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Field Testing of Copper Carboxylate Preservatives

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ABSTRACT

This paper details our ongoing experience with field testing of copper naphthenate and other copper carboxylate preservative systems. Results from field stake tests at an AWPA Hazard Zone 4 test site are presented. In general, copper carboxylates made with 'synthetics' yielded results equivalent to or only slightly lower than systems with straight nap acids or nap acids amended with synthetic neo acid bottoms.

Keywords: copper carboxylates, preservatives, copper naphthenate, copper neodecanoate, copper propionate, copper abietate, copper oleate, stake tests

INTRODUCTION

For many years, the search for new preservative systems has centered on compounds and formulations considered more environmentally benign and having lower mammalian toxicity or using existing biocides which have proven effective as agricultural fungicides. Copper carboxylates have been among the systems researched. This paper details our experience with field stake testing of these types of compounds.

Copper carboxylate systems have been studied as wood preservatives for several years (Preston *et al*. 1985), and much of the early work forms the basis for the copper-based systems currently in the marketplace. One of the principal systems is copper naphthenate which is finding use in both oil- and waterborne systems. A series of recent articles on copper naphthenate as a wood preservative (Barnes & Freeman, 2000, Barnes *et al*. 2000, 2001a,b, 2002 , Brient & Webb 2002, McIntyre 2000, Morris 1989, Nicholas & Freeman 2000) are available and several others can be found on the web at http://www.merichem.com/copper/Index.htm. One question often asked is 'what is the impact of 'synthetic' acids on the performance of copper naphthenate?'

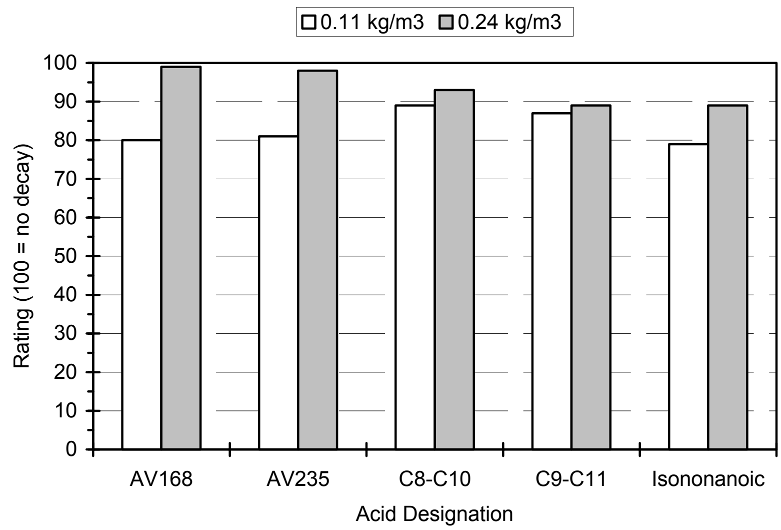

Figure 1. Stake test data from Sparks (1978)

Four-year field stake data were reported by Sparks (1978) to the BWPA for stakes treated using a dip treatment in mineral spirit solutions. Acids included a mixture of C-8 and C-10 iso acids, mixture of C-9, C-11 neo-acids, isononanoic, nap acids with acid values of 168 and 235. These data are shown in Figure 1 for two copper loadings. The three synthetic acids yielded copper carboxylates that performed as well as the 168 and 235 nap acid copper naphthenates. Hilditch (1983) reported on tests of similar stakes (Figure 2). These data

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show that at similar retentions the 168 nap acid is better than the synthetic acid copper carboxylate. A series of field tests with copper carboxylate systems is described below.

