CONSIDERATIONS FOR THE EFFECTIVE USE OF TRIBUTYLTINS IN WOOD PRESERVATION

By: Charles B. Beiter
M&T Chemicals Inc., Rahway, N.J. U.S.A.

1. Introduction

Organotin compounds are characterized by one to four alkyl or aryl radicals which are chemica bonded to tin by a carbon linkage (Figure 1). The activity varies, depending on the number a form of the organic groups attached to the tin[1]. For instance, biological activity peaks with triorganotins, three carbon to tin bonds. The trimethyltins are effective insecticides; however, t are also extremely toxic to man, precluding their use commercially. As the chain length increased, the mammalian toxicity is reduced and activity is more selective[2,3] (Table 1). T tributyltins are broad spectrum biocides inhibiting the growth of a long list of micro-organis They have moderate toxicity to man and have been safely used to control pests responsible biodeterioration and fouling. Their antimicrobial activity is illustrated by the inhibition values TBTO®, bis(tributyltin) oxide, established against bacteria (Table 2) and fungi in broth dilut tests (Table 3).

2. Commercial Applications

The evolution of organotin industrial biocides began in the 1950's when the interest in t biological activity was stimulated by the investigations of van der Kerk and Luitjen (Figure 2). T first commercial wood preservatives based on TBTO followed in 1959. In the 1960's, vari tributyltins were introduced for use in antifouling systems, water treatment, paint biocides, tex preservatives and other miscellaneous applications[4,5]. The 1970's saw refinement of the perfo ance through formulation and chemical modification of the organotins. This has resulted in f major commercial applications for the organotins in the 1980's:

Agricultural Fungicides and Insecticides,
Slimicides,
Marine Antifoulants, and
Wood Preservatives

PRESENTED AT CANADIAN WOOD PRESERVATION ASSOCIATION, NINTH ANNUAL MEETING, TORONTO, CANADA, NOVEMBER 2, 1988.

urrent commercial industrial biocide applications for the tributyltins include:

- Cooling Water Treatment for control of slime produced by bacteria, algae and fungi.
- Marine Ship Bottom Paint additives for control of a variety of plant and animal forms; algae, barnacles, bryozoans etc.
- Wood Preservatives for control of wood rot fungi.

Effective Use

he effective use of the tributyltins in specific applications generally requires the development of a urefully designed formulation or a structural modification to obtain properties which enhance the rformance under the use conditions.

Cooling Water Treatment

One of the early applications for TBTO was slime control. Here, performance was erratic until two limitations were compensated for: 1) a weakness in control of gram negative bacteria (Table 1), and 2) low water solubility.

In this use, TBTO/Quaternary ammonium compound complexes provided a water-dispersible product with broad spectrum control of bacteria, fungi, and algae (Table 4). Products of this type are generally recommended where particularly severe fouling conditions exist.

Marine Antifoulants

Marine fouling control was another early use of the tributyltins compounds, particularly TBTO and TBTF (tributyltin fluoride). Acceptance in the pleasure-craft market was based on their broad spectrum control of marine fouling organisms, compatibility with aluminum, and the ability to achieve a wide range of attractive colors in bottom paints.[6]

The first systems developed had limited utility outside the pleasure-craft market due to their short service life and poor control of algae. The marginal performance was attributed to poorly controlled release of the antifoulant. Long-term performance required by commercial and military vessels was achieved in recent years by:

1) Chemical modification of the tributyl tin compound by incorporating it in acrylate polymer. Hydrolysis occurs at a steady rate in water, controlling t release of the antifoulant, and

2) Use of a cotoxicant (usually cuprous oxide) to provide an improved spectrum control, especially against algae.

Wood Preservatives

As wood preservatives, the tributyltins have a proven service record in Europe in treatm of millwork and in other above ground applications[7]. In the US, TBTO is used in exter pigmented stains, in conjunction with Folpet and Chlorothalonil, to control fungi resp sible for rot, mold, and stain.

