

# **COPPER NAPHTHENATE AND COPPER NAPHTHENATE TREATED WOOD – A REVIEW AND UPDATE**

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## **ABSTRACT**

Copper naphthenate has been used as a wood preservative since 1889 and has been an EPA-registered product since 1972, when the US EPA was formed following FIFRA. Prior to that date, it was registered by the USDA. CuNap did not gain wide use for pressure treatments until the late 1980s, when it began to be used for cross arms, bridges, utility poles, fence posts and lumber. One of the principal reasons that CuNap has gained market acceptance is its low mammalian toxicity. CuNap exhibits less copper tolerance in resistant fungal species than that observed in water borne formulations. Unlike creosote and penta, CuNap is classified by the EPA as a non-restricted preservative, commonly sold over the counter. This paper reviews the efficacy of CuNap, compares its efficacy in laboratory and long term field tests against standard preservatives CCA, creosote and penta. Evaluation in both softwoods and hardwoods is compared. It also reviews causes of premature failures that occurred in treated poles in the earlier years mostly when the industry was learning how to handle and apply the preservative and changes that have been adopted by industry and the AWPA since then. Other topics covered include treating cycles for copper naphthenate poles and evaluation for use in poles and crossties.

## **INTRODUCTION**

### **Oil-borne /Oil Type wood preservatives**

Oil borne preservatives fall into two groups; the first group includes creosote-coal tar, and creosote-petroleum formulations. The second group consists of solutions of chemicals dissolved in a non aqueous carrier and were added to the AWPA book of standards in 1948. They include penta, copper naphthenate, copper-8-quinolinolate, bis(tri-n-butyltin)oxide, alkyl

ammonium compound, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one,3-iodo-2-propynyl butyl carbamate (IPBC), chlorothalonil, the triazoles, chlorpyrifos, and chlorothalonil/chlorpyrifos. The most common of these are creosote, penta, and copper naphthenate. Petroleum-base carriers are commonly used in oil-borne preservative formulations which form a resistant envelope on the wood surface, act as water repellants, allow treatment of wood after machining, reduce splitting and checking and eliminate renewed wetting after treatment (Lebow and Tippie 2001).

### **Copper based organic wood preservatives- Organometalics**

Copper based formulations may be divided into four groups: water-borne, solvent based, oil borne, organo-metallics and micronized copper formulations. Copper based preservatives have been widely and successfully used for more than a century. Fungicidal properties of copper were realized in the 1800's. The volume of wood products treated with copper based preservatives grew exponentially during the 1970s and 1980s and remains high. Copper compounds are relatively easy to formulate, easy to analyze and determine penetration in wood, slow to photodegradation and hydrolysis (Archer and Preston 2006). The voluntary withdrawal of CCA from residential applications resulted in increased use of arsenic and chromium free preservatives. Because the arsenic component controlled copper-tolerant fungi, there was concern about the capability of this group of fungi (Steenkjær Hastrup 2006). Although borates and organic biocides have gained importance, copper remains the primary biocide used to protect wood in ground contact or fully exposed to weather. In the absence of copper is extremely challenging as very few organic molecules, other than creosote, possess activity towards soft rot fungi (Hughes 2004).

Organometallic compounds used in wood preservation include organotin compounds, copper HDO and copper naphthenate. In recent years oxine copper has been increasingly used as an alternative to copper naphthenate. However, oxine copper is not standardized for use below ground unless combined with other biocides. It does not present the distinctive naphthenic acid odor, is odorless and is resistant to hydrolysis. Possible advantages of organometalics include: (i) a relatively low metal content, which may make future disposal of treated wood easier, (ii) this systems have much fewer metal corrosion problems than preservative systems formulated

with uncomplexed copper(II) and (iii) the metal coordination sites that are not complexed with the ligand could bind to the carboxylic or phenolic groups in wood to make the formulation relatively leach-resistant (Schultz et al. 2003).

## **MANUFACTURE AND HISTORY OF COPPER NAPHTHENATE**

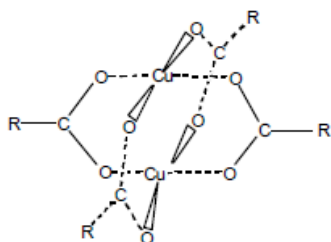
Copper naphthenate has been used as a wood preservative since 1889. It was first used in Germany and has been in commercial use since 1911. It was used as a creosote extender during world war II (Brient and Freeman 2004). CuNap began its strong entry into the wood preservation business in the mid 1940's 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, and of petroleum products, was in short supply. The AWPA began a search for combination biocides that could be added to creosote to effectively extend its service life. CuNap was determined as a likely extender for creosote. It did not cause some of the corrosion problems that addition of penta as a phenolic acid would pose (Freeman 2002). CuNap did not gain wide use for pressure treatments until the late 1980s, when it began to be used for cross arms, bridges, utility poles, fence posts and lumber. Also in the 1980s, regulatory activities stimulated interest in CuNap because of its general use classification. Environmental concerns about CCA, Penta, and Creosote stimulated CuNap's use in utility poles and other wood products. Trade names for copper naphthenate in commercial use include CuNap-8, Perm-E8, Cop-R-Nap, Cunapsol, and Cuprinol (copper in oil). Probably, some of the other metallic naphthenates have considerable value as wood preservatives.

CuNap is prepared by reacting copper or copper salts with naphthenic acid or with sodium naphthenate. Naphthenic acids are carboxylic acids recovered from kerosene and diesel fractions during petroleum refining. Their major use is in production of oil-soluble metal naphthenates, including copper, cobalt, iron and zinc (Brient 2004). Naphthenic acids are alicyclic acids with the formula  $C_nH_{2n-2}O_2$  (Barnes et al., 2001). Naphthenic acids contain a mixture of monocarboxylic acids which contain cyclopentane and cyclohexane groups with an acid number ranging from 150 to 300. The three commercial methods of producing copper naphthenate are direct metal, melt (fusion), or double decomposition methods. Manufactured

by Merichem Chemicals & Refinery Services LLC (MCRS), CuNap is available as an oil-borne or water-borne formulation in the United States.

The interest in naphthenates as preservatives arose from the increasing quantities of naphthenic acids being produced as byproducts of the petroleum industry and the urge to find markets for them (Blew 1946). Since then a number of exposure tests have been published to adequately develop retention standards for CuNap and now it is readily available and extensively used. CuNap is effective against wood-destroying fungi and insects. CuNap is not a restricted-use pesticide but should be handled as an industrial pesticide. It may be used for superficial treatment, by brushing with solutions with a copper content of 1-2% (approx. 10-20%) copper naphthenate (Ibach 1999).

The proposed chemical structure for Cu-Nap is shown below:



**Fig. 1. Structure of Copper Naphethnate**

## **PHYSICAL AND CHEMICAL PROPERTIES**

CuNap is a dark-green liquid and imparts this color to the wood. Weathering turns the color of the treated wood to light brown after exposure. The wood may vary from light brown to chocolate-brown if heat is used in the treating process (Ibach 1999). This organometallic preservative system is freely soluble in various organic solvents, including diesel fuel, mineral spirits, fuel oil, pole treating oil, and creosote-petroleum mixtures (Freeman 2002). CuNap is supplied as an 8% concentrate for dilution. Like pentachlorophenol, the properties of copper naphthenate are dependent on the type of oil used as the carrier. The most commonly used oils are fuel oil and mineral spirits (Lebow and Tippie 2001). The color of the treated wood may vary from light brown to dark green depending on the type of oil and the treating process. The

odor of the oil may be noticeable near the treated wood. It is difficult to paint or stain unless the copper naphthenate was treated using a light carrier solvent. Typical properties for the 8% concentrate and for a 1 % (copper as metal) solution (- ready to use) are shown in Table I.

