Chapter 15

Discussion on Prior Commercial Wood Preservation Systems That Performed Less Well Than Expected

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This article reviews five prior commercial wood preservatives that had efficacy concerns. A common factor among all five systems was minimal or no field testing of the proposed system prior to commercialization. Also, the formulation of a successful preservative was twice changed, and one successful system was employed with a new wood species. There is no intent to hold responsible any individual(s), company(ies), or organization(s) for these failures; the purpose is to simply discuss systems which performed less well than expected and report on failure factors. Because it appears that longer field evaluations prior to commercialization might have identified poor performance, a preliminary study of the effect of exposure time was performed. Data from three ground-contact studies of the fungal efficacy of experimental systems run at two sites were compared to the efficacies of positive control biocides which have long provided adequate commercial wood protection. Systems that were "poor" because of low initial biocide treatment required an exposure of three or fewer years to detect differences from a positive control. However, some systems which were treated to moderate biocide levels, and initially

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performed adequately, suffered greater fungal degradation than the positive controls after four or more years. This study indicates that exposure times longer than the currently-required three years may be needed to determine if a system treated to the proposed commercial retentions will perform adequately for the long service life expected by consumers.

Introduction

Because some untreated wood products may perform favorably for years in outdoor exposure, especially when used above ground, predicting the long-term durability of a wood preservative system requires years of field tests at multiple sites (*1*). Similarly, it may be years before consumers become aware that a wood product is not performing as expected, such as a structural member failing below the ground level where decay or termite degradation is not visible. No company that has been in business for any length of time wants, or even considers, the possibility of providing a product with the potential to fail with the resulting financial loss and negative publicity. However, failures do happen. While many types of failure can occur with treated wood products, in this chapter we focus only on biodegradation of commercially-treated wood where deterioration occurred with a frequency that caused concern within the forest products industry and was likely due to poor performance of the wood preservative system.

A system must protect a treated wood product against a wide variety of fungi and/or insects, of which any single species can invade and degrade the product over its expected long service life. It is impossible to test a system in the laboratory against all possible organisms which can attack wood, or to conduct ground-contact field studies in the many soil environments to which a treated wood product will be exposed. Furthermore, biocides can be depleted over time and depletion is best measured by long-term field studies, but outdoor ground-contact depletion data among replicate samples are typically very erratic (*e.g.* (*2*, *3*)). Finally, many technically complex factors can be involved and more than one cause can lead to failure under different circumstances – and human factors at the treating facility can also be involved in some circumstances.

For this chapter, we choose five major prior commercial preservatives which had efficacy concerns after commercialization and discuss each in chronological order in a balanced and factual manner. We then list the common factors among the five systems discussed. Finally, we examine preliminary data on the effect of outdoor ground-contact exposure test time and site on the significance of the fungal efficacy of experimental compared to well-recognized commercial systems.

Prior Commercial Systems with Efficacy Concerns

Volatile Solvent Pentachlorophenol Treatment

The first/earliest system discussed is pentachlorophenol (penta)-treated utility poles. Penta in heavy oil carriers, which gives the wood an oily surface, have been employed to treat utility poles and crossarms for at least 60 years. In the early

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1960's volatile solvents, specifically liquefied propane or butane (the CELLON™ process) or methylene chloride, were employed to formulate penta with the volatile solvent recycled after use (*4–8*). The treated poles had a dry and visually-appealing surface that could be stained or painted. This also eliminated the heavy oil carrier and enabled recycling of the volatile solvent which reduced costs. Poles with these treatments were extensively used. However, in a relatively short time soft-rot decay problems were noticed in both poles and research stakes (*9*). Much resulting discussion ensued on whether a problem existed and, if so, possible causes considered such as the penta retention gradient in small research stakes versus commercial-sized poles or interpretation of the rating index of research stakes.

Eventually, it was generally agreed that serious problems indeed existed and a number of factors were identified. One major problem was that the poles emerged so dry and uncolored after treatment that any untreated or partially treated poles, especially poles on the top layer in cylinders which were only partially filled, could not be readily identified. When employed, the entire pole or untreated portion quickly experienced decay or termite attack. By contrast, poles treated with a heavy oil carrier that were only partially treated could be visually observed and set aside for retreatment.

