COMPARATIVE PERFORMANCE OF PENTACHLOROPHENOL AND COPPER NAPHTHENATE IN A LONG TERM FIELD STAKE TEST

By

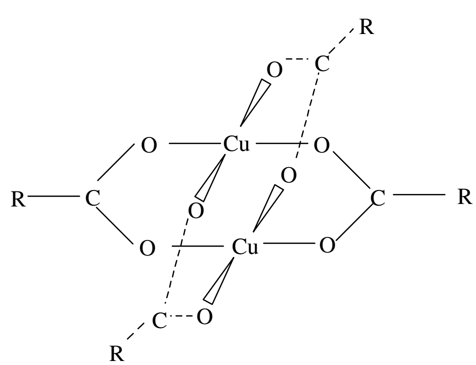
Darrel Nicholas & Michael Freeman

ABSTRACT

In this study the performance of copper naphthenate (Cu-Nap) and pentachlorophenol (Penta) treated pine stakes against decay and termite attack were compared at two test sites in Mississippi. Four different petroleum oils meeting AWPA Standard P9-A were used as carriers for these wood preservatives. After ten years exposure, the efficacy of Cu-Nap at a retention level of 0.05 pcf Cu was equivalent or slightly better than Penta at a retention level of 0.40 pcf. The type of carrier oil had an effect on the performance, but this was variable for both the type of preservative and test site. In comparing the two test sites, the performance of both preservatives was consistently better at the Dorman Lake test site. Wood treated with the oil carriers alone performed reasonably well against both wood decay fungi and termites, but the activity decreased rapidly after about six years exposure. Like the preservatives, the performance of the oils was consistently better at the Dorman Lake test site.

INTRODUCTION

Cu-Nap was developed in Denmark in 1911 and has been used as a preservative for a variety of wood and textile products over the years. Cu-Nap is generally prepared by reacting copper or copper salts with naphthenic acid. Or with sodium naphthenate. The three commercial methods of producing copper naphthenate are direct metal, melt (fusion), or double decomposition methods. Naphthenic acid is a by-product of petroleum refining and contains a mixture of monocarboxylic acids which contain cyclopentane and cyclohexane groups with an acid number ranging from 150 to 300. The proposed chemical structure for Cu-Nap is (Nicholas et. al., 1996):



The use of Cu-Nap as a commercial wood preservative in the United States has been limited, but recent environmental concerns with CCA, Penta, and Creosote has stimulated its use in utility poles and other wood products. In the mid-1980's, the Electrical Power Research Institute (EPRI) reviewed their own use of oil-borne preservatives within their member systems and determined that they should investigate possible safer and more environmentally benign preservatives and funded this research project to investigate alternatives to pentachlorophenol. Since there was limited data available on the performance of Cu-Nap treated wood exposed to soil contact, this study[1] was initiated. The objective of this study was to evaluate the comparative performance of Cu-Nap and Penta formulated with several different commercial carrier oils.

EXPERIMENTAL

Preservatives

Technical grade Penta (>96 % active ingredient) and Cu-Nap (8% Copper as metal) were obtained from various manufacturers within the United States.

Carrier Oils

A total of four carrier oils that met AWPA Standard P9-A were selected for this study. These were:

1. California Shell Oil from Shell Chemical Company
2. Base Oil L from Lillyblad Petroleum Inc.
3. Ashland Oil from Ashland Petroleum Company
4. #2 Diesel Oil + KB3 + B11 (KB3 & B11 from Eastman Chemical Products Company).

The physical properties of these oils are shown in Table 1. Oils 1-3 were diluted with toluene (20% oil and 80% toluene) before using them to treat the fungus cellar and field stake test specimens. The treating solution for Oil 4 was formulated with 17% diesel + 2% B11 + 1% KB3 + 80% toluene before treatment of these test specimens.

Soil Block Test

This test was carried out in accordance with AWPA Standard M10-77, using kiln-dried southern yellow pine (SYP)(*Pinus sp.*) sapwood. The oils were diluted with toluene to provide appropriate concentrations. The treated cubes were exposed to a brown-rot fungus (*Gloeophyllum trabeum*) and a white-rot fungus (*Trametes versicolor*).