**Table 1: Properties of Cu-Nap Solutions for pressure treatment (Freeman 2002)**

	<b>8% Concentrate</b>	<b>1 % copper as metal Ready to use (RTU)</b>
% Copper	8±0.50%	1±0.50%
% Solvent	20	90
Color	Dark green/Blue green	Dark green/Blue green
Freezes	No	No
Pour Point °F	0	-25
Viscosity, cps at 75°F	2240±500	38±12
Viscosity, cps at 180°F	94	14
Flash point, °F	180 (104)*	170*
Density, LB/Gal	8.5*	7.4*

**\*Depending on diluents flash point and /or specific gravity**

Copper naphthenate free of any solvent exists as an amorphous, glassy solid with the copper content ranging from 9.3-12.5% by weight, depending on the acid value of the naphthenic acid used.

### **USES OF COPPER NAPHTHENATE**

Copper naphthenate is not a restricted-use pesticide and can be purchased at retail lumberyards and hardware stores. It is widely applied as a field treatment on end cuts or holes bored into pressure treated wood during construction (Lebow and Tippie 2001). It is diluted in diesel or heavier oils for pressure treating (Brient 2004). A review of the literature cites many applications for ground contact and above ground purposes. When pressure treated it is used for: utility poles, cross arms, piling, fence posts, guardrail posts, glulam beams, railroad crossties/switch ties, bridge timbers. CuNap is used for bridge timbers, particularly over

environmentally sensitive areas where preservative drippage is a concern. CuNap is also used in non-pressure applications ( brush-on, spray, dip, remedial and coatings) for use in wood shingles, millwork, pallets, beehives, non-wood applications, such as tents, canvas fishnets, cordage and other fabrics Freeman 2002; Brient 2004). CuNap is a proven cellulosic fiber preservative. It has a high degree of permanence when used to preserve cellulose and also has the ability to prevent mildew, rot, and decay from occurring in fiber substrates (Freeman et al., 2002). CuNap is frequently being used as an alternative to CCA in pressure-treated wood for residential uses. It is appropriate for poles originally treated with other preservatives, including waterborne preservatives. A Certified applicators license not required for field treatment (Brient 2004).

One of the principal reasons that Cu-Nap is gaining market acceptance and is being compared to other oil-borne wood preservatives is its low mammalian toxicity. Almost all former penta plants in Missouri and the western states of Montana, Wyoming, and Colorado have switched over to CuNap.

## **AWPA STANDARDS**

Over the years the AWPA has revised its standards covering Copper naphthenate to include the following specifications:

- i. The acid used in the manufacture 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. The AWPA P8 Standard was revised to specifically exclude the use of synthetic carboxylic acids in the manufacture of CuNap. Using non-naphthenics leads to reduced preservative performance, emulsion problems during treatment and increased leaching potential (McIntyre 2000). An analytical method was developed to determine the presence of synthetic acids and other non-naphthenic adulterants in copper naphthenate (Brient et al., 2000).
- ii. The copper naphthenate concentrate used to prepare wood preserving solutions shall contain not less than 6%, nor more than 8%, copper in the form of copper naphthenate.
- iii. All of the copper present in the concentrate shall be combined as copper naphthenate.
- iv. The copper naphthenate concentrate shall not contain more than 0.5% water.

- v. The foregoing tests shall be made in accordance with the standard methods of the AWPA Standards A-5.
- vi. Solvents used to prepare solutions of copper naphthenate shall comply with the standards of the AWPA Standard P-9, solvents and formulations for organic preservative systems
- vii. The copper naphthenate concentrate shall not contain more than 2% (relative) of the total copper in the concentrate as being water extractable as determined by the analytical method A-14 (AWPA Book of standards 2008).

These standards have been revised since early failure problems with CuNap use were identified in the earlier years. Today there are over 25 Standards in the AWPA Book of Standards that relate to CuNap and treated wood commodities that have been treated with it (Baileys and Freeman 2002). Currently, the AWPA lists CuNap in over a two dozen commodity standards. These standards, approved by both the preservatives committees and/or the treatments committees, signify that the purchaser and user of CuNap treated wood commodities can be assured of the expected service life of commodities when properly treated in accordance with these standards (Freeman 2002).

CuNap is standardized by the AWPA for treatment of timbers in U1 (Sawn Products) of southern pine, Douglas fir, and Hem-fir. UC3 (exterior, non-ground contact) at 0.04 pcf copper, UC4A (exterior, ground contact) at 0.06 pcf copper, UC4B and 4C (exterior, ground contact, severe hazard) at 0.075 pcf copper (Brient 2004). For Douglas Fir poles, outer zone: 0.075, 0.095, and 0.150 pcf copper is required. In Southern Pine: 0.06, 0.08, and 0.13 pcf copper is required. For round timber piling 0.10 pcf copper Southern Pine and 0.14 pcf as copper in Douglas fir is specified (Brient 2004). In 2005, the AWPA approved guidelines CuNap for treating Oak and mixed hardwood crossties. AWPA M4 standard provides guidelines for the use of copper naphthenate for remedial and non-pressure applications and specifies 1-2% minimum copper, in solvent or waterborne systems.

For copper, as metal, analysis in CuNap, X-ray Fluorescence Spectroscopy (AWPA A9), Atomic Absorption Spectroscopy (AWPA A11) or Inductively Coupled Plasma Spectroscopy

(AWPA A21) may be used. For determining penetration of CuNap, AWPA A3 (Section 2) is appropriate. Waterborne CuNap formulations are also currently listed in AWPA Book of Standards, but will not be discussed here in detail.

AWPA P9 Type A (Hydrocarbon solvent type A) for preparing solutions CuNap and other oil borne preservatives shall be composed of petroleum distillates or a blend of petroleum distillates and co solvents. It is preferable for maximum protection, particularly when the wood is used in ground contact. Heavy oils remain in the wood for a long time but do not provide a clean or paintable surface. Type A solvent-heavy oil, is preferred for bridge applications. Hydrocarbon solvent type B Volatile petroleum solvent - LPG (butane) was removed without prejudice due to lack of use. Type B leaves a clean surface. AWPA P9 Type C solvent (light Petroleum solvent light oil / mineral spirits ) is used when treating glulam before gluing. Type D is similar to B. (Ibach 1999).

## RETENTIONS

AWPA retention standards for various commodities treated with CuNap are listed in Table 2. Standards for Southern pine and Douglas Fir are well established for most commodities. The standards for oaks and other hardwoods have not been finalized although research on efficacy on this species has been conducted.

**Table 2. Former/Older AWPA Retention Standards for Copper Naphthenate (pcf).**

<b>Standard</b>	<b>Southern pine</b>	<b>Douglas Fir</b>	<b>Western red cedar</b>	<b>Ponderosa pine</b>
C2-lumber above ground	0.04	0.04	0.04	-
C2-lumber, soil/fresh water	0.06	0.06	-	-
C3-land/fresh water piles (in P9A)	0.10	0.14	-	-
C4-Poles (in P9A)	0.06-0.13	0.06-0.15	0.12	0.06-0.13
C5-fence posts	0.055	0.055	-	-
C14-Highway construction	0.055-0.08	0.055-0.095	0.055-0.095	0.055-0.095



C16-farms, soil contact	0.055-0.075	0.055-0.075	0.055-0.075	0.055-0.075
C25-crossarms	0.04-0.06	0.04-0.08	-	-
C28-glulam-above ground	0.04	0.04	-	-
C28-glulam-above ground	0.06	0.06	-	-
C32-glulam poles	0.08-0.13	0.095-0.15	-	-
C33-PSL structural composite lumber	0.04-0.06	0.04-0.06	-	-
C35-poles by thermal process	-	-	0.15	-

A comparison of AWP retention comparisons for poles (C4) for the major oilborne preservatives are shown in Table 3.

