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Section 3 **Wood Protecting Chemicals**

Polymeric Betaine as a Wood Preservative

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ABSTRACT

Didecyl polyoxyethyl ammonium borate (DPAB), also known as Polymeric Betaine, was developed as a co-biocide for chromium-free copper based wood preservatives in Europe in the 1980's. This paper summarizes the properties of DPAB as a wood preservative. Unique properties related to the betaine nature of DPAB are discussed in terms of the structure-property relationship. Physical properties of DPAB treated wood and properties of DPAB formulations are discussed. Unlike many preservative systems which have negative impact on strength and other physical properties of wood composites, it was discovered that DPAB based formulations were especially suitable for treating wood furnish before composite manufacturing. Typical laboratory and field performance data of DPAB formulations are presented.

Keywords: Polymeric Betaine, DPAB, quaternary ammonium compounds, AAC, didecyl bis(hydroxyethyl) ammonium borate, distribution gradient, fixation

1. INTRODUCTION

During the 1980`s a lot of work was done in Europe to introduce new chromium-free water born products for wood preservation to address environmental concerns. During the development of wood preservatives, the consideration of environmental impact of new products has to be an important part of the strategy due to lack of control over the environmental fate of preservatives if leached during service or from waste wood. For wood protection in ground contact, all these second generation water born products were based on a copper and an organic co-biocide. Suitable organic co-biocides for wood preservatives include triazoles, and quaternary ammonium compounds.

Alkyl ammonium compounds (AAC) have good biological efficacy, acceptable environmental characteristics, and are cost effective. However, AAC's have some disadvantages as wood preservatives due to surface spotting and non-uniform penetration. This was the starting point of our development with the objective to overcome the disadvantages of AAC´s without loss of efficacy and other desirable properties.

When the details of the performance of quaternary ammonium compounds were analysed, the excellent activity of DPAB against copper tolerant fungi was discovered (Fig. 1).

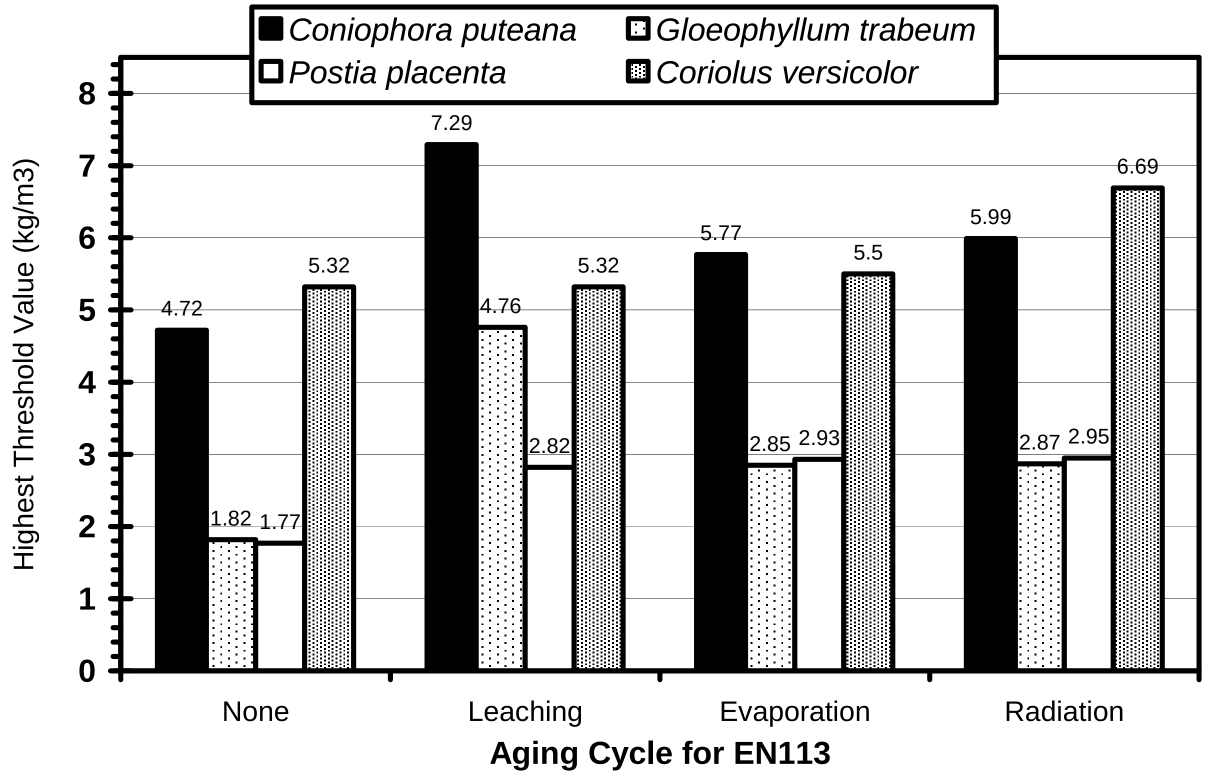

Figure 1. EN113 highest thresholds of DPAB for four fungi and four aging techniques.

