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Performance of Zinc-Based Systems

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Abstract: Zinc naphthenate and its analogs were investigated as potential ground contact preservatives in field stake tests. A water-dispersible formulation, a solvent-borne formulation, and an oilborne system were investigated. Performance of the water-dispersible and solvent-borne systems was poor in ground contact. However, when carried in heavy oil, performance was markedly improved and was comparable to a similar copper naphthenate system. The replacement of some copper by zinc in naphthenic systems shows promise but requires additional study.

Keywords: zinc naphthenate, water-dispersible, oilborne, insecticides, water repellents, neodecanoate, LOSP

Introduction: For about two decades, metal carboxylate systems have been investigated as wood preservatives. Predominate among these systems has been copper naphthenate. Numerous papers have shown it to be an efficacious ground contact system (Merichem 2004, Barnes *et al.* 2003). Less information is available for zinc naphthenate (ZN), an analogous system. Barnes (1986) reported on the treatment of log home logs with the zinc system. ZN yields a colorless treatment, an obvious advantage over copper naphthenate. Subsequently, ZN was marketed for above-ground applications. Zinc-based systems are also attractive because they are cheaper than copper naphthenate. Additionally, there is less environmental concern with zinc than with other heavy metals. Previous work has shown wood treated with water-dispersible formulations of zinc naphthenate or copper naphthenate to be no more corrosive to metals than untreated wood (Barnes, *et al.* 1984). This paper reports our results with ground contact testing of ZN systems. The objectives of this research were to determine how zinc naphthenate systems would perform in ground contact, to ascertain the impact of additives on performance, to determine performance differences due to the carrier system, and to compare the performance of zinc systems to similar ones based on copper.

Methods and Materials

End-matched southern pine (*Pinus* spp.) stakes measuring 19- x 19-mm (0.75- x 0.75-in) in cross section x 457-mm (18-in) long were pressure treated with ZN solutions using a full-cell treating cycle. The cycle consisted of a full intensity vacuum (-88 kPa = 28 in Hg) for 30 minutes followed by a one hour pressure cycle at 1035 kPa (150 psig). Retention was varied by varying treating solution strength. Retention was calculated by weight gain. Four different systems were evaluated. The first was a water-dispersible formulation diluted with water. The second formulation was an oilborne formulation diluted with toluene to make a light organic solvent (LOSP) preservative system. The same oilborne formulation was also diluted with an AWWA P9 Type A oil to yield a heavy oil system (AWPA 2003). The oil carrier was a one to three mixture of Base Oil L to toluene which yielded an oil retention of 96-128 kg/m³ (6-8 pcf), an oil retention range commonly found with oilborne preservative systems such as pentachlorophenol. An LOSP zinc neodecanoate system was also evaluated. Ten replicate stakes per combination of preservative formulation, carrier system, and retention were treated for evaluation.

To test the effect of various additives on performance, additional stakes were treated with insecticide added to water-dispersible (WD) ZN to see if the addition would improve the performance against termites. For one set of stakes, chlorpyrifos [Dursban[®]-(O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate] at 0.01% and 0.1% (w/w) was added to the treating solution prior to treatment. In a second stake test, permethrin [Pounce[®]-(3-phenoxybenzyl(1RS)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] at 0.2% (w/w) was added to the treating solution. An additional set of stakes were treated with a commercial water repellent (approximately 1% w/w) added to ZN carried in water, toluene, or AWWA P9 Type A oil to see if the decay resistance of wood was improved.

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After treatment, end-matched stakes were placed in ground contact in our Dorman Lake test site (AWPA Deterioration Zone 4) and our Saucier, MS test site (AWPA Deterioration Zone 5). Stakes were evaluated annually using the 10-point rating scale (10 = no deterioration, 0 = complete failure) given in the AWPA E7 standard (AWPA 2003). For purposes of this paper, only the data from our Dorman Lake test site will be reported as the results from the Saucier site were very similar. The Dorman Lake site is located on the Starr Memorial Forest, Oktibbeha County, 10 miles south of Starkville, MS. The soil is characterized as acidic (pH = 4.8) heavy clay (Falkner) on a poorly drained site. This site is known to have copper-tolerant fungi and is very active for decay and termites. A detailed description can be found in the literature (Schultz *et al.* 2002).