Data is available which confirms the activity of the tributyltins against a broad spectrum wood-destroying fungi[8,9,10] and insects (Tables 5, 6 and 7). Under actual use conditio however, performance is more selective.[11]

Limitations in performance of TBTO are related to its poor control of surface mold staining. TBTO, in combination with Folpet and Chlorothalonil, is effective in pigmen preservative systems. These products, however, have limited solubility in conventio wood treating solvents.[12,13] Little information is available on formulation approaches improve performance and provide a product with wider application potential.

4. Current Studies on Tributyltin Based Wood Preservatives

Testing is underway at Mississippi State Forest Products Lab to establish the performance of TB TBTX and candidate formulations employing commercially available cotoxicants.

1. The first study, designed to determine the influence of the anion (X) on the efficacy tributyltin X, compares TBTO and tributyltin methyacrylate/methyl methacryl Volatility and migration of the TBTM/MMA copolymers should be minimal compa with TBTO because of its high molecular weight. It might also prove to provide gre resistance to dealkylation of the organotin in wood.[14]

   Preliminary results with TBTM/MMA copolymer demonstrate reduced effective against stain and mold compared with TBTO at equal TBT-treatment levels. This sugge

that improved performance against surface attack will require greater mobility from the biocide since growth of the mold can develop on surface contamination without actually attacking the wood. The fact that TBTO is substantive to the wood accounts for its success in rot control at the sacrifice of mold and stain control.[15] Loss of the preservative due to volatilization is less of a factor.

2. The second study underway is evaluating cotoxicants which would complement the properties of TBTO. Products with greater water solubility, such as tributyltin ethanesulfonate, or with lower volatility, such as the TBTM/MMA copolymer, tributyltin phosphate, and tributyltin naphthenate, may provide some improvement in specific applications based on the structural modifications, but they will also require cotoxicants for broad spectrum control. The use of mildewcides (cotoxicants) compatible with conventional treating solvents and offering greater mobility in wood (less affinity for wood fibers) would appear, to us, to offer the best opportunity for improved TBTO wood treatments.

Laboratory tests conducted according to AWPA Method M12-72, have demonstrated control of termites with TBTO by both dip (Table 6) and vacuum (Table 7) treatments. These results, shown in tables 6 and 7, have encouraged us to utilize a field test described by Carter and Beal[16] which provides above ground challenge against mold, rot, and termites. The test employs treated dowels inserted in holes drilled in stakes. The dowels can be removed and inspected throughout the test. Preliminary results are shown in Table 8.

TBTO is controlling termites and rot-producing fungi after nine months exposure in Mississippi. The copolymer, at equal TBT levels, is slightly less effective. Both show a higher degree of termite control, compared to Polyphase. Long term exposure results will be necessary to confirm this early trend.

5. Cotoxicant Evaluations

The cotoxicant studies were initiated with an accelerated sap stain test in which wet and dry southe pine sapwood, treated with the test formulations, is stored for 4 to 6 weeks under high humidit Candidates selected for testing in combination with TBTO were:

Diiodomethyl-p-tolylsulfone (Amical® 48), Angus Chemical.
Isothiazolone (RH 287), Rohm & Haas.
2-bromo-2-nitropropane-1,3 diol (Biocide M95), Thompson-Hayward
Azaconazole (Rodewod), Janssen Pharmaceutica.
Dichlofluanid (Preventol® A4-S) Mobay.
2-iodo-2-propynylbutylcarbamate (Polyphase®), Troy Chemical
Undecylenic acid, Atochem.
Alkyl (50% C_{14}, 40% C_{12}, 10% C_{16}) dimethylbenzylammonium chloride (MaQuat MC 1412), Mason Chemical.

The performance of the TBTO preservative was improved with the addition of RH 287, Rodewo and Preventol A4 S. No significant benefit was seen when formulated with Amical 48, Polyphas and MaQuat (Table 9). On the other hand, an antagonistic effect was noted with Biocide M95 a undecylenic acid.

The TBTO preservative solutions containing RH 287, Rodewod, and Preventol A4-S warra further testing.

