

Impralit™ KDS and KDS-B

Helmut Härtner

Futong Cui

Stefan Schmitt

Rütgers Organics GmbH

Mannheim, Germany

H. Michael Barnes

Department of Forest Products,

Mississippi State University

ABSTRACT

Impralit™ KDS and KDS-B are copper-based waterborne heavy duty preservatives using polymeric betaine as a co-biocide. These systems were developed in Europe in the 1980's as chromium-free preservatives. Performance of KDS and polymeric betaine is summarized briefly. Focus is given to the chemistry of polymeric betaine and its impact on the properties of the preservative formulations and the treated wood.

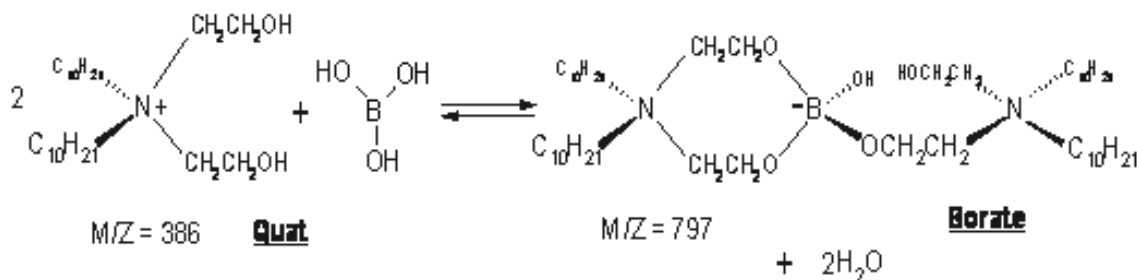
INTRODUCTION

Quaternary ammonium compounds (quats) are cost effective biocides and co-biocides for widespread industrial applications, including wood preservation. They have a number of advantages including good water solubility, good efficacy, and excellent fixation in wood. However, conventional quats also have a number of disadvantages as wood preservatives, such as distribution problems and corrosion problems related to early generations of quat chlorides. To overcome the disadvantages of conventional quats, polymeric betaine was developed. Impralit™ KDS and KDS-B contain 12.5% CuO and 10% polymeric betaine TGAI (Technical Grade Active Ingredient). KDS has 8% boric acid (BAE) while KDS-B does not contain additional boric acid as a biocide.

The chemistry of polymeric betaine

Polymeric betaine is synthesized from didecyl amine and ethylene oxide in the presence of boric acid and glycols. In its simple form, polymeric betaine is didecyl bis(hydroxyethyl) ammonium borate also known as didecyl polyoxyethyl ammonium borate, or DPAB.

Polymeric betaine (DPAB) belongs to the family of quaternary ammonium compounds because it exists as an equilibrium between the monomer didecyl bis(hydroxyethyl) ammonium cation form and the dimer borate ester form. The equilibrium shifts depends on the concentration and solution pH. At high dilutions and low pH, such as under physiological conditions, polymeric betaine exists as the monomer cation form as shown below:



$$K_{eq} = [\text{Borate}][\text{H}_2\text{O}]^2 / [\text{B}(\text{OH})_3][\text{Quat}]^2$$

Figures 1 and 2 show the direct infusion mass spectra of DPAB at two different dilutions. At 100 fold dilution, the dimer molecular ion dominates. At 1000 fold dilution, the molecular ion of the monomer dominates.

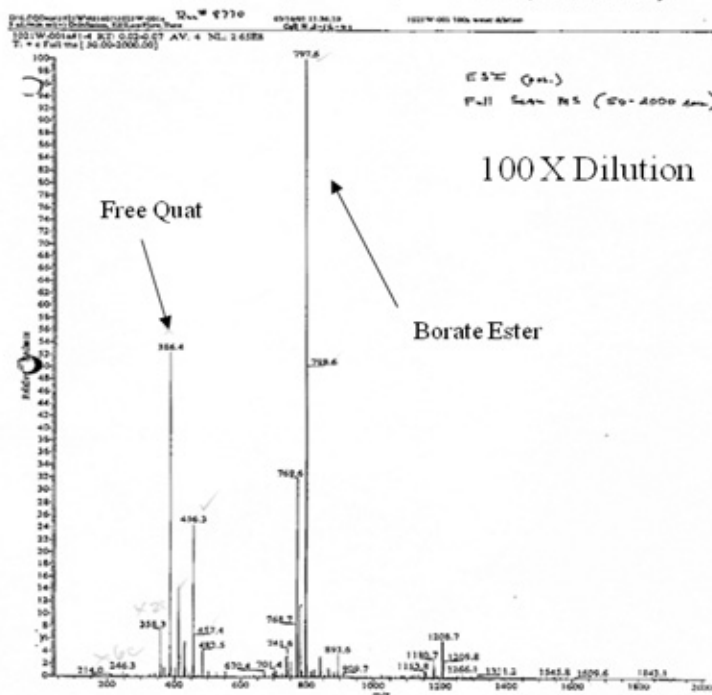


Figure 1. ESI (+) MS of polymeric betaine at 100 fold dilution.