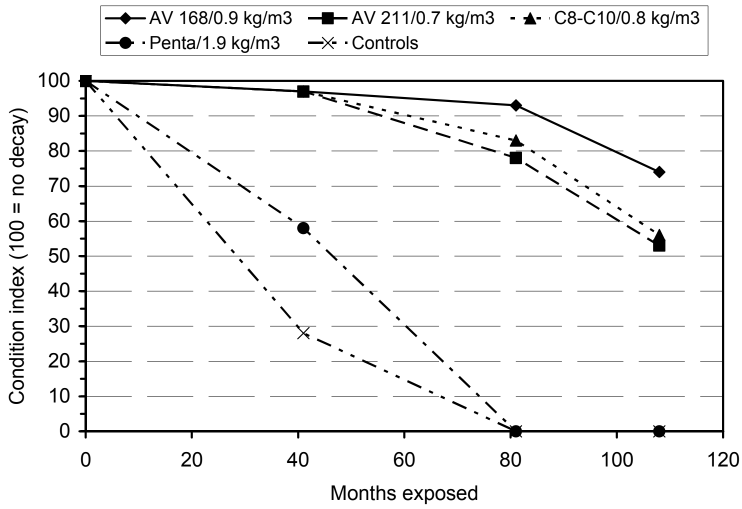

Figure 2. Stake test data from Hilditch *et al*. (1983).

EXPERIMENTAL PROCEDURE

Southern pine stakes measuring 19- x 19-mm in cross-section x 560-mm long were used in these studies. Stakes were selected and treated in accordance with AWPA Standard E-7 (AWPA 2002) using a Bethell (full-cell) cycle to refusal. Retention was calculated by weight-gain. Ten replicates for each combination of formulation/solvent were tested. Prior to installation in the test plots, stakes were air-dried at ambient conditions and cut to 457 mm in length. The 102-mm cutoff was retained for future reference.

All stakes were inspected annually for decay and termite attack using the AWPA E-7 rating scale shown in Table 1. Untreated control and reference preservative stakes were installed with each test. Data herein are reported for our Dorman Lake test plot located on the Starr Memorial Forest, Oktibbeha County, 10 miles south of Starkville, MS [UTM Zone 16N, NAD27: 325,466.14 m East, 3,690,416.68 m North]. The soil is characterized as acidic (pH=4.8) heavy clay (Falkner) on a poorly drained site. This site is known to have copper-tolerant fungi. This site is very active for decay and termites and is located in AWPA Hazard Zone 4.

Table 1. AWPA E-7 grading scale for decay.

Grade	Decay Condition
10	Sound; suspicion permitted
9	Trace decay to 3% of cross-section (x)
8	Decay 3-10% of x
7	10-30% of x
6	30-50% of x
4	50-75% of x
0	Failure (>75% of x)

A description of the formulations tested, solvent systems, etc. is given in Table 3. Included are

Table 3. Listing of formulations tested in this study.

Designation	Preservative	Carriers	Description
CuWD	Cu naphthenate	Water (W)	Water dispersible (WD)
ND	Cu neodecanoate	Toluene (T), P9A	Oilborne (OB)
CuNn	Cu naphthenate[1]	T, P9A, Mix[2], Acetone	OB
CuN	Cu naphthenate[3]	T, P9A	OB
CuWDi	Cu naphthenate with insecticide	W	WD
CuOc	Cu Octoate	P9A, T	OB
CuP	Cu propionate	W	
NOP	ND:CuOc: CuP[4]	P9A	OB
CuA	Cu abietate	T, P9A	OB
CuNAm	Cu naphthenate	W	Ammoniacal system

[1] CuNn formulation with a small amount of neo acid bottoms added; [2] Mix = Base Oil-L:toluene:dimethylformamide (70:25:5); [3] CuN with no synthetics added; [4] ND:CuOc:CuP (30:24:18); CuP contains 70% propionic acid equivalents + 30% Cu

waterborne, oilborne, and water-dispersible formulations. When listed, the P9A solvent conforms to AWPA (2002) Standard P-9 Type A solvent. Unless otherwise noted, it is a 1:3 mixture of #2 fuel oil:toluene and meets the distillation ranges specified by the standard.

RESULTS & DISCUSSION

Oilborne Systems

Unless otherwise noted, the data for these tests are presented in the form of dose-response curves for 5 years ± 2 months of exposure at our Dorman Lake test plot which is characterized as an AWPA (2002) Hazard Zone 4 location. Only decay data are presented as decay was more severe than termite attack in all cases.

