# Performance of Copper Naphthenate in Fence Posts

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Abstract

This paper reviews the efficacy and field trials of copper naphthenate in various wood species. Included in this discussion are chemical and physical characteristics of copper naphthenate preservative systems, the effect on wood treated with copper naphthenate or copper naphthenate wood preservative systems, and a review of the long-term efficacy trials, in various species of wooden fence posts. Included in this discussion are independent results from the USDA- Forest Products Lab testing in Harrison Experimental Forest near Gulfport, MS, results from the Tennessee Valley Authority on Fence Post Tests in Tennessee, summary of Test results from fence post tests in Canada and a brief mention of ongoing tests in Auburn, AL and Corvallis, OR. Included in this discussion is the typical plant handling characteristics of copper naphthenate and its diluted solutions. Based on all the data, copper naphthenate is an excellent preservative choice for both pressure and non-pressure treatment of wooden posts of all species.

## Background and History

The use of copper naphthenate as an industrial biocide and wood preservative has been well established since the turn of the century. Copper naphthenate is basically the metallic salt of a metal ion reacted with naphthenic acids. Naphthenic acids are by-products of petroleum, typically removed from petroleum oil, kerosene and fuel fractions by caustic quenching, then resulting acidification. Typical crude petroleum oils contained 0.5 to 2 percent crude naphthenic acid by weight, with the highest concentrations of crude found in South America, western North America, Romania, Russian, and Central America. The naphthenic acids are typically alicyclic acids. They are broadly classified as acids of the formulae $C_nH_{2n-z}\ O_{2.}$ The naphthenic acids them selves exhibit efficacy toward wood destroying organisms and bacteria. Chemically speaking, these compounds are known as cupric cyclopentane carboxylates or cyclohexane carboxylates. The physical and chemical characteristics of copper naphthenate and naphthenic acids have been described in detail and their use in wood preservation discussed by many researchers. Broadly speaking, many naphthenic acids can find their way into wood preservation, since the specifications written for copper naphthenate include a wide variety of acid values, all nap acids of which are known to perform extremely well in ground contact. Trade names for copper naphthenate in commercial use include Perm-E8, Cop-R-Nap, CuNap8, Cunapsol, and Cuprinol. Of these, the most common name is Cuprinol, dating back to the Danish of over a century ago, meaning, “copper in oil”. A review of the literature cites many applications for use, including field boxes, beehives, benches, flats, fenceposts, water tanks, canvas, burlap, ropes, nets, greenhouses, posts, utility poles, crossarms, and wooden structures in ground contact and above ground contact. This paper will focus mainly on the use in small round and sawn stock, namely posts. Copper naphthenate is known to control many decay fungi, molds, mildew, dry rot, certain marine growths, termites, wood parasites, and bacteria. Recent studies have also proven copper naphthenate to be effective in preventing the consumption of wood by the aggressive Formosan termite in Hawaiian field tests, Mississippi field tests, and lab tests.

Copper naphthenate began its strong leap into the wood preservation business with the need to extend the useful volume of creosote available in the postwar effort and for the use by the many penta fence post treaters who did not want to become licensed pesticide applicators to buy and use pentachlorophenol. Due to a modification of operating practices of the steel mills, creosote, whose main source is the coking of coal and of petroleum products, was in short supply. The American Wood Preservers’ Association (AWPA) began a search for combination biocides that could be added to creosote to effectively extend its service life. Colley et al. determined that copper naphthenate was a likely extender for creosote and did not offer some of the proposed problems that addition of pentachlorophenol (penta) as a phenolic acid would pose in treating plant corrosion.

Resulting papers presented by Minich and Goll included a broad background of the technical aspects of copper naphthenate as a wood preserving chemical, including its solubility in inorganic solvents, relative vapor pressure, electrical conductivity properties, compatibility with commercially available oils, and the effectiveness of copper naphthenate against wood decay fungi. A specification was proposed to add copper naphthenate to the AWPA Book of Standards. The key issues brought about by the proposal by Minich and Goll included copper naphthenate as a chemical compound of uniform performance, its highly effective nature, and as a permanent wood preservative, its easy application, and its safety in handling to workers.

Copper naphthenate exists in the AWPA Wood Preservative Standards, P-8, with the following specifications:

- The acid used in the manufacture of copper naphthenate shall be naphthenic acid of the group of alicyclic carboxylic acids occurring in petroleum and shall have an acid number of not less than 180 and not more than 250 on an oil-free basis.
- The copper naphthenate concentrate used to prepare wood preserving solutions shall contain not less than 6 percent, nor more than 8 percent, copper in the form of copper naphthenate.
- All of the copper present in the concentrate shall be combined as copper naphthenate.
- The copper naphthenate concentrate shall not contain more than 0.5 percent water.