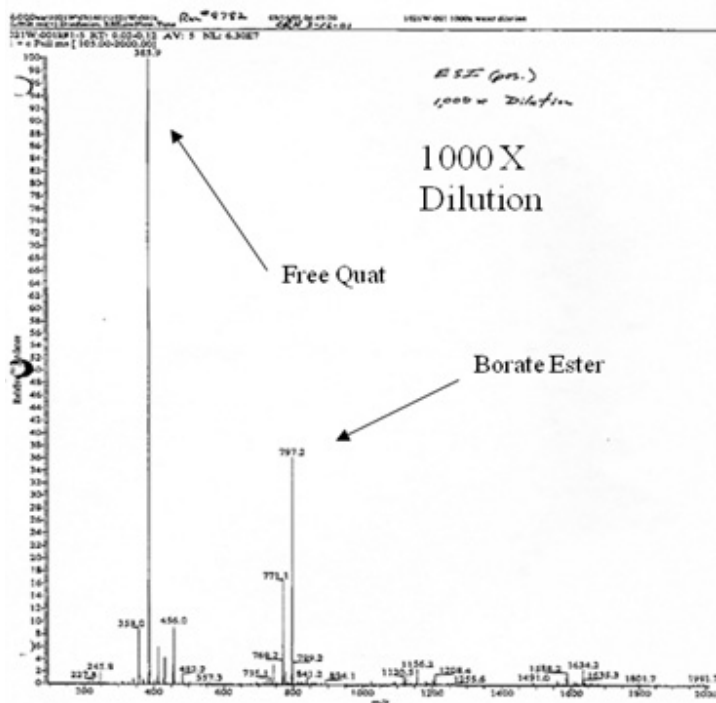


Figure 2. ESI (+) MS of polymeric betaine at 1000 fold dilution

Figure 3 shows the relative percentage of dimer and monomer at different dilutions. At the typical work solution concentrations, more than 80% of the material exists in the dimer form. Research has concluded that in the leaching water and dislodgeable residue of KDS treated wood, only the monomer quat form was identified. Since DPAB exists predominantly in the dimer betaine form at concentrations typical for wood treating, it is expected to behave different in the wood treating process.

Figure 4 shows the distribution gradient of DPAB in SYP 4x4s comparing with the copper component of KDS and the CuO in CCA. DPAB had a very flat distribution gradient similar to that of CuO in CCA. This is to be expected based on the betaine nature of DPAB. The flat distribution gradient would indicate reduced leaching and dislodgeable residue comparing with conventional quats. Conventional quats have a steep distribution gradient in the treated wood due to the strong interactions (Jin and Preston 1991) between the quat cation and wood components.

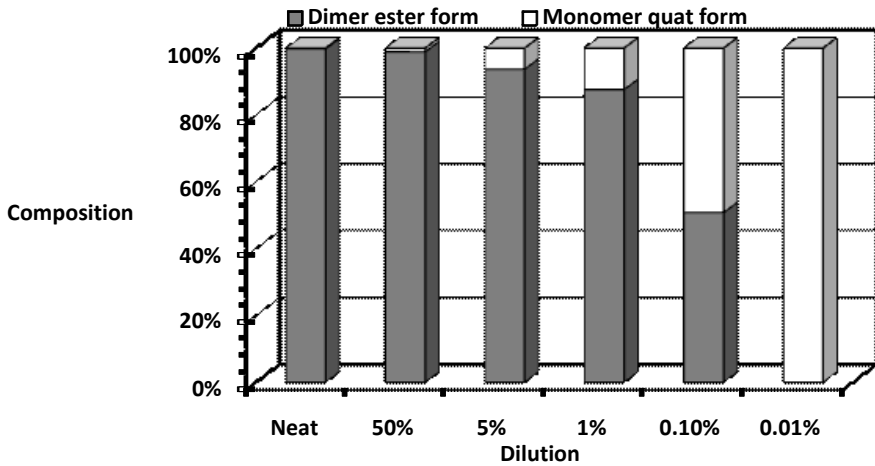


Figure 3. Relative percentage of dimer and monomer at different dilutions at the natural pH of polymeric betaine.