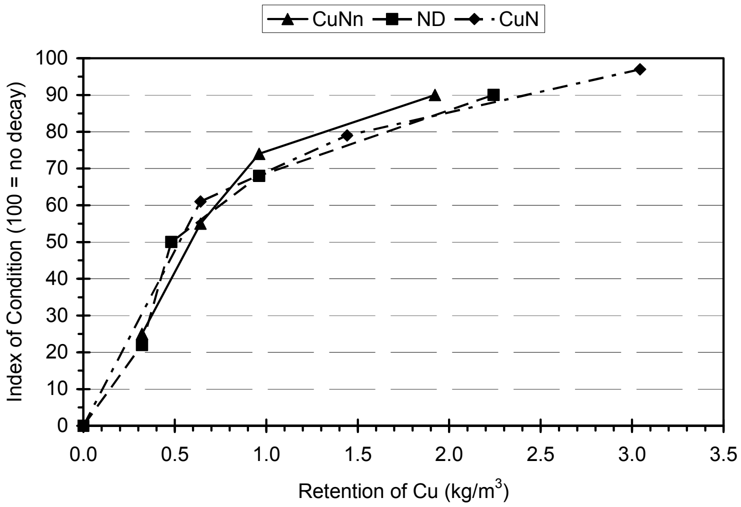

Figure 3. Dose-response curves comparing copper naphthenate with (CuNn) and without (CuN) neo acid bottoms and copper neodecanoate (ND) carried in toluene after 5 years of exposure

In the first test, copper naphthenate with (CuNn) and without (CuN) neo acid bottoms and copper neodecanoate (ND) in toluene are compared. As shown in Figure 3, there is little to separate the performance of all three formulations after five years of exposure. These data suggest that only a slight decrease in performance may be expected when synthetic acids are incorporated in copper naphthenate formulations.

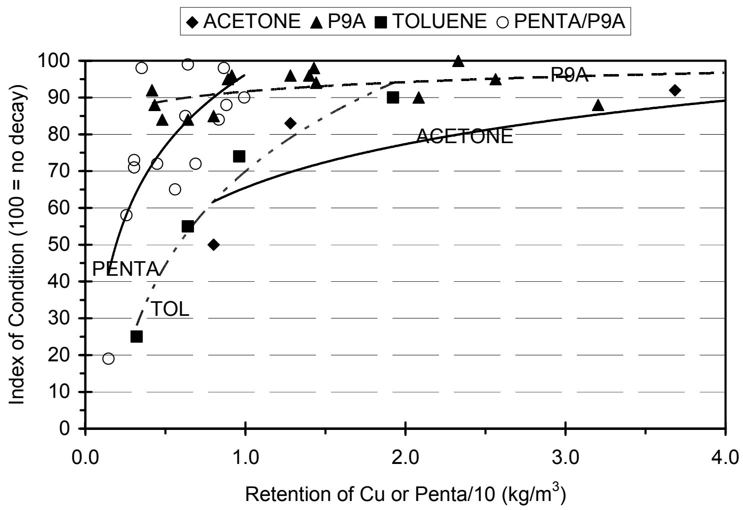

Figure 4. Performance of copper naphthenate in various solvents compared to pentachlorophenol in P9A solvent.

In the next set of data, CuNn in a variety of carriers is presented (Figure 4). No difference between the performance in P9A solvent and P9A solvent with 5% DMF added was noted, so these data are combined for plotting purposes. These data indicate that better ground contact performance is achieved when heavier solvents are used as the carrier system. Performance in a P9A carrier is about equivalent to that of pentachlorophenol for penta:Cu (as metal) ratios in the range of 8:1 to 10:1.

The next set of data compares the performance of CuN and CuNn with that of copper octoate in P9A solvent. These data are shown in Figure 5. Clearly, copper octoate performs in a manner similar to that of copper naphthenate (with and without added neo acid bottoms). It appears that the addition of copper octoate does not negatively impact the performance of copper naphthenate in these tests.

In Figure 3, the performance of copper naphthenate and copper neodecanoate in toluene were compared. In Figure 6, the same systems in a P9A carrier are compared along with a mixture of copper neodecanoate, copper octoate, and copper propionate. Again, the performance of the synthetics mimics that for copper naphthenate. When compared to Figure 3, the data in Figure 6 show that the performance is enhanced in heavier oil carriers.

Figure 7 compares the performance of copper abietate and copper oleate in heavy (P9A) and light (toluene) carriers. In this test, copper naphthenate in P9A carrier is out performing the synthetics especially at the lower end of the retentions. In toluene all systems are performing the same.For all systems, the P9A carrier is better than the light solvent. In like solvents copper oleate and copper abietate perform equivalently.

