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Update on Research with Non-Metal Based Wood Preservative Systems

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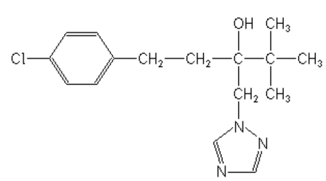
This paper is intended to be an update of an earlier presentation entitled "Opportunities and Challenges in the Development of non-metallic Wood Preservatives" made at the 28th CWPA conference held in Quebec City in 2007 (Archer, 2007)   In that presentation the case was made that the development of non-metal based wood preservatives is challenging on a number of fronts that include regulatory, performance and costs. Two years down the road those same challenges remain but significant progress has been made as exemplified by the introduction of non-metal based wood preservative systems into the North American marketplace.

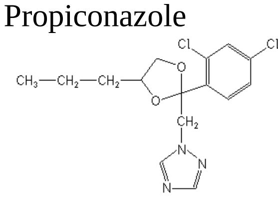
In the 2007 presentation the comment was made that the number of active ingredients available for wood preservation uses was limited. While the list of actives that are available has not changed significantly in the last two years it is important to realize that the fungicides and insecticides that are available include some very cost effective biocides. Most, if not all, were originally developed for agriculture or for other applications.

Examples of fungicides currently in use as wood preservative include members of the triazole family:

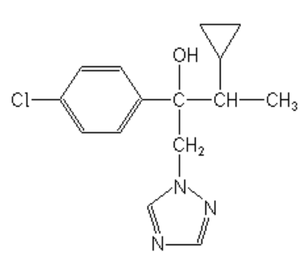
Tebuconazole



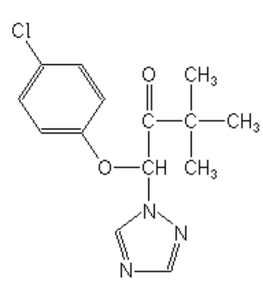
Propiconazole



Cyproconazole



Triadmephon



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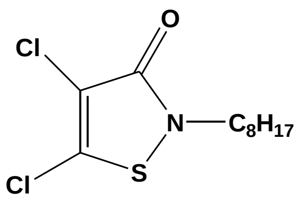
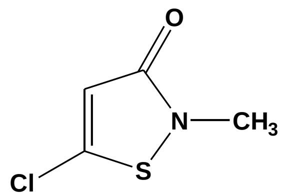
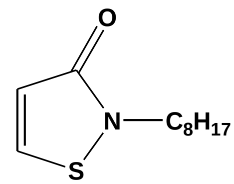
The isothiazolinone family:



DCOIT



CMI



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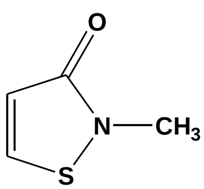

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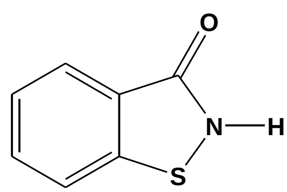
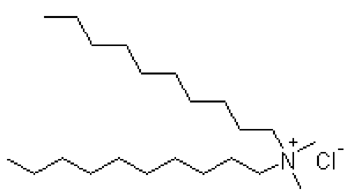


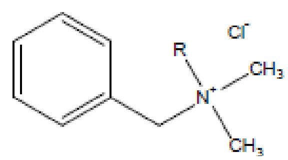
BIT

and quaternary ammonium compounds:

DDAC



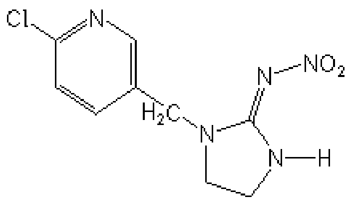
ADBAC



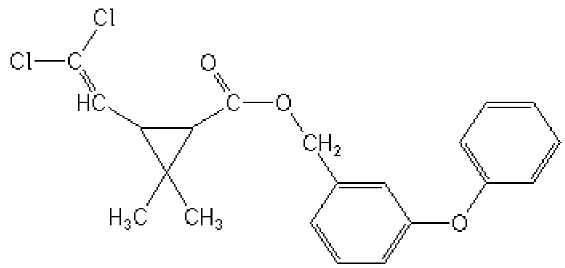
The spectrum of activity for the older generation of copper based biocides used in wood preservatives was very broad. Copper provided fungicidal and insecticidal activity. With the newer non-metallic active ingredients the spread of activity is much more restricted. This is especially true with respect to insecticidal activity where the non-metallic fungicides typically have limited or no activity. As a consequence insecticides such as imidacloprid and permethrin are often found in combination with non-metallic fungicides.

