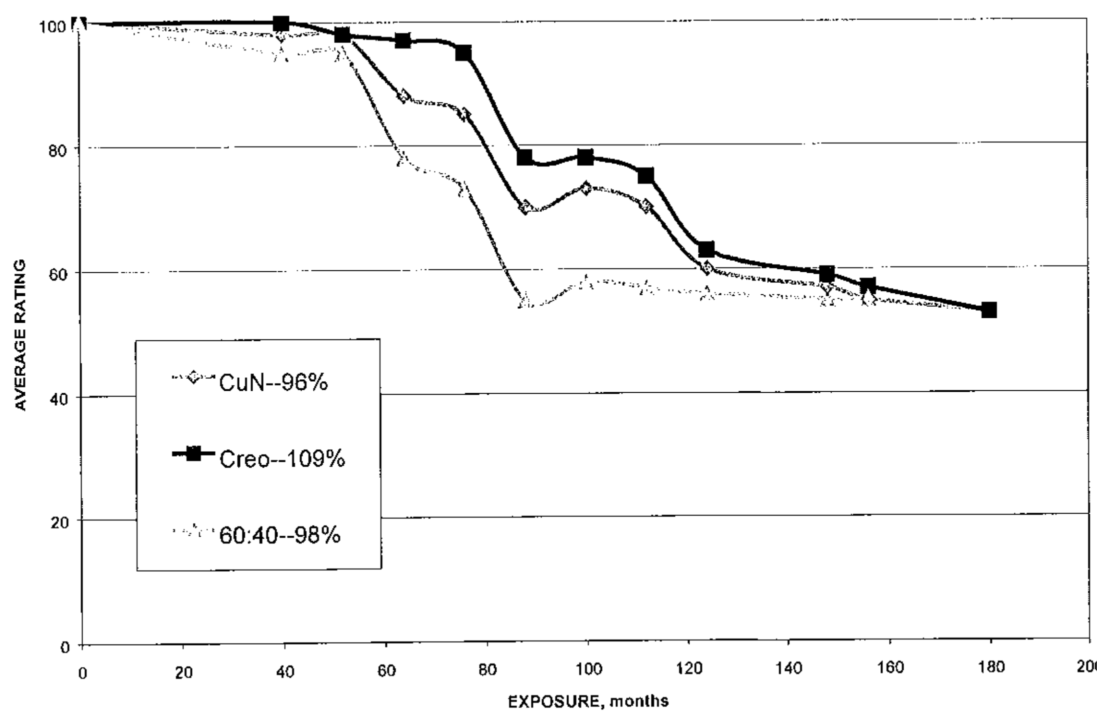


Figure 3. Red Oak Data from Florida - 100% of AREA retention

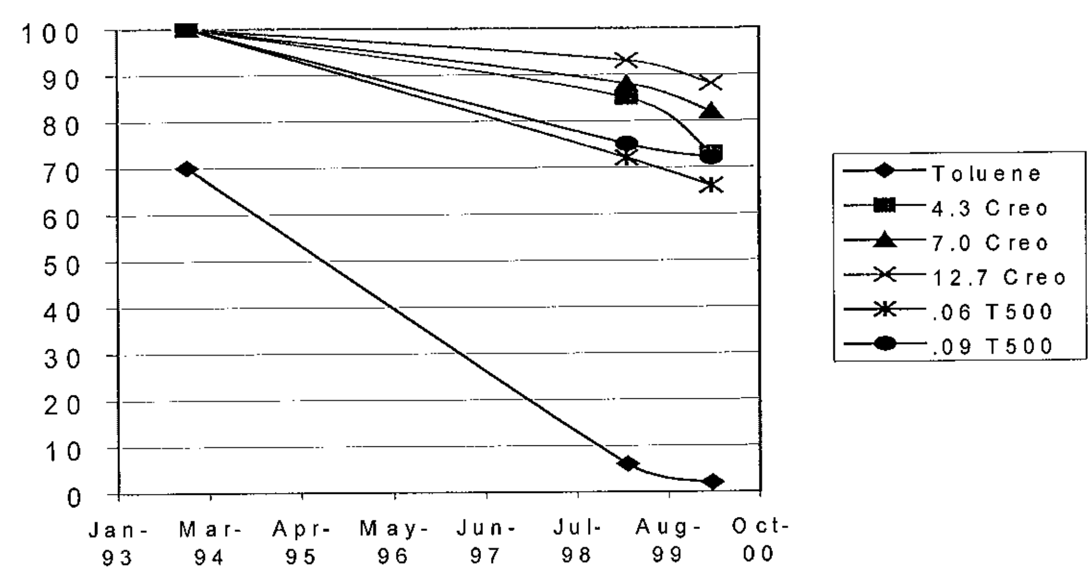