Fungus Cellar Test

The test specimens measuring 0.5 x 0.75 x 10 inches long were prepared from kiln-dried SYP sapwood. A total of five replicate stakes were treated with each of the four different levels of Penta (ranging from 0.09 to 0.80 pcf) and Cu-Nap (ranging from 0.010 to 0.090 pcf copper metal) using the four carrier oils listed above. After allowing the toluene to evaporate, the stakes

1 This research was funded by the Electrical Power Research Institute under Contract No. WO2797-01.

were positioned vertically in a soil bed maintained at a moisture content of approximately 100% of the soil water holding capacity. The fungus cellar room was maintained at a temperature of approximately 80°F with a humidity of 90%. The stakes were removed at three month intervals and evaluated for decay, using a 10 to 0 rating scale with 10 denoting sound and 0 denoting failure.

Field Stake Test

The field stake test was performed in accordance with AWPA Standard E 7, using 1 x 2 x 22 inch southern pine sapwood stakes. A total of 20 replicate stakes were treated with each of the field stake formulations listed in Table 2.1. After air drying, a 4-inch section was cut from the end of each stake and reserved for possible depletion analysis.

The field stakes were installed at the following sites on the dates indicated:

Dorman Lake, MS	May 2, 1988
Saucier, MS	April 22, 1988

These field stakes were pulled and evaluated for decay and termite damage annually, using the AWPA E7-93 rating system where 10 denotes sound and 0 denotes failure.

Biocide Depletion from Field Stakes

The field stake depletion test was carried out with 1 ½-inch square by 22-inch long southern pine sapwood stakes. Before exposure in the test plot, these stakes were treated with Penta and Cu-Nap formulations using the oil carriers listed above. After air drying, a 4-inch section was cut from the end of each stake and reserved for the initial retention analysis. These 18-inch long stakes were then installed at the Saucier test plot by inserting them vertically into the ground to a depth of 14 inches. A total of 5 stakes were installed for each retention level and these were removed after two years. After cleaning, a section was removed from the stakes at two locations-1-inch below the top of the stake and at a location slightly below the ground line. These wafers were ground in a Wiley mill and analyzed on an Asoma XRF unit.

RESULTS AND DISCUSSION

The importance of carrier oil properties on the performance of organic wood preservatives is well known and serves as the basis for the AWPA Standard P9-A. In this standard physical properties such as viscosity, specific gravity, penta solvency and distillation range of the carrier oils must meet specified criteria in order to be acceptable because they influence the plant operation and performance of the treated wood product. With regard to performance, the major factor is the effect of the carrier oil on depletion rate of the biocide. (Arsenault, 1973). Another possible factor that may influence the performance of wood preservative systems is the inherent toxicity of the carrier oils to wood decay fungi. The data in Figure 1, which includes the oils used in this study as well as others, clearly shows that some of the oils are toxic to wood decay fungi. However, it should be pointed out that this data is based on a pure culture basidiomycete test which does not necessarily predict the performance of treated wood in service. Nevertheless, the data in Figures 2 and 3 demonstrate that the carrier oils provide some degree of protection to wood exposed in soil contact. However, the performance is limited and most of the oil treated wood is failing after about nine years exposure.

An accelerated fungus cellar test was also carried out in this study and a summary of the results is shown in Table 2 and Figure 4. It is apparent from this figure that Cu-Nap formulations with CA Shell, Base Oil, and Diesel/KB3/B11 performed considerably better than any of the penta formulations.

Results for the field stake test after 11 years exposure at two test sites in Mississippi are presented in Table 3. This data clearly shows that both penta and Cu-Nap are performing very well against both decay fungi and termite attack. Comparative data for Cu-Nap at a copper retention level of 0.05 pcf and penta at a retention level of 0.4 pcf at both test sites are shown in Figures 5 and 6. From this data it is apparent that overall the performance of Cu-Nap is somewhat better than that of penta. The only exception to this is for the diesel/KB3/B11 formulation the performance of Cu-Nap is slightly worse than penta. Consequently, on the basis of this data it can be concluded that wood treated at a copper retention level of 0.05 pcf will perform satisfactorily.

In reviewing the data in Figures 5 and 6 it is of interest to note that the performance of both penta and Cu-Nap treated wood is slightly lower at the Saucier test site. There are two possible explanations for this difference.