- The foregoing tests shall be made in accordance with the standard methods of the AWPA Standards A-5.
- Solvents used to prepare solutions of copper naphthenate shall comply with the standards of the AWPA Standard P-9.
- The copper naphthenate concentrate shall not contain more than 2 percent (relative) of the total copper in the concentrate as being water extractable as determined by the analytical method A-14 on Page 248 of the 1987 AWPA Proceedings.

- [1] A gas chromatographic method for determining conformity with part 2.1 and 2.3 will be published in the 1999 AWPA Proceedings as an appendix to the Subcommittee P-5 Report.

Data has been presented to the Association as well as to the International Research Group on Wood Preservation that certain carboxylic acids do not provide adequate protection. Of these, the synthetic carboxylic acids which have the acid numbers in excess of 250 and less than 750, have proven to be highly leachable and insufficient wood preservatives for ground contact. Additionally, the use of low molecular weight acids 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 solutions propensity for the formation of stable emulsions and may help create sludges even in non-pressure applications. Copper naphthenate, when produced commercially, consists of an amorphous, glassy solid with the copper content ranging from 9.2 percent to 10.8 percent by weight. When using a total acid value number (TAN) for copper naphthenate of approximately 200, the ratio of copper to total copper naphthenate fraction is approximately 1 to 10. This means that if you are treating with a solution that is roughly 10% copper naphthenate, it contains approx. 1% copper (as metal).

Penta, an effective wood preservative, has undergone intensive environmental reviews by the U.S. EPA from 1978 to 1986. The result of this review was the final publication of a RPAR position document IV and a settlement agreement between industry and the EPA. Although penta remains an extremely viable wood preservative for the treatment of utility poles, many people concerned over hexachlorobenzene and chlorinated dioxins have begun to specify and user copper naphthenate, due to the bad press received by penta over the last number of years as well as a perceived problem with penta-treated products. The increase in use of copper naphthenate-treated wood posts and in the companies producing them can be easily seen in the conversion of almost all former penta plants in Missouri and the western states like Montana, Wyoming, and Colorado over to CuNap over the past 12 years.

Copper naphthenate is typically supplied as an 8 percent concentrate dilutable with a wide variety of organic solvents. Typical properties for the 8 percent concentrate and for a 1 percent (copper as metal) solution (RTU - ready to use) when the 8 percent concentrate is diluted with 8.3parts fuel oil is well documented in earlier publications.

One of the principal reasons that copper naphthenate is gaining market acceptance and is being compared to other oil-borne wood preservatives is its low mammalian toxicity. The acute toxicity profile of copper naphthenate (8%) has been well published and documented, including studies conducted by the U.S. Army Industrial Hygiene

Group. The current Task Force answering the questions on the U.S. EPA Data Call-In, dated 1985, have reviewed the acute and chronic toxicity package of copper naphthenate and copper naphthenate treating solutions. A complete review of the regulatory status by Talereck has been performed and is summarized in earlier published works, including a short white paper entitled" Regulatory Status of Copper Naphthenate".

## Forest Products Laboratory Tests

Test Location: Southern Mississippi ( Saucier)
Size: Posts
Number: 25 per retention

| | | PER CENT POSTS STILL SERVICABLE AT YEAR | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Preservative | Retention | 0 | 15 | 17 | 19 | 21 | 23 | 25 | 27 |
| CN/OIL | 0.03 Cu | 100 | 96 | 96 | 96 | 96 | 88 | 88 | 88 |
| PCP/OIL | 0.18 PCP | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| PCP/OIL | 0.30 PCP | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| OIL | 5.9 lb. Oil only | 100 | 96 | 88 | 88 | 84 | 76 | 76 | 68 |

Oil is No.4 Aromatic Residual

**Oregon State Arboretum Tests**

Test Location: Western Oregon
Size: Posts
Number: 25 per species/preservative

| COLD SOAK | | | |
|---|---|---|---|
| | | | Service |
| Species | Treatment | Retention | Life, yrs |
| Douglas fir | UNT | - | 4 |
| Cottonwood | UNT | - | 4 |
| | | | |
| Douglas fir | CuN | 0.03 | 9 |
| Douglas fir | CuN | 0.03 | 9 |
| Douglas fir | CuN | 0.05 | 15 |
| Douglas fir | CuN | 0.12 | 24 |
| | | | |
| Douglas fir | PCP | 0.35 | 15 |
| Douglas fir | PCP | 0.37 | 16 |
| Douglas fir | PCP | 0.5 | 29 |
| Douglas fir | PCP | 0.65 | 30 |
| | | | |
| Cottonwood | CuN | 0.10 | 8 |
| Cottonwood | NaPCP | 0.15 | 11 |
| Cottonwood | PCP | 0.15 | 37 |
| | | | |
| BRUSH ON--2 coats | | | |
| | | | |
| Douglas fir | CuN | 1% Cu | 11 |
| Douglas fir | PCP | 5% | 14 |
| Douglas fir | CREO | - | 9 |
| | | | |