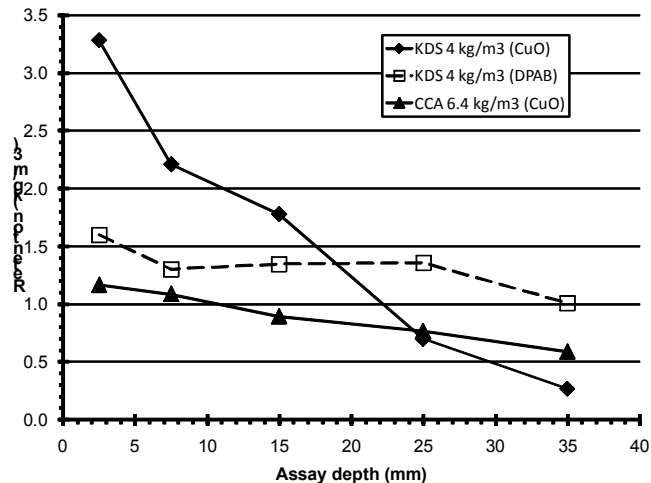


Figure 4. Distribution gradient of DPAB and copper in KDS-treated southern pine (SYP) 4x4s compared to copper distribution in CCA treated southern pine.

The unique property of DPAB is that due to the dimer-monomer equilibrium shift, it fixes in the wood similar or better than a conventional Quat. Because of the hydroxyl groups, DPAB is expected to form hydrogen bonds (Figure 5) with wood components in addition to other mechanisms of fixation.

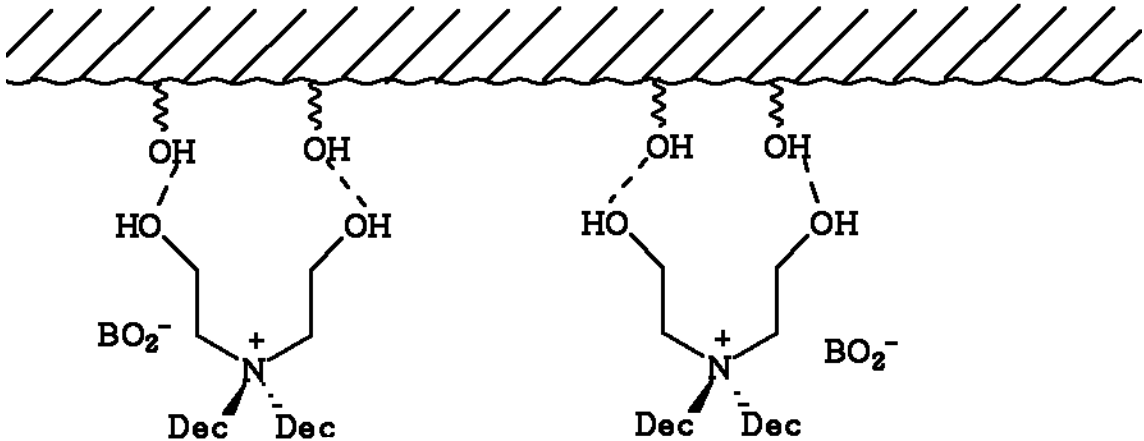


Figure 5. Proposed hydrogen bonding between DPAB and wood structure

In another study (Figure 6), DPAB concentration was higher in the inner zone than the outer zone of KDS treated 2x2 stakes.

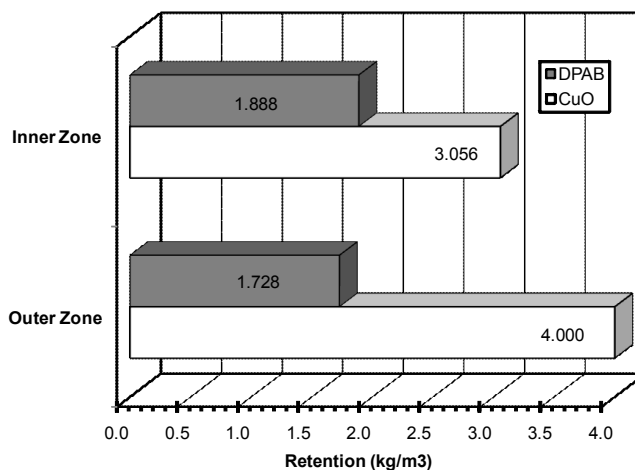


Figure 6. Distribution gradient of DPAB and CuO in KDS-treated SYP 39x39 mm stakes.

