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**Section 3** **Wood protecting chemicals**

# The Chemical and Biological Properties of Polymeric Betaine


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# 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. DPAB as a wood preservative has been reported previously. This paper summarizes the chemical, physical, and biological properties of DPAB.

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

## 1. INTRODUCTION

Alkyl ammonium compounds (AAC) are a group of cationics that have important industrial applications such as textiles, antiseptics, antistatic agents, ore flotation, corrosion inhibitors, and special emulsifiers. With appropriate alkyl chain length and chain distribution, AAC are cost effective antimicrobials that find application in a number of fields. For the wood preservative industry, AAC can be used for both heavy duty pressure treatment and dip treatment applications. Conventional AAC, however, has a number of drawbacks such as poor distribution and corrosion. Didecyl polyoxyethyl ammonium borate (DPAB), also known as Polymeric Betaine, was designed to overcome these drawbacks. In addition to the desirable properties the inventors had in mind, a number of unique properties were found during research and development. This paper intends to report the chemical, physical, and biological properties of DPAB.

## 2. STRUCTURE

The first batches synthesized in the laboratory had >70% active and had very high viscosity. The characterisation of the product in the early stages of research was very complicated. The first analytical findings indicate a polymeric structure. Therefore the product was named "Polymeric Betaine".

Modern analytical techniques such as NMR and direct fusion mass spectrometry results in a new view of the structure of polymeric betaine. Depending on the concentration and pH in aqueous solutions polymeric betaine exist in an equilibrium mixture between the dimer and monomers and the shift of equilibrium is very rapid and completely reversible.

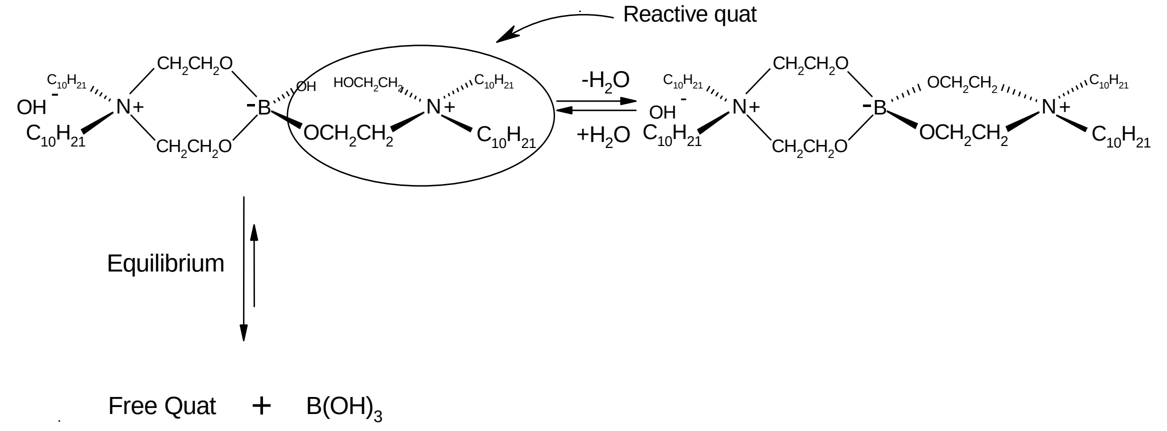


**Figure 1**. Equilibrium of Polymeric Betaine (DPAB) in solution

## 3. THE EFFECT OF BETAINE STRUCTURE ON WOOD TREATMENT

Because the dimer and monomer forms of DPAB are in equilibrium, and most of the material is in the monomer Quat form at low concentrations and/or low pH, DPAB can be analyzed by methods applicable for conventional Quats. For example, all AWPA analytical methods for quaternary ammonium compounds are applicable to DPAB analysis.

Because substantial amount of DPAB exists in the dimer form at work solution concentration typically used for wood protection (Figure 2), the betaine nature has a significant impact on the interaction with the wood structure.