Another problem was penta migrating to the surface of the poles as the volatile solvent was removed, causing blooming [crystallizing] on the wood surface. The pole surface was sometimes washed with aqueous alkali to remove the surface residue (*10*), but this wash also removed some of the penta in the thin outermost layer of the pole. The lower penta retention in the vulnerable surface layer afforded an opportunity for soft-rot fungi to become established, as soft-rot fungi are more resistant to penta than brown- or white-rot fungi. It was also reported that various additives may have been employed to reduce blooming, and a few of these may have negatively affected treatment efficacy and/or enhanced penta leaching (*11*).

The heavy oil carrier was originally assumed to be biologically inert. However, extensive studies have now conclusively shown that stakes treated with heavy oils alone are more durable than untreated stakes (*12*). Today, most professionals agree that heavy oil carriers impart some biological efficacy against decay and termites (*13*) and enhance the activity of penta as a wood preservative. Further, heavy oils impart some water repellency which reduces decay potential.

Another possible problem was penta leaching. Penta is a highly acidic phenol with a pKa of about 5, which meant that this biocide readily forms the ionized, water soluble salt form when exposed to water at normal pHs. Thus, some researchers suspected that any crystallized penta without a heavy oil carrier might be easily solubilized and leached by free water in the ground-contact area of the pole. While some penta in the outer zone of the pole initially depleted relatively rapidly, the depletion rate decreased over time and only slightly higher penta levels were found to be retained in poles with heavy oils (*5*, *8*). The only poles which had severe penta depletion were those installed in alkaline and/or water-saturated soils, and reportedly even penta in heavy oil will leach from utility poles in highly alkaline soils (*14*).

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CCA Treatment of Eucalypts Utility Poles

CCA is a waterborne preservative that was extensively employed in both residential and industrial applications and is still employed in industrial and agricultural uses where it provides excellent and cost-effective service for a wide variety of applications. The vast majority of treated wood is cut from gymnosperms (softwoods) that include pines, spruces, and firs. Thus, the wood treating profession has had a long and positive experience with CCA in protecting softwood products.

Softwood pole availability was limited in Australia, however, so poles from certain hardwood (angiosperm) Eucalyptus species were employed with the assumption that the highly effective CCA would continue to perform well with hardwoods to give a durable product. This assumption quickly proved wrong, however, as initial reports of soft-rot attack on CCA-treated Eucalyptus poles was later verified by extensive field research (*15*, *16*). In an exhaustive study, slight to severe fungal deterioration was observed in all 1,000 CCA-treated Eucalyptus poles examined (*16*). The problem was successfully addressed by inspection of standing poles and a remedial treatment applied where necessary (*17*).

The reasons identified appear rather subtle at first but, perhaps, with hindsight should have been considered before large volumes of Eucalyptus poles were treated. Specifically, hardwoods have a more complex anatomy, and different lignin chemical structure and lower lignin levels, than softwoods. As CCA components are fixed within softwood, often to lignin, the relatively simple anatomy and uniform lignin structure and distribution in softwoods means that the CCA is relatively homogenously distributed. However, hardwoods have a more complex anatomy which results in hardwood fibers sometimes being poorly treated, and pockets of untreated fiber cells existed with CCA-treated hardwoods (*18*, *19*), Further, as the lignin structure in hardwoods differ among the various cell types, and the metallic biocides preferentially fix to lignin, CCA microdistribution within hardwoods was more variable than in softwoods. Finally, hardwoods are generally more susceptible than softwoods to soft-rot fungi (*10*).

To summarize the possible reasons for the failure observed with hardwoods treated with CCA; 1) hardwoods are more susceptible to soft- and white-rot fungi than softwoods; 2) CCA fixes to the wood, especially the lignin component, and hardwoods have a more complex lignin structure than softwoods that varies among the cell types and the different layers of the cell wall; 3) hardwood fibers are more difficult to treat than softwood fibers; so 4) due to 2 and 3 above a non-uniform CCA microdistribution exists in hardwoods; and 5) metallic biocides have smaller zone of inhibitation compared to organic biocides, so that decay fungi can grow in untreated cells that border cells treated with copper.