The excellent fixation of DPAB in KDS treated wood was demonstrated in an extraction study (Table 1). In this study, ¹⁴C labeled DPAB was used so that the material can be accurately analyzed and positively identified without interference. KDS treated wood dust was consecutively extracted in 6 steps and the

remaining residue was combusted to confirm the total radio activity for validation. As shown in Table 1, after six harsh extraction procedures, near 50% of the DPAB remained in the wood residue.

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°C in 0.05 M sodium acetate buffer	Cellulose breakdown	10.3%
0.05 M Sodium acetate/0.05 M EDTA, 15 hrs at 70 °C	Dissolve pectin	3.8%
Acetic acid/NaClO ₂ , 4 hrs at 70°C	Breakdown lignin	2.8%
24% KOH, 15 hrs at 25°C	Hemicellulose extraction	27.8%
72% H ₂ SO ₄ , 4 hrs at 25°C	Cellulose hydrolysis	0.4%
Residue combustion	Recovering remaining bound ¹⁴ C	48.0%
Total recovery		94.8%

Efficacy of polymeric betaine and KDS

The synergy between polymeric betaine and copper is clearly demonstrated in the toxic threshold values of amine copper, 2:1 Cu:polymeric betaine, and 1:1 Cu:polymeric betaine as shown in Figure 7.

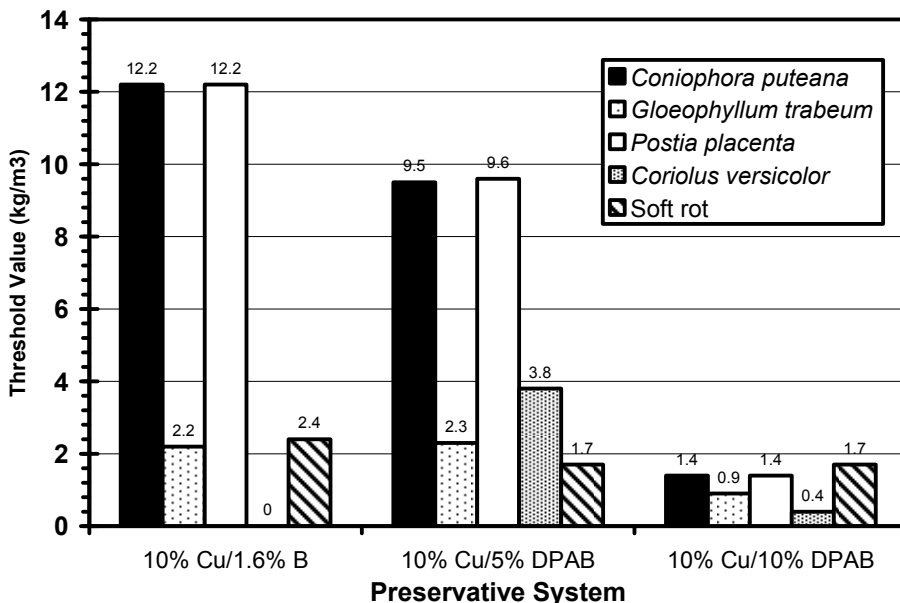


Figure 7. Threshold values from EN113 tests and soft-rot tests after leaching.

In a 7 year fungal cellar test (Figure 8), KDS outperformed CCA. In 10-year field tests in Norway and Sweden, KDS had similar or better performance than CCA (Figures 9 and 10).