First, the average temperature and rainfall at the Saucier site is somewhat greater than that experienced at the Dorman test site. Secondly, the soil types at the two test sites are quite different. The soil at Dorman is high in clay content and is classified as silty clay loam, whereas the soil at Saucier is characterized as a loamy sand type soil. These differences may possibly result in different oil carrier and biocide depletion rates. The fact that the Saucier test site has higher rainfall and soil with good drainage properties may possibly result in higher biocide and carrier oil depletion rates. This possibility, at least for the carrier oil, is supported by the data for stakes treated with carrier oils alone. That is to say, the stakes treated with the oils have somewhat higher decay ratings at the Dorman test site than at the Saucier test site.

In addition to the broad spectrum efficacy of biocides against microorganisms and insects, the depletion rate of biocides plays a major role in the performance of treated wood. Hence, a biocide depletion analysis was included in this study and the results are presented in Table 4. In general, the biocide loss from the above ground section of these field stakes is lower than the below ground section. Furthermore, on a percentage basis the loss of penta is somewhat greater than that for Cu-Nap. However, it should be emphasized that due to the relatively small sample size this data does not represent statistically significant differences. Nevertheless, this data does suggest that the depletion rate of Cu-Nap compares favorably to that of penta.

REFERENCES

Nicholas, D.D., W.P. Henry, and R.C. Vasishth. 1996. The role of copper in wood preservation. In: Handbook of Copper Compounds and Applications. W. Richardson (ed.). Marcel Dekker, Inc.

Arsenault, R.D. 1973. Factors influencing the effectiveness of preservative systems. In: Wood deterioration and its prevention by preservative treatment. (D.D. Nicholas, ed.) Vol. II, pp. 121-278.

TABLE 1. PHYSICAL PROPERTIES OF CARRIER (P9-A) OILS					
PROPERTY		**CALIFORNIA SHELL**	**BASE OIL L**	**ASHLAND**	**#2 DIESEL (90%)/ KB3 (10%)**
Specific Gravity @ 72°F		.9548	.9740	.9452	.9124
Viscosity SUS @ 100°F (ASTM D-88)	Whole Oil	46	37	35	35
	Fraction above 500°F	53	40	37	--
	Bottom 25%	--	67	47	--
Viscosity SUS @ 100°F with Penta	0% a.i.	49.4	39.7	37.6	35.5
	7% a.i.	54.1	40.8	37.5	36.8
Interfacial Surface Tension Dynes/cm (ASTM D1871) Fraction above 500°F		24.3	23.5	24.5	--
Penta Solvency-AWPA P-5(%)	Whole Oil	15	18.4	8.15	15
	Fraction above 500°F	16	10	8	--
	Bottom 25%	14.4	12.5	9.2	--
Volume Distilled (ASTM D-86)	Distillation Temperature of Various Fractions				
	Initial Boiling Point	464°F	480°F	470°F	410°F
	10%	492°F	515°F	500°F	456°F
	20%	516°F	532°F	520°F	480°F
	30%	530°F	545°F	532°F	495°F
	40%	548°F	560°F	545°F	514°F
	50%	575°F	575°F	558°F	530°F
	60%	604°F	595°F	575°F	550°F
	70%	637°F	610°F	595°F	568°F
	75%	650°F	625°F	604°F	577°F
	80%	666°F	640°F	618°F	590°F
	90%	673°F	670°F	648°F	623°F
% Above 500°F		86	95	90	68

le 2. Comparative Decay Ratings for Stakes Treated with Cu Nap and Penta in Four Different Oils and Exposed in a Fungus Ce

	Decay Ratings							
	Ashland		CA Shell		Base Oil L		Diesel/KB3/B11	
xposure ime (mo)	Cu Nap. Retn (pcf) 0.048	Penta Retn (pcf) 0.372	Cu Nap. Retn (pcf) 0.046	Penta Retn (pcf) 0.398	Cu Nap. Retn (pcf) 0.052	Penta Retn (pcf) 0.390	Cu Nap. Retn (pcf) 0.057	Penta Retn (pcf) 0.439
3	10	9.7	10	10	10	10	10	10
6	10	9.9	10	10	9.7	9.8	7.2	7.4
9	9.9	9.7	9.9	9.0	9.9	9.2	4.6	3.7
12	2.9	2.3	8.4	4.0	5.5	3.1	4.0	3.6
15	2.8	2.3	8.0	3.6	5.2	2.2	4.0	3.4
18	2.9	2.2	8.1	3.6	5.4	2.2	4.0	3.0
21	2.5	2.0	7.8	3.2	5.4	1.8	3.4	1.8
24	2.5	1.8	6.6	2.8	5.0	1.8	2.4	1.4

verage Decay and Termite Ratings for Field Stakes Located at Saucier and Dorman After 11-Years Exposure.