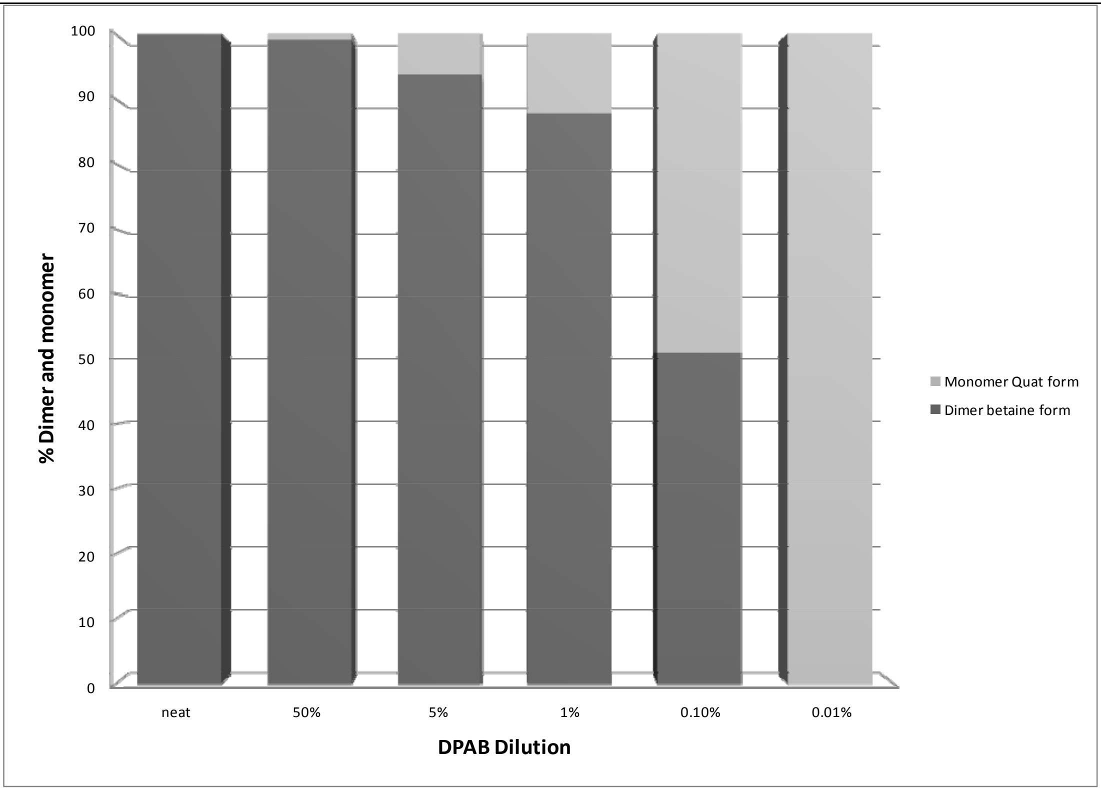


**Figure 2**. Equilibrium shift of DPAB as a function of dilution

Research has shown (Jin and Preston 1991) that Quats interact with wood components very strongly. As a result, Quats have a steep distribution gradient in the treated wood. Because

DPAB exist mostly in the dimer betaine form at work solution concentration, it does not behave like a Quat during the wood treating process. With a drop in pH during the fixation process, DPAB is converted to the monomer Quat form which is fixed strongly in the wood. Leaching studies indicated that DPAB is fixed in wood as well as or better than conventional Quats, probably as a result of hydrogen bonding as shown in Figure 3.