The above fungicides are not currently registered in the US for use as wood preservatives, b approval is anticipated by the suppliers.

Reformulation of systems containing Amical 48, Polyphase, and MaQuat, which are registere would be of interest to establish whether an additive or antagonistic action exists with TBTO.

6. Handling Considerations For The Tributyltin Wood Preservatives

A major concern for all microbial control agents is safety in handling. The latest toxicological studies on TBTO relative to health and safety were reviewed by H. Schweinfurth at the 1987 Convention of The British Wood Preserving Association.[17] All our information, including plant experience in handling the organotins, indicates that tributyltin based wood preservatives can be handled safely. Ongoing studies conducted for the EPA, in support of TBTO registrations, continue to confirm that TBTO wood preservatives are safe to use.

Current studies on the toxicology of the organotins assure us that there are no long term adverse effects due to low level exposure to the tributyltin compounds. We should, however, be aware of the potential responses from exposure to the organotins which cause discomfort (Figure 3) and the simple precautions that should be taken by applicators (Figure 4).

1. Skin burns if material which contacts the skin is not washed off immediately.
2. Irritation to mucous membranes which may lead to nose bleeds with over exposure.

The quidelines for safe handling, supported by our plant experience, require:

1. Protective equipment against skin and eye contact.
   a) Gloves, long sleeve shirt and impermeable aprons.
   b) Chemical goggles.
2. Adequate ventilation to remove solvent vapors. TBTO has very low vapor pressure but high odor threshhold.
3. Good personal hygiene and discarding of contaminated garments.

The closed treating systems, or Vac-Vac as used in Europe, provide safer handling of wood preservatives as well as better performance. These systems are currently under evaluation at Forintek and, hopefully, will lead to wider acceptance of closed systems in North America. Sophisticated designs available for dip and electrostatic spray treating systems also provide for the safe and effective use of wood preservatives in special applications.

7. Summary

Bis(tributyltin) oxide has a history of over 25 years of successful performance in slime contr marine fouling control, and wood preservation. The in-service effectiveness of the tributyltin bas wood preservatives can be broadened through the use of cotoxicants for mold, stain, and inse control.

The growth in use of the tributyltins in wood preservation is tied to several key factors whi contribute to assuring extended service life with treated timbers.

1. Identification of cotoxicants to complement the activity of TBTO.
2. Selection of tributyltin derivatives (TBTX) to improve performance in specific applic tions, e.g., water-based systems.
3. Implementation of closed treating systems such as employed in Europe.

Biologically active chemicals will generally have undesirable human health effects. However, t careful handling of TBTO will minimize or eliminate any potential dermal effects received fr contact with the preservative concentrates or treating solutions. There are no known chronic effe related to low level TBTO exposure.

M&T has and will continue to support registration of TBT-based products. There are no restrictio on the use of TBTO as an active ingredient in wood preservative solutions in the U.S. and Cana when used according to the registered label.

FIGURE 1

CLASSES OF ORGANOTINS

$RSn X_3$	
$R_2Sn X_2$	**X Represents a Halogen**
$R_3Sn X$	**or Other Electronegative Group**
R_4Sn	

TABLE 1

INFLUENCE OF THE ORGANIC GROUP ON BIOLOGICAL ACTIVITY

TRIORGANOTIN	ACTIVITY	TOXICIT
Trimethyltin	Insecticidal	High
Triethyltin	Antimicrobial/Broad spectrum	High
Tripropyltin	Antimicrobial/Broad spectrum	Moderate
Tributyltin	Antimicrobial/Selective	Moderate
Triphenyltin	Antimicrobial/Selective	Moderate

Table 2

TBTO - ANTIBACTERIAL PROPERTIES

	MIC[1] ppm
Staphlococcus aureus	1
Bacillus ammoniagenes	<1
Bacillus subtilis	<1
Bacillus mycoides	1
Aerobacter aerogenes[2]	>500
Escherichia coli[2]	>500
Pseudomonus aeruginosa[2]	>500
Proteus vulgaris[2]	>500
Lactobacillus bifidus	50
Lactobacillus casei	50
Sphaerotilus	<1
Desulfovibrio desulfuricans[2]	10

[1]Minimum Inhibitory Concentration determined by Broth Dilution Method

[2]Gram Negative Bacteria.