Quaternary Ammonium Compounds in Australia and Asia

A variety of quats, or quaternary ammonium compounds, are employed in wood preservatives. Quats have many positive properties including being extremely economical per unit weight and a relatively broad efficacy against a

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wide variety of fungi and insects. They are also waterborne but fix in wood upon treatment by ion-exchange reactions. Quats were tested as a wood preservative using approved laboratory tests and one outdoor above-ground test with painted wood (*20*). After favorable test results (*21*), quats were employed to treat wood for above ground applications in Australia and New Zealand. An above-ground test run shortly thereafter in North America with unpainted wood suggested some concerns, however, and decay problems later surfaced in applications with high decay potential.

Relatively little data was made publicly available from studies on the causes. One cause was likely poor penetration of quats in some cases. Under alkaline conditions quats sometimes rapidly fixed within the wood so that only the outer shell of commercial-sized lumber was treated, leaving the center core untreated as observed by one author, DDN, in field trials in Houston, TX. This effect would not necessarily have been observed with the small samples typically employed in laboratory efficacy tests. Secondly, a supposedly less active benzalkonium chloride (BAC) quat was used rather than the more active dimethyl didecylammonium chloride (DDAC) (*22*), although a later field study found little efficacy differences between BAC and DDAC (*23*). Some bacterial degradation of the quat may have also occurred (*24*, *25*). Overall, it appears that a large number of factors and special circumstances occurred in the various failures, and hindsight suggested that more and longer field tests should have been conducted (*20*).

Companies in Japan later examined quats and, upon favorable results (*26*, *27*), employed them. A few decay problems later appeared in certain high-decay hazard applications (*20*).

Quats have many advantages, as listed above, and when combined with other biocide(s) to ensure greater and/or broader activity they provide good protection against a wide variety of fungi and insects in some current systems.

Waterborne Pentachlorophenol

In the late 1970's waterborne penta [the salt of pentachlorophenol] was employed to treat wood (*28*). While the salts were water soluble, upon treatment and exposure to the naturally acidic wood the salt was protonated and the penta precipitated in the wood. As with the volatile solvent penta-treated poles discussed above, the surface of the resulting product was clean and could be painted, individually-treated wood could be glued together to form composites, and the cost of the process was reduced by not employing a heavy oil carrier. However, in a relatively short time concern was expressed over decay seen in some research stakes that further exposure time confirmed in commercially treated wood products (*9*, *12*, *29*).

Many of the problems identified were similar to the volatile solvent-formulated penta poles discussed earlier, including the lack of a heavy oil carrier making the wood more susceptible to decay, especially by soft-rot fungi. Another factor included the possible use of a surfactant in the formulation which may have increased penta leaching (*30*). Further, the aqueous alkali treating solution

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solubilized wood extractives such as sugars and resin acids which, along with any remaining soluble penta salts, crystallized on the surface. The treated poles were washed with an alkaline solution to remove the unsightly surface deposits, but this also resulted in reduced penta levels in the outer pole surface to make it more vulnerable to initial fungal colonization and subsequent fungal movement into the inner/deeper zones (*10*). Finally, soft-rot fungi appeared to "grow around" areas with penta crystals.

Tributytin Oxide

Tributyltin oxide (TBTO), a colorless biocide with low mammalian toxicity, was not patented and so was freely available for commercial use. A number of factors suggested that TBTO would be a good wood preservative, including laboratory decay tests which indicated it would be effective in above-ground applications and a long and positive history in other biocidal applications. Also, the treated wood had good appearance and no strength loss, and TBTO has low volatility and good water leach resistance. Based on the promising laboratory fungal efficacy tests and the good TBTO properties (*31*), it was extensively used in millwork and other low-deterioration hazard applications in North America and Europe. Unfortunately, initial reports of deterioration appeared within a few years, which were later confirmed as the TBTO-treated products aged.