**Table 3. A comparison of AWP retention comparisons for poles (C4 or U-1). (PCF)**

	SYP	Douglas Fir
Penta	0.38, 0.43, 0.45	0.45, 0.60
Creosote	6, 7.5, 9	9, 12
Cu* (as CuNap)	0.06, 0.08, 0.13	0.075, 0.095, 0.15

### PREMATURE FAILURE PROBLEMS

In the 1990's some performance problems with CuNap treated poles were reported and resulted in a series of litigation. Some of these poles failed within 18 months of service, faster than untreated poles would be expected to fail (Freeman 2002). The earliest instance of premature failures occurred in 1992 in the Midwest. Instead of failing at the ground line these poles exhibited a variety of decay pockets in the aerial portions. A number of other utilities reported problems of sporadic decay. Both southern pine and Douglas fir poles are treated with CuNap but the widespread failure problems were only been reported in approximately 1500 southern pine poles. The problems were investigated and a number of reasons pinpointed. McIntyre & Freeman(2000) reviews the test history of CuNap and comments on the various potential causes for the failures below

## Causes of premature failure

- i. Possible use of non-naphthenic synthetic acids that do not conform to AWPA P8. To address this issue, AWPA P8 was revised to preclude the use of non-naphthenic or synthetic acids. Naphthenic acid is an extremely variable commodity and manufacturers of CuNap may have blended synthetic acids with natural naphthenic acids to produce a more uniform product and reduce costs. Many grades of naphthenic acids can be used in wood preservation since the specifications allow a range of acid values that are known to perform extremely well (Freeman 2002). Some naphthenic acids have considerable amounts of low molecular weight compounds, synthetic acids and other undesirable components (Niemi et al., 1998). Archer and Van der Waals (1990) related CuNap poor performance and the chemical composition of a range of naphthenates. The chemical composition of a range of naphthenates procured for several international sources was studied by GC-MS. However during the 1990's no US manufacturer of CuNap used imported naphthenic acids. All of the naphthenic acid used came from two chemical plants in the Southeast that used exclusively natural sources. Data shows certain carboxylic acids do not provide adequate protection. Synthetic carboxylic acids with acid numbers more than 250 and less than 350 have proven to be highly leachable and less effective for wood preservatives for ground contact. Low molecular weight acids can cause increased water solubility of both the copper and act as a coupling agent for water/hydrophobic sections of the naphthenate molecule and increase the solution tendency to form stable emulsions.
- ii. Treating with too high a water content in the treating solution. This results in the treatment solution water phase penetrating the wood pole and the oil-phase coating the pole exterior surfaces causing a "greenhouse-like" effect of keeping a high moisture content in the pole, even if it was effectively dried. It makes the exterior surface water repellent but keeps the pole interior MC elevated (Freeman 2002). It also results in emulsion problems.
- iii. Resultant retention distribution and threshold of CuNap:-One theory states that treatment with CuNap results in a different distribution of retentions compared with that of other oil

borne preservatives. A larger percentage of the poles end up with extremely low retention due to an extremely wide range of retentions. To investigate this claim, the distribution of retentions found in about 1000 CuNap poles was compared with that for 900 creosote poles. For both cases slightly skewed 'bells' were obtained but the curves are essentially the same. Other works have shown that retention distributions for creosote and penta in oil are also the same; one can extend the conclusion to include CuNap. A random sampling of 150 southern pine poles from 11 utilities nationwide showed that less than 5% of the poles had retentions below 50% of the mean (Barnes et al., 1999).

- iv. Post treatment steaming:-there have been indications that post-treatment steaming may inactivate copper naphthenate (Kamdem et al., 1998). Elevated temperatures for extended periods in laboratory tests can reduce a portion of CuNap to biologically inactive copper oxide. It is uncertain if conditions necessary to effect this transformation in the laboratory are available in full-size treatment to appreciable extent. Also, since the pole surfaces would be hottest, one would expect that the inactive copper oxide would be on the surface of the poles and thus a uniform surface decay would result. This is not the pattern seen in the field.
- v. Other reasons may include incipient decay, improper pretreatment conditioning, improper sterilization or conditioning, inadequate copper penetration and retention in high AWP hazard zones, and improper and insufficient post treatment inspections. It is important to note that none of these have anything to do with the efficacy of copper naphthenate. In fact, all of these reasons could lead to early failures with any preservative and it is reasonable to believe that some of the premature failures attributed to copper naphthenate are indeed due to some of these causes (McIntyre 2000).

### **Change in Guidelines and Specifications to Eliminate premature failure**

Numerous changes have been instituted to address all suspected causes of early failures in CuNap treated poles. Since then no significant failures have been known in southern pine poles and there have never been any reports of any early failures in Douglas Fir or any other species. Today's CuNap is substantially different than the product used in the introductory

phases. Numerous steps have been taken to avoid future premature failures. In many cases the precautions have involved revision of existing AWWA preservative and commodity standards. In others operating procedures were revised to address specific issues. Enhanced procedures, revised specifications, redundant safeguards and increased awareness of all parties involved have combined to provide the utility industry a high quality long lasting product (McIntyre and Freeman).

Today's CuNap pole is produced under significantly different guidelines and specifications. For example

- i. Brient et al (2000) identified an analytical method to verify the conformance of copper naphthenate to AWWA P8.2 standard for naphthenic acid component. The Analytical method was included in AWWA to differentiate acids.
- ii. Since mid-1990's, all southern pine is Kiln-dried before treatment to avoid incipient decay. The high temperature ensures sterilization and low moisture content gives improved treatment. Potential for incipient decay is negligible now. To improve sapwood penetration, poles are properly dried to low moisture contents. Treater quality assurance procedures have been revised to ensure good drying.
- iii. There is now 100% inspection of SYP poles regardless of size. The inspection of CuNap poles is extremely vigilant exceeding that of other preservatives due to procedural changes at inspection agencies and treating plants.
- iv. There is improved control of solution moisture content by controlling/minimizing emulsion formation. Closely monitoring the solution moisture content, removing excess water from the solution by distillation and or separation and using formulations that are easily separable from water. Inspection agencies are paying close attention to the moisture content of treating solutions.
- v. There is increased awareness against the inadvertent use of low retention levels in high AWWA hazard zones to provide a safe guard.
- vi. The chemical manufacturing method used today yields the lowest amount of byproducts –solids, impurities reducing any problem due to these impurities. All material is filtered to remove solids and the quality assurance program has rigid specifications for product consistency.

- vii. Supplier support is ensured by acquiring deep knowledge about all aspects of CuNap chemistry, and procedures. Their support of the wood treating industry and registered use of ISO 9002 manufacturing procedures ensures product consistency (McIntyre and Freeman--).

For the last decade, CuNap has been predominately used as a heavy duty industrial wood preservative. A conclusion can be made that the premature failures that occurred with treated poles were mostly due to learning how to handle and apply the preservative in a treating plant; a learning curve similar to those associated with either penta or creosote treatment modifications when they were first introduced. Both treaters and the manufacturer did not initially know how to effectively handle and use this newer preservative, thinking it would effectively be the same as either penta or creosote in handling characteristics. The relatively large number of failures in early years rapidly decreased as familiarity with the product grew (McIntyre 2000). Since 1995, the quality of the CuNap treated poles has improved as treaters and chemical suppliers have learned to control water emulsions and treatment variables. Knowledge on CuNap behavior has increased over time. Quality assurance techniques have been refined and documented and numerous plant personnel have undergone various training resulting in high quality southern pine poles produced today (McIntyre and Freeman--).