Table 3

TBTO - ANTIFUNGAL PROPERTIES

	MIC[1] ppm
Penicillium digitatum	3
Penicillium piscarium	1
Penicillium funiculosum	3
Penicillium expansum	1
Aspergillus niger	0.5
Aspergillus terrus	0.5
Chaetomium globosum	1
Pullularia pullulans	0.5
Trichoderma viride	1
Saccharomyces cerevisiae	1
Candida albicans	1
Microsporum audouini	0.5

[1]Minimum Inhibitory Concentration determined by Broth Dilution Method

FIGURE 2

EVOLUTION OF INDUSTRIAL ORGANOTIN BIOCIDES

1950's	Interest in biological activity stimulated by the investigations of van der Kerk and Luitjen.
1959	First commercial wood preservative based on TBTO.
1960's	Introduction of tributyltins for use as: Antifoulants Water Treatment Paint Biocides Textiles Preservatives Misc. Biocide Applications
1970's	Refinement of performance through formulation and chemical modification.
1980's	Four Major Commercial Applications Agricultural Fungicides and Insecticides Slimicides Marine Antifoulants Wood Preservatives

Table 4

TBTO / QUAT[1] - ANTIMICROBIAL PROPERTIES

	MIC[2] ppm
Bacteria	
Bacillus mycoides	2
Staphylococcus aureus	2
Aerobacter aerogenes	8
Pseudomonas aeruginosa	16
Desulfovibrio desulfuricans	5
Fungi	
Aspergillus flavus	2
Penicillium funiculosum	2
Algae	
Chlorella vulgaris (green)	2.5
Chlorella pyrenoidosa (green)	0.5
Scenedesmus dimorpha (green)	1.2
Dictyosphaerium pulchellium (green)	0.08
Phormidium retzii (blue green)	0.3
Gonphoema (diatom)	0.15

[1]Alkyldimethylbenzylammonium chloride used at ratio of 5 parts to 1 part TBTO.
[2]Minimum Inhibitory Concentration determined by Broth Dilution Method

Table 5

TOXIC VALUES FOR TBTO ON UNLEACHED SCOTS PINE BLOCKS AGAINST BASIDIOMYCETE FUNGI, ACCORDING TO BS 838[1]

Fungus	Toxic Values (Kg/m^3)
Poria vaporaria	0.013 - 0.03
Coriolus versicolor	0.15 - 0.37
Coniophora puteana	0.12 - 0.32
Poria vaporaria	0.008 - 0.016
Coniophora puteana	0.16 - 0.28
Merulius lacrymans	0.02 - 0.06
Poria monticola	0.02 - 0.06
Coniophora puteana	0.73 - 0.81
Coriolus versicolor	1.18 - 1.33

[1]Reported by Hill & Killmeyer - AWPA Annual Meeting, 1988

Table 6

Resistance of dip-treated[1] southern yellow pine blocks to the subterranean termite Reticulitermes flavipes.