	Retention	Average Decay and Termite Ratings at Saucier and Dorman with Different Carrier Oils														
t	(pcf)	Ashland				CA Shell				Base Oil				Diesel/KB3/		
		Dorman		Saucier		Dorman		Saucier		Dorman		Saucier		Dorman		S
		Decay	Ter-mite	Decay	Ter-mite	Decay	Ter-mite	Decay	Ter-mite	Decay	Ter-mite	Decay	Ter-mite	Decay	Ter-mite	Decay
	0.025[1]	9.1	9.6	7.9	8.2	9.9	10	9.7	9.9	8.6	8.8	8.2	8.2	8.2	8.4	5.3
	0.050	9.7	9.9	9.0	8.6	9.7	9.9	9.6	9.6	9.2	9.7	8.2	8.6	9.0	9.3	7.3
	0.100	9.7	10	9.5	9.2	9.9	9.9	9.8	9.9	10	10	9.8	9.6	9.7	9.9	9.2
	0.20	8.2	8.3	8.1	7.7	8.2	8.3	6.6	6.9	8.0	8.3	7.7	7.4	7.5	8.0	6.9
	0.40	8.9	9.1	8.7	8.6	9.3	9.7	7.8	7.7	8.7	8.8	8.6	8.3	8.4	8.3	7.6
	0.80	9.7	9.8	9.8	9.6	8.9	9.3	8.5	8.6	9.7	9.8	9.5	8.9	9.0	9.2	8.5
	0.00	2.6	5.3	2.7	2.0	7.8	8.7	3.4	3.6	4.4	7.4	2.4	3.0	4.1	7.6	1.6
		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Copper

Table 4. Average Percent Depletion of Cu Nap and Penta from Above and Below Ground sections of 1 ½-inch square stakes Treated with several Different Carrier oils, and exposed at Saucier for 2-years.

Carrier Oil	Preservative Initial retn. (pcf)	Average Percent Loss After 2-Years Exposure[1]	
		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

[1]Cu Nap retentions and depletion is based on Cu content.