Figure 4. Decay Ratings for Red Oak in Gainesville, FL

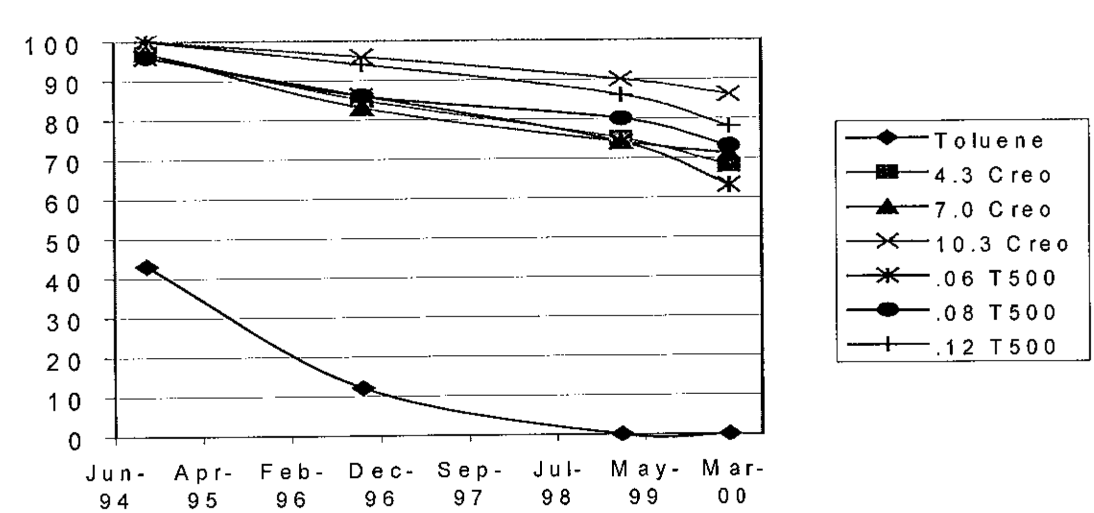
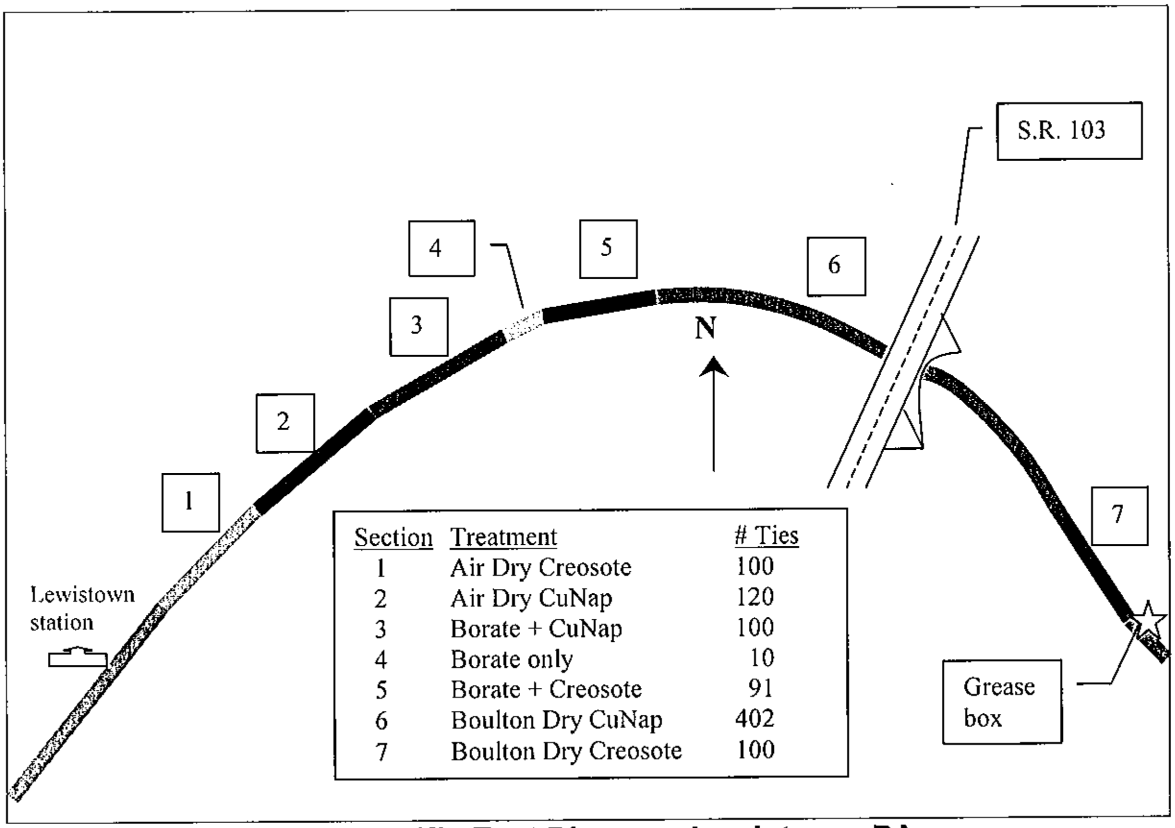


