POSSIBILITIES AND PITFALLS – THE FUTURE OF WOOD PRESERVATION

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"The future is not a result of choices among alternative paths offered by the present, but a place that is created— created first in the mind and will, created next in activity. The future is not some place we are going to, but one we are creating. The paths are not to be found, but made, and the activity of making them, changes both the maker and the destination." - John Schaar

Predicting the future as can be seen by the thoughts of John Schaar is fraught with difficulties not because choices are not clear, but because the future is actively entwined with the path and those creating it. But the forces of change are clear. The wood preserving industry has changed dramatically during the past 20 years. It began to change the day the industry introduced the preserved wood foundation and marketed treated wood for use by the consumer (Ruddick, 1999). This resulted in a different mindset being required. The industry is now servicing the consumer – a group that may not have a great deal of technical knowledge but who could influence the industry by their preferences – preferences often defined by their view of life style formed from a holistic thinking. When recycling of paper becomes a norm then recycling of everything else becomes a way of thinking – as does the use of recycled products. The wood preserving industry is currently ill-equipped to respond to the consumerism that it now faces. Introducing new products based on consumer demand can not take the decade required to gain standardization through agreed testing protocols. However, the industry has a powerful and strong message to provide to consumer – that sustainable use of the forest resource can never be achieved without the critical advantages provided through the extension of service life achieved solely by enhancing wood durability. And an equally powerful message - that the more wood that is kept in service, the better we are able to address carbon balance. So it is very appropriate for the wood preservation industry to examine which of the options will ensure that it remains at the centre of wood use, in chemically, physically and biologically hazardous environments. Today we will consider the role that non-metallic based chemicals can play in enhancing wood performance, and in particular the part that carbon based wood preservatives could play in this future.

It is interesting to reflect on the origins of the modern age wood preservation. In the mid19[th] Century stimulated by the need to overcome the problems of "dry rot" in ships of the Royal Navy in the UK, one of the first successful commercial wood preservatives was creosote. While John Bethell gained a patent in 1838 for a "creosoting process" which used bituminous substances, he did not mention the word "creosote". This came from an earlier patent granted to Franz Moll in 1836, who introduced a more complex process part of which involved a heavy oil extract of coal tar which he termed "Kreosote". This may have been derived from the Greek "kreas = flesh" and "soter = preserver". The term creosote up to that time had been applied to the distillation product of wood but it was retained when the coal tar distillation product gained wide acceptance as an effective wood preservative. If we consider some of the desirable properties of a modern day

preservative, (Table 1) it can be seen that creosote did meet many of these needs. The first modern commercially successful wood preservative was organic in nature and derived from a naturally occurring recyclable material – although the renewal rate is several million years – which does not meet the modern day requirement of sustainability!! In addition, the toxicity of several of the components present in the creosote is not well established although several have been identified as belonging to potentially carcinogenic chemicals.

Table 1. Desirable properties of a wood preservative

¾ Derived from a naturally occurring material ¾ Totally organic ¾ Effective against a wide range of organisms including fungi and insects ¾ Can be readily biodegraded ¾ Non-toxic against non-target organisms ¾ Easily disposed ¾ Low cost ¾ Renewable and sustainable source

While several inorganic salts were introduced in the early part of the 20th Century the next major commercially successful preservative – pentachlorophenol - was also organic. Easily produced by the chlorination of phenol using, an aluminum trichloride catalyst, pentachlorophenol like creosote suffered from being toxic. However, perhaps its main problem has been its association with dioxins (Figure 1) through a condensation reaction – one of which has long been known to be extremely toxic (Hartford, 1973). However, even though the dioxins formed in pentachlorophenol treated wood have been shown to be the relatively nontoxic highly halogenated dioxins (Cui and Ruddick, 2001) the use of pentachlorophenol has been gradually replaced for most uses with the fixed inorganic
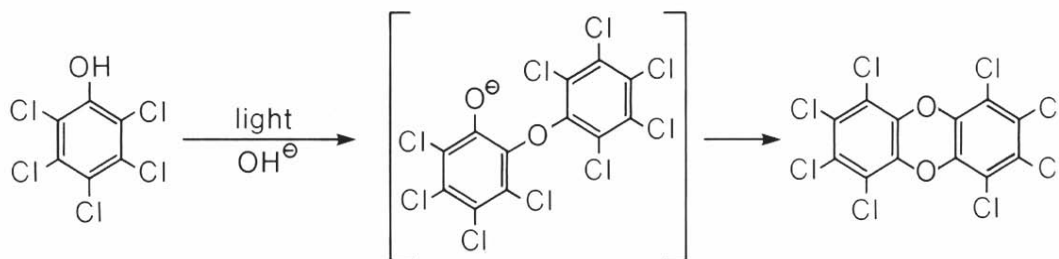

Figure 1 Formation of octochlorodibenzo-p-dioxin (OCDD) from pentachlorophenol

In the mid 1970's the treated wood industry introduced the Preserved Wood Foundation method of residential building, in which treated wood could be used to construct a full basement home. The advantages claimed included: all year round construction; savings since when a concrete basement was built, a wall and floor system still had to be built within the concrete to create a living space; an enhanced drainage system which was able to ensure a dry basement; and a system that could be built in the more remote regions of Canada where concrete was not easily obtained. With the acceptance of treated wood around homes this created the platform for a broader acceptance of chromated copper arsenate (CCA) treated wood for "Do It-Yourself" projects. Decking, siding, fencing, shingle and shakes, and landscape products rapidly followed leading to a dominant position for this preservative. By the end of the 20th Century almost 90 % of the treated wood produced in North America was protected with CCA. In addition, almost 70 % of this market targeted residential end uses most of which were out of ground contact.