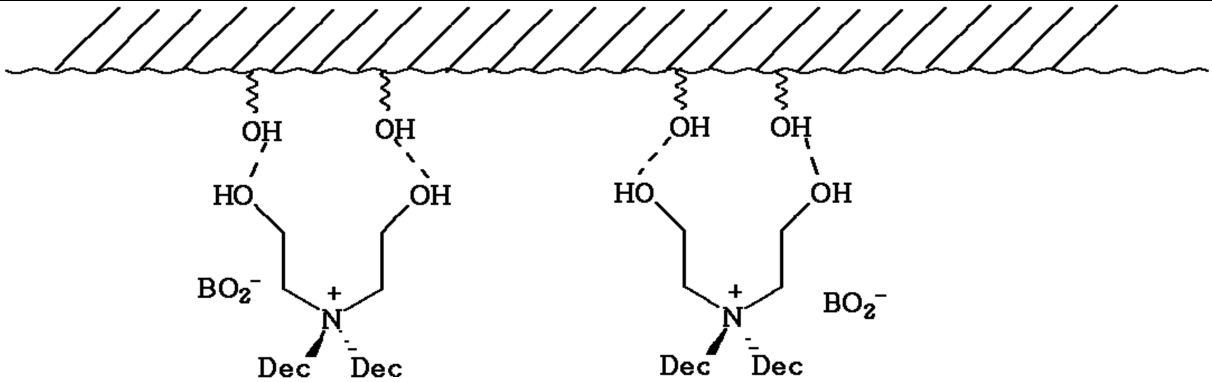


**Figure 3**. Proposed hydrogen bonding between DPAB and wood structure

Zonal analysis of DPAB in the treated wood indicates that it has a very flat distribution gradient in the cross section of treated wood. Figure 4 shows the distribution gradient of DPAB in KDS treated Southern Yellow pine 4x4 (89x89 mm). The copper component of KDS has a typical gradient expected for alkaline copper preservatives.

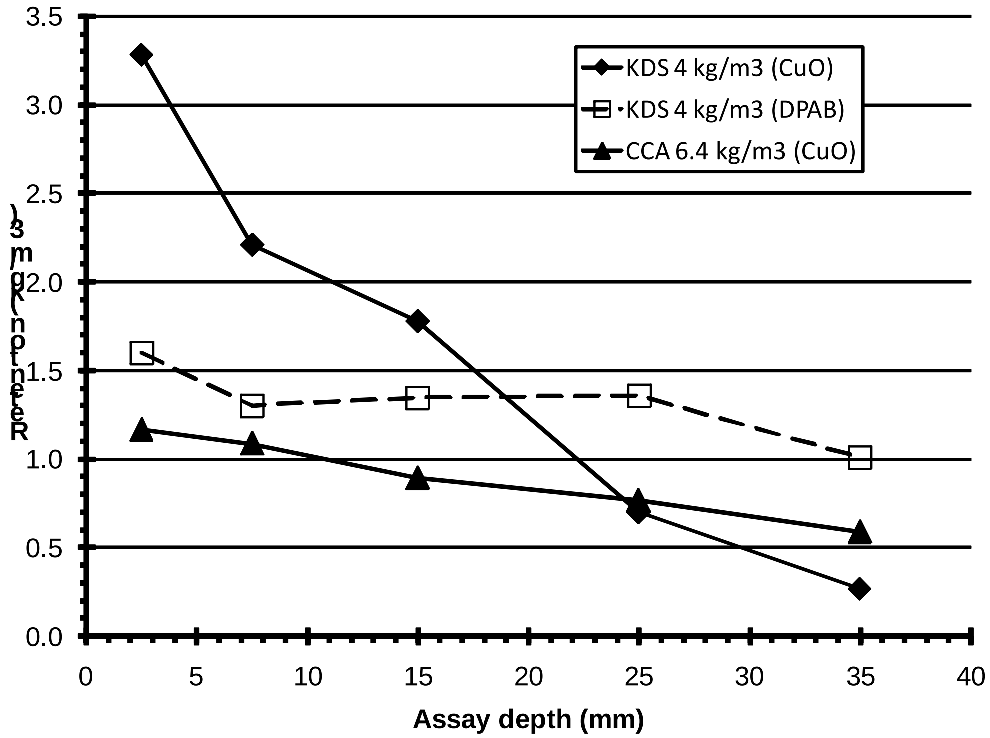


**Figure 4**. Distribution gradient of DPAB and copper in KDS-treated southern pine (SYP) 2x4s compared to copper distribution in CCA treated southern pine.

In another study, KDS treated 2x2 (50x50 mm) were sectioned into two zones and DPAB analyzed. As shown in Figure 5, the copper component shows the typical gradient while DPAB has a higher concentration in the inner zone.