Figure 5. Decay Ratings for Red Oak in Dorman, MS



Section	Treatment	# Ties
1	Air Dry Creosote	100
2	Air Dry CuNap	120
3	Borate + CuNap	100
4	Borate only	10
5	Borate + Creosote	91
6	Boulton Dry CuNap	402
7	Boulton Dry Creosote	100

Figure 6. Tie Test Diagram, Lewistown, PA

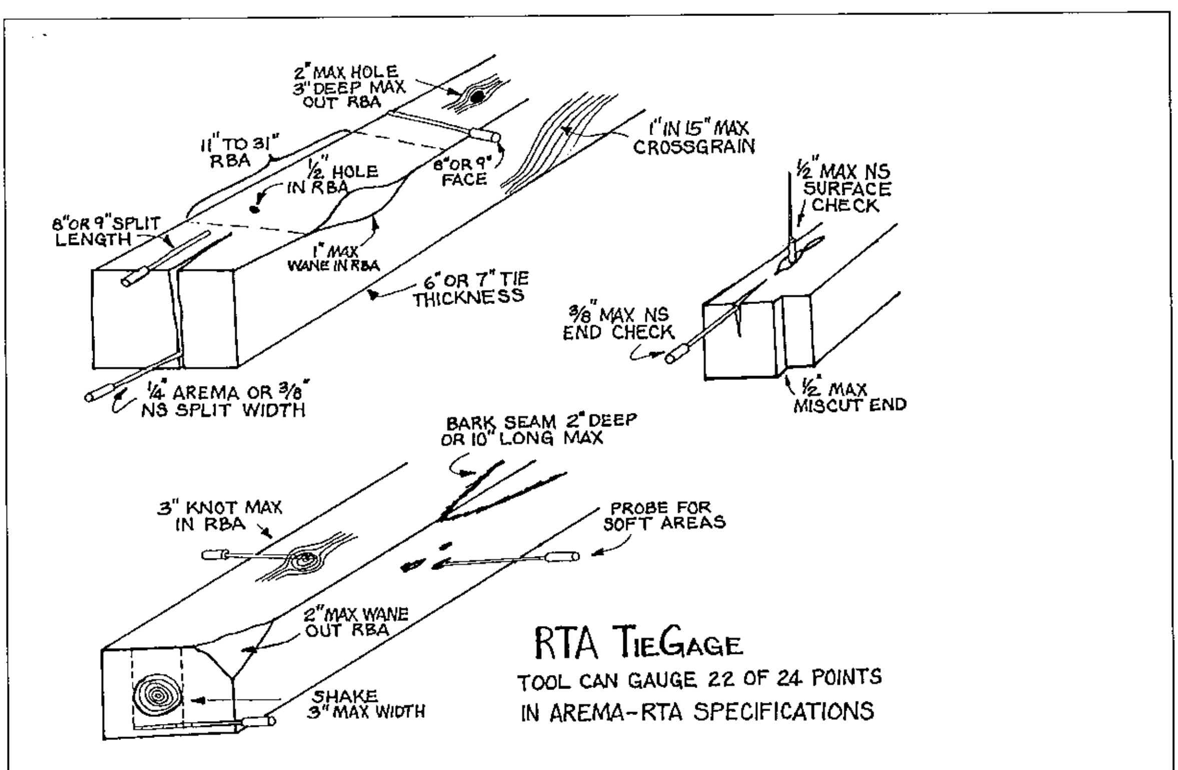


Figure 7. RTA's TieGage inspection instrument

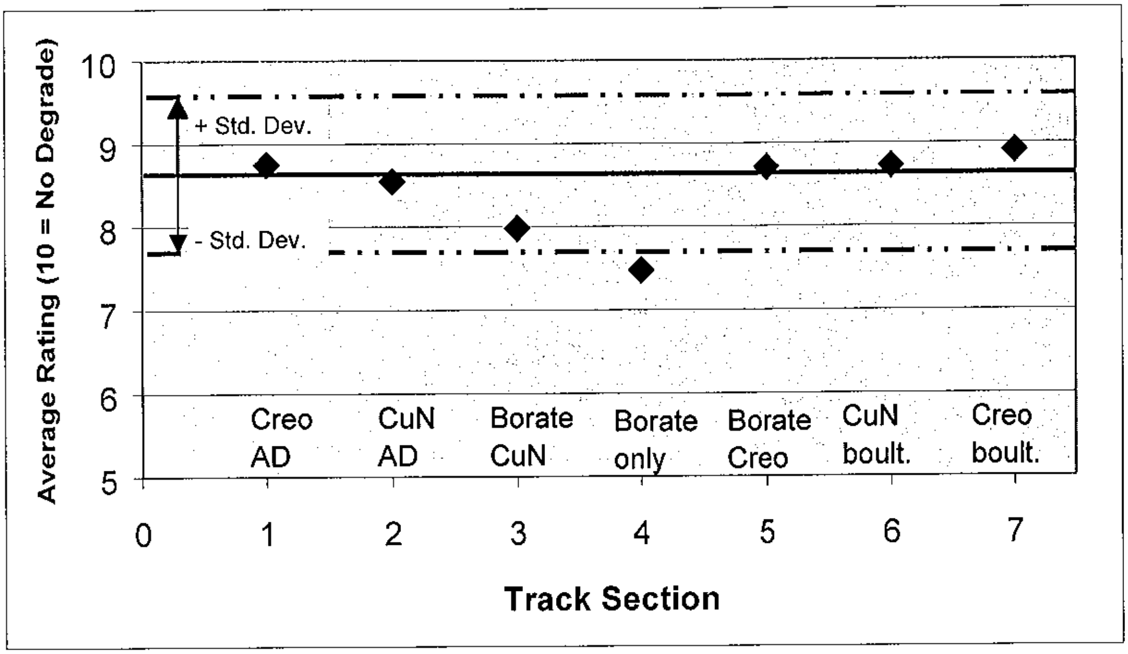


Figure 8. Average Rating of Ties after 13 Years

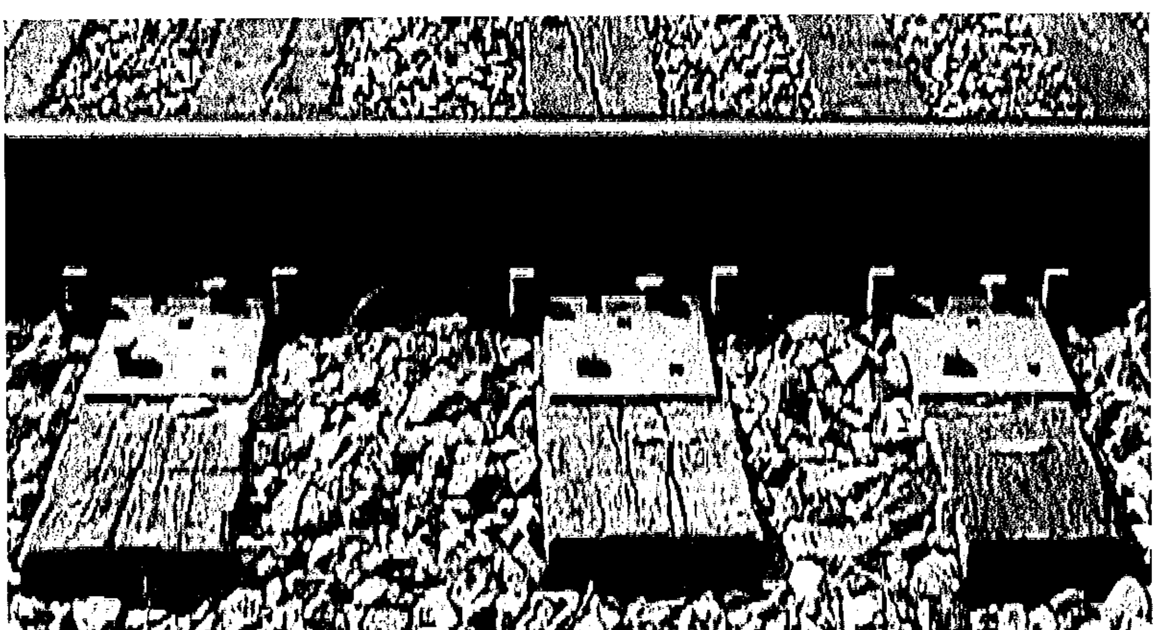


