Copper Naphthenate: An Effective Wood Pole and Crossarm Preservative

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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 and copper naphthenate preservative systems, the effect on wood treated with copper naphthenate or copper naphthenate wood preservative systems, a review of the long-term efficacy trials, typical plant handling characteristics of copper napthenate and its diluted solutions, and information relating to conversion of oilborne pressure treating plants to copper naphthenate.

Background and history

The use of copper naphthenate as an industrial biocide has been well established since the turn of the century (29). Copper naphthenate is basically the metallic salt of a metal ion reacted with naphthenic acids. Naphthenic acids are byproducts of petroleum, typically removed from crude petroleum 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, Rumania, Russia, and Central America. The naphthenic acids are typically alicyclic acids. They are broadly classified as acids of the formula CnH_2n-$2O_2$ having the typical formula in Figure 1.

Chemically speaking, these compounds are known as cupric cyclopentane carboxylates or cyclohexanecarboxylates. The physical and chemical characteristics of copper naphthenate and naphthenic acids have been described in detail (33) and their use in wood preservation discussed by Hartford et al. (23). 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 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, CuNap, Cunapsol, Cuprinol, and M-Gard. Of these, the most common name is Cuprinol, dating back to the Danish of over a century ago, meaning "copper in oil" (6). A review of the literature cites many applications for use, including field boxes, beehives, benches, flats, fenceposts, water tanks, canvas, burlap, ropes, nets, greenhouses, utility poles, crossarms, and wooden structures in ground contact and above ground contact (35). Copper naphthenate is known to control many decay fungi, molds,

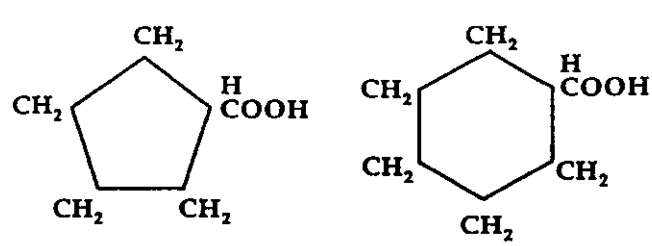

Figure 1. — *Chemical structures of typical alicyclic naphthenic acids.*

mildew, dry rot, certain marine growths, termites, wood parasites, and bacteria.

Copper naphthenate began its strong leap into the wood preservation business with the need to extend the useful volume of creosote available in the postwar effort. Due to a modification of operating practices of the steel mills, creosote, whose main source is the coking of coal 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 (29) 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 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 naphthenic acid used in the manufacture of copper naphthenate shall be 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 Standard 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.

These values in the current AWPA Standards vary slightly from the original proposal prepared by Minich and Goll, including an upper limitation of the naphthenic acid value to preclude the use of synthetic carboxylic acids in preparing copper carboxylate solutions. 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 molecular weights and acid numbers in excess of 250 and less than 350, have proven to be highly leachable and insufficient wood preservatives for ground contact. 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 an acid value number for copper naphthenate of approximately 200, the ratio of copper to copper naphthenate is approximately 1 to 10.

In the United States today, there are approximately 132 million standing utility poles. An excess of 95 percent of these standing utility poles are constructed of wooden materials. Data published by EPRI (1987) indicate that of these poles, approximately 65 percent are treated with penta, 17 percent are treated with creosote, and another 17 percent are treated with inorganic arsenicals. The trendline for these wood commodities indicates that poles treated with oilborne preservatives, although perceived as easier to climb than poles treated with water-based preservatives, maintain a steady market share. The use of inorganic arsenicals in wood poles and crossarms is a growing percentage (Micklewright, 1950-1991). There appears to be a drop in creosote usage and an increase in the inorganic arsenicals.

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 an RPAR position document and a settlement agreement between industry and the EPA. Although penta remains an extremely viable wood preservative, many people concerned over hexachlorobenzene and chlorinated dioxins have begun to specify and use 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 utility poles. Recent data, published by the Electrical Power Research Institute, however, indicate that TCLP testing on penta utility poles gave no positive response, indicating the penta-treated wood would not similarly be considered a hazardous waste. The increase in use of copper naphthenate-treated wood and an increasing amount of utility specifications, however, have shown that a gradual increase in copper naphthenate is occurring with expected values for pole purchases in 1992 to exceed 2 percent of the total market.