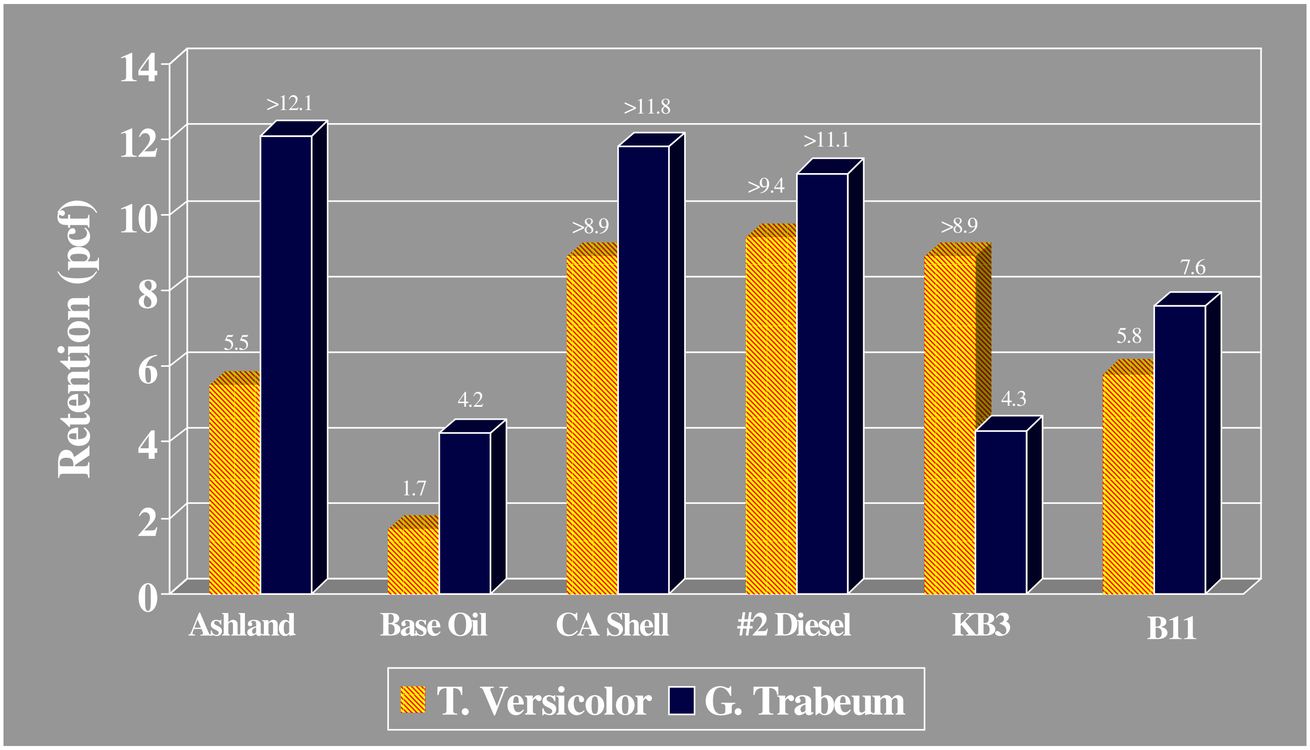


Figure 1. Approximate Toxic Threshold Values (pcf) of Several Oils Exposed to Fungi in a Soil-Block Test

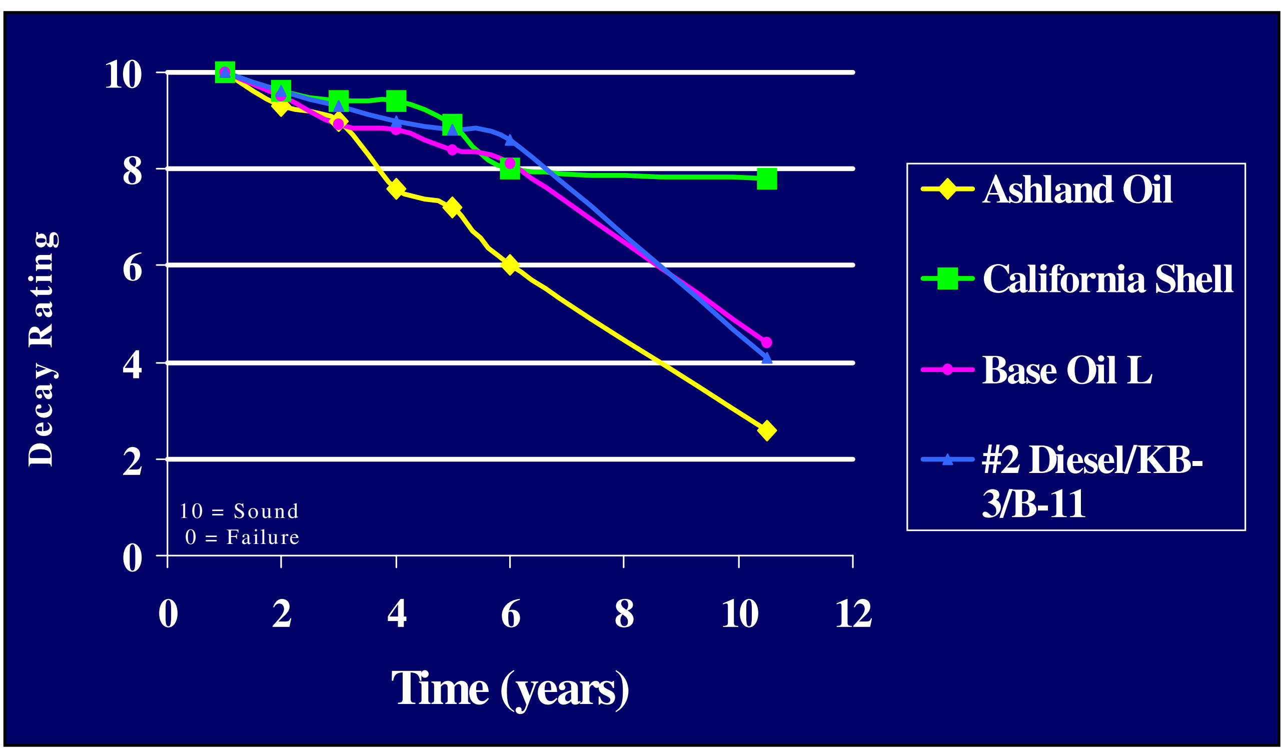


Figure 2. Average Decay Rating for Stakes Treated with Carrier Oils/Toluene (20%/80%) After Exposure at Dorman