Figure 2. CCA-treated residential products

However, the importance of the environmental impact of preservative treated wood had already been established by the Rebuttable Presumptions Against Registration (RPAR) notices issued by the Environmental Protection Agency (EPA) on October 18, 1978. As a result the industry had to document the economic importance of the treated wood industry and also to identify the risks associated with the production and use of treated wood. This required an enormous commitment of resources and served as a notice, that in the future acceptable toxicity levels and minimal environmental impacts would be key requirements for the future well-being of the industry. This action in the USA, lead directly to the creation in Canada of a Technical Steering Committee under the Chairmanship of Environment Canada. This group was created a Technical Recommendation Document (TRD) for each preservative system used in Canada, which identified the correct procedure to be used to minimize the exposure and environmental risk associated with the production of treated wood. In producing these TRDs, Canada was the first country to produce such Guidelines, and they have since served as a model for many other risk management strategies for treated wood producers in other countries. At the same time it served notice that future use of wood preservatives would be subject to environmental scrutiny. This was further elaborated by the Strategic Options Process (SOP) in which chemicals on the Priority 1 substance list were to be reviewed to determine the conditions necessary for their continued use. Aquatic environments were also addressed in the development of a "Best Management Practices for the use of treated wood in aquatic environments" also known as BMPs, in 1995 (Figure 3). These BMPs identified methods to assess the acceptable conditions under which preservative treated wood could be recommended for use in aquatic environments and were site specific.

Figure 3 Best Management Practices Guide addressed the use of treated wood in aquatic environments.

In May 2003 the wood preservative suppliers agreed to phase out the use of arsenical based wood preservatives from wood used in residential dwellings. This has eliminated CCA-treated dimensional wood from the residential market although some products such as CCA-treated plywood, shingles and shakes, and PWF components remain until suitable alternatives are available. This change followed several months of lobbying by environmental groups for its removal and the appearance of several negative press articles (Figure 4). Under the agreement in Canada the Pest Management Regulatory Agency of Health Canada agreed to work with the industry to ensure that alternative

Figure 4 News articles directed to consumers

preservatives could receive a label provided there was no evidence of unacceptable toxicity or environmental hazard. Since the alternative preservative formulations were based on alkaline copper solutions combined with known biocides from other industries and which had already been proposed for uses in wood protection in Canada, the industry was able to phase out the use of CCA by December 31, 2003. Understandably the industry has been engaged in strategic thinking about future directions for enhancing the durability of wood, particularly the production of wood for the residential market where appearance is as important as long term durability. In addition, in Europe there has been a resurgence of interest in alternative strategies for enhancing

wood durability including the use of thermal treatments and wood modification. While these alternatives undoubtedly will be important in the future development of the wood products industry, the major focus in this paper will be to identify the potential for organic based wood preservatives for use in protecting residential timber products.

1. Biocide options

There are several factors to consider when examining the potential for carbon based wood preservatives to replace the metal based formulations currently dominating the marketplace. Perhaps the first limitation is the size of the industry. Not being a large industry the cost of developing formulations or actives specifically for the industry is prohibitive, so that future biocides are likely to be based on those already identified for other larger industrial uses. However, the demands of these other industries are often not aligned with those of the wood preservation industry. For example an important characteristic of agricultural biocides is that they must break down rapidly after application so that they do not accumulate in the environment. This is not appropriate for a wood preservative, where the treated wood must remain durable for decades. One attribute of metal based preservatives that is important is their ability to slow down the weathering of the treated wood. Even though treated wood decks do not rot, they are frequently replaced after 15 to 20 years because they do not have a good appearance or the boards are physically damaged by the weathering process. When considering totally organic formulations, the lack of an inherent mechanism to prevent or slow down weathering, will result in an unacceptably short service life. Cost also is an important consideration. Totally organic formulations tend to be costly and so must be used at low concentrations. These concentrations which are an order of magnitude lower than metal based systems, may raise concern over their micro-distribution in difficult to treat wood species. However, totally organic wood preservatives could provide some advantages, including potentially lower corrosion of metal connectors and fasteners, and once placed within the wood many organic biocides have low leachability. During the past 20 years several organic biocides have been studied for their potential to prevent decay in wood. Some of these are listed in Figure 5 below. They include quaternary ammonium compounds, triazoles, thiazalinones and carbamates.
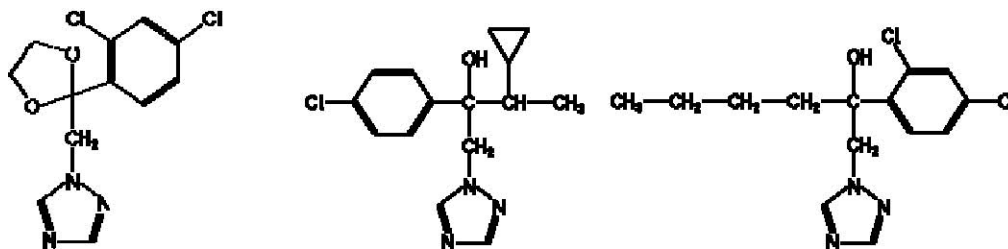
Figure 5 Examples of carbon based biocides for wood preservation

A. Quaternary ammonium compounds

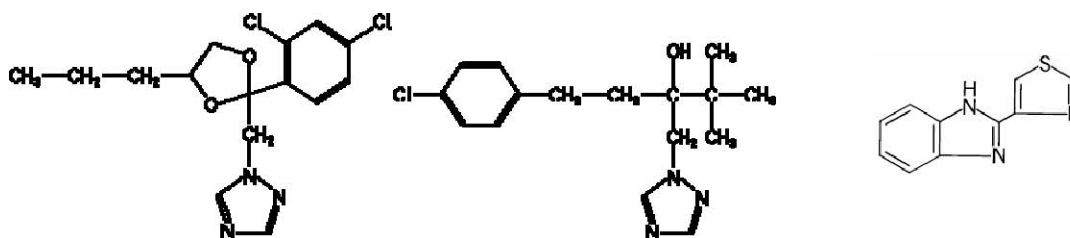Didecyldimethyammonium chloride   Benzalkonium chloride