Results and Discussion

Results are presented in the form of dose-response curves with a logarithm fit of the Index of Condition (IC) vs. preservative retention. IC is obtained by summing the results from the ten replicate stakes to yield a 100 point scale (100 = no deterioration).

Effect of insecticide addition—Figure 1 shows the five-year exposure dose-response curve for termite attack on stakes for both levels of added Dursban[®]. At higher retentions, a slight improvement with the added insecticide was noted. The data for Pounce[®] addition indicates a slight, but non-significant, improvement in termite resistance (Figure 2). The addition of insecticides used in these studies for improving the resistance of wood treated with WD ZN to termite attack cannot be recommended.

Effect of water repellent addition—Figure 3 shows at best a marginal, non-significant improvement after five years of exposure for the WD and LOSP systems. No improvement was noted for the oilborne system. Perhaps the addition of higher concentrations of water repellent would have increased the efficacy of one or more of these systems.

Carrier effects—Performance of the water-dispersible system in ground contact was poor as is shown in Figure 4. After five years of exposure, only the highest retentions were above an IC of 70, the lowest level of performance generally considered acceptable. A decay grade of 70 indicates that 10-30% of the cross section is decayed. After five years of exposure, no retention in this study was acceptable. These data would indicate that water-dispersible zinc naphthenate would not qualify as a ground contact system at anything approaching a reasonable economic retention. The same is true, only more so, for LOSP ZN or zinc neodecanoate systems (Figure 5). For the LOSP systems, no retention studied was effective after three years of exposure.

When ZN is carried in a heavy oil (AWPA P9 Type A solvent), the performance was tremendously improved. An IC of 70 or below was reached only after 7-10 years of exposure, as is clear from Figure 6. These data would indicate that ZN might qualify as a ground contact preservative when carried in a heavy oil solvent. The data suggest that performance in above ground usages would certainly be adequate.

Comparison with copper naphthenate—Copper naphthenate (CN) was evaluated in parallel studies as has been reported previously (Barnes *et al.* 2003). Comparison between the two preservative systems generally shows the copper-based system to be superior as can be seen in Figures 7, 8, and 9 for five years of exposure of the water-dispersible, solvent-borne (LOSP), and heavy oil (AWPA P9 Type A) systems, respectively. After 10 years of exposure, the performance of both the Zn and Cu systems is similar (Figure 9), with CN showing better performance. As cautioned by John Leutritz in discussions at AWPA meetings, care should be exercised in interpreting data on small stakes after seven years of exposure. This is in part due to the 'reservoir' effect being small in small-sized samples as compared to that for wood in larger structural sizes.

Figure 10 compares the dose-response curves for a combination zinc/copper (2.67:1 Zn:Cu) naphthenate LOSP system with both copper naphthenate and ZN LOSP systems after five years of exposure. The significant improvement in performance of the Zn/Cu system as compared to ZN alone can be attributed to the addition of the copper. The extent to which zinc could replace copper in a combination system from both a performance and economic standpoint requires additional study.

Summary and Conclusions

This paper reports on the effectiveness on zinc naphthenate in ground contact in various carriers and with different additives. The addition of insecticides or water repellants did little to improve the

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performance of zinc naphthenate systems at the concentrations tested. As has been shown with other systems, the carrier system used had the greatest effect on performance (Nicholas *et al.* 1994). When formulated as a water-dispersible or LOSP system, performance would not qualify zinc naphthenate as a ground contact preservative. However, in a heavy oil (AWPA P9 Type A) carrier performance was greatly improved, suggesting that zinc naphthenate might be effective in some ground contact applications such as deck structural members, glue laminated beams, agricultural and highway uses. Performance lagged slightly behind that for copper naphthenate in heavy oil. The replacement of copper with zinc in a naphthenic system showed some promise but will require additional study.