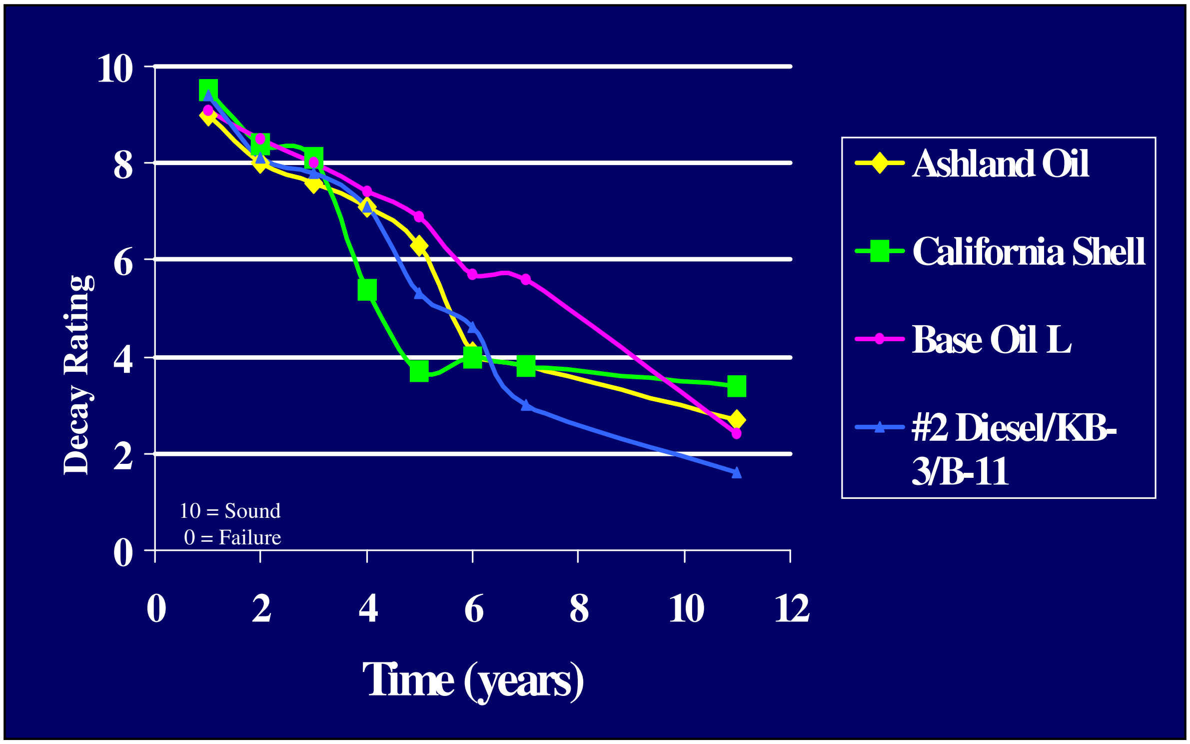


Figure 3. Average Decay Rating for Stakes Treated with Carrier Oils/Toluene (20%/80%) After Exposure at Saucier