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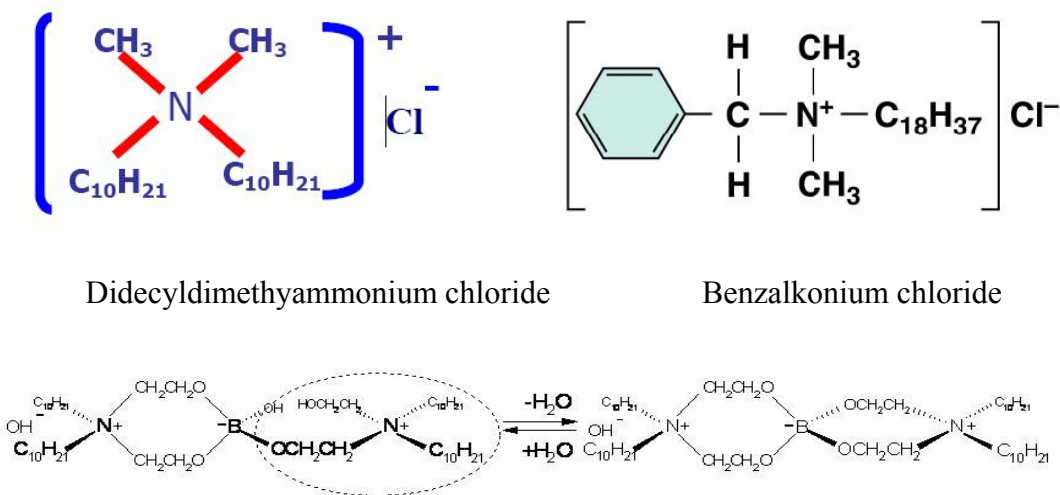
Betaines – a combination of boron and a quaternary ammonium compound
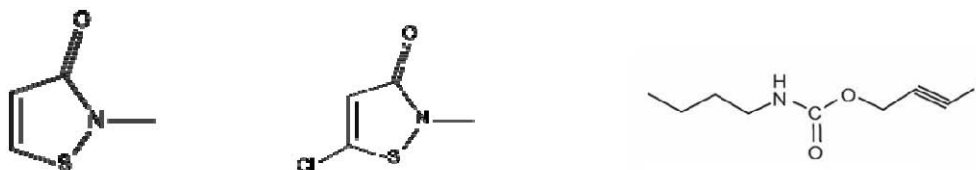
B. Triazoles

Azaconazole Cyproconazole Hexaconazole

Propiconazole Tebuconazole Thiabendazole

C. Other

Methylisothiazalinone   chloromethylisothiazalinone 3-iodopropynylbutylcarbamate

2. Challenges facing the development of organic based wood preservatives

An immediate challenge facing anyone researching organic based wood preservatives is which decay fungi should be selected in screening for fungal efficacy. Currently the standardized procedure recommends fungi that have been selected based on historical approaches to wood preservative development. Consequently the fungi recommended often have known tolerance to metals such as copper as in *Coniophora puteana* or *Postia placenta*, or arsenic as in *Gloeophyllum trabeum*. However, there is little information as to which fungi are tolerant to organic biocides in general. In addition previous research has shown that non-decay fungi can dramatically influence the performance of organic wood preservatives. For example while quaternary ammonium compounds demonstrated excellent performance against the standard decay fungi under laboratory conditions, field experiments quickly identified problems in their resistance to non-decay fungi, (Ruddick, 1982 and 1983). From the field experiments it was observed that staining fungi were able to colonize treated stakes more rapidly even than controls. In a subsequent experiment in which treated wood blocks were first exposed to a mixture of non-decay fungi isolated from field stakes, and then exposed to standard decay fungi, the toxic threshold for all fungi increased dramatically (Ruddick, 1986). For example blocks exposed (without leaching) against *G. trabeum* the toxic threshold increased from about 2 kg/m^3 to almost

10 kg/m^3. The addition of leaching caused very minor changes, (Figure 6). Further research investigated the possible action of the non-decay fungi on didecyldimethylammonium chloride (DDAC) treated wood (Doyle, and Ruddick, 1993; Burgel, Dubois and Ruddick, 1996a; Burgel; Dubois and Ruddick, 1996b; Zheng, and Ruddick, 1995.) It was shown that a dominant degradation product (P1) which was similar to the DDAC (Figure 7) was formed relatively quickly. ^{1}H NMR analysis revealed that the carbon skeleton of P1 had the same proton total as DDAC and the splitting suggested a hydroxyl bond on the second carbon from the terminal methyl group
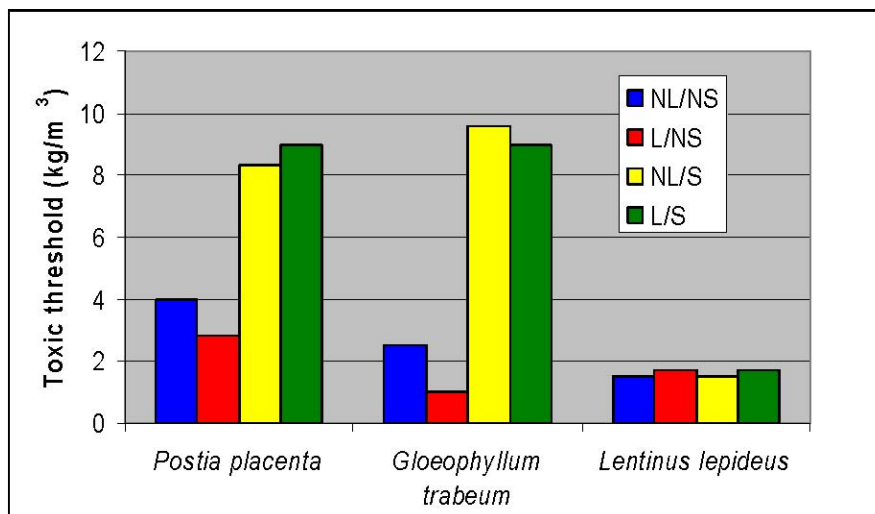
Figure 6. Effect of pre-exposure of soil blocks to staining fungi (S) or leaching (L) on the toxic threshold of alkyldimethylbenzylammonium chloride exposed to *Lentinus lepideus*, *Gloeophyllum trabeum* and *Postia placenta*. Reference blocks were not leached (NL) or not pre-exposed to staining fungi (NS).