As of the year 2000, over 1.2 million poles had been treated with CuNap since 1988, and less than 4000 (< 0.5%) were cited as having early decay problems, less than one would expect based on a normal distribution curve for wood poles with a mean life of 35 years. Another nation wide inspection of CuNap poles treated between 1988-1999 included poles in all hazard zones and included poles installed by twelve different utilities and eight different treaters. In all 307 poles were sounded and bored and only 2 poles had early decay Barnes et al (1999). No allegation has ever been made that copper naphthenate is itself an ineffective preservative. In fact, with a proper inspection and remedial treatment program treated poles may well last over 80 years.

## **EFFICACY STUDIES**

Copper naphthenate is known to control decay fungi, molds, mildew, dry rot, certain marine growths, termites, wood parasites, and bacteria. By the year 2000 CuNap was used at eight different treating plants and three chemical companies supplied the vast majority of the product. A number of exposure tests have been performed to adequately develop retention standards for CuNap and now it is readily available and used for pole treatments. Through the years, there have been numerous efficacy tests done on CuNap. The tests have ranged from laboratory investigations such as agar plate and soil block bioassays with pure monocultures to full-size pole trials installed in test lines. These tests all show good efficacy for copper naphthenate.

CuNap test history spans several decades and involves a variety of oil-carriers, test plots, sample sizes, rating systems and exposure conditions. It is difficult if not impossible, to structure all of this data in a rational manner if the typical individual plots are generated. CuNap has been typically tested as a stand-alone oil-borne preservative but it sometimes was incorporated as an additive for creosote or other standard preservatives (McIntyre 2000). Railroad companies are continuously looking for ways to improve crosstie life in high-decay areas. Studies have shown that CuNap -treated crossties provide service life comparable to creosote treated crossties.

### **Mode of action of organometallics**

Toxic metals exert harmful effects in many ways but principally as a result of their strong coordinating abilities, they block functional groups of biologically important molecules (e.g. enzymes and transport systems for essential nutrients and ions), displace and/or substitute essential metal ions from biomolecules and functional cellular units, conformational modification, denaturation and inactivation of enzymes and disruption of cellular and organellar membrane integrity. Almost every aspect of their metabolism, growth and differentiation may be affected. The cell membrane is an initial site of action for a toxic metal species and membrane damage can result in loss of mobile cellular solutes. Organometallics are generally more toxic towards fungi than corresponding free metal ions. Toxicity of these compounds varies with the number and with the identity of the organic groups. Organometallics may

damage cell membranes and mitochondrial membranes by the production of free radicals since the carbon-metal bond readily reacts with available radicals to produce peroxyalkyl radicals which can result in lipid peroxidation and hence breakdown of biological macromolecules. Organometallic compounds may also exert a disruptive effect on cell membranes by causing a loss of  $K^+$  (Gadd 1999).

### **Copper Tolerance studies with CuNap**

Organometallics exhibit less copper tolerance by inhibiting oxalic acid production in resistant fungi. The relative tolerance of strains to copper-containing preservatives varies with the formulation. The same strains of *S. lacrymans* used in agar plate assays against copper citrate (CC) and CCA and in agar block tests against CuNap show a difference in relative tolerance of the isolates against the two preservatives (De Groot and Woodward 1999). Sutter et al (1983) postulated that the oil component in CuNap and oxine copper physically prevents movement of precipitated copper oxalate to the exterior of the wood surface. Eleven out of 12 isolates of *S. lacrymans* are tolerant towards CC because it induces high levels of oxalic acid early in the decay process (Sutter et al., 1983). CC is used to study copper-tolerant fungi because it lacks co-biocides found in most copper-based preservatives (Clausen et al., 2000).

### **Efficacy against termites**

Studies by Grace et al. (1993) have proven CuNap to be effective in preventing the consumption of wood by Formosan termites in Hawaiian field and lab tests. Southern pine and Douglas fir wafers pressure-treated with CuNap in AWWA P9 Type A oil or in toluene were evaluated for resistance to attack by the Formosan subterranean termite by Grace and Yamamoto (1993). Wood samples were treated to target copper retentions of 0.040, 0.075, 0.095, or 0.150 pcf, conditioned to simulate field exposure, and exposed to termites in choice and no choice lab tests. An approx. 20 % loss of copper after weathering and termite exposure was noted in samples treated to target retentions of 0.095 and 0.150 pcf Cu. With or without a heavy oil carrier, CuNap showed toxicity to termites and deterred termites. At the highest target retentions of 0.095 and 0.150 pcf Cu, southern pine wt. losses from termite feeding did not exceed 4 % in no-choice tests or 1 % in two-choice tests. Using a 3-min. cold soak treatment, Tynes (1968) found CuNap to be a better termite deterrent than penta. In fact,

chlordane and CuNap naphthenate had about the same degree of termite attack after 8 years exposure.

### **Efficacy studies against fungi**

Numerous reports for the AWPA Copper Naphthenate Task Force reviewing the efficacy of CuNap against decay fungi in various petroleum solvents in both soil block and agar block techniques have indicated excellent control over decay organisms tested in the 0.02 to 0.044 lb/ft.<sup>3</sup> (as copper) range in southern yellow pine sapwood including efficacy against copper tolerant fungi such as *poria placenta* (Freeman 2002).

### **Long term Efficacy Field studies**

Stake tests have demonstrated that CuNap provides years of extended service life and performance of CuNap in softwood species has been widely reported. In a one study (Nicholas and Freeman 2000) compared the performance of CuNap and penta-treated pine stakes in ground contact at two test sites in Mississippi corresponding to a high hazard (AWPA zone 4) and a severe hazard (AWPA zone 5). After 10 years exposure, the efficacy of CuNap at 0.80 kg/m<sup>3</sup> Cu retention was equivalent or slightly better than penta at 0.64 kg/m<sup>3</sup> retention. Oil-borne CuNap gives equivalent performance to creosote or penta at appropriate comparable retentions. As reported to Freeman (2002) CuNap under test at Oregon State University continues to give excellent performance in brush-treated, soaked, and pressure-treated Douglas-fir posts after greater than three decades of exposure.

Results from Southern Pine stakes installed in MS in 1943 and evaluated after 20 years compared

CuNap at 0.5% copper metal in naphtha and 5% penta in pine oil naphtha. At 20 years, 60% of penta stakes had been removed from service while only 30% of Cu-Nap stakes had been removed due to decay and termite attack. Projected life's of the stakes was 20 for penta stakes and 25 years for CuNap stakes respectively (Crawford 2000). Long-term efficacy trials on 2x4 lumber treated by dip, soak, brush-on, and pressure treating methods are published in USDA Forest Service Technical Note FPL-02 (Crawford et al 2000). These data indicate that CuNap dissolved in No. 2 diesel oil gives an average predicted lifespan of 38 to 42 years, comparable



to that of either creosote or penta in heavy oil. In addition to these data compiled in USDA Forest Service Publication FPL-01 that compares wood preservatives in Post Tests shows that CuNap treated round stock gives excellent service life when compared to standard preservatives CCA, creosote, or penta in P9 Type A oils (Freeman 2002).