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 when the 8 percent concentrate is diluted with 8.3 parts fuel oil is shown in Table 1.

One of the principal reasons that copper naphthenate is gaining market acceptance and is being compared to other oilborne 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 typical acute toxicity profile of copper naphthenate concentrate is published in Table 2 (22,24,26,36).

Table 1. — *Properties of typical copper naphthenate solutions.*

	Concentrate	Ready-to-use concentrations
Percent copper	8	1
Percent solvent	20	90
Color	Dark green	Dark green
Freezes	No	No
Pour point (°F)	0	–25
Viscosity (cps at 75°F)	2240	38
Viscosity (cps at 180°F)	94	14
Flash point (°F)	180 (104)	170
Density (lb./gal.)	8.5	7.4

Efficacy of copper naphthenate

Copper naphthenate exhibits a wide range of efficacy toward most decay fungi (basidiomycetes), termites, and many other wood-destroying insects. Duncan (13-15) performed efficacy trials of copper naphthenate in soil block tests, comparing these to penta, coal tar creosote, and petroleum fractions. In addition to these data, reports for the AWPA Copper Naphthenate Task Force reviewed the efficacy of copper naphthenate against six decay fungi (white rot and brown rot) and data was reviewed by Morrell to determine effectiveness against copper-tolerant fungi (*Poria, Postia*). Overall performance of copper naphthenate in various petroleum solvents have indicated that both soil block and agar block techniques were applicable to this preservative system with excellent control over decay organisms tested in the 0.02 to 0.044 lb./ft.^{3} copper (as metal) range in southern yellow pine sapwood.

Long-term efficacy trials on 2 by 4s treated by dip, soak, brush-on, and pressure-treating methods have been evaluated by Davidson (11) and Gjovik and Gutzmer (20,21). These data, published in USDA Forest Service Technical Note FPL-02, "Comparison of Wood Preservatives in Stake Tests" (Table 3), are illustrated graphically in Figure 2. These data indicate that copper naphthenate 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, USDA Forest Service Publication FPL-01, "Comparison of Wood Preservatives in Post Tests," indicates that copper naphthenate-treated round stock gives excellent service life when compared to standard preservatives such as CCA, creosote, or penta in P9 Type A oils.

Review of the severity of the tests, including test sites at Madison, Wis., Gulfport, Miss., and

Table 2. — *Acute toxicity properties of copper napthenate (Perm-E8).*

Acute oral toxicity (LD_{50})	>5 g/kg
Acute dermal toxicity	>2020 mg/kg or >2 g/kg
Primary dermal irritiation	Slightly irritating to skin
Dermal sensitization	None
Primary eye irritation	Mildly irritating
Acute inhalation toxicity	>1.17 mg/L
EPA label class	Caution