After numerous studies in different laboratories it was generally acknowledged that with long-term exposure TBTO underwent chemical and/or biological dealkylation to form dibutyl and monobutyl compounds that had reduced fungal activity (*32–38*). While the initial laboratory efficacy tests were encouraging, the abiotic and/or biotic transformation of the biocide which resulted in reduced fungal protection were relatively slow reactions - so that the resulting lower efficacy was not observed in the relatively short-duration laboratory tests employed to test TBTO prior to commercialization. Thus, the fundamental cause for the efficacy problem with TBTO was the lack of long-term outdoor above-ground efficacy and depletion tests prior to commercialization. Further, retention of TBTO in millwork and other wood products was determined by analysis of only the tin, rather than determining the amount of the actual organotin biocide (*39*). Consequently, the tin retention deceivingly remained almost constant while the organotin biocide underwent dealkylation reactions in the treated wood to give an altered, less biocidal compound.

Summary of Common Factors

The mostly frequently occurring factors associated with the five systems discussed above are:

- Minimal or no valid outdoor, long-term efficacy and/or depletion trials prior to commercialization, including the need to employ multiple test sites for systems intended for ground-exposure applications. This apparently occurred with all five systems discussed.

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- A change in the formulation of an established system with the assumption that the biocide would continue to be effective even when formulated in a different carrier (*e.g.* the volatile solvents and waterborne penta systems), or using a successful system with a new wood species (*e.g.* CCA/Eucalypts poles).

Preliminary Study on the Effect of Field Ground-Contact Exposure Time

One common factor which occurred in all five of the systems discussed above was minimal or no valid outdoor efficacy and depletion tests. For ground-contact applications, systems proposed for American Wood Protection Association (AWPA) standardization are required to be exposed for a minimum of three years at two different sites with high or severe deterioration hazard along with depletion analyses ((*40*), Appendix A). Similar requirements exist for systems being submitted for International Code Council-Evaluation Service (ICC-ES) Standardization (*41*). Recently, much discussion has occurred on the sufficiency of three years of field exposure at two sites to determine if a proposed system will be effective for the many years of service expected by consumers.

To address the question of exposure time, long-term field AWPA E7 test data were obtained from multiple studies conducted by the USDA-Forest Products Laboratory and Mississippi State University. Results from a preliminary analysis of three field data sets established at the Dorman (AWPA Deterioration Hazard Zone 4/High, with copper tolerant fungi present) and Saucier (AWPA Deterioration Hazard Zone 5/Severe) test sites in Mississippi were conducted. All three field stake tests included positive control samples of a long-established commercial biocide. One set consists of the synergistic copper/Cu-8 combination (*42*, *43*) with CCA as the positive controls. The other two sets examined the organic PXTS (polymeric xylenol polysulfide) system, a potential creosote substitute which tests showed to be about twice as effective as creosote (*44*). The two PXTS sets employed different formulations, with one set having CCA and the other creosote positive controls. As this is a preliminary analysis only the fungal decay results were examined. The results were modeled over a 12-year period. Fungal efficacies were statistically compared at the 0.05 significance level, adjusted for multiple time comparisons, using as a comparison a commercial preservative system at the specified retention for residential (Cu/Cu8) or industrial applications (PXTS). The objective was to determine whether three years of field exposure is sufficient to decide if a proposed ground-contact system is comparable to a commercial system and, if three years is insufficient, how long a test exposure period is necessary.

The first system examined was PXTS with creosote as the positive control. The results were statistically different between Saucier and Dorman sites. At Saucier, the positive control was 144.5 kg/m^3 creosote, and at Dorman the positive control was 113.1 kg/m^3 creosote. What would be anticipated as poor systems, e.g. low retentions of creosote [19.7 to 75.4 kg/m^3] or PXTS [18.9 and 39.8 kg/m^3], gave statistically poorer results compared to the positive control after only one

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year of exposure at Saucier. PXTS at levels of 112.5 and 159.2 kg/m^3 at the same site required seven and eight years of exposure before they performed significantly better than creosote at 144.5 kg/m^3. Similarly, at Dorman PXTS with relatively high levels of 112.5 and 159.2 kg/m^3 performed better than the creosote positive control after only four years of exposure. For low biocide retention levels which would be expected to have "poor" performance, the two lowest creosote levels of 19.7 and 38.7 kg/m^3 took only one year of exposure at Dorman to show they had poor decay performance. However, the efficacy of stakes treated with the relatively low PXTS retention of 39.8 kg/m^3 at Dorman was statistically similar to the positive control, and after five years of exposure PXTS at 76.6 kg/m^3 performed statistically better than the positive control.