Insecticides:

Imidacloprid



Permethrin



Combinations of different fungicides are being tested with and without insecticides are to create broader spectrum or even synergistic wood preservative formulations. Proprietary combinations of azoles e.g. Triademefon and Tebuconazole (Preventol® A20) or Propiconazole and Tebuconazole illustrate the concept. Figure 1 shows the relative performance of different azoles in combination when tested against a range of decay fungi using the EN 113 agar block procedure with EN73 leaching. Data on the 'Y' axis are reported as toxic values in kg a.i,/m^3.

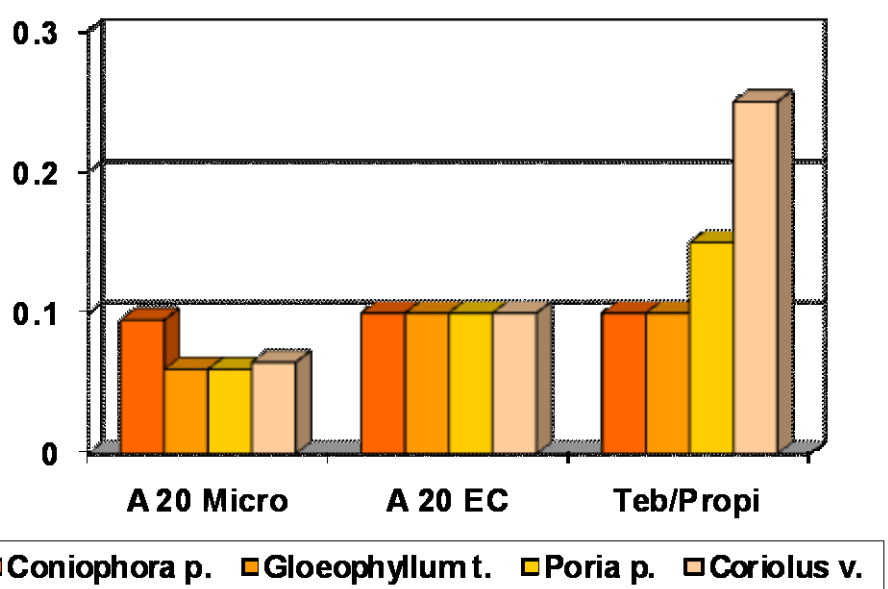


Figure 1

The US Environmental Protection Agency (EPA) and the Canadian Pest Management Regulatory Agency (PMRA) regulate the use of pesticides in North America.

Fortunately for the wood preservation industry previous registration activity for non metal active ingredients used in agriculture has led to the development of extensive toxicity and product chemistry dossiers that are useful for wood preservation registration submissions. In recent years the PMRA and EPA have expressed a desire to conduct joint reviews on new actives citing the potential for improvements in efficiency, a reduction in costs and shortening the length of time to market. Industry has been slow to take advantage of the joint review concept primarily because of the perception that a joint review by the two agencies will increase the timeframe for the process significantly. EPA and PMRA are working with industry to ensure that that is not the case. A number of registration submissions for non-metallic formulations for use as wood preservatives are purportedly in the pipeline but, given the proprietary nature of registration submissions, specific information is not available.

In the Canadian standards arena there appears to be little indication of any significant activity with respect to standardization of non-metallic preservative systems for wood preservative uses. The Canadian Standards Association Technical Committee A366-TC has a standing subcommittee (subcommittee “Q”) chaired by Dr. Paul Morris. At the time of writing there are no submissions under consideration by the subcommittee but within the next 12-24 months it seems likely that proposals might be brought before A366. In preparation for that event minimum data criteria have been drafted to provide guidelines for wood preservative manufacturers. On the Canadian Building Code front there has been talk about the Canadian Construction Materials Centre (CCMC) developing wood preservative evaluation reports to support Canadian national building standards but nothing tangible has materialized to date.