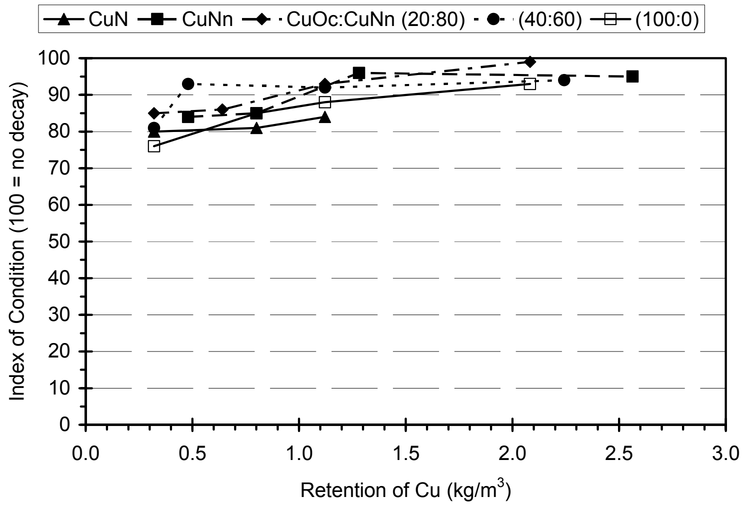

Figure 5. Comparison of copper naphthenate with and without neo acid bottoms with mixtures of copper octoate in P9A solvent.

Waterborne Systems

Data for waterborne systems are shown in Figure 8. Included for comparison are a water-dispersible pentachlorophenol system, a water-dispersible copper naphthenate system, an ammoniacal copper naphthenate system, and copper propionate. These systems show remarkably similar performance. The water-soluble propionate system is performing as well as either the dispersible copper naphthenate system (CuWD) or the solublized ammoniacal (AmCuN) system. To compare oilborne and water-dispersible systems, Figure 9 combines all the data for copper naphthenate carried in P9A solvent. As expected, the oilborne system outperforms the water-dispersible formulation and the light organic solvent preservative system (LOSP-AWPA P9 Type C). However, the water-dispersible and LOSP systems show good efficacy, which indicates that copper naphthenate preservatives formulated for these carrier systems should find acceptance in commercial systems.

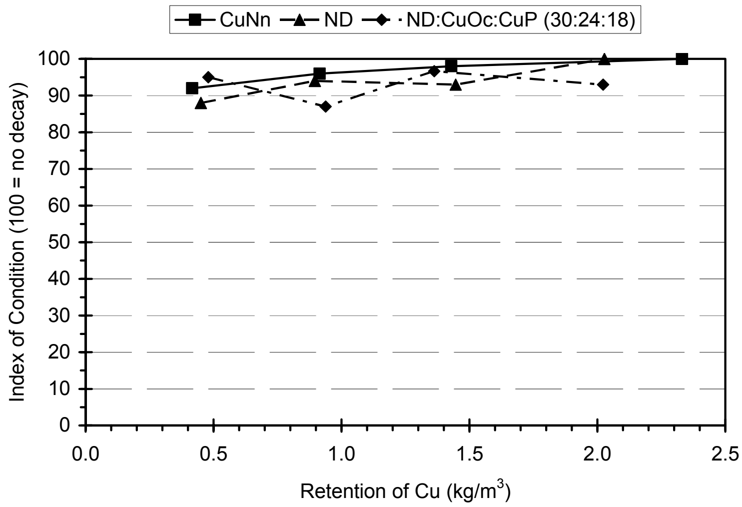

Figure 6. Comparison of copper naphthenate with copper neodecanoate and a mixture of copper neodecanoate, octoate, and propionate in P9A carrier.

SUMMARY & CONCLUSIONS

This study has shown that the addition of 'synthetics' to copper naphthenate has little deleterious effect on the performance of CuN preservatives. In fact, many formulations based on 'synthetic' acids gave satisfactory biological performance, especially in heavy oil carriers.

Heavy oil carriers generally outperformed light organic solvent carriers and water. LOSP and water-based systems performed sufficiently to qualify for both ground contact and above ground applications depending on the retention chosen.