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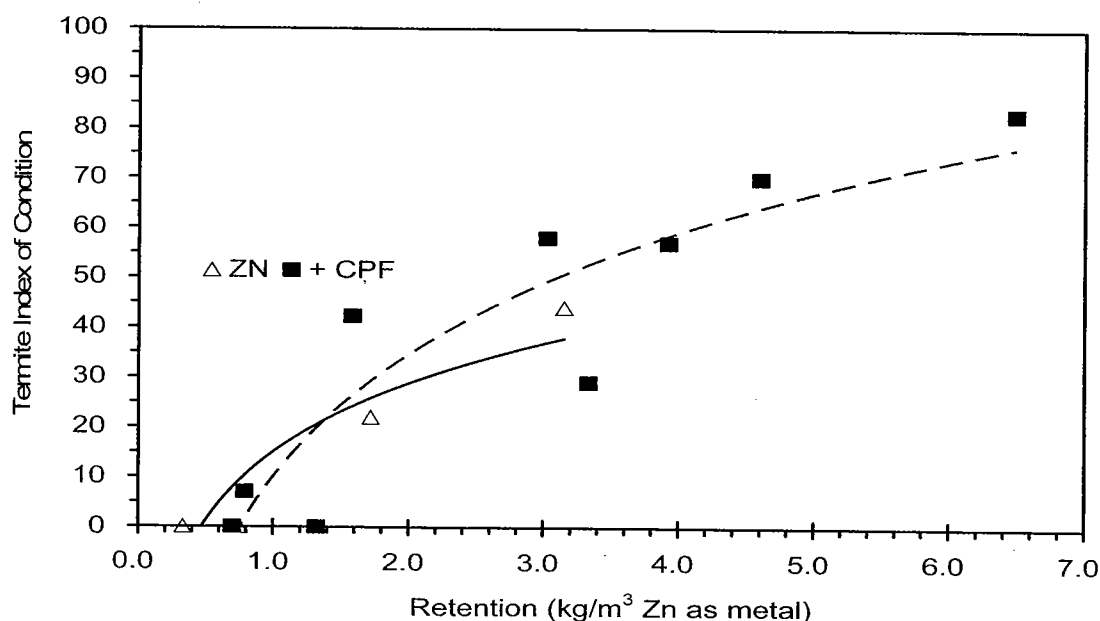


Figure 1. Effect of chlorpyrifos (Dursban[®] = + CPF) addition on the performance of wood treated with water-dispersible zinc naphthenate after five years of exposure in ground contact.

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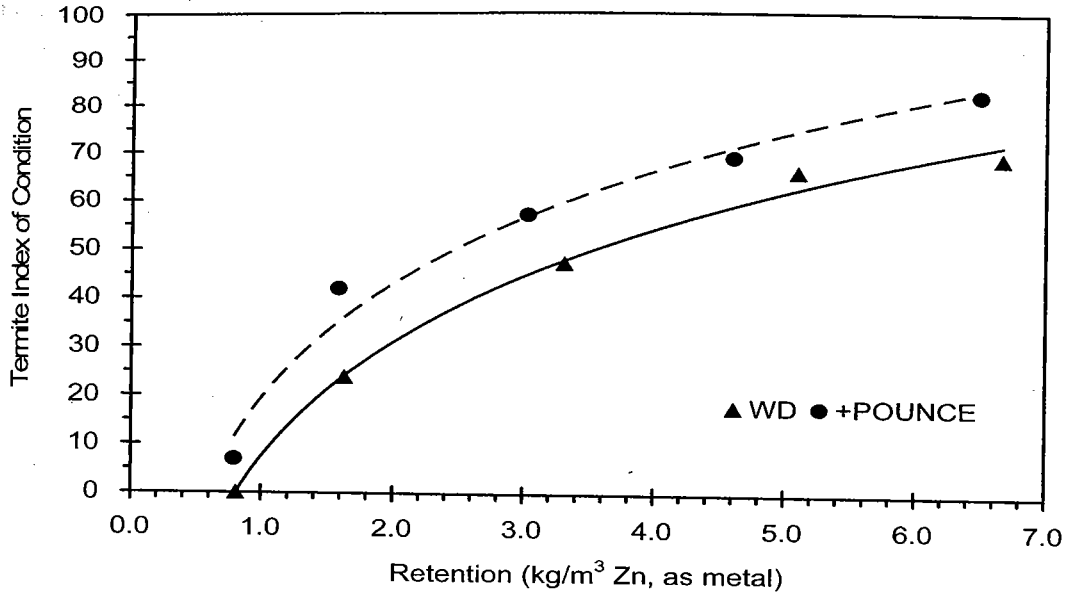


Figure 2. Effect of permethrin (0.2% Pounce®) addition on the performance of wood treated with water-dispersible zinc naphthenate after five years exposure in ground contact.