Over 50 years ago, the USDA-Forest Products Lab established tests in a high decay and high termite hazard zone in southern Mississippi to evaluate performance of over 100 wood preservatives using SYP fence posts with an average diameter of 4-5 inches. During the last five decades, periodic reports have been issued on the efficacy and performance of southern pine fence posts treated with a variety of wood preservatives. Davidson (1977) gives an evaluation of the effectiveness of the various wood preservatives. Freeman et al. (2005) reassessed the condition of the treated wood posts, and statistically calculated and re-updated the expected post life span (Table 4). In estimating service life prior to 100% failure, average service life was approximated by the time when 60% of the posts in a group have failed. They evaluated 50 remaining wood preservatives in the test posts by a standard 50 lb lateral load pull test. After 53 years many of the posts failed upon to the stress load. Table 5 shows some of the preservatives, retention, posts remaining, and percentages of posts that passed or failed the test. It was determined that penta in oil, creosote, and CuNap in oil, provided life spans calculated to exceed 60 years. Creosote, with low residue, (clean creosote) did not perform as well, giving a service life of 37 years from the 1977 inspection, and 45 years in the 2005 evaluation. Surprisingly, creosote and penta treated posts at 75% (0.30 pcf penta in # 2 fuel oil) of the recommended AWPA retention, had a calculated service life of 74 years and CuNap at 50% of the required AWPA retention for fence posts had a calculated service life of 65 years; an excellent performance in this AWPA Hazard Zone 5 site and an even better performance when dissolved in aromatic residue. Untreated southern pine posts lasted 2 years. CuNap SYP poles used in AWPA Hazard Zone 5 require a retention of 0.13 pcf ( Cu as metal), and these posts treated to less than one-quarter of that specified retention, in this severe exposure hazard zone have a calculated service life > 65 years (Freeman et al., 2005).

**Table 4. Average service lives of penta, creosote and Cu-Nap treatments in Mississippi.**

<b>Preservative</b>	<b>Predicted service life (Davidson et al.,1977)</b>	<b>Predicted service life (Freeman et al., 2005)</b>
Ammoniacal copper arsenate (ACA)	42	59.5
Coal-tar creosote, straight run, low residue	37	45.7
Coal-tar creosote, straight run, medium residue	40	54.0
Coal-tar creosote, medium residue, low in fraction from 235° to 270° C, crystals removed	40	71.7
<b>Copper naphthenate (5%)-petroleum</b>	<b>42</b>	<b>72</b>
Pentachlorophenol (5%)-petroleum oil (No. 2 distillate)	42	74
Pentachlorophenol (5%)-petroleum oil (Wyoming residual)	36	
Penta 5% in Petroleum Oil		55.5
Penta 5% in #4 Aromatic Res.		119.4
Penta 3% In #4 Aromatic Res.		122.1
untreated controls	3.6	2.4

**Table 5. Preservative retention, posts remaining and percentages of pass, fail posts evaluated.**

<b>Chemical</b>	<b>Ret.</b>	<b>% Remaining</b>	<b>Fail</b>	<b>Pass</b>
Ammoniacal copper	0.34	64	4 (25%)	12 (75%)

arsenate ACA				
<b>CuNap 5% Cu in Petroleum Oil</b>	<b>6</b>	<b>68</b>	<b>4 (24%)</b>	<b>13 (76%)</b>
Penta 5% in #2 Distillate	6.3	68	0 (0%)	17 (100%)
Penta 5% in #4 Aromatic Res.	5.9	88	1 (5%)	21 (95%)
Penta 3% In #4 Aromatic Res.	6	100	2 (8%)	23 (92%)
Penta 5% in Petroleum Oil	6	64	6 (38%)	10 (63%)
Penta 5% Cu Nap in Petro	6.2	92	2 (9%)	21 (91%)
Creo Straight Run High Res	6	72	2 (11%)	16 (89%)
Creo Straight Run Low Res	5.9	28	4 (57%)	3(43%)
Control	0	0	0	0

(Freeman et al., 2005)

### Efficacy studies on hardwoods

Early studies with CuNap used southern pine and Douglas Fir. More recently efficacy of CuNap has been studied in hardwoods. Kamdem and Chow (1999) investigated the treatability of hardwoods with CuNap. For applied pressures of ~150 psi or higher, no difference in the preservative absorption or gradient for a given species was seen. Absorption followed the trend beech < red oak < sugar maple < red maple. Cu-Nap did not adversely affect bending strength. In an earlier study, Kamdem et al.,(1995) used Northern red oak sapwood cubes pressure-treated with CuNap in toluene to test decay resistance after exposure to brown and white rot fungi for 16 weeks. Cubes were pressure-treated to a target elemental Cu retention ranging from 0.112 - 4 kg/m<sup>3</sup>. At 1.28 kg/m<sup>3</sup>, elemental Cu retention, wt. loss of northern red oak cubes exposed to brown rot *Gloeophyllum trabeum* or white rot *Pleurotus ostreatus* or *Trametes versicolor* fungi was ≤3%. A higher elemental Cu retention of 1.6 kg/m<sup>3</sup> was needed to protect red oak against the Cu-tolerant brown rot *Poria placenta*.

Field stake studies by Barnes et al. (2001) show that CuNap is an effective preservative for a wide variety of hardwoods. In this test, Red oak, sweetgum, and southern pine stakes were treated by the full-cell process with M-Guard™ T500 CuNap, Creosote and 60/40 Creosote/Coal Tar. Cu-Nap compared favorably with creosote or creosote-coal tar systems after 7.5 years. Crossties treated using Cu-Nap and inspected after 12 year in Lewistown, PA. showed that CuNap and creosote crosstie performance, whether air dried and Boulton seasoned, was not significantly different. CuNap at retentions as low as 0.03-0.04 pcf Cu gave outstanding performance with all preservative treatments (Barnes et al., 2001). For treatment of ties recommendations to the AWPA include 0.055 pcf Cu or refusal for oak, 0.06 pcf Cu for mixed hardwoods (MHW), SYP, Douglas fir, with penetration requirements similar to those of creosote and penta. CuNap treated hardwood stakes tested in FL and MS and rated for decay and insect attack by AWPA E7 found the rating for 4.5 pcf creosote is roughly equivalent to 0.08 pcf (Cu as metal) in oak.

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 was investigated (Crawford et al. 2000). Wood treated with CuNap in oil at retentions as low as 0.26 kg/m<sup>3</sup> performed satisfactorily in an AWPA zone 5 region in South Mississippi. CuNap treated hardwood stakes tested in FL and MS and rated for decay and insect attack by AWPA E7 showed that 4.5 pcf creosote is roughly equivalent to 0.08 pcf (Cu as metal) in oak (Barnes et al., 2003). Similarly Brient and Webb (2002) showed that CuNap treated ties with 0.03-0.05 pcf Cu, in actual service for 13 years, were equivalent to ties treated with 7.8 pcf creosote.

### **Evaluation for crossties**

CuNap has been evaluated in lab and field stake tests studies as a preservative for oak and other hardwood species Oak is readily treatable with CuNap with no adverse effects on bending strength of the treated wood. In 1975, the American Railway Engineering Association (AREA) submitted data recommending minimum retentions of CuNap as Cu and creosote of 0.10 and 8.0 pcf respectively. Oak samples treated to these retentions and half of them gave comparable ratings over 15 years when exposed in Florida. More recently an inspection of CuNap, creosote and borate treated oak ties installed on a Norfolk-southern main line in

Pennsylvania was made. The ties were treated with 0.031-0.046 pcf as Cu. CuNap is not listed in the AWPA standard C6 for crossties or other commodities using oak or mixed hardwoods. The minimum retention for SYP poles under AWPA is 0.06 pcf as Cu greater than the retention in these ties. Creosote ties were treated to 7.8 pcf retention slightly above AWPA C6 retention of 7.0 pcf. Samples were either air dried or Boulton dried. Satisfactory and comparable penetration and retention of both the CuNap and creosote preservatives were achieved in mixed red and white oak ties. Two groups of borate dipped crossties were treated with secondary treatments of CuNap and creosote. Except for the borate dip only ties, all combinations of treatments fell within one standard deviation of the mean rating for all ties and are still supporting the track system. There was no significant difference in performance after 13 years in the preservatives and treating schemes. No significant difference as noted between creosote and CuNap treatments (Brient et al--).