DPAB was found to be synergistic with copper as shown in Figure 2. Impralit KDS was designed as a heavy duty preservative for pressure treatment for in-ground and above-ground

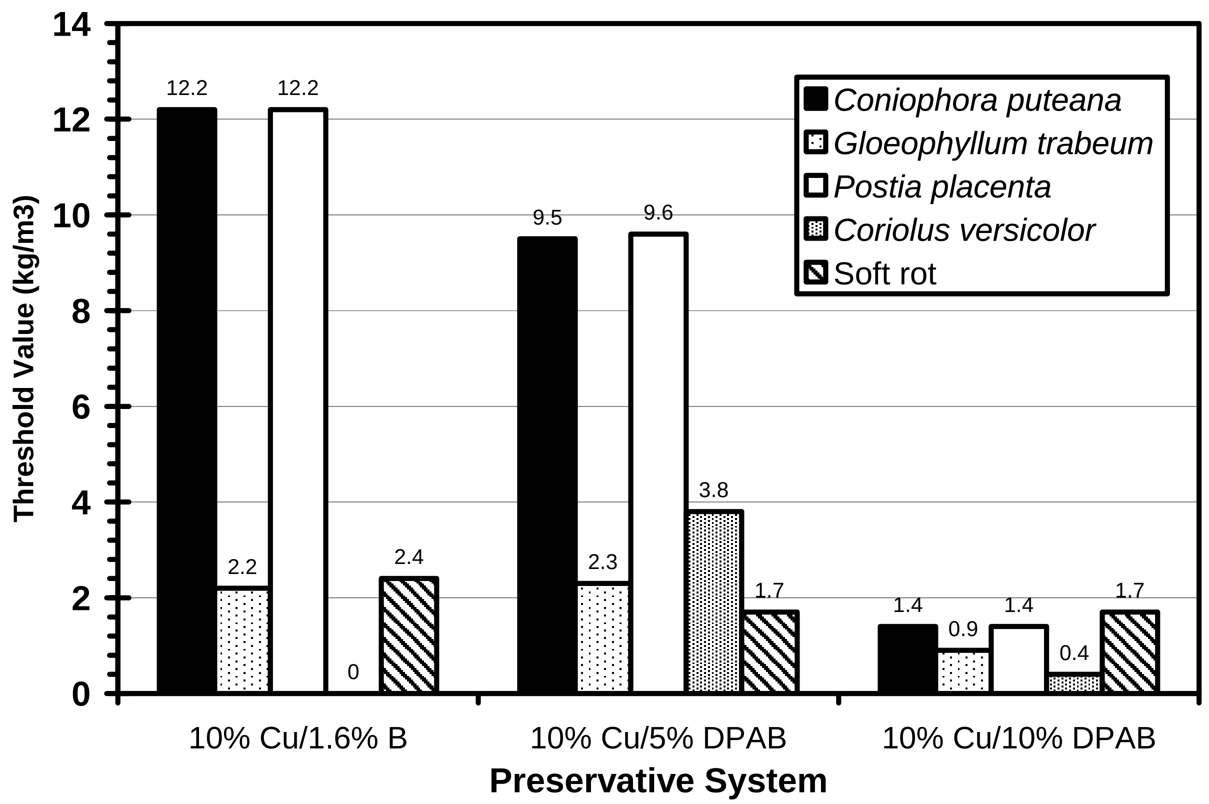

Figure 2. Effect of DPAB on the threshold values from EN113 tests and soft-rot tests after leaching.

applications based on this synergy. Impralit KDS contains copper, DPAB, and boric acid. KDS was commercialized in Europe in 1992. The Impralit KDS-B formulation is identical to KDS except no additional boric acid is added. KDS-B still has borate as counter ion for DPAB. In recent years other formulations based on DPAB has been developed. One of these formulations is Impralit TSK10 which contains DPAB and Fenoxycarb.

2. THE CHEMISTRY OF DPAB

Typical alkyl ammonium compounds are synthesized by reacting an amine and an alkylating agent such as alkyl halide, sulfate esters, or carbonate esters. Didecyl polyoxyethyl ammonium borate (DPAB), or more precisely didecyl bis(hydroxyethyl) ammonium borate, was synthesized by the reaction of a dialkylamine with ethylene oxide and boric acid. The resulting quaternary ammonium compounds are very stable under alkaline and strong acidic conditions.

DPAB exists as a mixture of monomer and dimers depending on the concentration, pH, and other factors. In the neat form which contains about 60% active DPAB, it exists as almost 100% dimer. At typical work solution strength for wood preservation, DPAB has about 70-80% in the dimer form. The monomer form dominates only at more than 100-1000 fold dilutions. Solution equilibrium for DPAB is shown in Figure 3.