Figure 9. Air-seasoned copper naphthenate ties

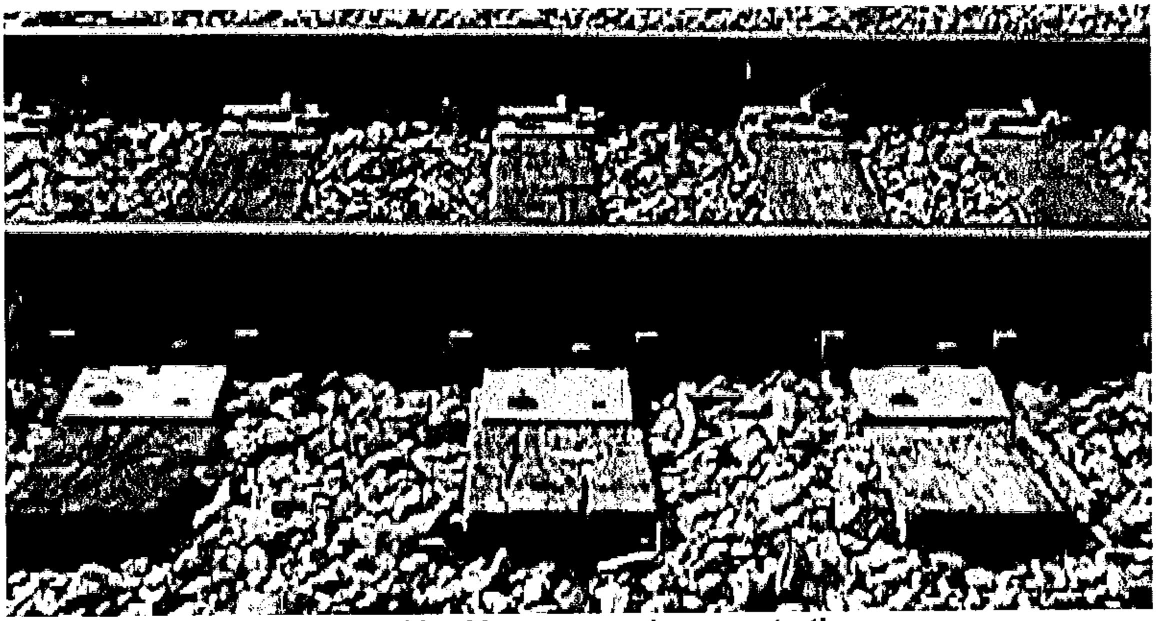


Figure 10. Air-seasoned creosote ties

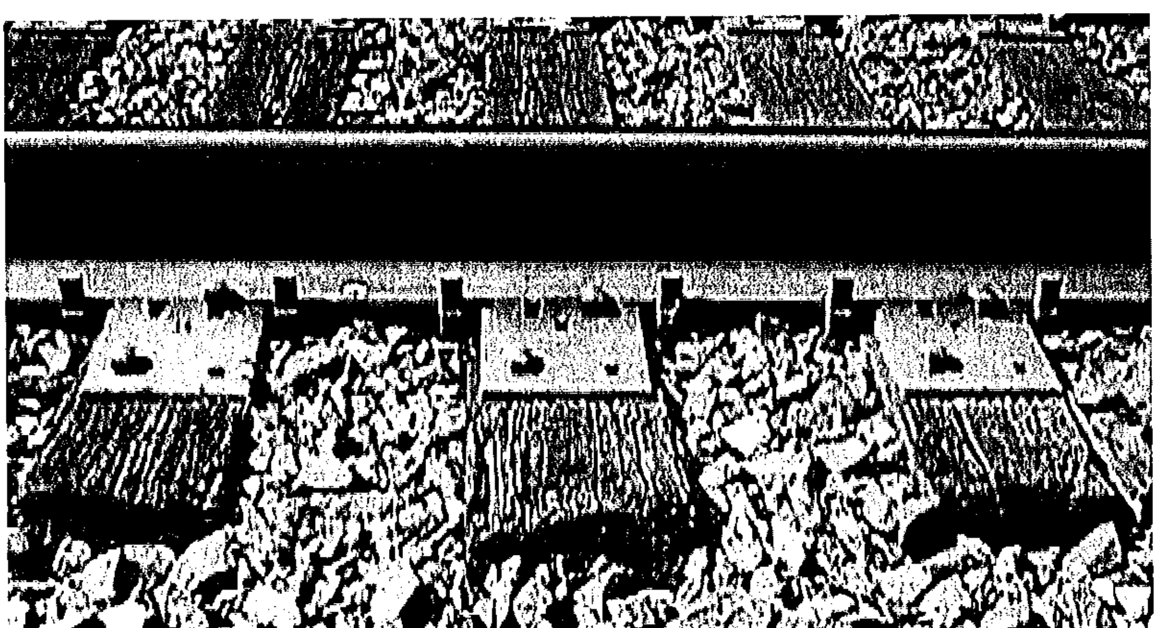


Figure 11. Borate-dipped ties

Table I. Copper Naphthenate Charge Summary			
BPB Charge No.	C-88-148	C-88-150	C-88-152
Number of Ties	210	225	210
Boulton Dry Time, Hrs.	17	--	18
Copper in Work Solution, %	0.77	0.91	0.91
Net Solution Retention, pcf	5.0	3.4	5.1
Creosote Equivalent*, pcf	6.6	4.5	6.7