### **Water borne CuNap formulations**

Waterborne CuNap is available for non-pressure treatment applications and has been an EPA-registered product since 1980. CuNap may be solubilized effectively using nitrogen based chemistry. Water-borne CuNap (WB-CuNap) presents advantages such as low volatile organic compound emissions and relatively low cost by using water as the carrier (Kamdem et al. 1996, Freeman et al., 2002). The active ingredient is dissolved in a solution of an alkanolamine and/or ammonia in water. Shaw (1994) tested water borne CuNap in field stake tests and compared it's performance to that of oil borne CuNap, CCA and penta. Samples were installed in a Hazard Zone 5 site. The performance of 0.15 pcf waterborne CuNap was equivalent to that of 0.13 pcf oil borne CuN and also equivalent to that of 0.60 pcf CCA. Waterborne CuNap performed as well as 0.45 pcf penta.

Freeman et al. (2003) tested softwood and hardwood field stakes treated and installed in MI, MS, and FL. Comparable ratings obtained after 5-7 years in various AWPA Hazard Zones included those of Waterborne CuNap at 0.08 pcf Cu, oil borne CuNap at 0.06 pcf Cu and CCA-C at 0.35 pcf in soft maple and SYP stakes. The results revealed that WB CuNap can be an effective, wood preservative for outdoor wood structures made from yellow pine and maple used in ground contact. The ratings of stakes treated with WB CuNap at 4-5 kg/m<sup>3</sup> (as Cu)

retention is comparable to ratings obtained for stakes treated with CCA at 4-5 kg/m<sup>3</sup> retention, oil borne CuNap at 3-4 kg/m<sup>3</sup> retention and ACQ-C at 6-8 kg/m<sup>3</sup> retention. The study proposes that retentions of 0.71±0.07 kg/m<sup>3</sup> Cu metal for yellow pine and 0.56kg/m<sup>3</sup> for soft maple using this waterborne CuNap formulation offers moderate ground contact protection for 7 years exposure in Mississippi, 7 years in Michigan and 5 years in Florida. At this copper retention, the performance of waterborne CuNap treated yellow pine is comparable to treatment with ACQ-C at 8.44 kg/m<sup>3</sup>, CCA at 5.63 kg/m<sup>3</sup> and oil borne CuNap at 3.94 kg/m<sup>3</sup>. The proposed retention for soft maple has a performance comparable to that of ACQ at 6.86 kg/m<sup>3</sup>, CCA at 4.37 kg/m<sup>3</sup> and OB CuNap at 3.12 kg/m<sup>3</sup>. Previously reported efficacy data on this system in long term stake tests in hazard zone 5 (Florida) indicate that 0.15 pcf (Cu as metal) in WB CuNap is roughly equivalent to 0.13 pcf (Cu as metal) oil-borne CuNap and 0.60 pcf (as oxides) CCA-C. Kamdem et al. (1996) suggested that water-borne CuNap with 2kg/m<sup>3</sup> copper retention was sufficient to protect red oak (*Quercus rubra*) and red maple (*Acer rubrum*) against some white rot and brown rot fungi.

The most common solubilizing agents for CuNap have historically been either ammonia or amines. In two independent studies, where ammonia was the primary solubilizing agent, results in test plots in both Central Florida and in Dorman Lake, MS (Hazard zones 5, and 4, respectively) indicate in SYP sapwood stakes in plots where both termites and decay fungi destroyed untreated controls in less than 2 years, stakes continued to perform well after 10 + years. Even the slightly lesser performing ammoniacal solubilized WB CuNap could be a very functional replacement product for the arsenic and chromium-containing CCA-Type C. The amine WB CuNap formulation has been used extensively for over the counter brush on and cold soak application for a number of years. WB CuNap is an excellent protectant for wood roofing materials, and superior to many other pesticidal and non-biocidal, water repellent only treatments. WB CuNap has also been used to successfully treat Aspen composites bound with Phenol-Formaldehyde (PF) resin systems. When WB CuNap incorporated into the PF resin system and then sprayed and tumbled onto the Aspen flakes, the OSB produced had significant resistance to decay from basidiomycete attack and no reduction in any mechanical properties such as MOR, MOE, and WPL. These studies clearly suggest that WB Cu-N can be used as a wood preservative for both above ground and ground contact applications.

Additional work on the amine –based formulation is necessary to ascertain effect on wood strength, corrosion to metal in contact with treated wood or any adverse wood conductivity.

## **CO-BIOCIDES**

CuNap combined with the insecticide permethrin is a well-established system used in a number of formulations designed to control both fungi and termites especially in Australia. Bioassay results using *Pinus radiata* sapwood indicate that the performance of copper naphthenate/permethrin could be enhanced against fungal decay and termite attack by co-formulating with synthetic polymer-based fire retardants. These fire retardants did not detract from the performance of the wood preservative against both the brown rot fungi and the termite species included in this study in lab tests (Marney et al., 2008).

CuNap-borate formulation combines the fungicidal effectiveness of copper-containing formulations with the fungicidal / insecticidal effectiveness of a diffusible borate. Several publications (Amburgey and West 1989, Amburgey and Freeman 1993a and 1993b, Freeman and Amburgey 1997 and Amburgey and Freeman 1997) document results of a field test with a CuNap-borate paste (Cu-Rap 20™) for treating the groundline of poles after varying periods of exposure at the Mississippi State University Dorman Lake test site. Southern pine pole stubs, were treated on one end with either a gel containing penta or a paste containing Cu-Rap 20™, covered with polyethylene and placed in holes so that the wraps extended two inches above ground. Untreated controls could easily be broken after 4.5 years by leaning on them. The lower portions of all treated stubs were essentially free of insect and decay damage through the 9+ years inspection. The stubs treated with Cu-Rap 20™ had less decay and fewer beetle exit holes than those treated with penta paste (Pol-Nu™), but stubs remained sound at groundline. After 15.5 years the groundline areas of most of the stubs had varying amounts of decay but none of them could be broken. Results with Cu-Rap 20™ indicated that either the copper is being transported into the wood by the diffusible borate or that a diffusible copper/borate complex is formed within the wood. Other studies with this formulation indicate its effectiveness in protecting standing utility poles even in semi-arid environments. Other tests in which unseasoned southern pine posts were diffusion-treated with the borate, dried, and butt-treated with CuNap have demonstrated the effectiveness of copper/borate treatments.

While the borate eventually leaches to below-threshold levels at the tops of the posts, the areas receiving both the copper and borate treatment (with no plastic wrap) remain sound after 10 years of exposure. CuNap borax paste continue to gain commercial use by both domestic and international utilities.

## **FACTORS AFFECTING PERFORMANCE OF CuNap Formulations**

Factors affecting the performance of CuNap are the same as those affecting other oil borne preservatives in treated wood. They include, conditioning method, soil type and soil chemistry of site of installation of the treated wood, solvent type (carrier solvent), amount of oil in solvent and presence of co-biocide.

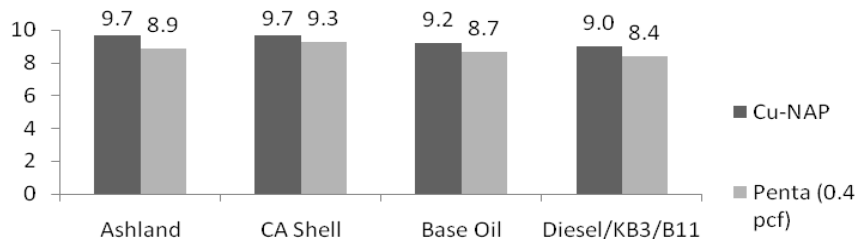
### **Test Site and carrier solvent**

Nicholas and Freeman (2000) compared the performance of CuNap and penta pine stakes against decay and termite attack at two test sites in Mississippi using four different petroleum oils meeting AWPA P9-A as carriers (Ashland, CA shell, Base oil, Diesel/KB3/B11). In this EPRI sponsored test program, the efficacy of CuNap at a retention of 0.05 pcf Cu was found equivalent or slightly better than penta at 0.40 pcf after ten years exposure. Untreated stakes typically fail in 3 years at the southern site. The type of carrier oil had an effect on the performance, but was variable for type of preservative and test site. A summary of the results is shown in Figure 2. All of the CuNap formulations performed better than comparable penta formulations except in the diesel/KB3/B11 and base oil formulations, for which the performance of CuNap is slightly lower than for penta at the Saucier test site. The depletion rate of penta was somewhat greater than that for CuNap. The depletion rate plays a major role in the performance of treated wood.