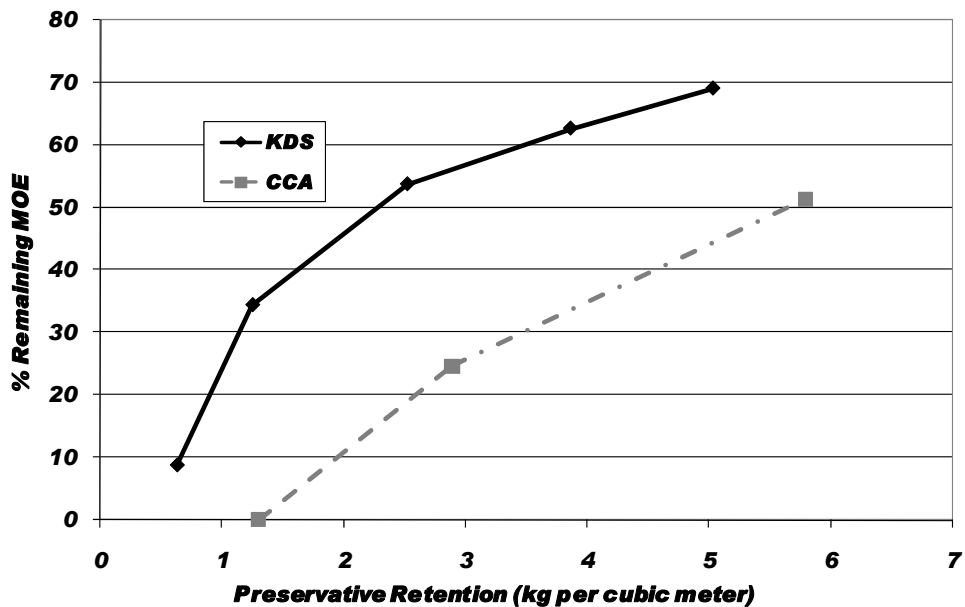


Figure 8. Relative performance of CCA and KDS in a 7 year fungal cellar test (EN252)

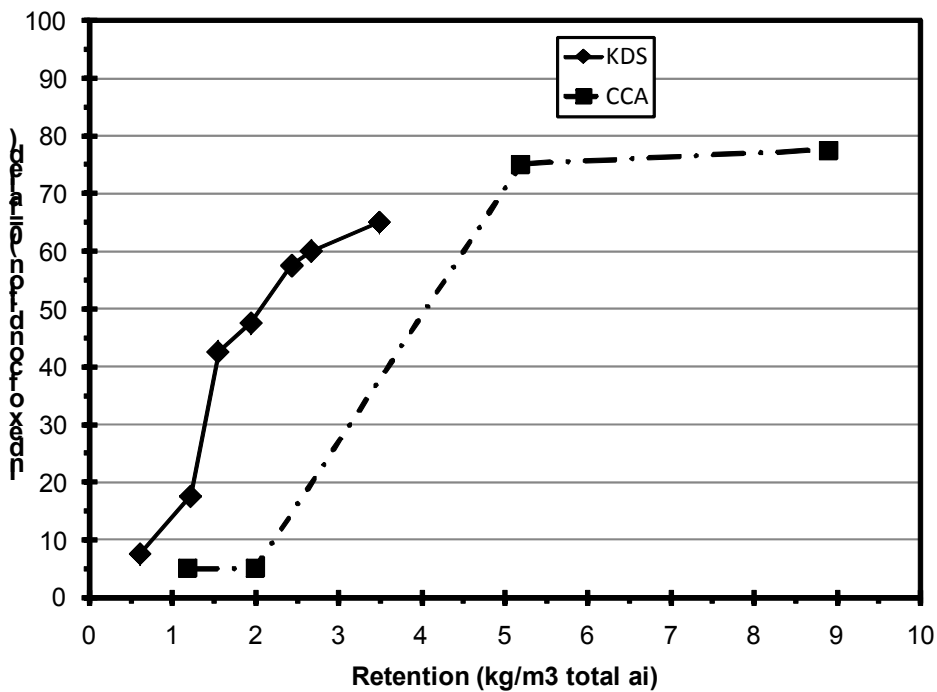


Figure 9. Dose response of KDS and CCA in a 10-year field test in Simlangsdalen, Norway.