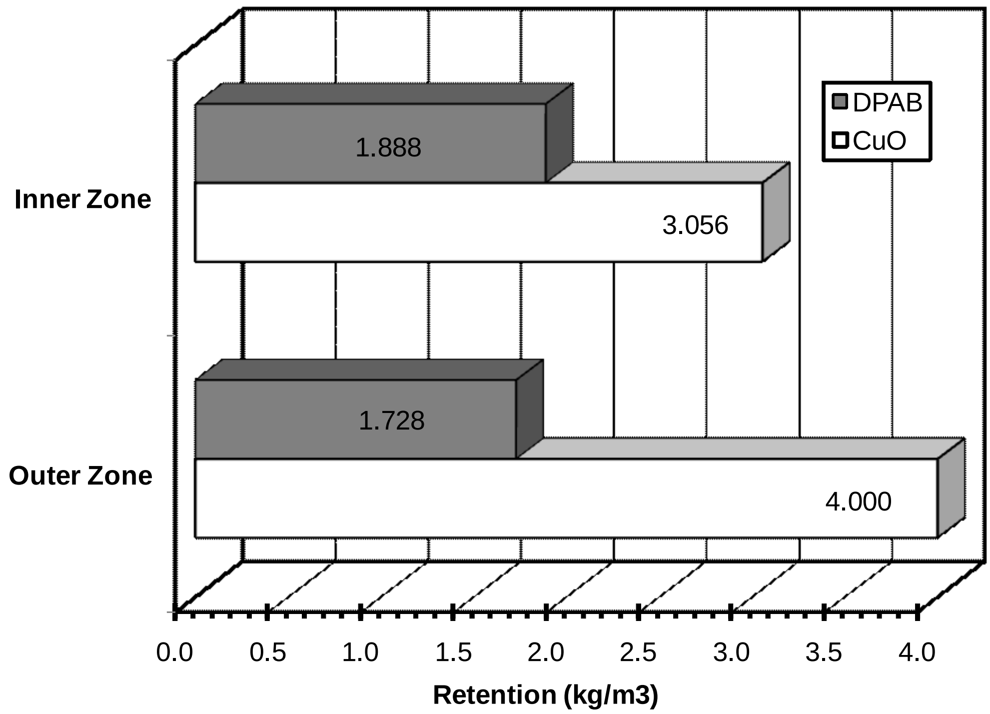


**Figure 5**. Distribution gradient of DPAB and CuO in KDS-treated SYP 39x39 mm stakes.

Also related to the betaine structure is the penetration of DPAB in dip treatments. Dip treatment of roof structures to prevent beetle infestation and decay is very important in certain European countries. impralit TSK 10, containing DPAB and Fenoxycarb, has good penetration for dip treatment. In comparision to products based on DDAC or other Quats the penetration depth of DPAB is 3-4 times better (Barth and Haertner 1993).

With increased use of engineered wood products, the protection of wood composites becomes very important. Unfortunately, the preservative treatment of common composites such as OSB and MDF is very difficult. Post treatment of finished composites with water-born preservatives is difficult due to severe swelling. On the other hand, treatment of wood furnishing before composite manufacturing also face difficulties due to the negative interaction between adhesives and wood preservatives. It was discovered (Barnes and Kirkpatrick 2005, Kirkpatrick and Barnes 2006) that DPAB and Impralit KDS can be used to treated wood flakes prior to OSB production and the treatment had little negative impact on strength and swelling of the finished products. This discovery is quite surprising since ACQ, a similar product, is known to have negative interactions with phenolic resins. Careful analysis of the behaviour of the two similar preservative systems suggests that the difference may be due to the distribution gradient. Wood treated with ACQ is expected to have a high DDAC concentration on the wood surface. Study by Lorenz and Frihart (2006) indicated possible interaction between Quat and phenolic resins.

## 4. ENVIRONMENTAL PROPERTIES

A common pathway for the biotransformation/biodegradation of synthetic chemicals by microorganisms and by animals is hydroxylation. Comparing to common alkyl ammonium compounds, DPAB has two hydroxyalkyl chains and is expected to have lower toxicity. Various tests confirmed this hypothesis. Typical toxicity data is shown in Table 1.

In a metabolism study, 95% of DPAB administered to the rat was excreted from the body within 48 hours, including >9% in the urine and >6% as volatiles. These data shows negligible bioaccumulation, poor absorption and rapid biodegradation.