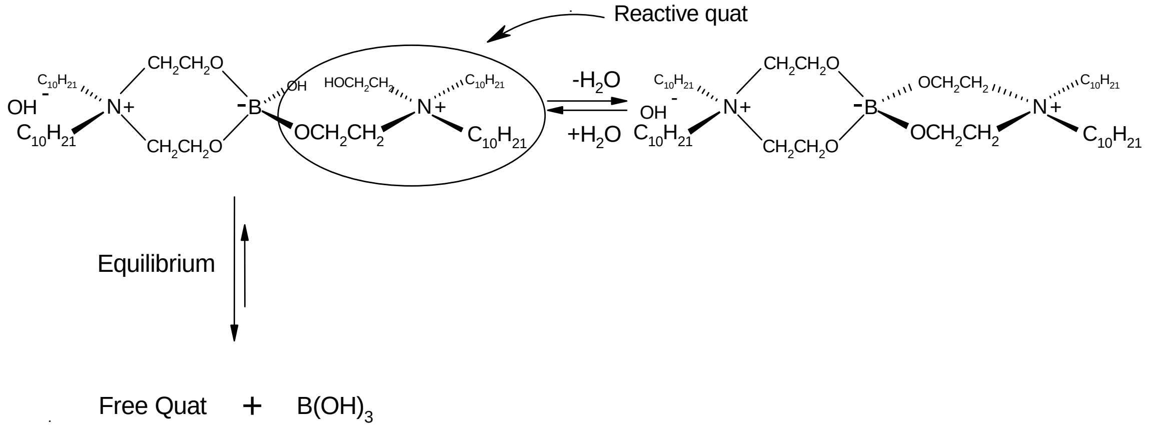

Figure 3. Equilibrium of Polymeric Betaine (DPAB) in solution

The existence of DPAB dimers and the equilibrium shift between the dimer and monomer can be monitored by using direct infusion electrospray mass spectrometry (Figure 4).

It is well known that typical quaternary ammonium compounds such as DDAC and ADBAC have strong interactions with wood components (Jin and Preston 1991, Jiang 2008). Because of this strong interaction, these cationic biocides have a steep distribution ingredient. The outer layers of the treated wood have much higher concentrations of the biocide than the inner layers. For some cationics under certain conditions, the center of the treated wood has such low levels that are below the toxic threshold. On the other hand, the strong interaction of quaternary ammonium compounds with wood also leads to excellent fixation in wood (Jin and Preston 1991).

The betaine nature of DPAB presents unique properties as a wood preservative. Since DPAB exists mostly in the betaine dimer form at work solution strength, it does not behave as a typical cationic molecule and therefore does not have strong interactions with wood components during the wood treating process. Upon fixation, however, DPAB behaves as a

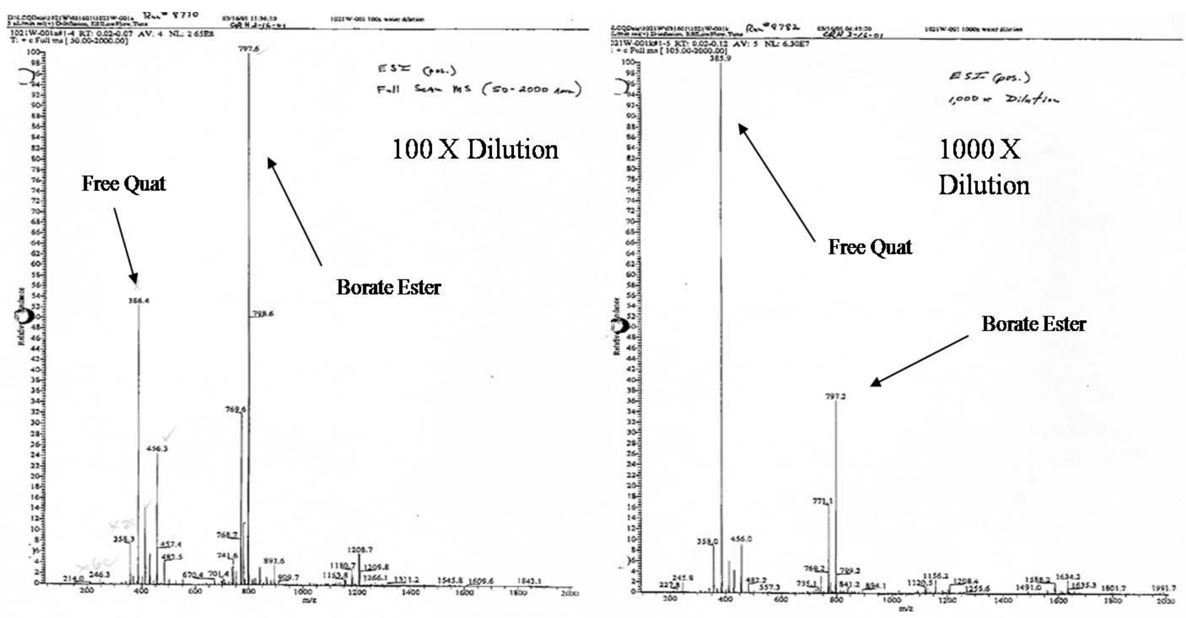

Figure 4. Mass spectrum of DPAB at different dilutions

cationic molecule and has excellent fixation properties in the treated wood. It is believed that the hydroxyl groups of DPAB also allow interaction with wood through hydrogen bonding. Typical AACs do not have hydroxyl groups and their fixation in wood does not involve hydrogen bonding.

2.1 Distribution gradient of DPAB in treated wood

The distribution gradient of DPAB in treated wood was studied in two separate tests. In the first test, the concentration of DPAB in Impralit KDS pressure treated SYP 2x4 (39x89 mm) was analyzed at different depth. As shown in Figure 5, the DPAB has almost flat distribution similar to that of the copper component of CCA at 6.4 kg/m^3. The copper component in KDS has a similar distribution gradient as other alkaline copper systems.