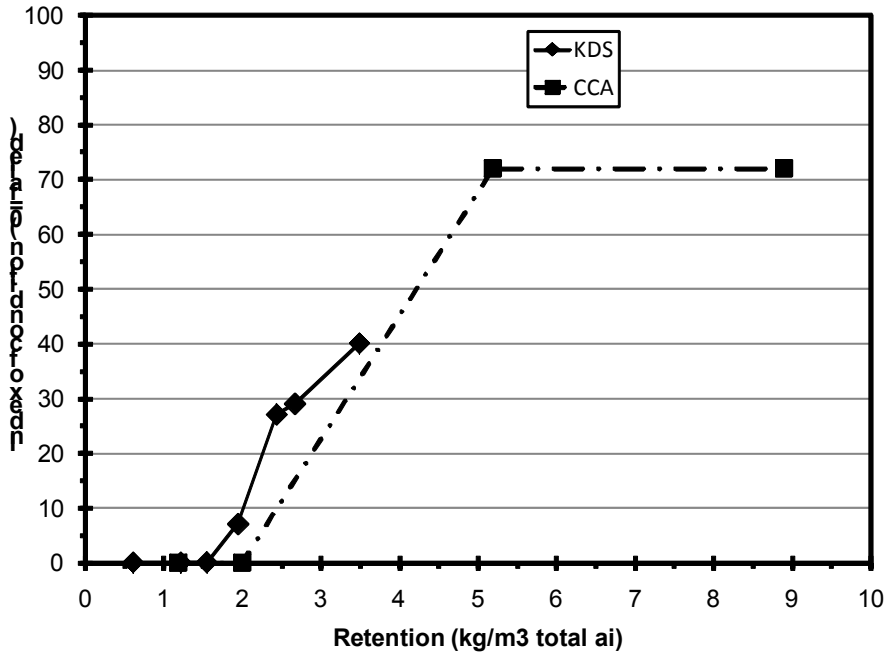


Figure 10. Dose response of KDS and CCA in a 10-year stake test in Sorkedalen, Sweden.

In anti-sapstain field trials carried out in North America and in Europe, DPAB based formulations outperformed the leading commercial products in both North American and European markets (Härtner et al 2009; Pfabigan *et al.* 2009). In addition to excellent efficacy against decay and mold/stain fungi, polymeric betaine based formulations also have good termite resistance. Table 2 shows the toxic threshold of KDS in comparison with CCA. In the same AWPA E-1 test, KDS showed termite repellency.

Table 2. Toxic threshold of Impralit KDS determined according to AWPA E-1 test.

Preservative	<i>Reticulitermes flavipes</i>		<i>Coptotermes formosanus</i>	
	(kg/m ³)		(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

Physical properties of KDS solutions and treated wood

In a modified AWPA E-12 corrosion test, KDS treated SYP was less corrosive than the standard ACQ at the same retentions (Table 3). The corrosion characteristics of KDS and KDS-B comparing with CCA were evaluated according to AWPA E-17 (Table 4). The lower corrosion rate of KDS-B is probably due to the relatively higher pH. Both KDS and KDS-B can be considered non-corrosive due to the very low

corrosion rate in mild steel. The low corrosion of KDS solutions and treated wood can be explained by the fact that polymeric betaine is a corrosion inhibitor for certain applications.

Table 3. Rate of corrosion of Impraliti 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 4. Solution corrosion (1.2% a.i.) of Impraliti KDS, KDS-B, and CCA

Preservative	CCA	KDS	KDS-B
Mild steel rate of corrosion (Mils per year)	0.018	0.029	0.012

Polymeric betaine based formulations for composite protection

Besides applications for pressure treating and anti-sapstain, polymeric betaine based formulations have shown great promise for composition protection (Barnes and Kirkpatrick 2005). In contrast to other preservatives which negatively impact the gluing properties of composites, OSB treated with polymeric betaine based formulations showed higher MOE and MOR values than untreated controls. This is believed to be due to properties related to the betaine nature of DPAB (Härtner *et al* 2009).

REFERENCES

1. Barnes H M, and Kirkpatrick J W (2005): Biocide treatments for composite panels. *In*: Proceedings, 39th International Wood Composites Symposium (R. Tichy, V. Yadama, eds.), Washington State University, April 5-7, 2005, Pullman, WA, p. 225-231.
2. Härtner H, Schmitt S T, Cui F, and Barnes H M. 2008. Polymeric betaine as a wood preservative. International Research Group on Wood Protection, Doc. No. 08-30487, 11 pp.
3. Härtner H, Schmitt S T, Cui F, and Barnes H M. 2009. The chemical and biological properties of polymeric betaine. International Research Group on Wood Protection, Doc. No. 09-30512, 8 pp.
4. Jin L and Preston A F. 1991. The interaction of wood preservatives with lignocellulosic substrates, I. Quaternary ammonium compounds. *Holzforschung* 45(6):455-459.
5. Pfabigan, N.; Gründlinger, R.; Härtner, H.; Cui, F.; Schmitt, S. 2009. Impraliti-BSK – New Field Tests of a Waterborne Preservative Against Blue-stain and Mould, Technical Forum Presentation, AWWA Annual Meeting, San Antonio, TX, April, 2009.