**Table 1**. Typical toxicity data of DPAB

| Test | Species | Results |
|---|---|---|
| Acute Oral | Male rat | $LD_{50}$ > 2000 mg/kg |
| | Female rat | $LD_{50}$ = 500-2000 mg/kg |
| 90-day Oral | Sprague Dawley rat | LOAEL = 85.5 mg/kg |
| | | NOAEL = 28.5 mg/kg |
| Avian toxicity | Northern bobwhite | 14-day $LD_{50}$ = 664 mg/kg<br>NOEL = 253 mg/kg |
| Fresh water fish toxicity | Bluegill sunfish | 96 h static $LC_{50}$ = 0.89 mg/L,<br>NOEC = 0.54 mg/L |
| Fresh water invertebrate toxicity | *Daphnia* magna | 48 h static $EC_{50}$ = 0.39 mg/L,<br>NOEC = 0.06 mg/L |

LOAEL = Lowest observed adverse effect level. NOAEL = No observed adverse effect level. NOEC = No observed effect concentration.

A lot of research has been carried out to study the safe disposal of treated wood after service. In the USA, residential treated wood waste is not considered hazardous and is currently disposed in landfills. Although incineration of treated wood is not generally recommended, some regulatory agencies require chemical suppliers to study the incineration of treated wood to safe guard the public.

Rütgers carried out a comprehensive incineration study of Impralit KDS treated wood in a pilot incineration plant. KDS treated Scots pine was dried, and chipped before burning. Flu gas analysis results are shown in Table 2.

**Table 2**. Flu gas analysis of KDS treated and untreated Scots pine during pilot plant incineration

| **Chemical** | **Untreated Scots pine** | **KDS treated Scots pine (2.7 kg/m$^3$)** |
|---|---|---|
| $NO_x$ (mg/Nm$^3$) | 70 | 124 |
| Boron (mg/Nm$^3$) | 0.013 | 1.5 |
| Cu (mg/Nm$^3$) | 0.0096 | 2.7 |
| HCl (mg/Nm$^3$) | 0.79 | 0.25 |
| $SO_2$ (mg/Nm$^3$) | 0.12 | 0.20 |
| PCDD/PCDF (ng/Nm$^3$) | 0.103 | 0.133 |

The higher nitrogen oxides, boron, and copper concentration in the KDS flu gas was expected since the preservative system has high levels of these elements. It is interesting to note that the KDS treated and untreated pine has similar levels of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/PCDF).

## 5. DPAB Efficacy

The excellent efficacy of DPAB is well documented. (Härtner etc, 2008, Barth and Haertner 1993, Haertner and Barth 1996). In addition to decay and termite resistance, DPAB based formulations have shown great promise for anti-sapstain applications.

The efficacy of DPAB alone as an anti-sapstain agent was compared with a commercial formulation (NP-1) in a 12 month test (Minchin and Byrne 1995). Freshly sawn Hem fir and Douglas fir were sprayed with DPAB or NP-1 at 27 g/m$^2$, inoculated with a mixture of common mold and staining fungi, and then warped to encourage fungal growth. At the end of the test, each board (replication of 80) was rated on a scale of 0-5. A rating of 0 means no growth, and 5 means very heavy fungal growth. As shown in Table 3, DPAB shows excellent protection for both Hem fir and Douglas fir. In a similar study in Europe, a DPAB based formulation demonstrated superior performance to a commercial product.

**Table 3**. Anti-sapstain performance of DPAB and NP-1 in a 12 month test. (Application rate 27 g/m2, rating = 0: no fungal growth; rating = 5: heavy fungal growth)

| Treatment | Concentration | Hem-fir | | Douglas fir | |
|---|---|---|---|---|---|
| | | Average rating | % Pieces acceptable | Average rating | % Pieces acceptable |
| Untreated | - | 4.0 | 6 | 4.1 | 6 |
| DPAB | 5.1% | 2.4 | 44 | 1.8 | 73 |
| | 6.3% | 1.4 | 73 | 1.4 | 81 |
| | 7.6% | 0.7 | 90 | 1.2 | 88 |
| NP-1 | 1.7% | 3.5 | 13 | 3.2 | 31 |
| | 3.3% | 2.9 | 34 | 2.0 | 63 |
| | 6.6% | 2.5 | 39 | 1.3 | 84 |

In an independent blind study of commercial and proprietary antisapstain formulations in Europe, the leaching of active ingredients and leachate toxicity were studied (Aschacher etc 1998). Treated lumber stacks were placed above collection pans and the leaching water was collected each month. Figure 7 clearly shows that DPAB had the least leaching. C1015 is a proprietary formulation from another chemical supplier.