In the second study, the concentrations of DPAB and copper in the inner and outer zones of five KDS pressure treated 2x2 (39x39 mm) stakes were analyzed. Average DPAB concentration varied little across the zones while some gradient was noted with the copper component (Figure 6).

2.2 Fixation and leaching of DPAB

As shown in a number of studies, DPAB fixes strongly in wood. In one study, wood treated with Impralit KDS containing ^{14}C labeled DPAB was reduced to wood dust and the dust was subject to six consecutive steps of extractions (Table 1). DPAB released to the extraction fluid was quantified by liquid scintillation counting. After the exhaustive extractions, the remaining solid was combusted and the radio carbon quantified.

In the first step, the wood dust was extracted with a mixture of 0.05 M pH 7 phosphate buffer and 0.05 M NaCl in order to remove the DPAB fixed through the ion exchange mechanism. Surprisingly, only 1.8% DPAB was removed. This may be due to the fact that DPAB solubility in water is decreased by the presence of salts, especially di- and tri-valent ions. Although DPAB is freely soluble in water, low concentration of salt can “oil out” DPAB.

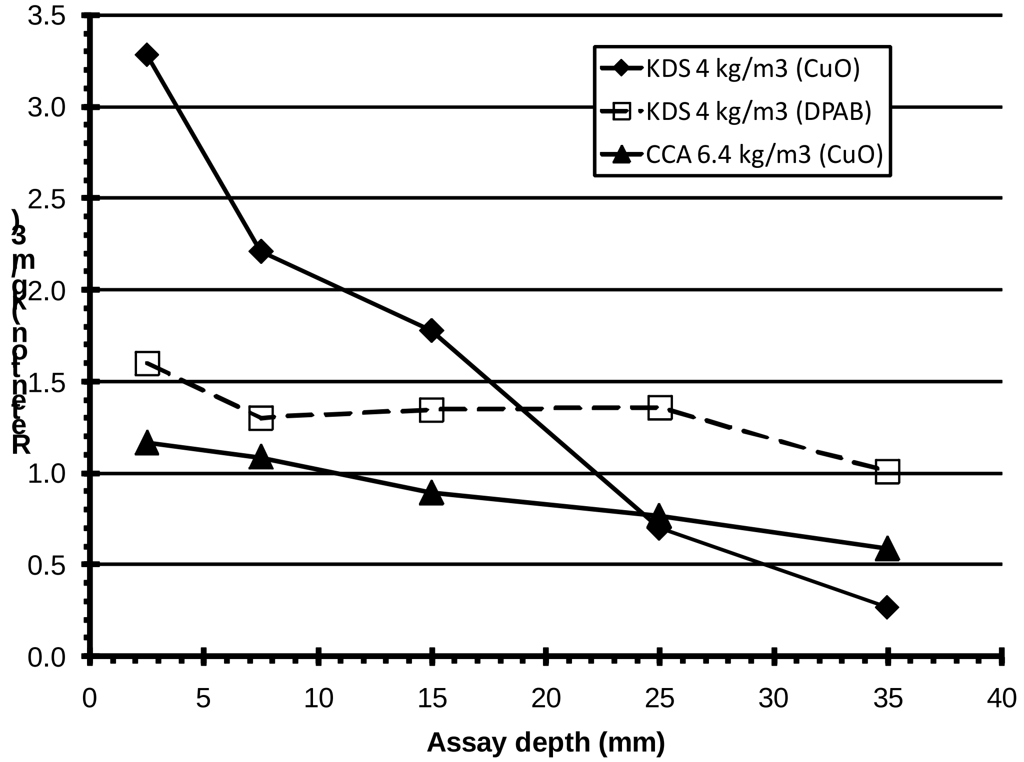

Figure 5. Distribution gradient of DPAB and copper in KDS-treated southern pine (SYP) 2x4s compared to copper distribution in CCA treated southern pine.