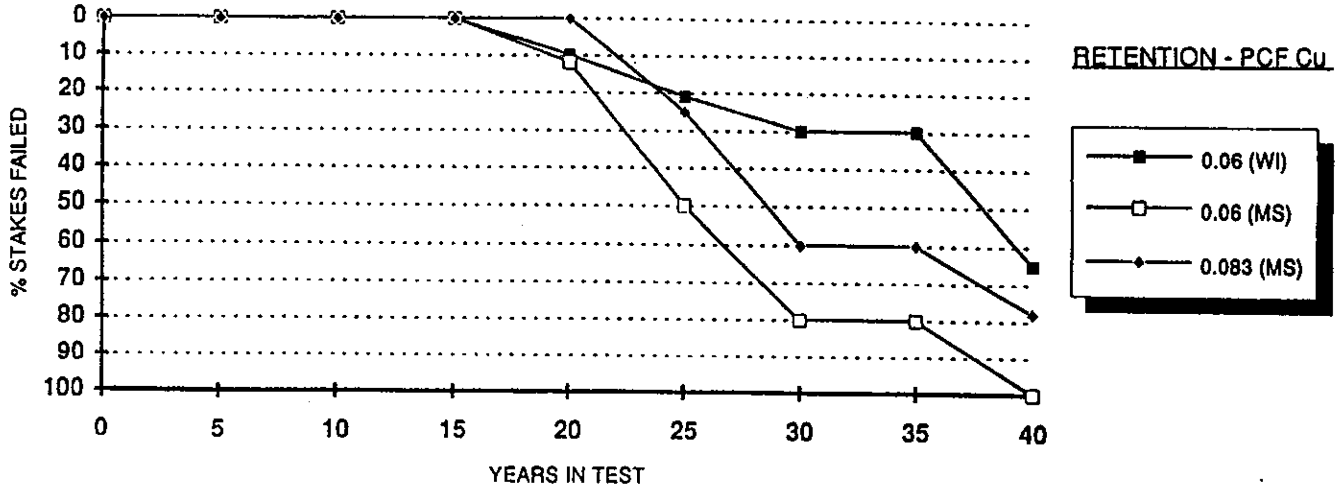

Figure 2. — *Comparison of copper naphthenate retention at Wisconsin and Mississippi stake test sites.*

Table 3. — *USDA tests of copper napthenate-treated southern yellow pine 2 by 4 stakes in ground contact.*

Copper	Average life span	Estimated life span
(pcf)	-------- (yr.) --------	
Mississippi (1942)		
None	2	
0.011	16	
0.030	22	
0.060	27	
0.083	8/10 (1981)[a]	
Wisconsin (1941)		
None	5	--
0.011	26	--
0.028	3/5[b]	40
0.060	5/8[b]	39
0.084	2/6[b]	49

[a] 8 removed, 2 left. Estimated average life span: 34 years.
[b] Removed for decay/total in test (1981). Solvent = No. 2 fuel oil.

Table 4. — *Proposed minimum retention levels of copper in wood commodities, using 0.75 percent copper in P9 oil (25).*

	Copper
	(pcf)
Lumber, plywood, timbers	
In ground contact or fresh water	0.075
Not in ground contact or fresh water	0.045
Piles for fresh water or land	0.090
Utility and building poles	0.033[a]
	0.060[b]
	0.075[c]
Posts	0.045

[a] for western redcedar.
[b] for poles <12 inches in diameter and in moderate service.
[c] for poles >12 inches in diameter or in severe service.

Dorman, Miss., indicate that severity of the test plot can alter the service life of wood products when placed in ground contact. However, by placing a standard control preservative into the test plot, the degree of severity of that test plot can be monitored, including the predictability of service life (Fig. 3). These data have been reviewed by Scheffer (1972) and Eslyn (17), including data on utility pole decay and growth temperature relationships of this decay, and by Scheffer in plotting average decay in North America by temperature humidity mapping (decay hazard map, Appendix B, AWPA Committee T-4, 1972). Hunt and Garratt (25) proposed levels of copper in copper naphthenate-treated wood commensurate with those in the current standard (Table 4).

In addition to these data, the post farm at Oregon State University continues to have excellent performance of brush-treated, soaked, and pressure-treated Douglas-fir posts after three decades of exposure (30). These data have also been published by Morrell, Scheffer, and Miller in the "Progress Report for the OSU Post Farm Test." Copper naphthenate is also a proven cellulosic fiber preservative. Data reviewed by Curwen (9) has shown that copper naphthenate has a high degree of permanence when used to preserve cellulosics and also has the ability to prevent mildew, rot, and decay from occurring in fiber substrates.