In the United States there has been significant activity related to non-metallic wood preservative systems by the American Wood Protection Association (AWPA) technical committees. In 2008 two products, one designated PTI (Propiconazole + Tebuconazole + Imidacloprid and the other EL2 (4, 5 dichloro-2-n-octyl -3(2H)-isothiazolone (DCOIT) combined with Imidacloprid and a moisture controlling stabilizer) were standardized for above ground uses. Both formulations combine fungicides with insecticides.

Minimum data requirements for the non-metallic systems are the same as those submitted for conventional metal based systems. Thus, the data submitted to the AWPA in support of the EL2 system included eight year AWPA E9 L-Joint test data after 8 years exposure in Hawaii and Florida, Seven to nine years exposure with the AWPA E 16 Lap-joint test procedure in Hawaii, Florida and Australia as well as 3.5 year AWPA E18 Ground proximity decay test data from Hawaii.

Out of concerns about potential fungal tolerance problems with non-metallic systems AWPA protocols recommend that pure culture laboratory test data are provided in support of a candidate wood preservative system. Weight loss data from an AWPA E10 soil block test of EL2 treated material are summarized below in Table 1.

Table 1 - E10 soil block results for the EL2 system

Treatment	Weightloss %				
	Trametes versicolor	*Gloeophyllum trabeum*	*Postia placenta*	*Neolentinus lepideus*	*Antrodia vaillantii*
Untreated	78	39.4	40	28.6	10.1
EL2 0.15 kg/m^3	-0.6	12	1.1	-0.1	2.7
EL2 0.21 kg/m^3	0.8	7	0.4	-0.8	1.0
EL2 0.3 kg/m^3	-1.3	-1.3	-3.9	-2.3	-0.9
EL2 0.4 kg/m^3	-1.6	-0.4	-2.6	-2.0	-0.7
EL2 0.6 kg/m^3	-1.6	-1.8	-3.3	-2.4	-1.7

The data demonstrate that the EL2 formulation controls white rot and brown rot decay fungi at relatively low retention levels.

Other alternative laboratory test procedures such as the AWPA E22 soil block test that relies on changes in compressive strength as a function of decay fungal activity have been successfully used with non-metallic systems. Table 2 summarizes the toxic threshold values of EL2 formulations with and without the moisture controlling stabilizer (MCS).

Table 2: AWPA E22 Soil block test results for EL2 exposed to *Gloeophyllum trabeum* for four weeks.

Formulation	Toxic Threshold Range (pcf)
DCOI	0.024-0.036
DCOI + 0.5% MCS	0.012-0.023
DCOI + 1% MCS	0.013-0.025

The data in Table 2 show that the MCS component reduces the toxic threshold level significantly. In fact, for the AWPA standardization of EL2, the MCS component was considered as part of the standard with a minimum specified retention level based on non-volatile solids content in addition to the minimum retention level for DCOIT + Imidacloprid actives.

In the United States over the last few years there has been considerable activity associated with non-metallic preservatives and the International Code Council Evaluation Service (ICC-ES). The ICC-ES has published a number evaluation reports ESR 1477 (Propiconazole+ Tebuconazole + Imidacloprid) for above ground applications; ESR 2067

(Tebuconazole + Imidacloprid) for above ground applications; ESR 1851 (DCOI + Imidacloprid) for above ground applications (ICC-ES, 2009).

The importance of penetration and retention to wood preservative performance has long been recognized. While the penetration of green color of traditional copper based preservative systems can be readily seen with the naked eye or after it has been enhanced with chemical reagents such as chrome azurol, rubeanic acid or PAN; the non-metallic formulations typically give no color to the treated wood and they do not form colored complexes with simple reagents. This creates a significant quality control issue for both the treating plants and third party inspection agents. One simple approach that has been suggested is to mark the presence of wet (treated wood) zones immediately after treatment (Photo 1).