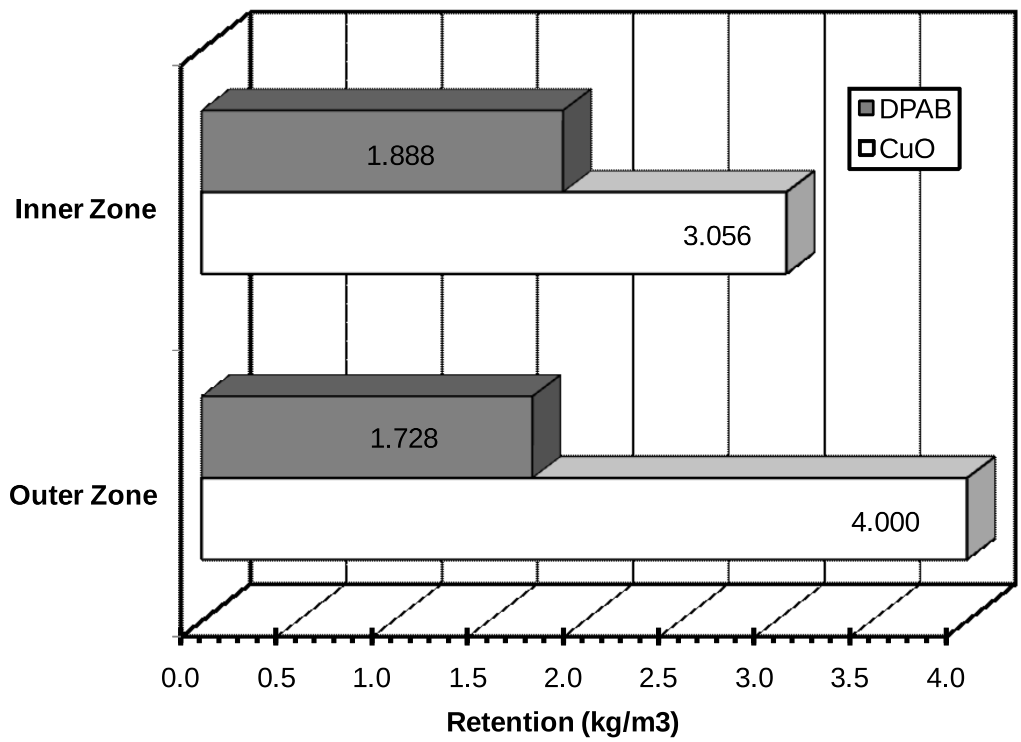

Figure 6. Distribution gradient of DPAB and CuO in KDS-treated SYP 39x39 mm stakes.

This property of DPAB, though advantageous in some aspects, poses formulations challenges. In the earlier stages of Impralit KDS development, formulation stability was problematic. This may be responsible for occasional poor results observed in competitor testing where samples were taken from un-agitated tanks at treating plants.

In the second step of the harsh extraction series, the solid was incubated with cellulase enzyme for 48 hours at 37 ^{o}C. Only 10.3% DPAB was found in the supernatant.

Table 1. Extraction of DPAB from Impralit KDS treated wood

Procedure	Purpose	DPAB removal/recovery
0.05 M pH 7 phosphate buffer + 0.05 M NaCl, 10 min. extraction	Ion exchange	1.8%
Cellulase enzyme, 48 hrs at 37^{o}C in 0.05 M sodium acetate buffer	Breakdown cellulose	10.3%
0.05 M Sodium acetate/0.05 M EDTA, 15 hrs at 70 ^{o}C	Dissolve pectin	3.8%
Acetic acid/$NaClO_2$, 4 hrs at 70^{o}C	Breakdown lignin	2.8%
24% KOH, 15 hrs at 25^{o}C	Hemicellulose extraction	27.8%
72% H_2SO_4, 4 hrs at 25^{o}C	Cellulose hydrolysis	0.4%
Residue combustion	Recovering remaining bound ^{14}C	48.0%
Total recovery		94.8%

A mixture of sodium acetate and EDTA used for extracting pectin removed 3.8% DPAB. A mixture of acetic acid and sodium chlorite, suitable for breaking down the lignin fraction of wood, removed 2.8% DPAB. Extracting the residue with 24% KOH for 15 hours at 25 ^{o}C, designed for the dissolution of hemicelluloses, removed 27.8% of DPAB.

Finally, reacting the residue with 72% sulfuric acid removed 0.4% DPAB. After the six-step consecutive harsh extraction procedures, 48% radio carbon remained in the final reside.

These results strongly support the excellent fixation of DPAB in the treated wood. It should be indicated, however, that the extraction procedures in this study were not designed to completely remove a certain fraction of wood. For example, sulfuric acid and other acids have been used to completely hydrolyze the polysaccharides in wood to prepare acid lignin or to determine the lignin content. The sulfuric acid treatment in the current study was insufficient to remove all carbohydrates.

3. EFFICACY OF DPAB FORMULATIONS AGAINST DECAY FUNGI

In a seven year fungus cellar test carried out by BAM, Impralit KDS showed excellent efficacy in comparison with CCA (Fig. 7).