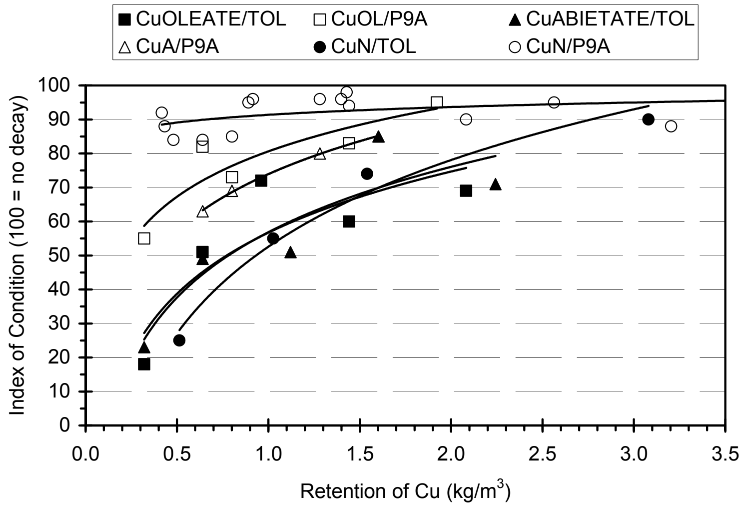

Figure 7. Performance of copper oleate and copper abietate in toluene (TOL) and P9A solvents compared to copper naphthenate.

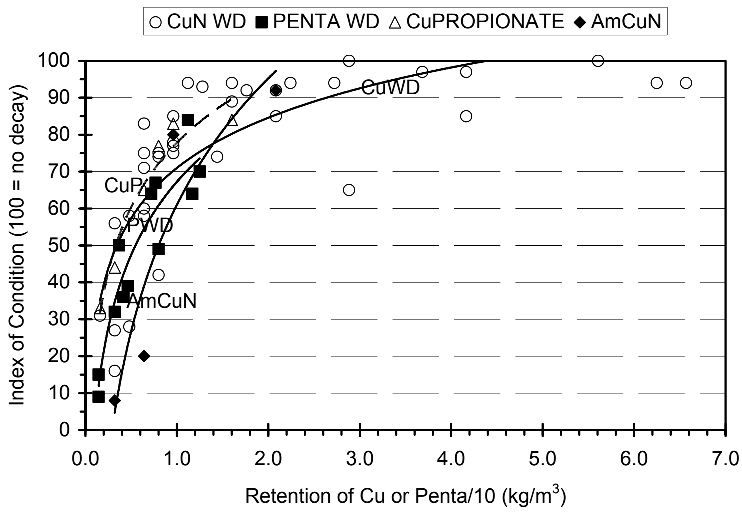

Figure 8. Performance of waterborne systems.

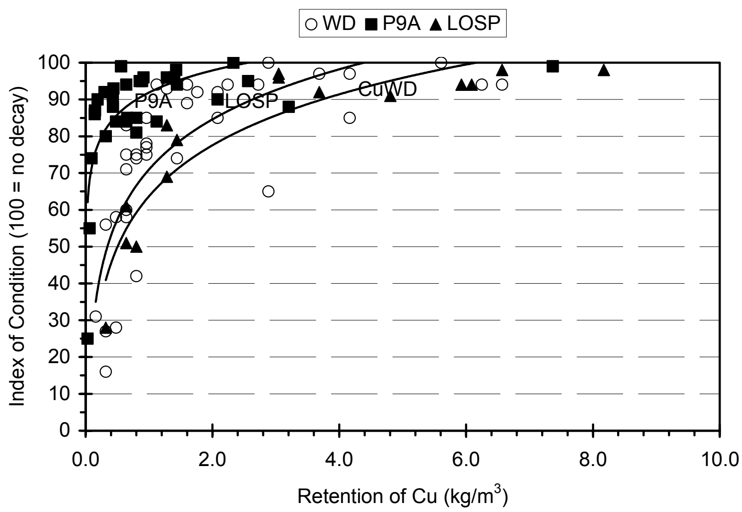

Figure 9. Effect of carrier type on the performance of copper naphthenate systems.

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