of the ten carbon chain. (Figure 8), and this was confirmed by FTIR which showed the functionality was similar to that of DDAC except for the presence of a secondary hydroxyl group (Dubois and Ruddick, 1998). It was concluded that the DDAC was biotransformed rather than biodegraded (Figure 9).
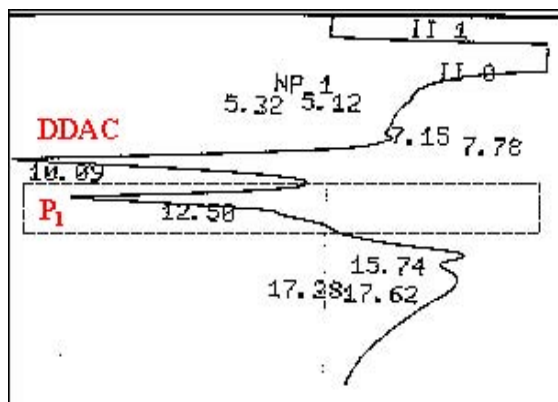

Figure 7. Chromatogram showing DDAC and the prime degradation product (P1) after exposure to *Gliocladium roseum*
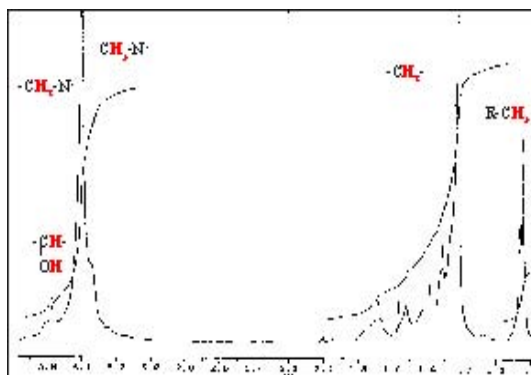
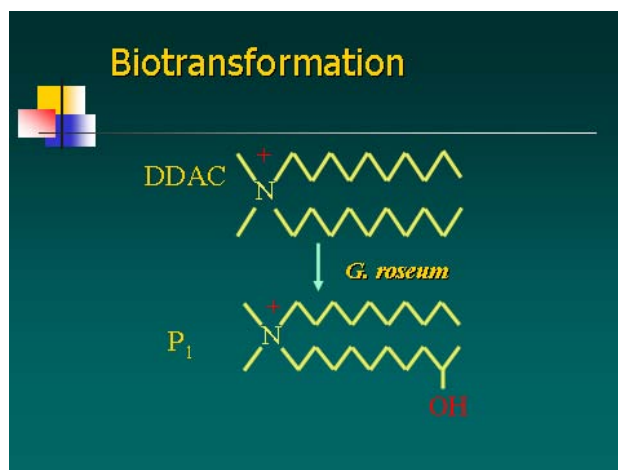**Figure 8.** ^{1}H NMR spectrum of the degradation product P$_1$