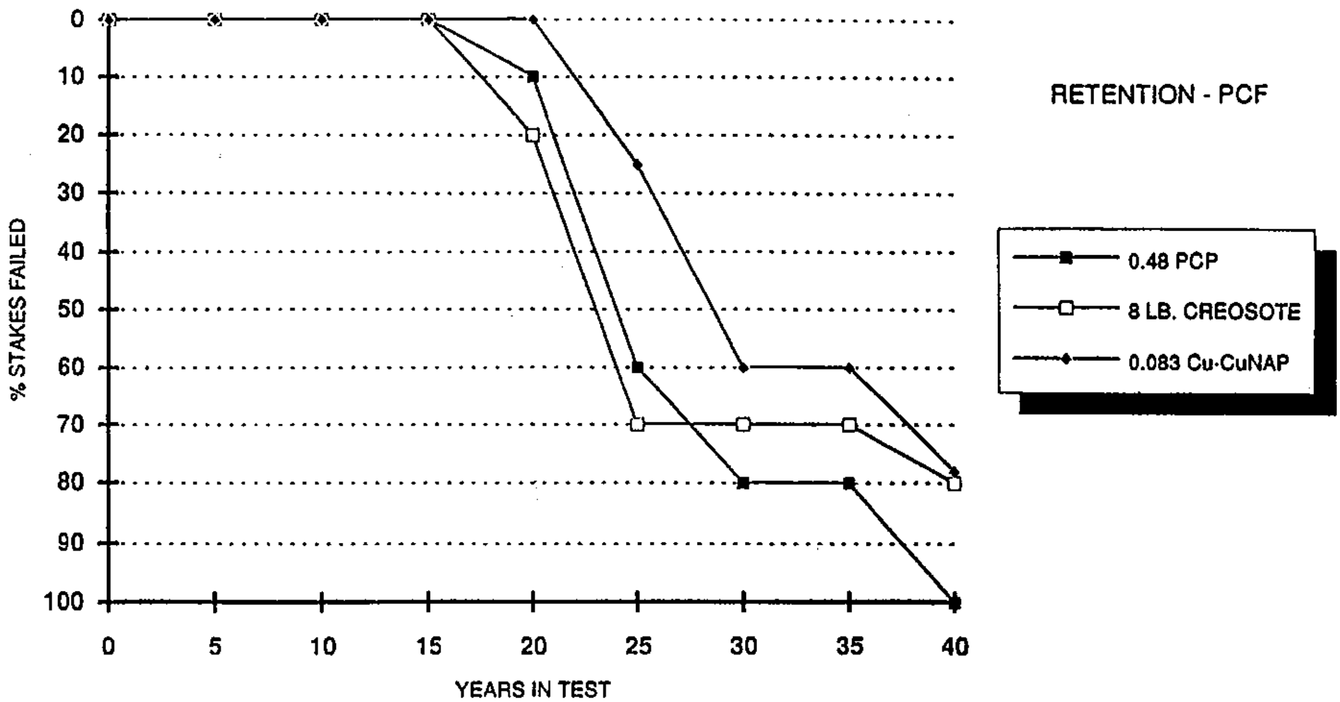

Figure 3. — *Comparison of wood preservatives at the USDA FPL Gulfport, Miss. stake test site.*

Table 5. — *AWPA Commodity C-4 copper naphthenate retention comparison.*

	Southern yellow pine	Douglas-fir
	- - - - - - - - - - (pcf) - - - - - - - - - -	
Penta	0.38, 0.43, 0.45	0.45, 0.60
Creosote	6, 7.5, 9	9, 12
Copper (CuNap)	0.06, 0.08, 0.13	0.075, 0.095, 0.15

Table 6. — *Leachability of oilborne wood preservative systems.*[a]

Preservative	Amount pcf	Percent leached
Copper naphthenate	0.134	0.49
Penta	0.346	11.40

[a] AWPA Standard Method M-11 was used with toluene solutions.

Copper naphthenate-treated wood

Copper naphthenate is a standard preservative listed in AWPA Standard P-8. This organometallic preservative system is freely soluble in various organic solvents, including mineral spirits, fuel oil, pole treating oil, and creosote-petroleum mixtures. Currently, the AWPA lists copper naphthenate in over a dozen commodity standards (Table 5). These standards, approved by either the preservatives committees or the treatments committees, indicate that the purchaser and user of copper naphthenate-treated wood commodities can be assured of the expected service life of commodities when properly treated in accordance with these standards.

When copper naphthenate is evaluated for treating utility poles and crossarms, four specific evaluation parameters should always be reviewed: 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.

Leachability

Standard wooden blocks, when treated with copper naphthenate and penta in a similar P9 oil, were tested in accordance to AWPA Standard M-11. Results of these tests are shown in Table 6. Results of this test indicate that the slight leachability of both preservative systems 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, which may be both chemical and physical, including copper lignin bond formation.