Copper Retention, pcf (Net Gauge)	0.039	0.031	0.046
Section No. of Track Installation	6	2	6

* Copper Naphthenate net retention times the ratio of densities, 9.2/7.0.

Table II. Ties in Test at Lewistown, PA						
Section	Treatment	Tie numbers	Total ties	Replaced	Still in test	% Replaced
1	Air Dry Creosote	1-100	100	16	84	16
2	Air Dry CuNap	101-220	120	33	87	28
3	Borate + CuNap	221-320	100	27	73	27
4	Borate only	321-330	10	2	8	20
5	Borate + Creosote	331-421	91	23	68	25
6	Boulton CuNap	422-823	402	64	338	16
7	Boulton Creosote*	824-923	100	0	100	0
Total			923	165	758	18

* Last 33 ties closest to grease box were not rated

Table III. Ratings of Ties in Test at Lewistown, PA			
Section	Treatment	Average rating	Average void volume, in^3
1	Air Dry Creosote	8.8	17.2
2	Air Dry CuNap	8.5	25.7
3	Borate + CuNap	8.0	39.7
4	Borate only	7.6	9.1
5	Borate + Creosote	8.8	46.5
6	Boulton Seasoned CuNap	8.8	24.0
7	Boulton Seasoned Creosote *	8.9	28.8

* Last 33 ties closest to grease box were not rated