Figure 9. Biotransformation of DDAC

3. Stability of triazoles when used as a fungicide in wood

Very little research has been published on the potential degradation pathways of triazoles when placed in wood. Perhaps one of the most detailed studies has been reported by Armstrong (1999). This research focused on the extraction and isolation of propiconazole from woody material and examined factors influencing its degradation. Propiconazole has been used to control Dutch elm disease which is caused by the fungus *Ophiostoma ulmi*. Studies by Owen and Donzel, (1986) led these authors to postulate that propiconazole undergoes a rapid hydrolysis reaction under acidic conditions. They proposed that the metabolites produced would include α, β and γ-hydroxypropiconazole, and that these metabolites could then be reduced to 1-(2,4-dichlorophenyl)-2-(1,2,4triazol-1-yl) ethanol under acidic conditions (Figure 10). Armstrong (1999) further examined the degradation of propiconazole under buffered acidic conditions with a pH of 6. The hydrolysis rates were calculated for the cis (Figure 11) and trans isomers of propiconazole.
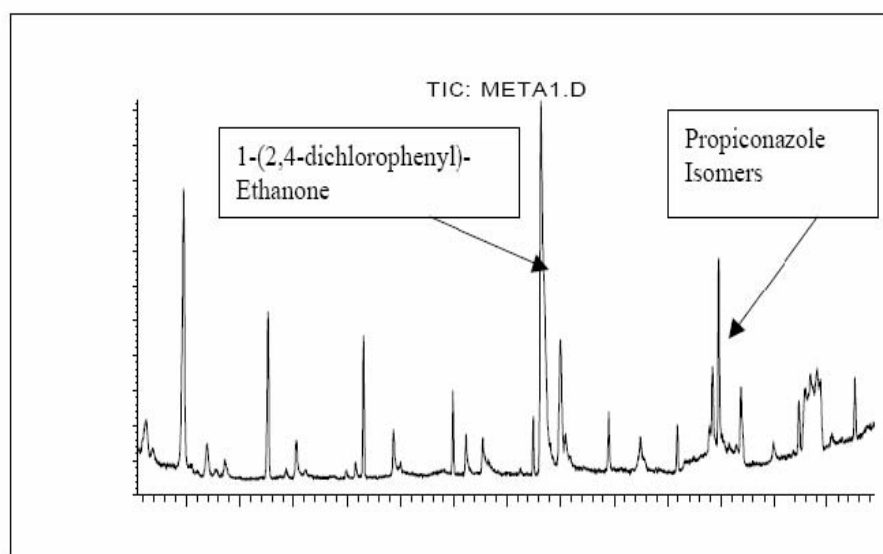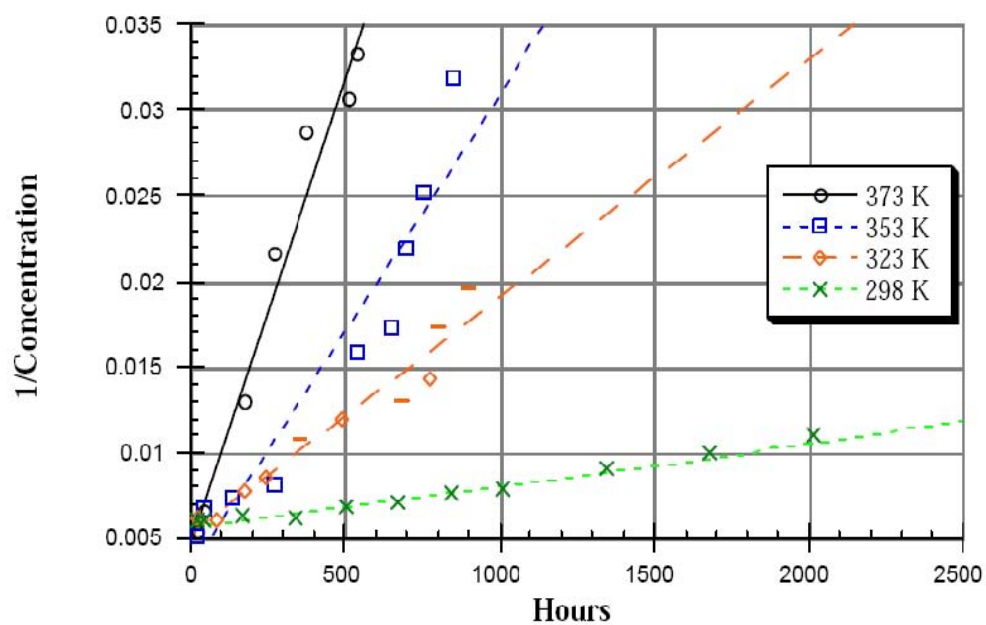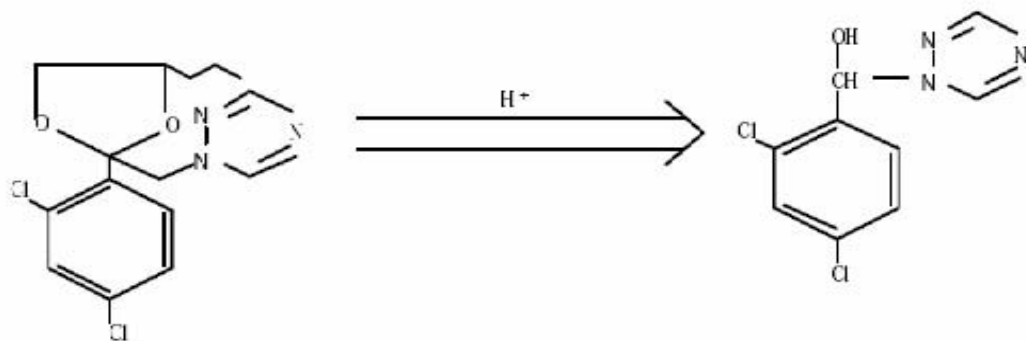
The hydrolysis rate (at 25 °C) for the trans isomer was ca. 102 days while that of the cis isomer was ca. 68 days. The predicted formation of the carbinol (Figure 10) suggested by Owen and Donzel (1986) was not detected. Instead positive identification of a degradation product 1-(2,4-dichlorophenyl)-ethanone was deduced based on total ion chromatography (Figure 12). According to Armstrong (1999) the GC/MS spectra were confirmed a cleavage of both the dioxolane and triazole and the production of 1,2pentanediol (Figure 13). Clearly much more research is needed to better understand the long term stability of the triazoles particularly with respect to their hydrolysis under the typically acidic conditions found in wood. It is know that wood has an excellent buffering
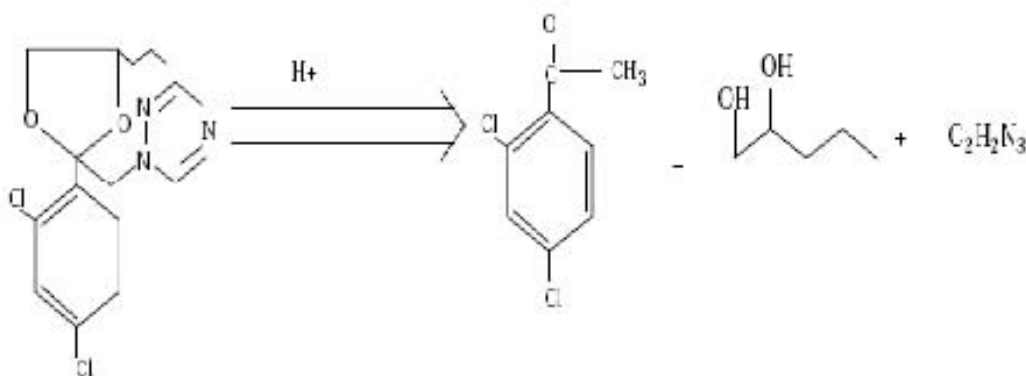
4. Is there a need for preservative mobility?

An intriguing question concerning the performance of treated wood used above ground, concerns the question of the minimum thickness of the treated wood shell that will provide long term protection to the untreated core, (Figure 14). For decades treated sawn-wood had to have a minimum penetration of 10 mm according to the Canadian Standard.
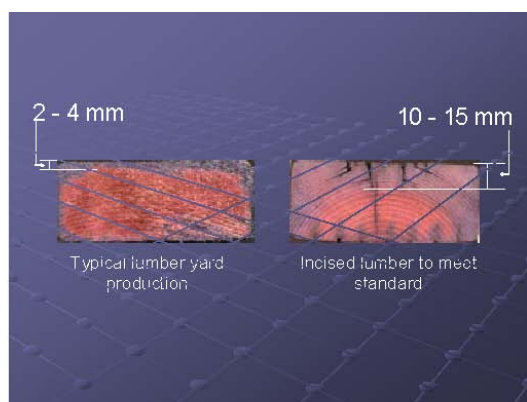