Table 7. — *Conductivity of clear southern yellow pine impregnated with ground contact loadings of two wood preservatives.*

Preservative	Kilo ohms
None	275
Copper naphthenate	315
CCA salt formulations	35

Table 8. — *Gaff penetration (1/2 in.) test of utility poles treated with three preservatives.*

	Southern yellow pine		Douglas-fir	
	Average	Range	Average	Range
	- - - - - - - - (lb.) - - - - - - - -			
Copper naphthenate/oil	230	137-317	204	109-301
Penta/oil	298	242-340	314	190-241
Untreated	358	310-404	317	248-397
CCA-C	405	324-488	357	302-397

Conductivity

When evaluating preservatives and preservative systems for both wooden utility poles and crossarms, conductivity of the treated wood is of utmost importance. Reduction in the conductivity of the treated wood may be achieved by simple reduction of moisture content of the treated wood commodity by displacing these with nonpolar organic solvents or by reducing the overall conductivity of the wood specimen. Review of conductivity testing includes data from Katz and Miller (AWPA Proceedings, 1963). This data indicates that either resistivity or conductivity of treated wood can greatly be affected by grain orientation, moisture content of the piece, temperature, and preservative system employed. Test results published by Asmus et al. (6) have shown that there is no increased conductivity of the treated wood utility pole or crossarm when treated with copper naphthenate in an oilborne preservative system. Results are published in Table 7.

Hardness/gaff penetration

When specifying and 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 very important. Hardness of the pole relates to surface hardness as well as the ability to flex under torsion. Many delivery firms typically roll utility poles off the back of either gondolas or flatbed trucks

Table 9. — *Corrosivity of copper naphthenate and penta treating solutions.*[a]

	Corrosion rate of mild steel	
P9A solvent	1% copper naphthenate	7% penta
	- - - - - - (mils/yr.) - - - - - -	
No. 2 fuel oil	<0.5	2.1
Medium aromatic treating oil	<0.5	23.8

[a] Refluxed at 230° to 260°F for 2 weeks in the presence of southern yellow pine wood and excess water.

at the destination site, rather than picking these up and moving them with knuckle-boom loaders. 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.

When evaluating the gaff penetration of copper naphthenate-treated wood in species such as southern yellow pine or Douglas-fir as compared to standard preservative systems, no significant difference was found in gaff penetration between it and penta in similar P9 Type A oils. It is a widely recognized fact that the oilborne petroleum solutions generally give a certain amount of lubrication for gaff penetration and an ease of penetration to the wood surface. Results of the gaff penetration tests by Pierce, conducted at the testing ground of Arizona Public Service Company, Phoenix, Ariz., are shown in Table 8 (31).

Corrosivity

The corrosivity of the free oil and copper naphthenate in treated wood offers no significant increase compared to untreated wood or preservative 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 have indicated no significant corrosivity from the treating solution and/or the treated wood specimens (Table 9).

Treating plant operating considerations

In evaluations of a new preservative system, the properties of the treated wood are important, but the operating characteristics of that preservative system are also important and should be considered when incorporating the system into an existing treating plant. Currently in the United States, there are 31 operating treating plants using copper naphthenate in various petroleum oils. It is estimated that over 1.5 million pounds of copper naphthenate concentrate are being sold into the wood preservation market into the United States as of this date. This amount of material, based on an 8 percent metallic copper content, indicates that approximately 2 million cubic feet of posts, poles, and lumber are being treated annually. Typical oilborne preservative plants can be converted over to use copper naphthenate with relative ease. Key issues in operating plants are:

- the tendency for preservatives to be compatible with available treating oils or diluents
- the tendency for preservatives and preservative systems to form emulsions and the resulting separation of these emulsions to allow wastewater discharge
- the propensity of a preservative or preservative system to form sludge within this treating cylinder, treating solution, or on the surface of wood
- typical items necessary to convert an existing operating plant.

Emulsion formation

Copper naphthenate solutions, produced from copper naphthenate concentrate and fuel oil, can form stable emulsions, especially when the emulsions contain wood extractives, wood acids, and wood sugars. These wood components tend to stabilize the emulsions by acting as either thixotropes or surfactants. Investigations into the tendency of copper naphthenate solutions have been well discussed by Freeman (18) and Accampo (4).

Two single factors play the greatest role in forming emulsions in copper naphthenate treating plants and treating equipment. In every single case investigated where emulsions have formed, insolubles were present in the wood treating solution. This would indicate that the tendency to form emulsions can be greatly reduced by incorporating filtration equipment into the treating plant equipment and filling lines prior to going into either the Boulton tank or the pressure treating cylinder. In fact, commercial treating plants of large scale today use multiple canister filters or multiple bag filters to remove solids from solutions. The incorporation of a filtration unit into a commercial treating plant reduces the amount of emulsions that form and also reduces surface solids deposited onto wood utility poles.