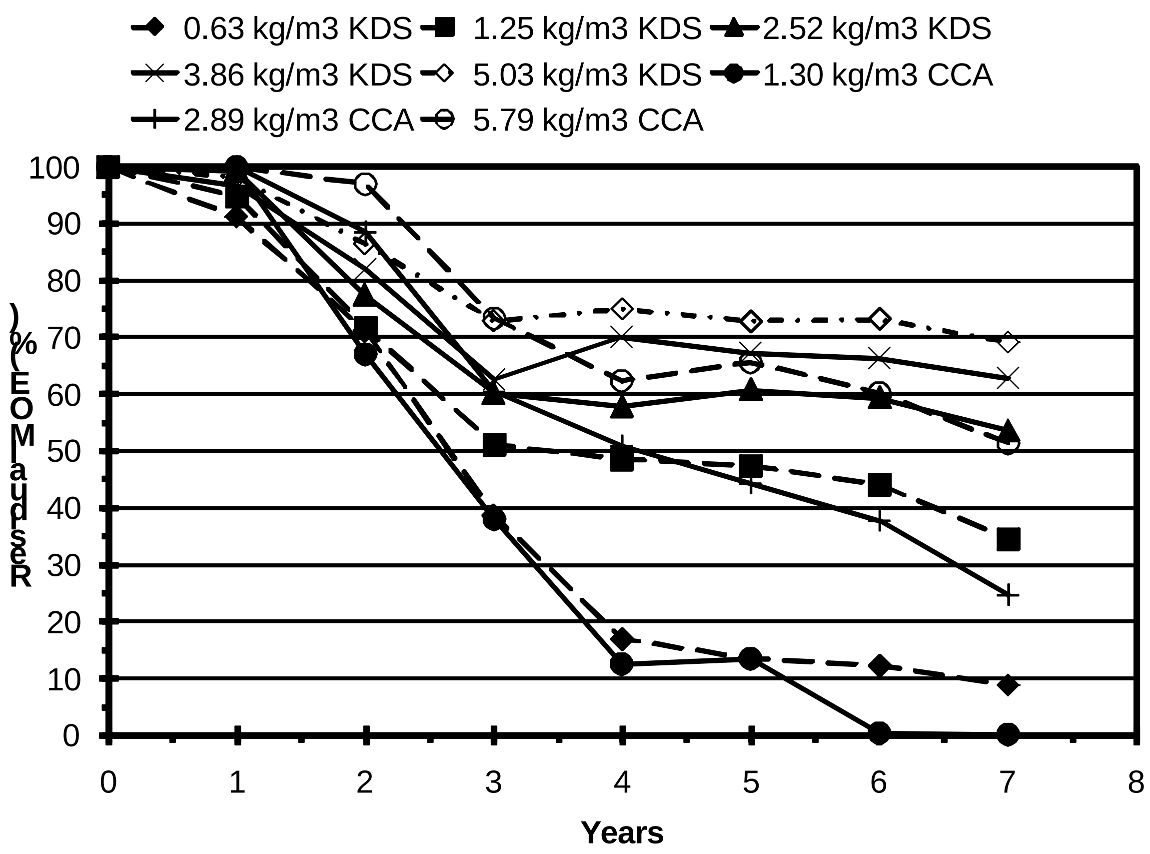

Figure 7. Residual MOE of fungus cellar stakes in a 7-year test at BAM.

In two separate 10-year field tests in Norway and Sweden, KDS showed similar or better performance than CCA (Figures 8, 9).

4. DPAB AS AN ACTIVE FOR ANTI-SAPSTAIN FORMULATIONS

Forintek Canada Corp. (Now FPInnovations) carried out a 12-month field trial comparing DPAB with NP-1(Minchin and Byrne, 1995). It was concluded that at 210 μg/cm^2, DPAB provided satisfactory 12-month protection of green Douglas fir and Hem-fir. In comparision, NP-1 at up to 180 μg/cm^2 retention did not provide satisfactory protection.

In a recent laborotary test in North America, a DPAB based formulaiton was found to be 1.5-2 times more effective than a popular commercial product in North America.

In an European field trial, a DPAB based formulation was found to be more effective than a popular commercial formulaiton for the protection of green pine and spruce.

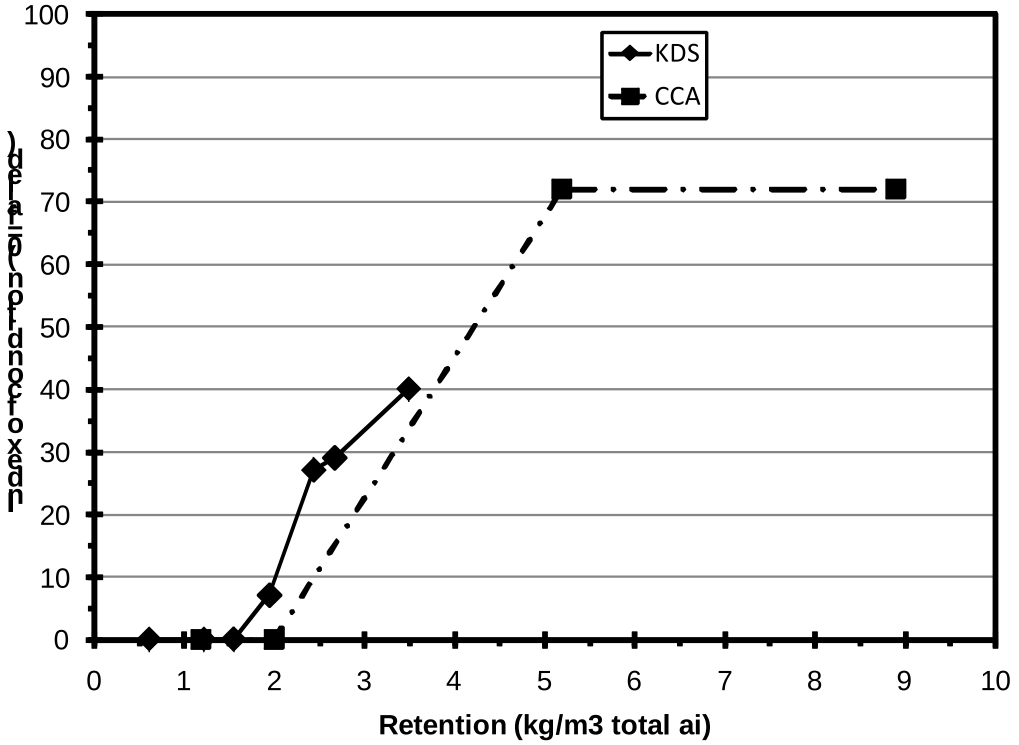

Figure 8. Dose response of KDS and CCA in a 10-year stake test in Sorkedalen, Sweden.