Figure 14. Comparison of un-incised shell treated wood with incised lumber

With the evolution of the residential lumber a new requirement for residential wood of 5 mm was introduced, based on the fact that much of the wood was being used above ground for where

appearance was important. Incising was not acceptable for these products so that penetration was much lower in Canadian softwoods which are mostly heartwood. The question therefore was why wood with a very thin shell of treatment, which was easily breached during the in-service check formation, did not fail rapidly. A second aspect related to performance, is the need to apply a wood preservative solution to the cross cut surfaces of sawn-wood to recreate the envelope of protection, required to protect the untreated core. It was clear that the majority of wood being used in the residential market was not being protected by end cut treatment. The mystery was that even so, it was not failing dramatically. Following extensive research, these mysteries were resolved by recognizing the importance of a small mobile component of the preservative which migrated into the checks during rain and fixed to the wood surface hereby protecting it. In CCA-treated decking it was shown that both copper, and to a lesser extend chrome and arsenic (Figure 15), were deposited onto the check surface, (Choi, Ruddick and Morris, 2001 and 2004). As wood weathers the rain causes the mobile component to migrate, some leaving the wood and being lost due to leaching, while a portion migrates and transfers to the exposed untreated wood by ion-exchange, (Choi, Ruddick and Morris, 2004; Chung and Ruddick, 2004a and 2004b). These same authors' developed a hypothesis that the principal mode of degradation for wood exposed out of ground contact was by spore germination. Earlier Choi *et al.* (2002) had shown that copper tolerant fungi were not tolerant at the spore stage. They were also able to confirm that a much lower level of copper was able to prevent spores germinating on softwood (Figure 16). Ultimately when the mobile copper was no longer available to protect the check surfaces which continue to develop during the life of the product the wood begins to decay, (Figure 17). The recognition that a small mobile component is necessary for the long term performance of shell treated wood, when used above ground, is extremely important when considering organic wood preservative formulations where mobility of the components will be very low.

CCA component of wood surface Short term exposure				
Time of exposure	Location	CCA (mg chemical/ g wood)		
		Cr	Cu	As
0.4 yr	Treated surface	11.56	7.30	5.47
	Check surface	0.07	0.29	0.11
	Untreated interior	0	0	0
1.0 yr	Treated surface	16.99	5.63	5.18
	Check surface	0.16	0.35	0.12
	Untreated interior	0.01	0.04	0.01

Figure 15. Deposition of chrome, copper and arsenic on untreated check surfaces
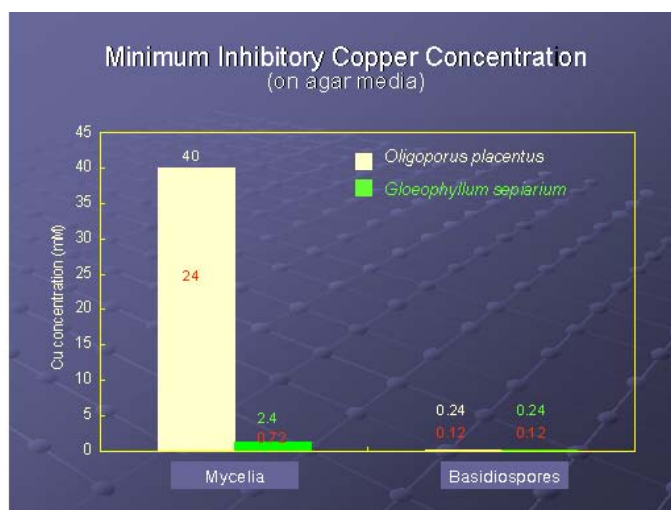
Figure 16. Minimum inhibitory copper concentration preventing spore and mycelial colonization of sapwood.

Figure 17. Decay in decking boards originating in checks.

5. Role of additives in supporting the performance of organic biocides

Several studies have examined the role of additives in enhancing the performance of treated wood. Recently a novel preservative which was based on three organic biocides (tebuconazole, propiconazole and imidacloprid) was proposed to the American Wood Protection Association (AWPA) for standardization. It was interesting to note that the formulation included provision for a water repellent stabilizer. The control of moisture and ultra-violet degradation is important for organic preservatives. A recent field study of the performance of organic preservative treated decking examined the influence of incorporating a water repellent additive, and the results graphically illustrates the value in limiting moisture uptake (Figures 18 and 19, Preston, personal communication). More research is needed on the factors influencing the long term performance of triazoles, and quaternary ammonium compounds, when formulated with additives.
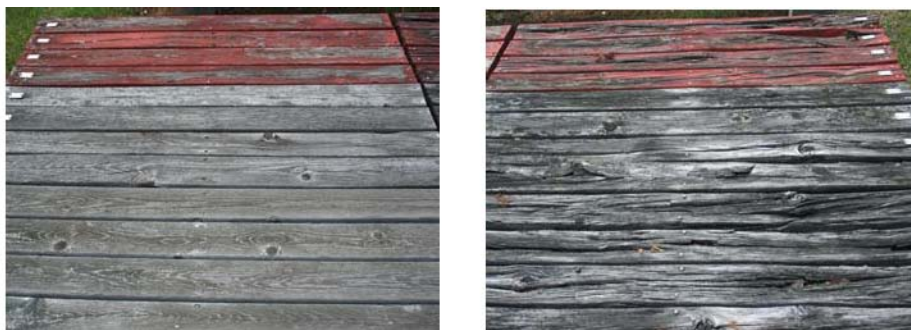
Figure 18. Effect of water repellent on the performance of organic preservative treated decking, with (left) and without (right) a water repellent additive.
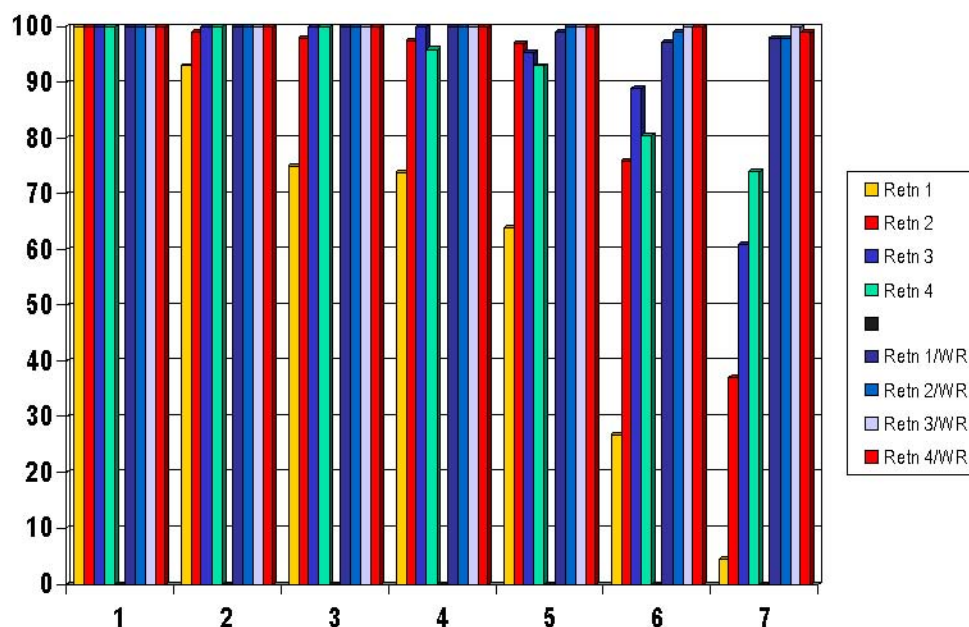