## Tennessee Valley Authority Tests

Test Location: Eastern Tennessee-
Size: Posts
Number: Varies per species/preservative

Cold Soak Treatment to ~6 pcf of 5% CN (0.5% Cu) and 5% PCP

Therefore retentions of 0.03 pcf Cu and 0.30 pcf of PCP

| | Service Life, yrs | | | Service Life, yrs | | | Service Life, yrs | |
|---|---|---|---|---|---|---|---|---|
| Species | UNT | No. | CuN | No. | Fail,% | PCP | No. | Fail,% |
| Southern Pine | 1.9 | 123 | *16-17* | 494 | 23 | *20+* | 175 | 1 |
| Willow | 2.4 | 25 | *12-13* | 50 | 52 | - | - | - |
| Hybrid Poplar | 2.4 | 25 | - | - | - | - | - | - |
| River birch | 2.6 | 25 | *11* | 49 | 84 | *14+* | 45 | 38 |
| Sycamore | 2.6 | 25 | *12-13* | 49 | 55 | - | - | - |
| Black oak | 2.8 | 25 | *15-16* | | | - | - | - |
| Yellow-poplar | 2.8 | 23 | *17+* | 50 | 12 | - | - | - |
| Black gum | 3.4 | 25 | *14-15* | 50 | 34 | *20+* | 25 | 4 |
| Sourwood | 3.6 | 50 | *17+* | 50 | 16 | *15+* | | |
| Red maple | 4 | 25 | *11-14* | 50 | 56 | *14+* | 25 | 40 |
| Hickory | 4.7 | 25 | *12-15* | 50 | 18 | - | - | - |
| Chestnut oak | 4.8 | 25 | *18+* | 50 | 6 | - | - | - |
| White oak | *11* | 17 | *14+* | 50 | 18 | - | - | - |
| Sassafras | *11* | 25 | *16+* | 50 | 20 | - | - | - |
| Black locust | *15* | 25 | *20+* | 25 | 0 | *20+* | 25 | 8 |
| E. Red cedar | *18* | 23 | *20+* | 25 | 4 | - | - | - |
| | | | | | | | | |
| | Estimated life in italics | | | | | | | |

**Forintek Canada Tests**

Service life of untreated softwood posts in Canada

| Species | Mean Service Life (years) |
|---|---|
| Eastern white cedar | 17.9 |
| Balsam fir | 3.7 |
| White spruce | 3.5 |
| Black spruce | 4.5 |
| Eastern hemlock | 4.4 |
| Red pine | 3.8 |
| White pine | 5.7 |
| Jack pine | 5.5 |
| Tamarack | 8.3 |

**: Pressure treatments with oil-borne preservatives in Canada**

| Preservative | Wood species | Retention ($kg/m^3$) | Year installed | Ratio of posts still in service in 1998 | Mean service life |
|---|---|---|---|---|---|
| **Full-cell** | | | | | |
| PCP in pole oil (boultonized) | Red pine | 8.0 | 1967 | 10/10 | > 31.0 |
| PCP in pole oil (steamed) | Red pine | 7.2 | 1967 | 13/13 | > 31.0 |
| PCP/Cellon (set in foamed plastic) | Red pine | 7.5 | 1967 | 4/4 | > 31.0 |
| PCP in methylene chloride | Jack pine | 8.3 | 1971 | 13/16 | > 25.3 |
| PCP in methylene chloride | Red pine | 8.3 | 1971 | 4/4 | > 27.0 |
| **Empty-cell** | | | | | |
| Oxine copper in pole oil | Jack pine | 6.3 | 1974 | 5/5 | > 24.0 |
| Oxine copper in pole oil | Jack pine | 11.7 | 1974 | 6/6 | > 24.0 |
| Copper naphthenate (1% Cu) in pole oil | Jack pine | 1.3 | 1950 | 14/14 | > 48.0 |
| Copper abietate (1% Cu) in pole oil | Jack pine | 1.4 | 1957 | 9/9 | > 41.0 |
| Copper abietate (1% Cu) in pole oil | Jack pine | 2.2 | 1957 | 32/32 | > 41.0 |

Approximately 3 – 8 years (depending on the species) of additional service, was added by brush treatment with pentachlorophenol, copper naphthenate, and creosote compared to untreated posts (Table 5).