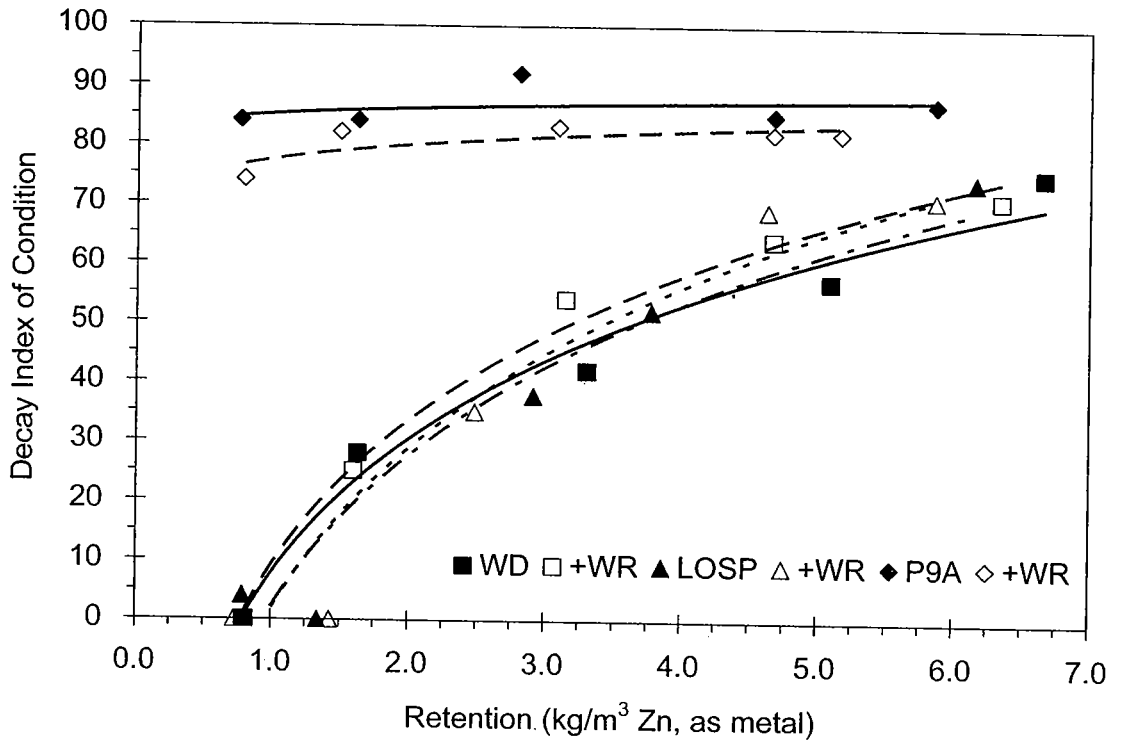


Figure 3. Effect of the addition of water repellent (WR) on the performance of wood treated with water-dispersible (WD), solvent-borne (LOSP), and oilborne (P9A) zinc naphthenate after five years of exposure in ground contact.

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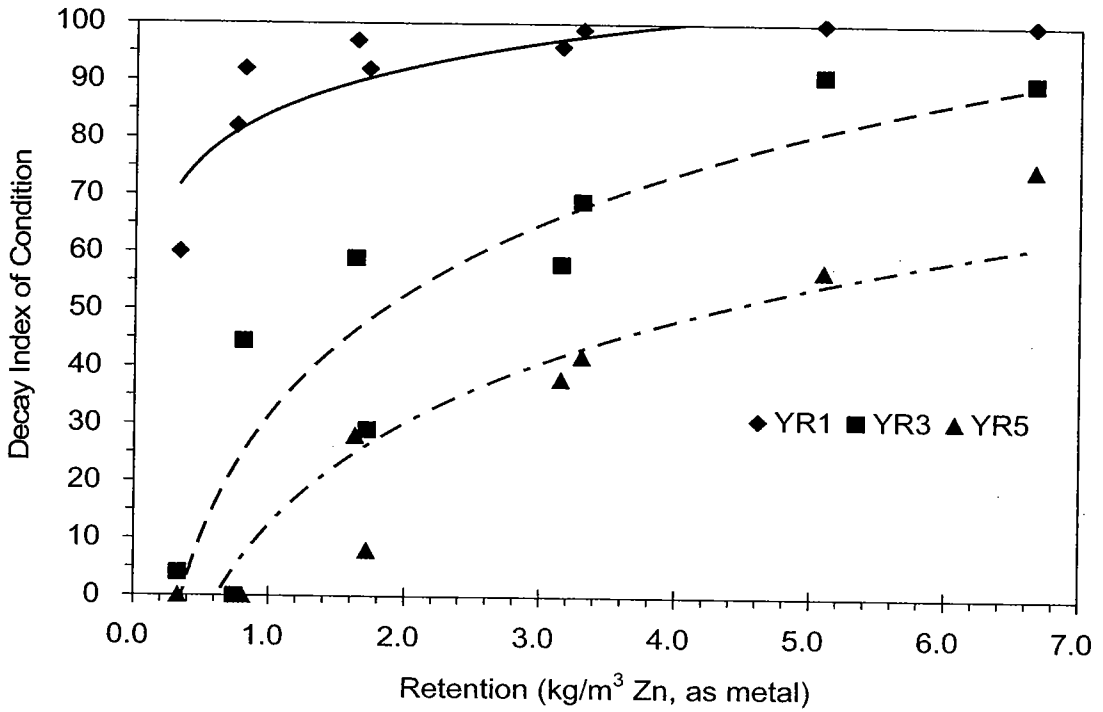