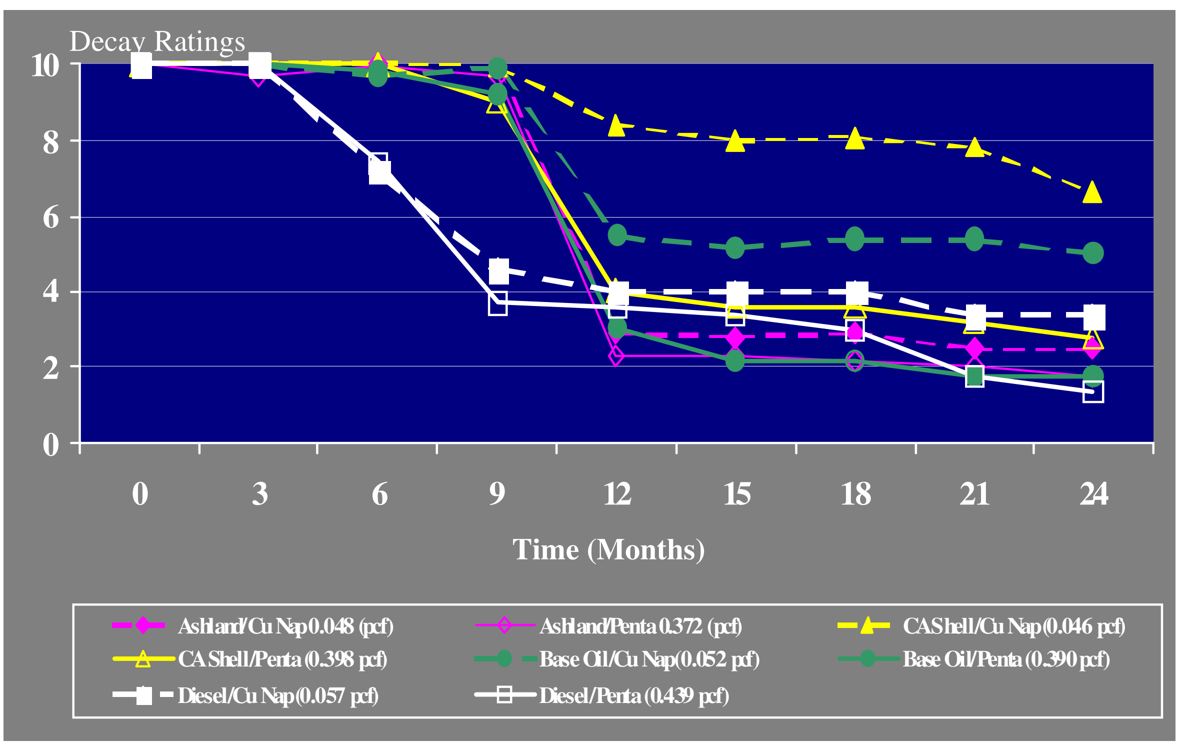


Figure 4. Comparative Decay Ratings for Stakes Treated with Cu Nap and Penta in Four Different Oils and Exposed in a Fungus Cellar