Photo 1: Use of the "wet zone" marking to indicate penetration of clear non-metallic preservative systems in the cross section of treated wood

Unfortunately this technique has little to no value to a third party monitoring program as the wood is generally dry at the time of inspection. Furthermore the technique does not work well with the traditional core samples routinely taken by in-plant or third party inspection agencies. It does however have limited potential if cross sections are available for example with pressure treated mill work. An interesting modification of this approach involves the use of dyes to more clearly delineate untreated zones. The dye approach is most useful when the wood has been treated with a preservative system containing a water repellent component. Photo 2 shows the cross sections of a number of treated pieces of dimensional lumber treated with a water repellent preservative formulation before and after spraying with a blue dye solution. The dye penetrates the zones where the water repellent and preservative has not penetrated.

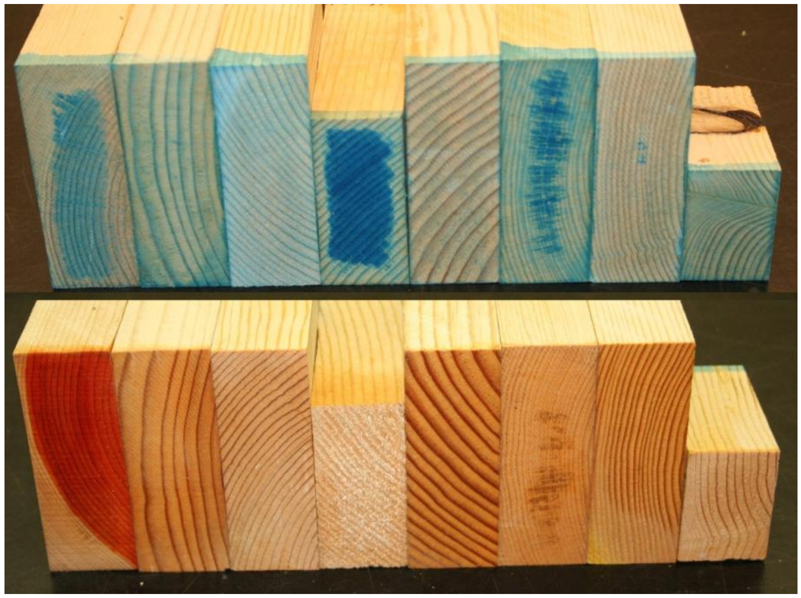


Photo 2: Freshly cut ends of millwork lumber treated with a clear non-metallic preservative system containing a water repellent additive before and after spraying with a blue dye. Untreated zones where the water repellent preservative has not penetrated are colored darker blue.

A third approach adopted with recent standardization of PTI and EL2 by the AWPA involves the use of surrogate penetration additives in the treating solution coupled with the use of reagents to detect the presence of the surrogate in treated wood. For example borate and phosphate additives can be used with PTI while copper based additives can be used with EL2. Concerns have been raised about whether or not the use of additives is valid if the non-metallic biocide is carried into the wood in the "organic" phase of the treating solution and the surrogate in carried in the "aqueous" phase. Work is ongoing to determine if the concern is valid.