**Brush treatments on Canadian Species**

| Preservative | Wood species | Treating solution uptake ($kg/m^3$) | Year installed | Ratio of posts still in service in 1998 | Mean service life |
|---|---|---|---|---|---|
| 5% Pentachlorophenol /pole oil | Jack pine | 12.5 | 1953 | 0/20 | 16.5 |
| | White spruce | 7.5 | 1953 | 0/20 | 12.6 |
| | White spruce | 13.0 | 1953 | 0/20 | 8.8 |
| 2% Copper naphthenate/pole oil | Jack pine | 15.9 | 1953 | 0/20 | 16.4 |
| | White spruce | 8.5 | 1953 | 0/20 | 9.7 |
| | White spruce | 10.6 | 1953 | 0/20 | 5.6 |
| Creosote | Jack pine | 14.9 | 1953 | 0/20 | 13.6 |
| | White spruce | 9.0 | 1953 | 0/20 | 11.3 |
| | White spruce | 21.5 | 1953 | 0/20 | 11.4 |

## Commercial Field Evaluation Experience

In 1986 The US EPA published the Settlement document on the three major wood preservatives: Inorganic arsenicals, creosote and Pentachlorophenol. Part of that settlement agreement was to make it difficult, if not impossible for an over-the counter consumer of wood preservatives to be able to buy, use, or re-sell one of the big three wood preservatives. The “big three” wood preservatives became restricted use pesticides and because of this new classifications label changes were made and it was also decided that you could not purchase and use these pesticides without being a certified pesticide applicator.

Many of the treating plants in the USA immediately had to get at least one person on their staff to become a certified pesticide applicator if they decided to continue to use either pentachorophenol, creosote or inorganic arsenical formulations. The contrary to this is that many of the other, sometimes smaller treating plants decided not to continue treating with the now restricted use pesticides and converted over to the use of Copper Naphthenate. More than 75% of the oil-borne treaters in the state of Missouri converted their plants after through cleaning of the plants, to copper naphthenate. The same was true of many=y of the western plants in Montana, Wyoming, and a few in Washington State. Many of these treaters were fence post producers.

A recent informal poll of the treaters using CuNap in the USA indicates that they have a very low replacement rate for failed fence posts and that they found the conversion over to CuNap from creosote or Pentachlorophenol was quite easy. Most noted that the CuNap concentrate was slightly more viscous in the wintertime, but found the thickness of the concentrate compared similarly to that of 40% penta concentrates. No significant changes were noted between the ready to use (R-T-U) solutions of CuNap and Penta for most of these customers. Today, fence posts treated with CuNap are performing well in fence post applications throughout the United States and have gained widespread industry and commercial acceptance.

## Summary and Conclusions

CuNap treated fence posts perform well in almost every posts tests installed in Canada and in the USA over the last 60+ years. In Canadian studies, with just a brush coating of CuNap on refractory species, useful service life as compared to an untreated post was ranged from doubling the service life to almost 5 times that of an untreated post. In Canadian pressure treating tests, Canadian species treated with CuNap were the longest lasting in fence post tests with useful average service life greater than 48 years.

In tests in western Oregon, CuNap extended the useful service life of fence posts from twice that of untreated to over six times the life of an untreated fence post. Even treatment by just brushing alone, gave good performance when compared to the reference preservatives, Pentachlorophenol and creosote. Treatment of posts in this same Oregon test by cold soaking were considerably better than brush treatments, even at very low to low retentions of active ingredient.

In cold soaking tests installed in Tennessee, CuNap did not last quite as long as Penta. This is probably due to the CuNap being at half of the AWPA retention for that of typical fence post, while penta performed well at retention of 0.30 pcf, which is 75% of the average, specified by The American Wood Preservers Association Book of Standards. Both preservatives, PCP and CuNap were effective in extending the useful service life of both hardwood and softwood posts in the TN tests.

In the USDA-FS tests on fence posts, in the highest hazard/decay zone, only CuNap treated fence posts compared to PCP treated post with both preservatives lasting an average life of 42 years.

Overall, fence posts treated with CuNap have been performing well in controlled field tests over the last 60 years. Commercially produced CuNap fence post have been performing well for over 15 years. Given the overall minimum hazards associated with CuNap and the fact that it appears to have no negative effects on livestock exposed to the treated wood and no significant strength or mechanical property degradation to fence posts, it makes an excellent alternative treatment for posts.

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