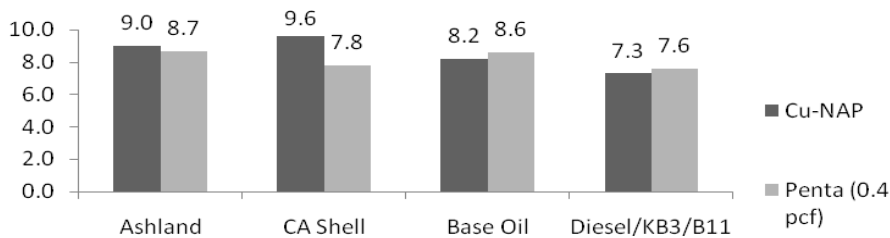
Test site is important when evaluating systems. In the test reported by Nicholas and Freeman (2000) in Mississippi, the performance of both penta and CuNap treated wood was slightly lower at Saucier test site where the average temperature and rainfall is higher and the soil is a loamy sand type with good drainage properties. The other site (Dorman) where performance was better had silty clay loam with poorer drainage and lower average temperature and rainfall. These differences possibly resulted from higher biocide and carrier oil depletion rates



at Saucier. Increasing oil content in the solvent carrier has a positive effect on the efficacy. Review of data from test sites at Madison, Wis., Gulfport, Miss., and Dorman, Miss., indicates that the severity of the test plot can alter the service life of wood products when placed in ground contact. In comparing the two test sites, the performance of both preservatives was consistently better at the Dorman Lake test site.



**Figure 2a. Comparative decay ratings of Cu-Nap and Penta treated Stakes using different carrier oils and exposed at Dorman MS. for 11 years.**



**Figure 2b. Comparative decay ratings of Cu-Nap and Penta treated Stakes using different carrier oils and exposed at Saucier MS. for 11 years**

The carrier solvent is designed to facilitate the penetration of the preservative into wood. The concept of the carrier oil having any impact on efficacy is not stated as a requirement. However, when selecting carrier oils, treaters need to ensure that the product does not reduce efficacy of the preservative, alter the physical properties of the wood, create compatibility problems in the treating plant, or introduce contaminants of regulatory concern (Brient 2009).

While the performance of a wood preservative formulation is first and foremost a function of the active ingredient, the carrier oil can have a major influence. The importance and impact of

the petroleum carrier on performance has been well documented in the literature (Nicholas 1988, Nicholas et al. 1994, Nicholas and Freeman 2000) and serves as the basis for the AWPA Standard P9.

## **EVALUATION OF CuNap FOR USE IN UTILITY POLES**

When copper naphthenate is evaluated for treating utility poles and cross arms, four specific evaluation important parameters reviewed are: leachability of the preservative system, conductivity of the treated wood commodity, hardness or gaff penetration of the treated wood, and corrosivity of the treating solution when placed in contact with metallic wafers while still in solution. Non-corrosive to mild steel or galvanized steel, insoluble in water, low leaching rate and is non-conductive (Brient 2004).

### **Leachability**

Standard wooden blocks, treated with copper naphthenate and penta in a similar P9 oil, were tested in accordance to AWPA Standard M-11 for leaching potential. Slight leachability of both preservative systems was observed: 0.49% of the CuNap was leached while 1.40% of the penta was leached. This may be one of the primary modes of protection of wood substrates by sterilization of the surrounding soil of the utility pole. Preliminary indications are that copper naphthenate is tightly bound to the wood substrate both chemically and physically, including copper-lignin bond formation, copper-holocellulose bond formation, and copper-extractives bond formation (Freeman 2002).

In addition to efficacy of biocides against microorganisms, Nicholas and Freeman (2000) compared the depletion rate of penta and CuNap in four different carrier oils at a site in Mississippi. On a percentage basis the loss of penta was found somewhat greater than that for CuNap (Table 6). However, due to the relatively small sample size this data does not represent statistically significant differences. Nevertheless this data suggests that the depletion rate of CuNap compares favorably to that of penta.

**Table 6. Average % Depletion of CuNap and Penta in stakes treated with several different carrier oils exposed at Saucer (MS) for 2-years.**

Career oil	Preservative Initial Retention (pcf)	Average % loss after 2-years exposure	
		Above ground	Below ground
Ashland	Cu Nap. (0.049).	20.3	30.1
	Penta (0.383)	8.4	39.2
CA Shell	Cu Nap. (0.045).	20.6	17.1
	Penta (0.383)	14.7	39.4
Base Oil	Cu Nap. (0.049).	17.9	21.8
	Penta (0.396)	11.2	43.2
Diesel/KB3/B11	Cu Nap. (0.051).	8.0	18.8
	Penta (0.394)	31.9	19.1

Cu Nap retention and depletion values are based on Cu Content.Penta . (>96 % active ingredient penta ) and Cu-Nap (8% Copper as metal)

### Conductivity

Conductivity of the treated wood is important when evaluating preservative systems for wooden utility poles and cross arms. Reduction in conductivity of treated wood may be achieved by reduction of moisture content of the treated wood by displacing these with non-polar organic solvents or by reducing the overall conductivity of the wood specimen. Resistivity or conductivity of treated wood can greatly be affected by grain orientation, moisture content, temperature, and preservative system employed. Many linemen and engineers are often concerned that a copper containing preservative may be dangerous to climb and be very conductive to electrical current. Test results published by Asmus et al. (1985) show that there is no increased conductivity of wood utility poles or cross-arms when treated with copper naphthenate in an oilborne preservative system. While untreated wood showed a resistance of 275 KΩ, CuNap wood had 315 KΩ and CCA treated wood showed 35 Kilo Ohms (Freeman 2002)

### Corrosivity

The corrosivity of copper naphthenate in treated wood offers no significant increase compared to untreated wood or treated wood using other oilborne preservative systems. Tests comparing

the corrosivity of the biocide dissolved in either No. 2 fuel oil or medium aromatic treating oil indicated no significant corrosivity from the treating solution and/or the treated wood specimens. Test specimens exposed in Michigan, Mississippi and Florida all showed no significant differences between corrosivity of oil borne CuNap treated stakes and those treated with CCA. Stakes treated with Water borne CuNap had higher corrosivity values but were lower than those of ACQ. Additionally Freeman (2002) reports on a survey concerning 30,000 poles inspected that were previously treated with CuNap in oil and none of these poles were found to have hardware corrosion problems.