Sludging

Sludging of copper naphthenate has been discussed in various documents such as Wood Treating Chemicals' documents CN-1400 and CN-1500. These documents indicate that the work done by Accampo (4) can be the result of emulsion formation and heating, which would tend to produce sludge within work tanks as well as treating equipment and on wood surfaces. When emulsions form in work tanks, standard industry practice is that the resulting water be driven off with heat. In copper naphthenate treating systems, if the water content exceeds 1 to 2 percent, elevation of the temperature of the work tank solution can cause the formation of black copper oxide. The black copper oxide can then form a "seed;" the resulting emulsion can either grow in size or can 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. Again, the secret to keeping sludge from forming in copper naphthenate treating equipment is to reduce the water content appreciably, continuously filter the solution, and prevent debris and trash from entering the wood treating equipment.

Plant conversion

Plant conversion is very simple when converting from either penta or creosote to copper naphthenate. 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 would have discharge going to a POTW or water discharge through NPDES permitting. Experience has shown that use of two work tanks, which would allow quiescent settling of solution after agitation and after removal of debris and water, greatly increases the operating efficiency of the facility and produces the cleanest treated wood. Having two work tanks requires keeping dual inventories of treating solution. A plant may also convert, using simple conversion from either a penta plant or a creosote plant, by simply converting the tanks, removing formerly used preservatives, and incorporating a filtration system into the material flow as well as a sludge dewatering system (Figs. 4 and 5).

Summary

Copper naphthenate, in field trials in 3/4-inch stakes, 2 by 4 stakes, posts, and pole-size sections, has proven its effectiveness as a ground-contact wood preservative. Copper naphthenate imposes no significant detrimental properties to treated wood as long as the treatment is in accordance