Figure 4. Dose-response curves after 1, 3, or 5 years exposure for wood treated with water-dispersible zinc naphthenate (data from two different stake tests).

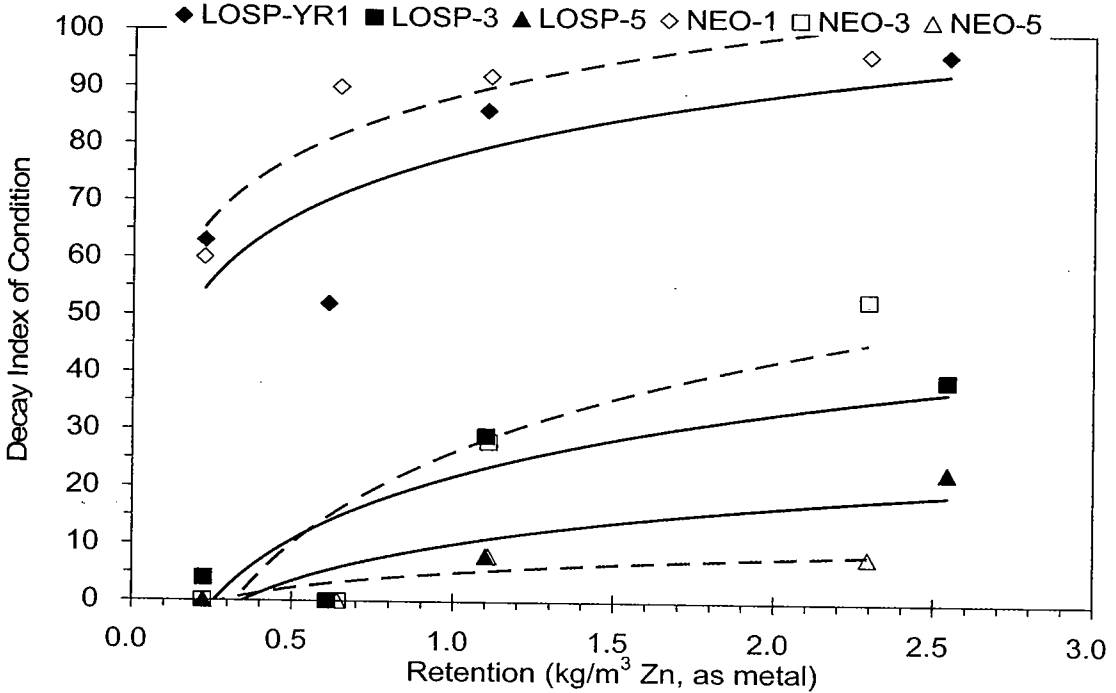


Figure 5. Dose-response curves after 1, 3, and 5 years exposure for wood treated with solvent-borne (LOSP) zinc naphthenate (solid lines) and zinc neodecanoate (NEO-dashed lines).