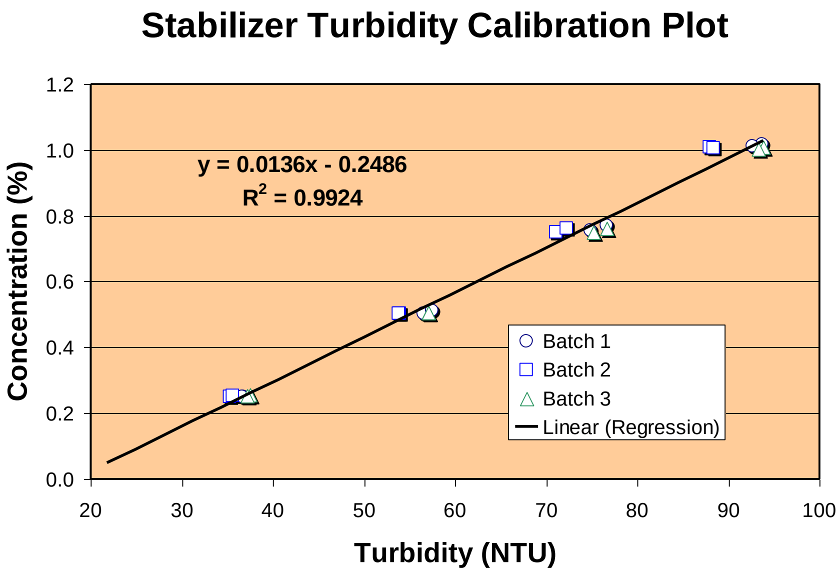
Development of standardized analytical procedures for non-metallic preservative system components at the treating plant level has also proved to be a challenge. For copper based systems X-ray fluorescence (XRF) analyzers have proven to be reliable tools for the rapid analysis of solutions and wood samples. The training required to use bench top XRF devices is minimal but in contrast the quantification of non-metallic biocide components in wood and solution relies on more sophisticated and complex analytical tools such as gas chromatography or high performance liquid chromatography. Standard procedures exist for the actives used in wood preservative formulations but more extensive training is required to use the equipment and for sample preparation. While experience has shown that in-plant QC personnel can be retrained successfully another approach has been to send samples back to the preservative supplier for analysis. The logistics of this approach can be a problem at a plant with high throughput. However, despite these limitations, with proper product stewardship and third party oversight it is possible to produce quality products in conformance with industry standards.

Given the importance of moisture controlling stabilizers and water repellents (i.e. non conventional active components) in non-metallic wood preservative formulations analytical procedures for those components have been developed to ensure that the treated products perform to an acceptable standard. For the AWPA standardized EL2 system a simple turbidometric procedure (AWPA A46) has been developed for the stabilizer in solution and an FTIR procedure (AWPA A47) has been developed for the stabilizer in wood. The simplicity and low cost of the turbidometer equipment required for solution analysis (Photo 3) lends itself to in-plant quality control.

Photo 3: A simple and inexpensive turbidity meter for in-plant QC of water repellent stabilizers in solution.

Using such a device it is possible to develop very strong turbidity/concentration curves for routine quality control in the plant as illustrated in Figure 1.

Figure 1: Stabilizer Turbidity Calibration plot. (from: Walcheski and Jin 2008)



Analysis of hydrocarbon wax based water repellent stabilizers in wood can be achieved through the use of Fourier Transformed Infrared (FTIR) analysis. Unfortunately interpretation of FTIR is inherently more complex than turbidity measurement and the equipment itself is more expensive. So much so that it is beyond the means of most treating plant QC environments. Nevertheless the concept is relatively simple and involves grinding the wood in a Wiley mill extraction with tetrachloroethylene, evaluation of the infrared C-H stretch region in absorbance mode and development of a calibration curve for peak height and % stabilizer. Example plots for the moisture controlling stabilizer system used with EL2 are provided in Figure 2 and Figure 3.

Figure 2:

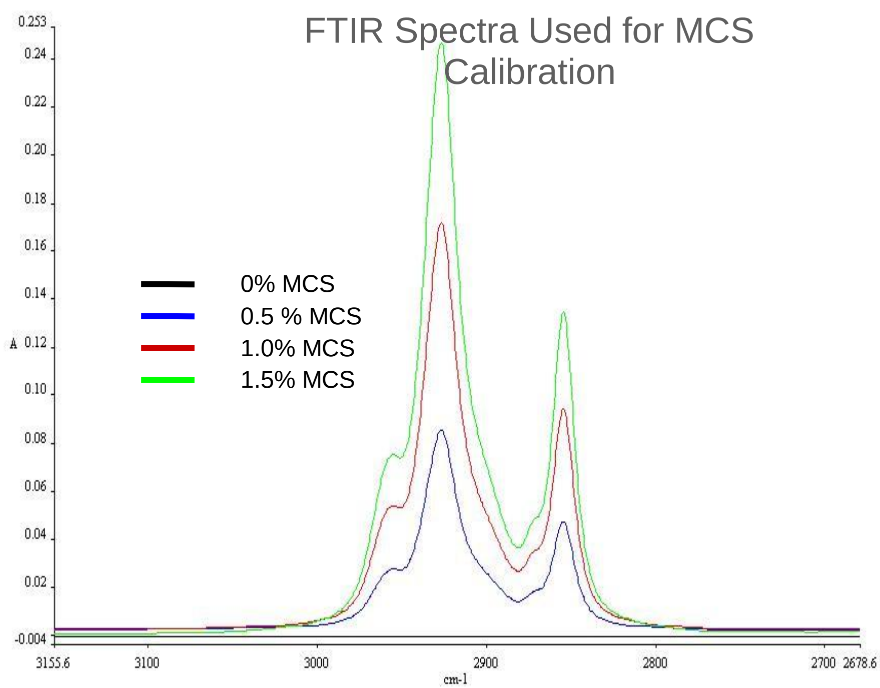
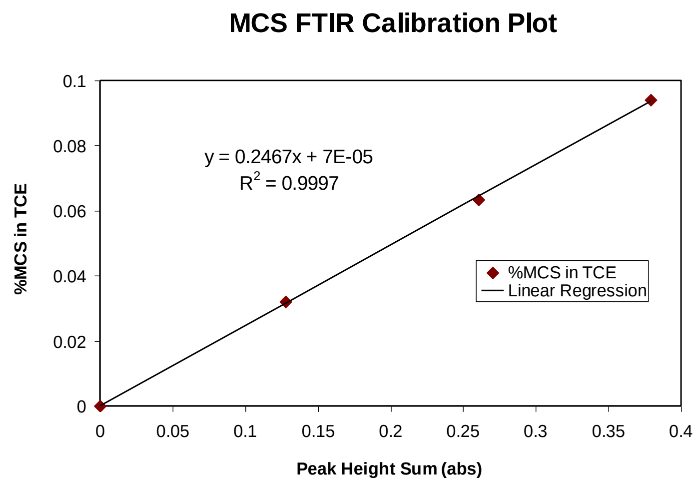


Figure 3:



The initial visual appeal of treated wood is high but without appropriate protection the surface of wood in service degrades, the color is lost and raised grain, checking and cracks as well warping and bowing manifest themselves. These unsightly changes are caused by ultraviolet light, repeated shrinking and swelling cycles from weathering events, bio-deterioration from mold and stain organisms and interactions from all three factors. Unlike copper based preservative systems the non-metallic biocides provide little weathering protection on their own. The inclusion of stabilizers and water repellents can help against cracking and splitting. Pigments can provide additional surface protection from UV while at the same time imparting color and enhancing product appearance. Of course the incorporation of these additives into a non-metallic wood preservative system creates the potential for significant cost performance issues. Research to find the "magic" combination of additives for non metallic preservative systems is on-going.

In common with metal based preservatives systems the performance of non metallic preservative systems is somewhat dependent of longevity of the active ingredient in the wood. Fortunately non-metallic biocides are generally non-polar and as a result then tend to be non-soluble or sparingly soluble in water. They "fix" by deposition or entrapment as opposed to chemical reaction with the wood substrate. Losses due to depletion can be reduced by the addition of moisture controlling additives such as water repellent emulsions to the preservative solution. Not only are losses of preservative active attributable to depletion they can also occur through biodegradation. Bacteria and stain and mold fungi are well known for their ability to degrade organic active ingredients. The problem is particularly acute in soil contact situations. A "cocktail" approach is generally considered to be a cost efficient strategy to counter biodegradation and a number or researchers are actively engaged in the evaluation of the benefits of antioxidants, metal chelators and water repellants. Another strategy is the control of mold in service. The incorporation of mold inhibitors into non-metallic wood preservative formulations can enhance the appearance of treated wood while at the same time minimizing the likelihood of degradation.

In summary, it is apparent that considerable progress has been made in the last few years in expanding the application of non-metal biocide technology to the wood preservative arena. Cost/performance parameters relative to conventional copper based technologies continue to be a limiting factor. Customer expectations about aesthetics of treated wood in service will continue to be a challenge with non-metallic preservative systems but the combination of fungicides, insecticides, mold control technology, water repellents and pigments offers the potential for successful high performance products.

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