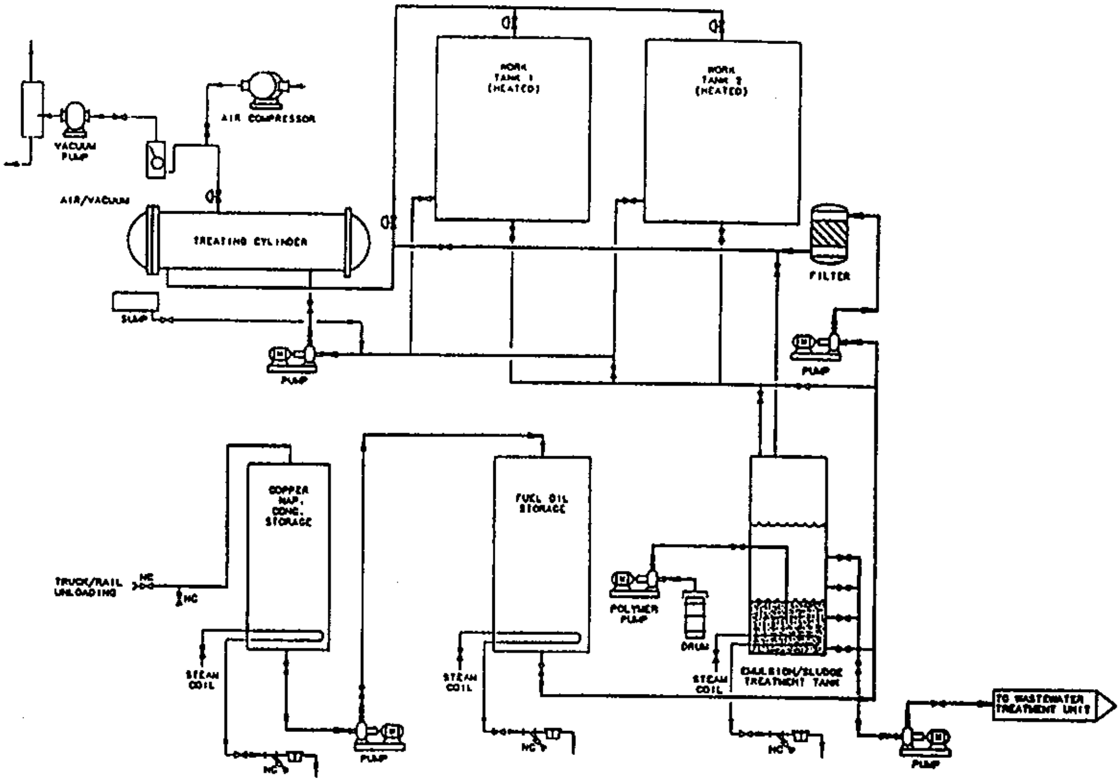

Figure 4. — *Copper naphthenate treating plant, version 1.*

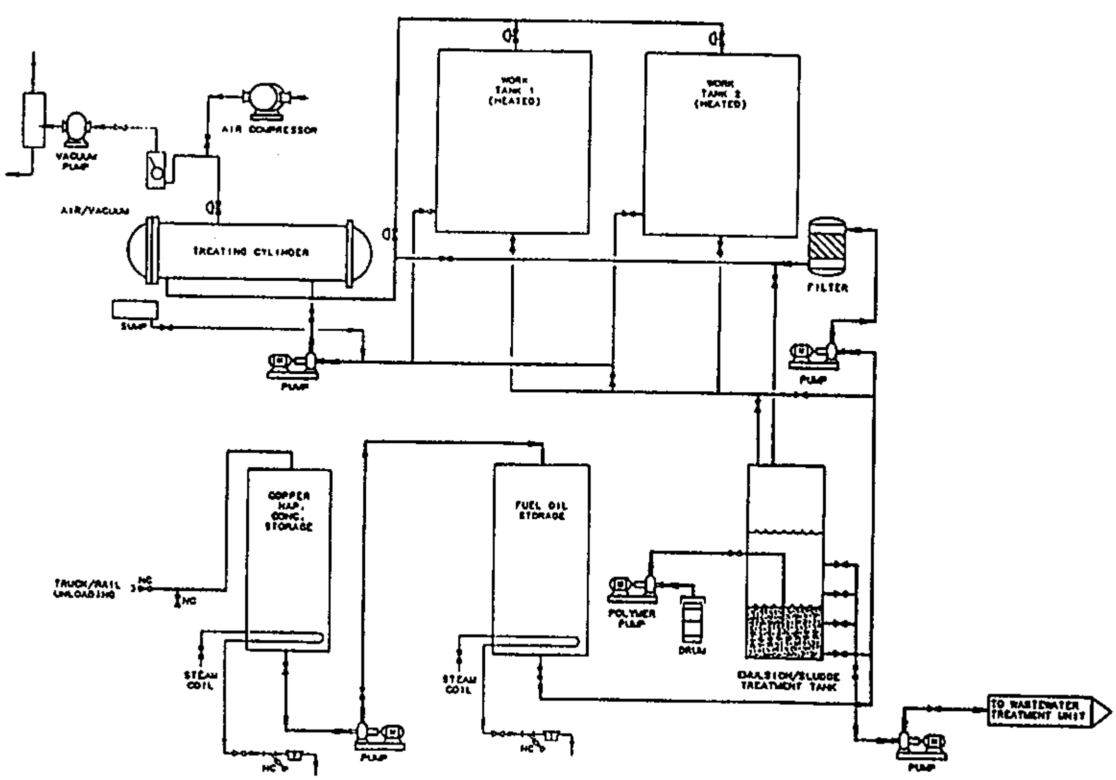

Figure 5. — *Copper naphthenate treating plant, version 2.*

with AWPA guidelines and in accordance with the commodity standards. Copper naphthenate is currently not considered a restricted use pesticide, and wastes containing copper naphthenate are currently not listed as hazardous. Certain wastes that are generated from a copper naphthenate treating plant may be characterized as characteristic hazardous waste, and disposal should only be undertaken after extensive product testing. Copper naphthenate offers a broad spectrum efficacy against termites and decay organisms, while offering a minimal worker exposure to operators handling both the chemical and the resulting treated wood. Plant conversion from an oilborne system can take place simply. Overall, copper naphthenate can be used as an effective wood pole and wood crossarm preservative, with service life expected to be equal to or exceeding typical creosote or penta treatments.

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