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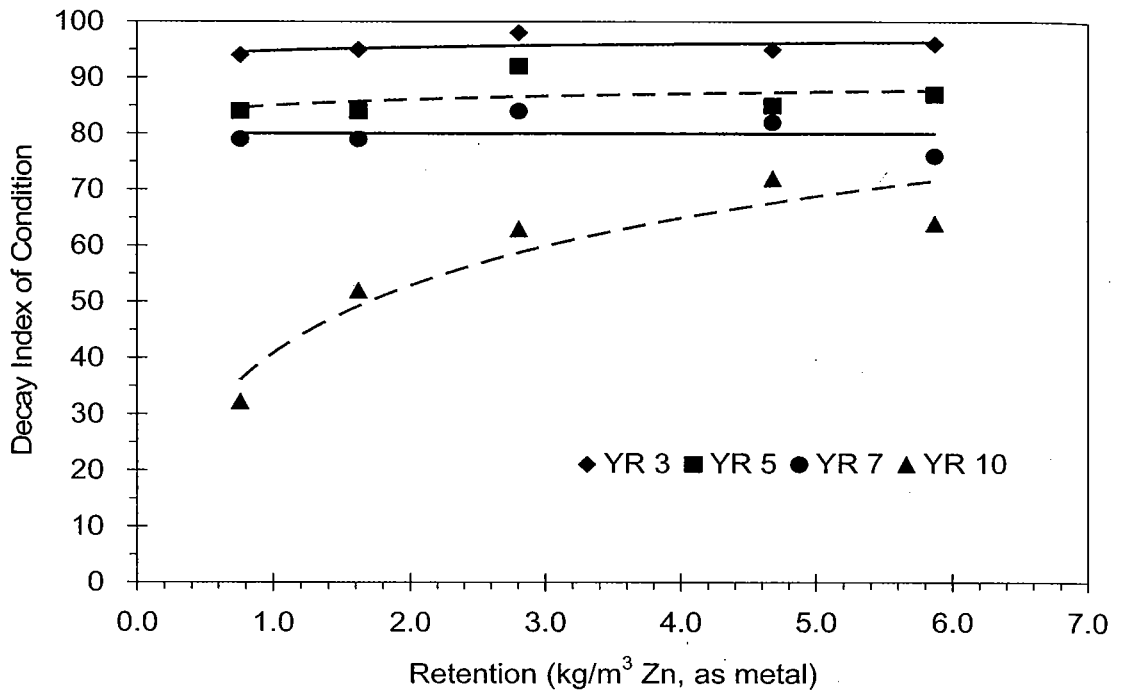


Figure 6. Dose-response curves at 3, 5, 7, and 10 years of exposure for wood treated with oilborne zinc naphthenate in an AWPA P9 type A solvent.

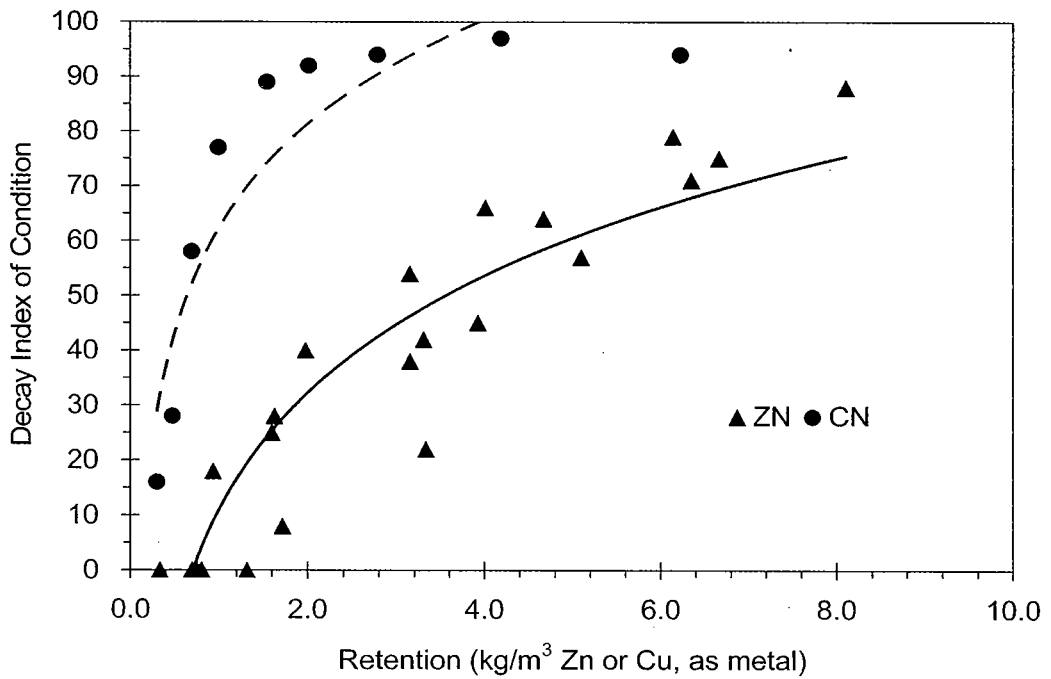


Figure 7. A comparison of dose-response curves for water-dispersible zinc naphthenate and copper naphthenate after five years of exposure.