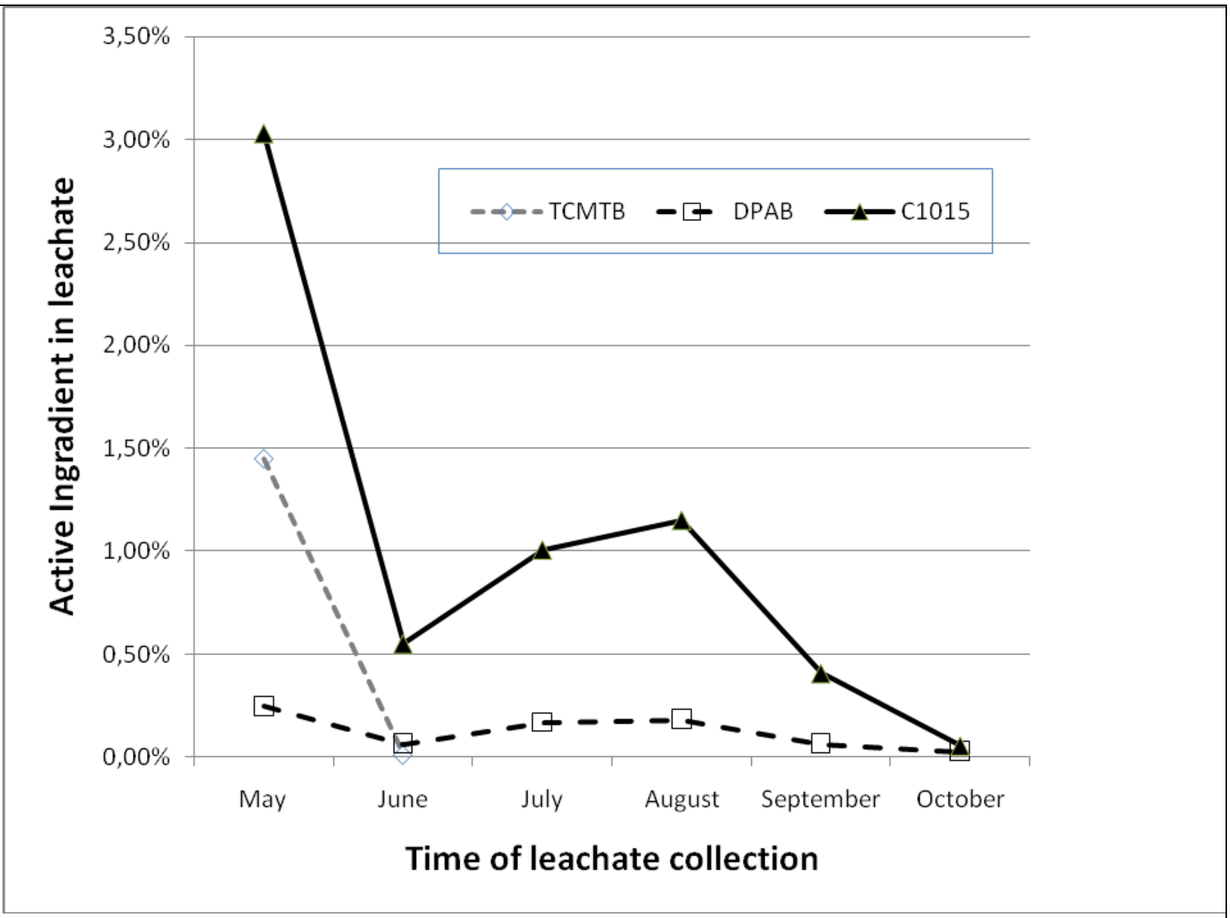


**Figure 7**. Active ingredient in leaching water

## 6. CONCLUSIONS

As a wood preservative, DPAB has some unique chemical and physical properties due to its betaine structure in the treating solution. Since the dimer betaine form and the monomer Quat form of DPAB exist as an equilibrium which shifts as a factor of concentration and pH, DPAB behaves like a Quat in terms of fixation. DPAB exists exclusively in the Quat form under physiological conditions, i.e. low concentration and low pH, explaining its similar toxicological properties as other Quats.

In addition to its applications for pressure and dip treatment, DPAB shows great promise for anti-sapstain formulations and wood composition protection.

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