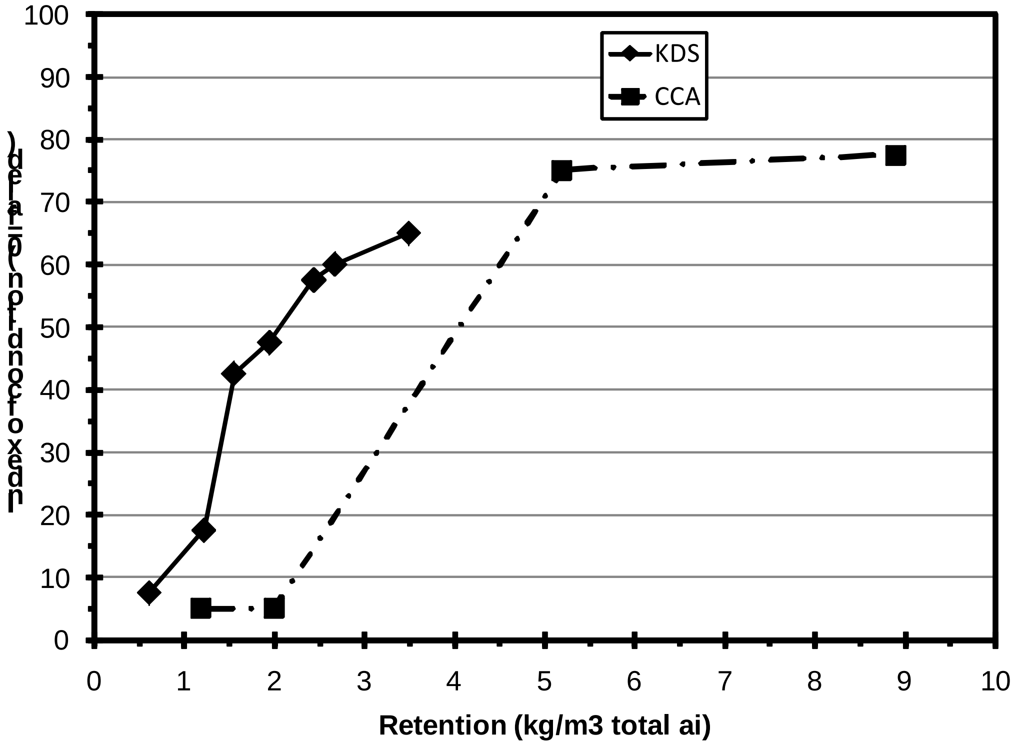

Figure 9. Dose response of KDS and CCA in a 10-year field test in Simlangsdalen, Norway.

5. EFFICACY OF DPAB FORMULATIONS AGAINST INSECTS

DPAB based formulations are efficacious against beetles, termites, and other insects as shown by the low toxic threshold values in Tables 2 and 3. In the AWPA E-1 laboratory termite test carried out at Mississippi State University, KDS showed termite repellency.

Table 2. Toxic threshold of Impralit KDS

Organism	Toxic Threshold (kg/m^3)
Hylotrupes bajulus	< 0.22
Reticulitermes santonensis	< 2.89
Mastotermes darwiniensis	< 1.83
Coptotermes acinaciformis	< 1.83

Table 3. Toxic threshold of Impralit KDS determined according to AWPA E-1 test.

	Reticulitermes flavipes (kg/m^3)		*Coptotermes formosanus* (kg/m^3)	
	Unleached	Leached	Unleached	Leached
KDS	2.1 – 3.2	< 2.1	3.2 – 4.3	2.1 – 3.2
CCA	< 2.1	< 2.1	4.0 – 6.4	< 2.1

6. CORROSION CHARACTERISTICS

The corrosion characteristics of KDS and ACQ treated SYP were compared using a modified AWPA E-12 method at Mississippi State University. Both ACQ and KDS were at 6.4 kg/m^3 retention. The sandwich assemblies were exposed at 50.5 ^{o}C and 91% relative humidity for 28 days. After cleaning, the rate of corrosion in mils per year (one mil equals to 0.025 mm) was calculated based on weight loss and surface area. As shown in Table 4, KDS treated wood is less corrosive than the industrial standard ACQ.

The solution corrosion characteristics of Impralit KDS and KDS-B (no additional boric acid) were evaluated using AWPA E-17. Both KDS formulations are non-corrosive compare to CCA (Table 5).

Table 4. Rate of corrosion of Impralit KDS and ACQ treated wood			
Treatment	Rate of Corrosion [Mils per year]		
	C1010 Mild steel	304 Stainless steel	Hot-dip galvanized steel
Untreated	2.9	0.1	2.3
ACQ (6.4 kg/m^3)	23.0	-0.01	13.9
KDS (6.4 kg/m^3)	17.4	0.3	9.4

Table 5. Solution corrosion (1.2% a.i.) of Impralit KDS, KDS-B, and CCA			
Preservative	CCA	KDS	KDS-B
Rate of corrosion (Mils per year)	0.018	0.029	0.012

The low corrosion of KDS treated wood and KDS formulations are not surprising since DPAB can be used as corrosion inhibitors for certain applications.