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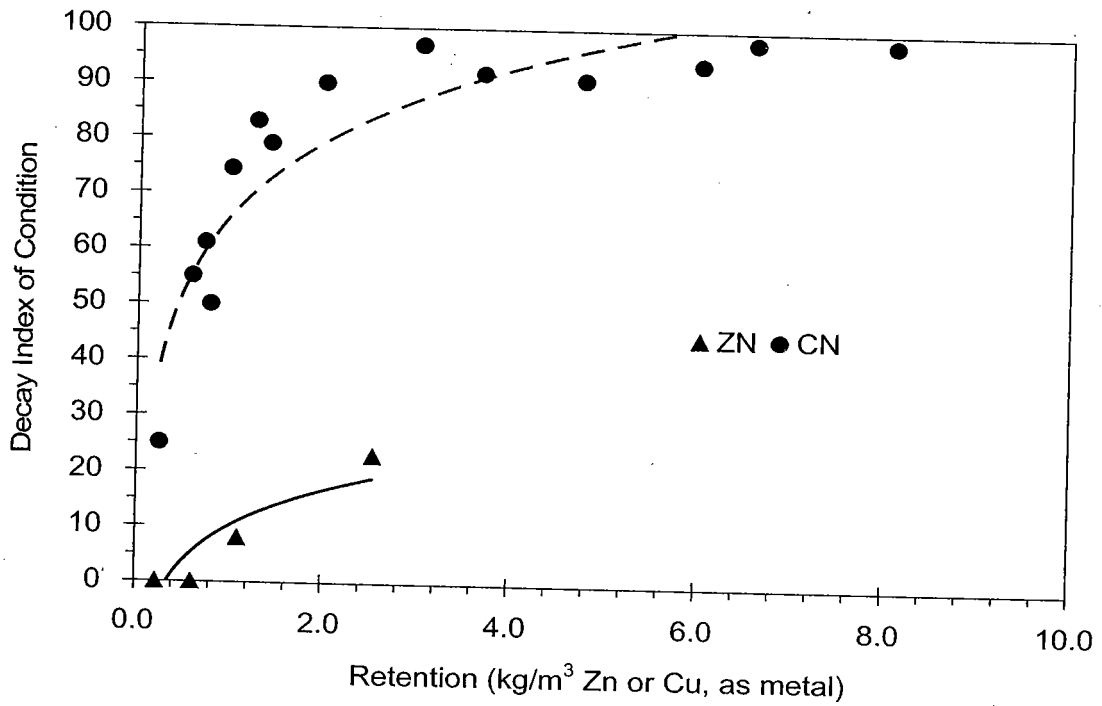


Figure 8. A comparison of dose-response curves for solvent-borne (LOSP) zinc naphthenate and copper naphthenate after five years of exposure.