Figure 19. Impact of water repellents on the performance of an organic biocide in a Lap-joint test at Hilo, Hawaii after 7 years. (A.F. Preston, personal communication.)

6. Other factors to consider when formulating organic based wood preservatives.

While factors influencing the performance of wood preservatives totally formulated from organic biocides have been discussed above, there are several other aspects which could influence their acceptability. For example, most require relatively sophisticated analytical methodology which complex extraction techniques to measure their presence quantitatively in wood. This is not easily supported in a treating plant. In addition, most of the organic wood preservatives are colourless when placed in wood, and do not have obvious reactions which lead to coloured products. Thus determination of preservative penetration, (a requirement of quality control procedures) will require either the use of coloured additives or novel procedures to enable the penetration to be assessed. Organic biocides tend to be more expensive than metal based formulations. Fortunately, they tend to have toxic thresholds to fungi which are an order of magnitude or more lower than the metal based wood preservatives. While this provides an economic basis for considering their use, it also poses potential problems of micro-distribution in sawn wood produced from refractory species. A major factor with organic biocides, most of

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which are relatively insoluble in water, is their delivery system used to impregnate timber. Several novel treating processes have been investigated, including micro-emulsions, nanoparticle technology and super critical fluid treatment. Nevertheless it is not clear that an acceptable micro-distribution of the wood preservatives can be achieved in difficult to treat wood species such as spruce or the heartwood of some pines and Douglas-fir. This is particularly so, where co-solvents are used to allow the concentrated preservative solution to be diluted with water. For example the use of emulsions has previously been recognized as being difficult in the treatment of the refractory heartwood of Douglas-fir. Clearly much research remains to be done if the rich potential of wood preservatives totally formulated from organic biocides is to be realized.