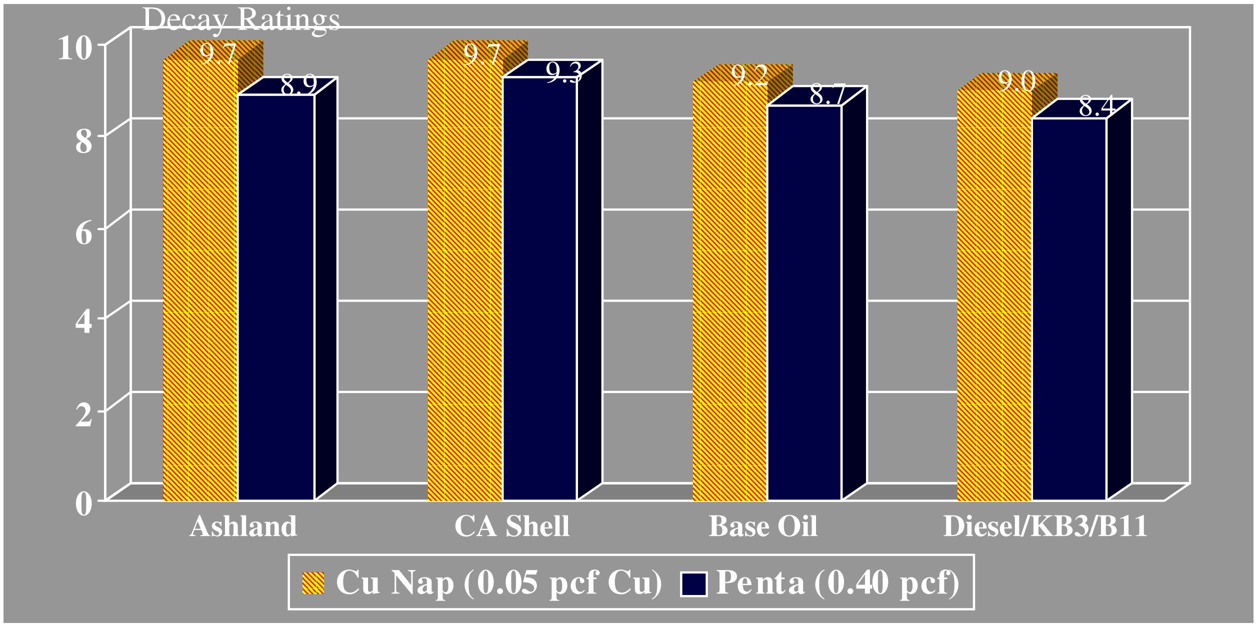


Figure 5. Comparative Decay Ratings for Cu Nap and Penta Treated Stakes Using Several Different Carrier Oils and Exposed at Dorman for 11-Years

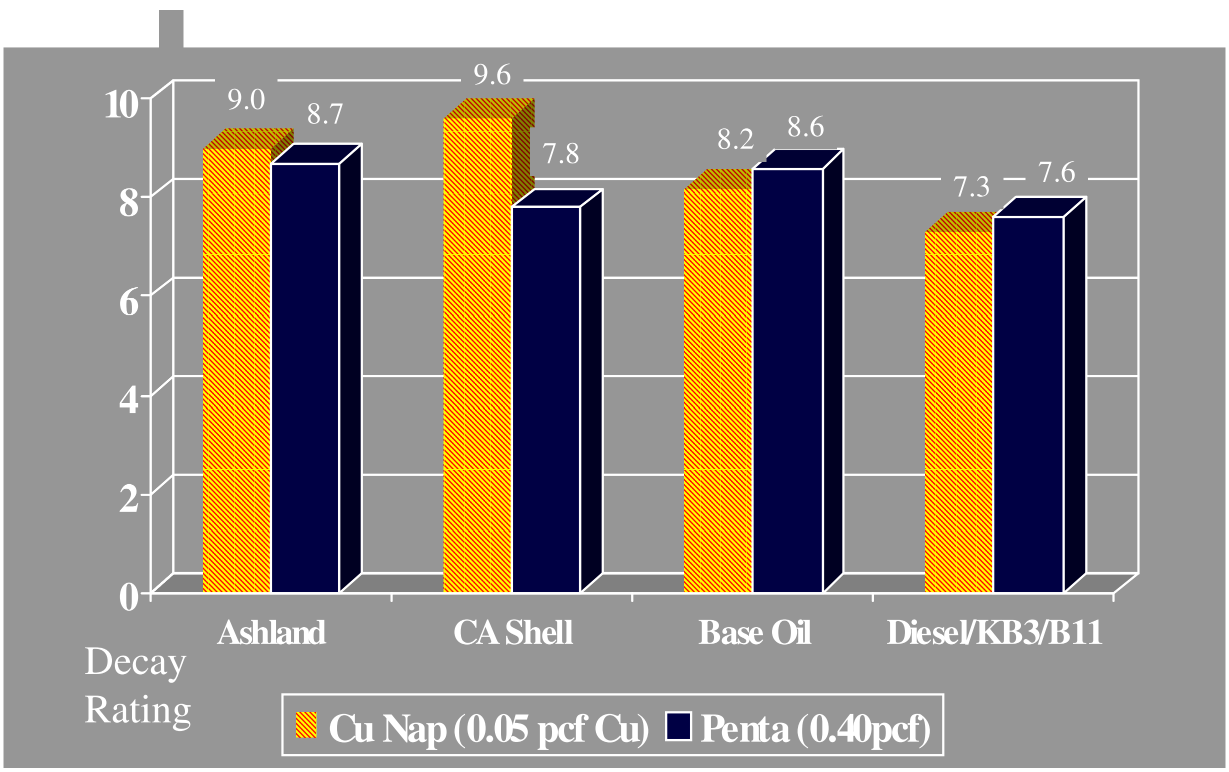


Figure 6. Comparative Decay Ratings for Cu Nap and Penta Treated Stakes Using Several Different Carrier Oils and Exposed at Saucier for 11-Years