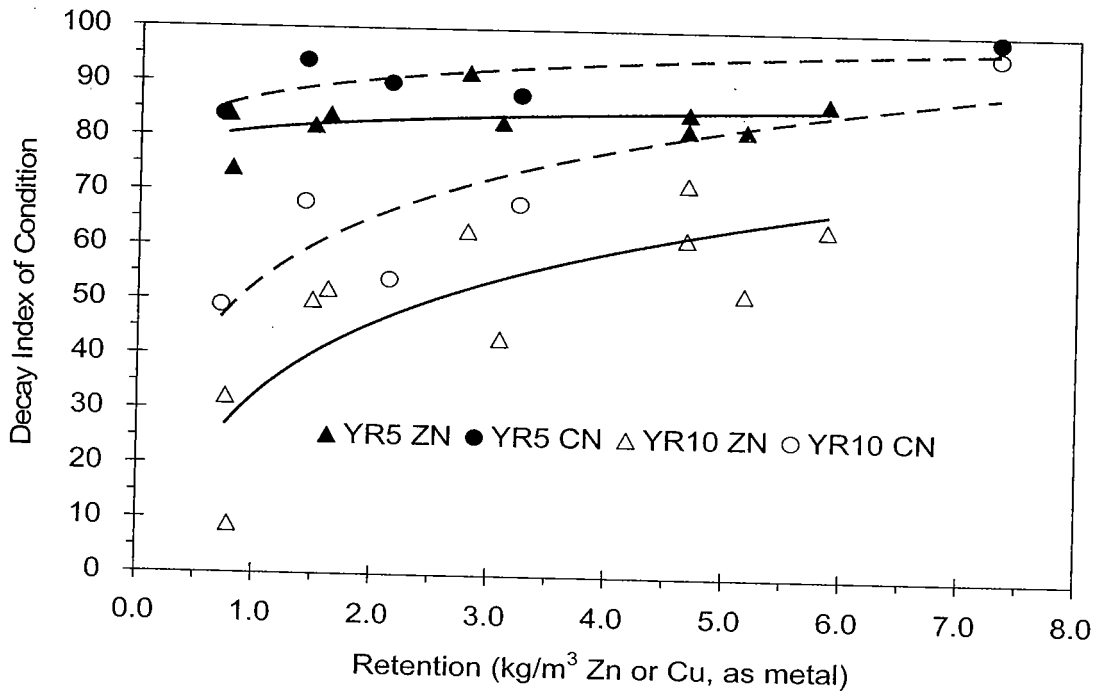


Figure 9. A comparison of dose-response curves for zinc naphthenate (solid lines) and copper naphthenate (dashed lines) in heavy oil (AWPA P9 type A) after five or ten years of exposure.

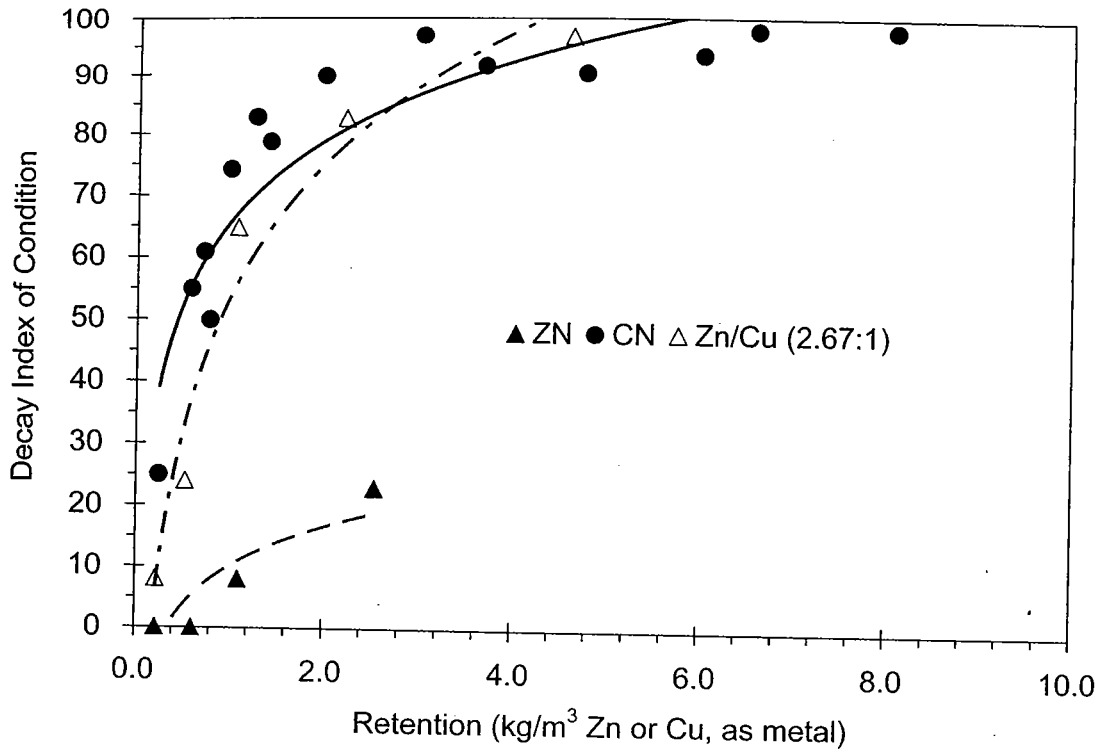


Figure 10. Dose-response curves for a 2.67:1 Zn:Cu LOSP system compared to zinc- and copper naphthenate systems after five years of exposure (Zn:Cu system is based on the Zn retention).