### **Hardness/gaff penetration**

When using a wood preservative to produce a utility pole, the hardness of the utility pole or the ability to penetrate that utility pole with the standard lineman's gaff is important. Hardness of the pole relates to surface hardness as well as the ability to flex under torsion. The hardness of a utility pole, or its ability to withstand impact, is greatly affected by the preservative system employed. Copper naphthenate-treated poles represent no significant increase in brittleness to a standard utility pole. Results of the gaff penetration tests at Arizona Public Service Company are summarized by Freeman (2002 ) and show that no significant difference exists in gaff penetration between CuNap and penta in similar P9 Type A oils in southern yellow pine or Douglas-fir. Oilborne petroleum solutions generally give a certain amount of lubrication for gaff penetration and an ease of penetration to the wood surface

## **TREATING CYCLES FOR COPPER NAPHTHENATE POLES**

### **Steaming**

Work in the development of CuNap as a preservative for poles led to the development of various treating cycles similar to other oilborne systems. It has been shown that post treatment steam conditioning southern pine converts CuNap to crystalline copper (I) oxide to a small degree. This cuprous species is less efficacious than cupric species such as CuNap in small laboratory tests. This gave cause to the AWPA copper naphthenate task force to review, the effect of pre and/or post steaming on the efficacy of CuNap preservative systems. Barnes et al., 2000a; 2000b; 2000c, reviewed the performance of pole stubs placed in a high hazard AWPA Hazard zone 4 location with termites and decay potential. Multiple treating cycles were

used to treat the pole stubs in these studies including various post-treatment conditioning methods. They found that the use of a post-treatment steam conditioning bath or open steaming cycle did not adversely affect the efficacy or overall performance of large size diameter wood poles in service for 1-12 years after post treatment steaming. Of all 44 pole stubs that were either post-or pre-treatment steamed, no decay colonization or termite attack was found on poles in service after 12 years in either the groundline or above-ground sections.

### **Treating plant operating conditions**

As of 2002 there were 31 operating treating plants using copper naphthenate in various petroleum oils in the United States. It is estimated that over 2.5 million pounds of copper naphthenate concentrate was being sold into the wood preservation market into the United States as of this date. Typical oilborne preservative plants can be converted over to use copper naphthenate with relative ease (Freeman 2002).

### **Plant conversion**

Plant conversion from either penta or creosote to copper naphthenate is very simple. Adequate cleaning is necessary to meet EPA guidelines if the user does not plan to obtain restricted use pesticide licensing or decontaminating/delisting the facility for use with copper naphthenate only. Incorporation of filtration equipment as well as sludge dewatering equipment is necessary for a copper naphthenate treating plant that will discharge water to a POTW or through NPDES permitting.

### **Emulsion formation and sludging**

CuNap work solutions produced from CuNap concentrate and fuel oil form stable emulsions, especially when the emulsions contain particulates and wood extractives such as acids and sugars. Experimental tests have also shown that CuNap manufactured from the direct metal process always forms more stable emulsions than CuNap produced from either the melt (fusion) process or the double decomposition process. Wood components tend to stabilize the emulsions by acting as either thixotropes or surfactants. Many factors play roles in forming emulsions in CuNap treating plants and treating equipment. In almost every single case where emulsions have formed, insolubles were present in the wood treating solution. The tendency to

form emulsions and formation of surface solids deposited onto wood utility poles can be greatly reduced by incorporating filtration equipment into the treating plant equipment and filling lines (Freeman 2002).

Emulsion formation and heating tend to produce sludge within work tanks and in treating equipment and on wood surfaces. When emulsions form in work tanks, industry practice is to drive the water off with heat. In CuNap treating systems, if the water content exceeds 1-2%, elevation of the temperature of the work tank solution can cause the formation of black copper oxide. Copper oxide can form a “seed” that allows the resulting emulsion to grow in size or precipitate to the bottom of the tank, since copper oxide is not soluble in organic solvents. This copper oxide increases the amount of xylene insolubles, or sludge, present in the solution. The best way to keep sludge from forming in CuNap treating equipment is to reduce the water content appreciably and continuously filter the solution to avoid debris and trash from entering the wood treating equipment (Freeman 2002).

Thermal treating pilot scale tests have been conducted using (CuNap) preservative solutions produced with base P9-type A oils to evaluate treating and process variations in Western red cedar (WRC) pole stubs. WRC was selected since it is currently used in commercial thermal production with Penta in oil. Penetration of the WRC sapwood and incised zone was very similar to commercially produced thermal treatment oil-penta poles (Baileys and Freeman 2002).

### **EPA REGULATORY STATUS**

CuNap has been an EPA-registered product since 1980. Unlike creosote and penta, CuNap is classified by the EPA as a general use preservative. Since it is a non-restricted preservative, it is commonly sold over the counter (Brient and Freeman 2004). It is a Non-hazardous waste or air pollutant with no reportable quantity required for spills. It is a logical choice when safety, environment and disposal are considerations. It is an attractive wood preservative because EPA imposes minimal requirements.

Compared to each restricted-use wood preservative, CuNap enjoys the following advantages:

- i. EPA does not require applicators of CuNap wood preservatives to be certified (some states may require applicator certification). EPA does not regulate CuNap wood preservative wastes as hazardous wastes and does not regulate CuNap emissions from wood-treating plants as hazardous air pollutants. Only the solvents that they are diluted with are regulated. Wood out of service can be disposed of in approved landfills or by incineration such as in cogen units. When CuNap treated wood is removed from service, it is commonly used for parking lot bumpers, landscape timbers and fences.
- ii. CuNap is not a regulated toxic substance to which the Clean air act (CAA) accidental release prevention requirements apply, it is neither a Clean water act (CWA) nor a CERCLA hazardous substance for which spills have to be reported and is not an EPCRA extremely hazardous substance for which emergency release notification requirements apply. Copper and CuNap are not listed as hazardous substances and, therefore, spills do not have to be reported. It is simply easier for total compliance for the treater and the user to use and specify CuNap when faced with many of the other regulations which constrain their business and business opportunities.

OSHA's hazard communication standard applies and requirements for material safety data sheets (MSDS) apply. Copper (but not copper naphthenate) is a priority pollutant for which effluent limitations and pretreatment standards have been prescribed for wood treatment plants.

## **HEALTH AND SAFETY**

Under FIFRA CuNap is not listed as an acute category I Chemical and has no significant sub-chronic, chronic or delayed toxic effects. CuNap has low acute mammalian toxicity by oral, dermal, inhalation routes of exposure (Brient 2004). Flammability of CuNap treated timber is similar to other oil borne preservatives and afterglow is not a factor with CuNap. Soil mobility tests demonstrate that CuNap is not transported through the soil by water. Environmental and toxicological studies show that it would have little or no impact on wildlife.

Brooks (2003) reports the results of a 30 day evaluation of copper in leachate water exposed to CuNap treated piles. Risk assessment is used to determine environmental risks associated with the use of piling immersed in freshwater. Copper losses from wood treated to 0.08 to 0.14 pcf copper are predicted to be  $18.9 \mu\text{g Cu/cm}^2\text{-day}$  on the first day of immersion. Initial loss rates decline exponentially and approach the long-term loss rate of  $1.2 \mu\text{g. Cu/cm}^2\text{-day}$  in about three or four weeks. CuNap leachate was found to be approximately 1/3 as toxic to *Daphnia* as ionic copper in a 21-day bioassay (Brooks 2003).

CuNap is non-corrosive to mild steel or galvanized steel, insoluble in water, low leaching rate and is non-conductive (Brient 2004). Copper in incinerator ash does not interfere with downstream usages in cement/concrete, and even increases compressive strength of concrete. Several cogeneration facilities contacted about incineration of ties treated with copper naphthenate did not identify any red flags based on its MSDS, chemical composition, and regulatory status (Brient 2004).

## **Summary and Conclusions**

Copper Naphthenate remains a viable wood preservative today after over 100 years of both industrial and residential use. Currently, the big box stores sell over two dozen different formulations and brand names of copper nap products for use by the consumer. In the USA alone, currently > 3% of all the annual production of utility poles are treated with copper naphthenate. Copper Naphthenate is not a Restricted Use Pesticide and remains a General Use pesticide. As these authors have indicated in previous papers, poor quality product and inferior treating practices lead to some 1500 Southern Pine pole failures from 1993-1997, but since then, roughly 0.1% of early failure poles have been found, indicating the CuNap pole performance issue is now a moot point. To date, no Douglas fir poles have been found to have early decay. And, although Copper Naphthate does have copper in the name, CuNap treated wood is non conductive and similar to untreated wood in conductivity and slightly easier to climb, due to the oil fraction contained therein, than untreated wooden poles.



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