The second set was PXTS, with CCA at 10.1 kg/m^3 as the positive control. The results were statistically different at the two sites, and differences with the positive control were detected more often and sooner at Saucier. PXTS at the relatively low level of 46.6 kg/m^3 required only three years of exposure at Saucier and four years at Dorman to show significantly poorer efficacies compared to the positive control. The moderate PXTS level of 70.9 kg/m^3 required four years of exposure at Saucier before it performed poorer than the positive control, while at Dorman this set performed equally to the positive control for all 12 years. PXTS at 94.2 kg/m^3 also performed equally to the positive control at Dorman for 12 years but statistically lower at Saucier after only two years of exposure; however, at the end of the study (12 years), the performance matched the controls at Saucier. Finally, CCA at a level of 3.4 kg/m^3, or about half of the UC4A retention and so would be considered to be a "fair" system, required nine and eight years of exposure at Dorman and Saucier, respectively, before it performed significantly poorer than the positive control.

The third set examined, copper/Cu-8, proposed to be a possible copper-based residential system so CCA at 6.1 kg/m^3 was employed as the positive control. Not unexpectedly, significant fungal efficacy differences were noted between Saucier and Dorman, with Dorman having lower ratings sooner. This was most likely due to copper-tolerant fungi present at Dorman. However, unlike the creosote studies an interaction between site and exposure time was not detected, indicating that although fungal attack occurred sooner at Dorman the ability to detect the differences between treatments did not occur any sooner at Dorman than Saucier. The systems which would be expected to be "poor", those treated with Cu8 alone (0.3, 1.0, and 1.9 kg/m^3) or relatively low levels of Cu/Cu8 mixtures (0.6/0.3, 1.6/0.2, and 1.3/0.3 kg/m^3), required only one to two years of exposure to show poor fungal performance. A moderate Cu/Cu8 level of 3.2/0.5 kg/m^3 required six years of exposure. Relatively high levels of Cu/Cu8, 3.7/0.6 to 5.0/1.1 kg/m^3, showed equal performance to the positive control of CCA at 6.1 kg/m^3 for all 12 years.

Overall, in this preliminary analysis it appears that three years of exposure at two sites is sufficient to show that treatments with relatively low retentions, which would be expected to give poor performance, did indeed perform poorly relatively to the positive controls. However, systems that would be considered as "fair" required longer exposure periods. For example, CCA at about half the UC4A retention required exposures of about eight years, and moderate Cu/Cu8 retentions

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of 3.2/0.5 kg/m^3 required six years of exposure, to show significantly poorer fungal efficacies than the positive controls. Conversely, PXTS at 76.6 kg/m^3 at five years of exposure performed better than the positive control. Thus, we conclude that exposure times longer than the currently-required three years may be necessary to determine if a system treated to a potential commercial retention would likely perform adequately in commercial service for the relatively long duration expected by consumers. However, longer field test exposure time will make it more difficult and expensive to develop new systems as quickly as the public currently demands.

This study is only a preliminary analysis of fungal efficacy data from three research studies. We hope to report more fully on further statistical analyses employing these and additional field stake data in the future.

Conclusions

A review of five prior commercial systems which had experienced poor service efficacy found that all systems underwent limited or no valid long-term outdoor efficacy and depletion testing prior to commercialization. In addition, formulations were changed in two systems which had a previously successful biocide, and one effective system was employed with a new wood species. A preliminary analysis of three AWPA E7 field test studies conducted at two sites suggests that a longer exposure period than the three years currently required may be necessary to adequately test the fungal efficacy of a proposed ground-contact preservative prior to commercialization.

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