7. Alternative strategies for enhancing wood durability

Any review of the potential replacement options for the current metal based wood preservatives, would be incomplete if the potential of alternative processes such as thermal treatments and wood modification was not recognized. These have been well described in the numerous reviews of this area of research and so will not be reviewed in detail here. Epmeier *et. al.* (2003) have described the comparison of the properties of wood which had been modified using one of eight different methods. The properties examined included durability, and the mechanical and physical properties of the treated wood. The methods studied were acetylation (Acetyl); maleoylation (MA); succinylation (SA); furfurylation (Falc); n-methylol acrylamide modification (NMA); reactive linseed oil (UZA); methylated melamine resin (MMF/Ac + MMF); and thermal modification (OHT). Only three modifications performed equally to CCA in both laboratory and field tests - acetylation, furfurylation (at medium and high loadings) and MMF (at medium and high loadings). All methods lead to a reduction in both the equilibrium moisture content (Figure 20) and impact bending strength (Figure 21). Field evaluation of modified wood in Hawaii after seven years again confirms the importance of additives in achieving an acceptable performance when used above ground, (Figure 22). Clearly further research is needed if these methods are to achieve widespread commercial acceptance.
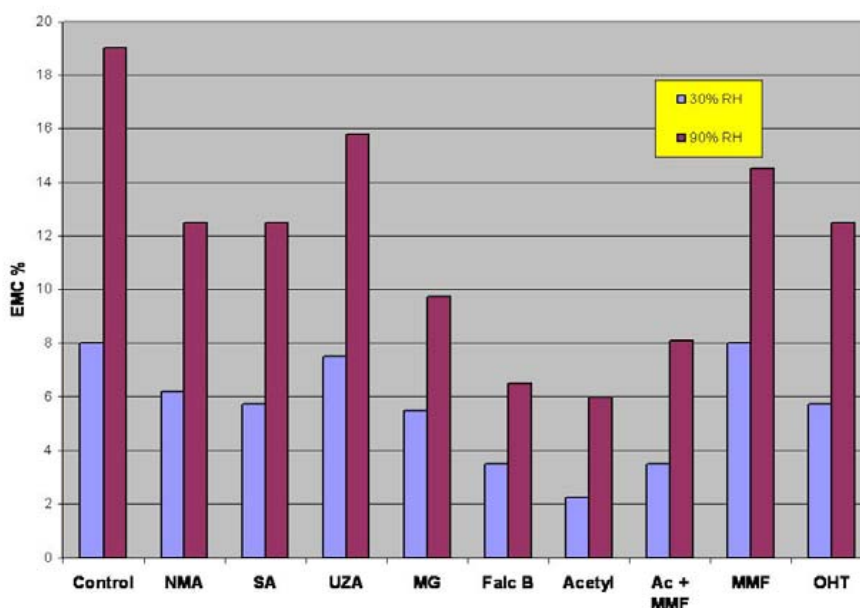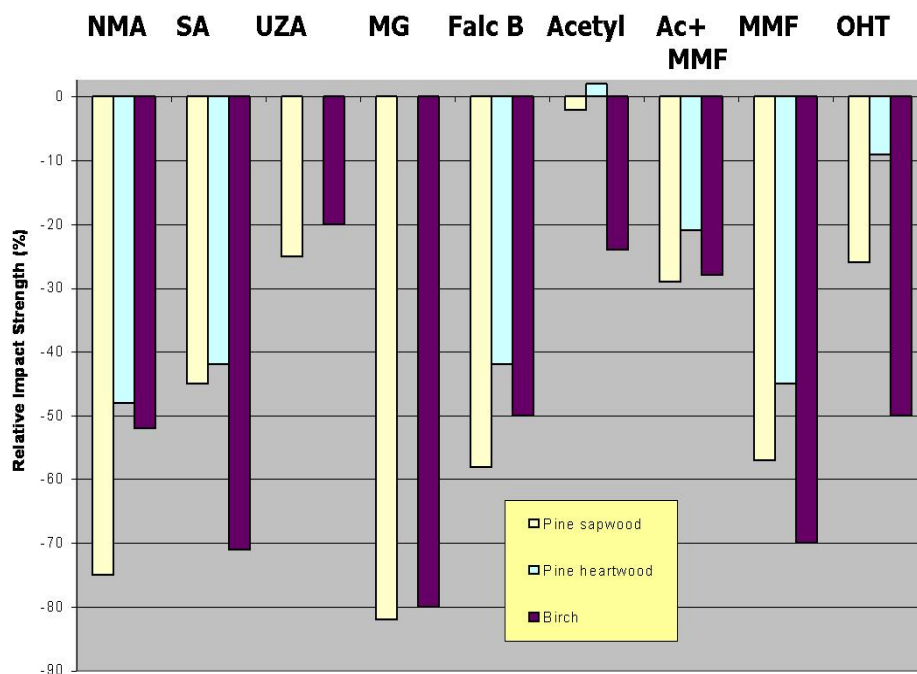
Another strategy that is receiving attention is the use of naturally occurring chemicals and research has been reported on the study of flavanones and antioxidants (Schultz and Nicholas, 2002), essential oils (Kartal *et al.* 2006; Yang and Clausen, 2006), pyrethroids, cinnamon, rosemary, carvacrol and other plant extracts (Shujun *et al.,* 2007; Maoz, *et al.* 2007), and extracts from durable woods such as teak. The cost effectiveness of such strategies remains ill-defined and many of the potential problems identified above for organic biocide formulations would apply equally well to these alternatives. The potential for producing synthetic analogues may provide one route to reducing the cost and addressing potential quality control issues.
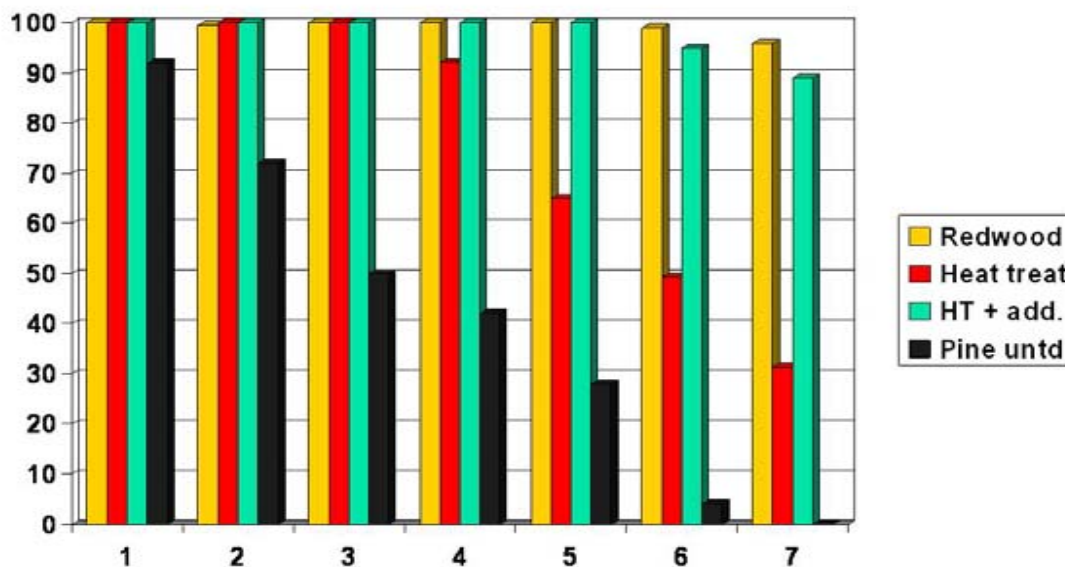
Summary

Many challenges face the replacement of metal based wood preservatives with formulations derived solely from organic biocides. However, the recent introduction of a commercial formulation indicates the interest of the industry in exploring this direction. Key difficulties to be addressed when evaluating the potential of organic biocides for use in wood preservation, include: the protection of the biocide and the wood during weathering; the role of non-decay fungi and bacteria in degrading the organic biocides; understanding the mechanisms by which the life of the wood preservative may be limited, while at the same time ensuring that the chemical can be ultimately be biodegraded to allow for recycling of treated wood; be cost effective; identify how shell treated wood will perform when no mobile component is present; identify the fungi resistant to common organic biocides and which colonize treated wood exposed abve ground, (Choi *et al.,* 2003) as having potential for use in wood preservation; develop appropriate laboratory testing methodologies for wood preservatives to be used above ground; and be able to apply quality control in terms of penetration of the biocide into the timber and quantify the amount present under treating plant conditions.

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