7. DPAB FOR WOOD COMPOSITE PROTECTION

The use of wood composites has been increasing in the last 30 years. The use of wood preservatives for composites has been limited due to a number of reasons. Products such as OSB and MDF cannot be treated with a waterborne preservative due to swelling. Addition of preservative during the manufacturing process is problematic due to the negative impact of most preservative systems on adhesive curing and physical properties of the composite product.

Research at Mississippi State University has revealed that DPAB is an excellent preservative for composite protection (Kirkpatrick and Barnes 2006, Barnes and Kirkpatrick 2005). Preservatives were sprayed to dry flakes before board fabrication. The retention of the different preservative systems was such that they provide adequate termite protection for the final product.

In the comprehensive study (Kirkpatrick and Barnes 2006, Barnes and Kirkpatrick 2005), the physical properties of phenol formaldehyde-bonded OSB treated with various preservative systems, including two DPAB formulations, were compared. DPAB treated boards have higher modulus of elasticity (MOE), modulus of rupture (MOR), work to maximum load, and work to proportional limit than untreated control. Boards treated with the two DPAB formulations have similar or less 24-hour linear expansion and thickness swelling than untreated boards. The internal bond (IB) strength of DPAB treated boards was somewhat lower than untreated control but was significantly higher than other preservatives. The MOE and MOR results are shown in Figure 10.

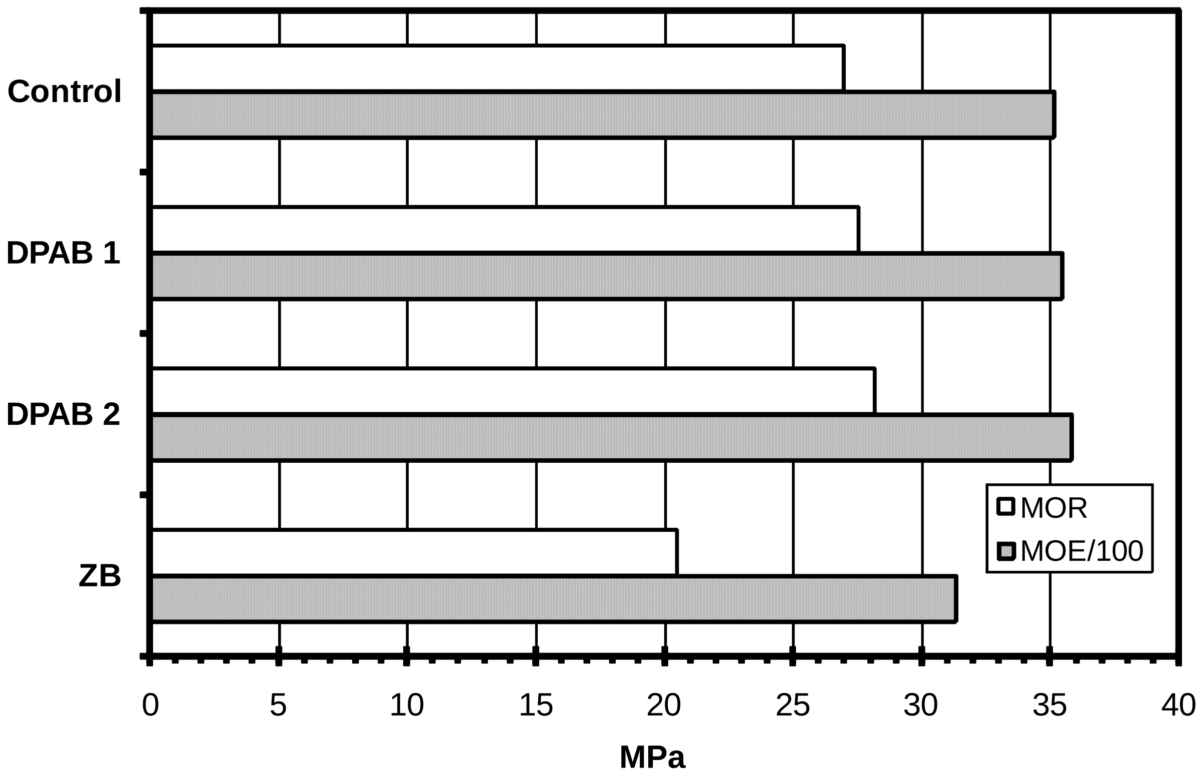

Figure 10. MOR and MOE values of untreated OSB in comparison with ZB (zinc borate) and DPAB-treated boards.

8. CONCLUSIONS

Although DPAB based preservatives have been used in Europe for almost 20 years, its use in the rest of world is limited. This paper has reviewed the unique chemistry and properties of DPAB-treated wood/composites in terms of research and new applications. In addition to heavy duty preservative applications, the performance of DPAB in antisapstain tests deserves more attention. The unique properties of DPAB as a composite preservative would probably lead to one of the most promising applications for this wood preservative active.

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