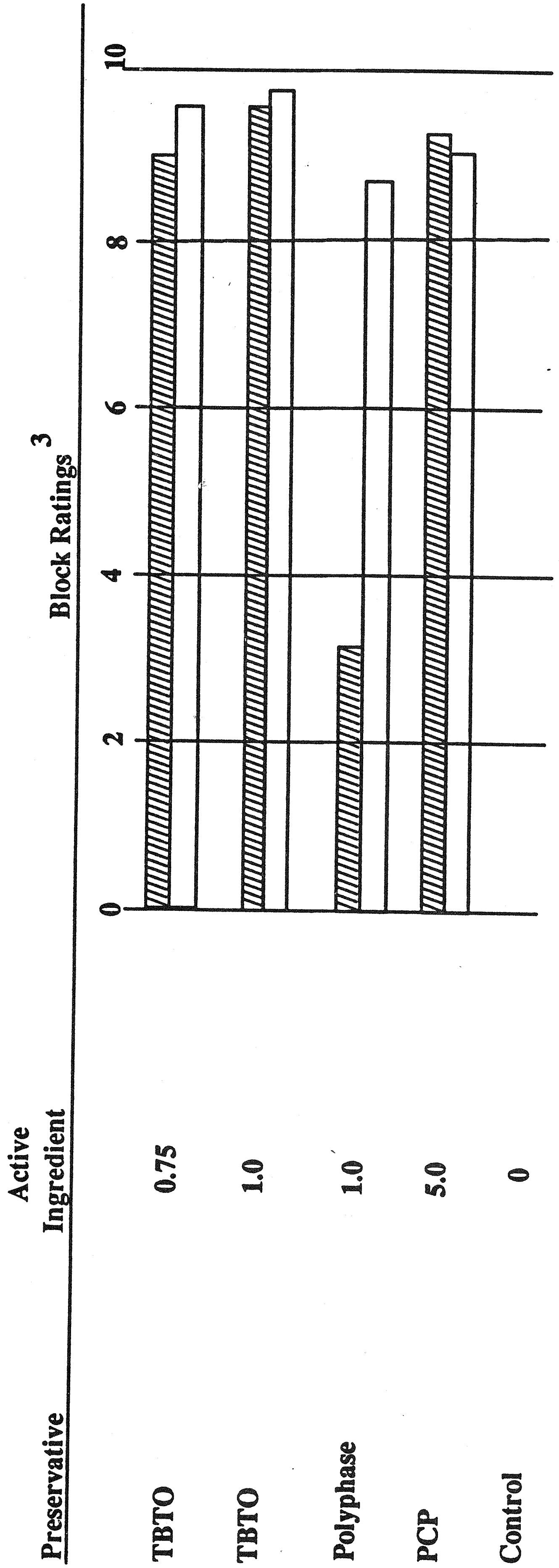
Preservative	Treating Solution Conc. (% a.i.)	Conditioning[2]	Weight (g) Solution Pick-up	% Wt. Loss	Block Rating[3]
TBTO	0.75	L	0.42	0.2 ± 0.5	9.0
TBTO	1.0	L	0.41	0.8 ± 0.5	9.6
Polyphase	1.0	L	0.44	29.7 ± 4.9	3.2
PCP	5.0	L	0.46	1.9 ± 0.6	9.2
Control	--	--	---	35.0 ± 6.4	0.0

[1]Dip treatment 1 minute.

[2]L = Leached

[3]Block Rating:
10 = Sound. Surface nibbles permitted.
9 = Light attack
8 = Moderate attack
4 = Heavy attack
0 = Failure

Termite (Reticulitermes flavipes) Control[1] with Dip - Treated Yellow Pine Blocks



Leached
Non-Leached

[1]AWPA Method M12 - 72

[2]Pressure - Treated AWPA M10 - 77

[3]Block Rating: 10 = Sound. Surface nibbles permitted
9 = Light attack
8 = Moderate attack
4 = Heavy attack
0 = Failure

Table 7

Resistance of pressure-treated[1] southern yellow pine blocks to the subterranean termite Reticulitermes flavipes.

Preservative	Treating Solution Conc. (% a.i.)	Conditioning[2]	Retention (pcf)	% Wt. Loss	Block Ratings[3]
TBTO	0.3	L	0.09	0.8 ± 0.3	9.6
TBTO	0.5	L	0.15	0.8 ± 0.3	10.0
TBTO	0.75	L	0.25	0.1 ± 0.3	9.8
TBTO	1.0	L	0.32	0.2 ± 0.5	10.0
Polyphase	0.5	L	0.16	17.3 ± 5.0	7.0
Polyphase	1.0	L	0.32	3.4 ± 1.5	9.0
PCP	2.5	L	0.85	1.7 ± 0.5	10.0
PCP	5.0	L	1.65	1.6 ± 0.6	10.0
Control	--	--	--	34.0 ± 6.4	0.0

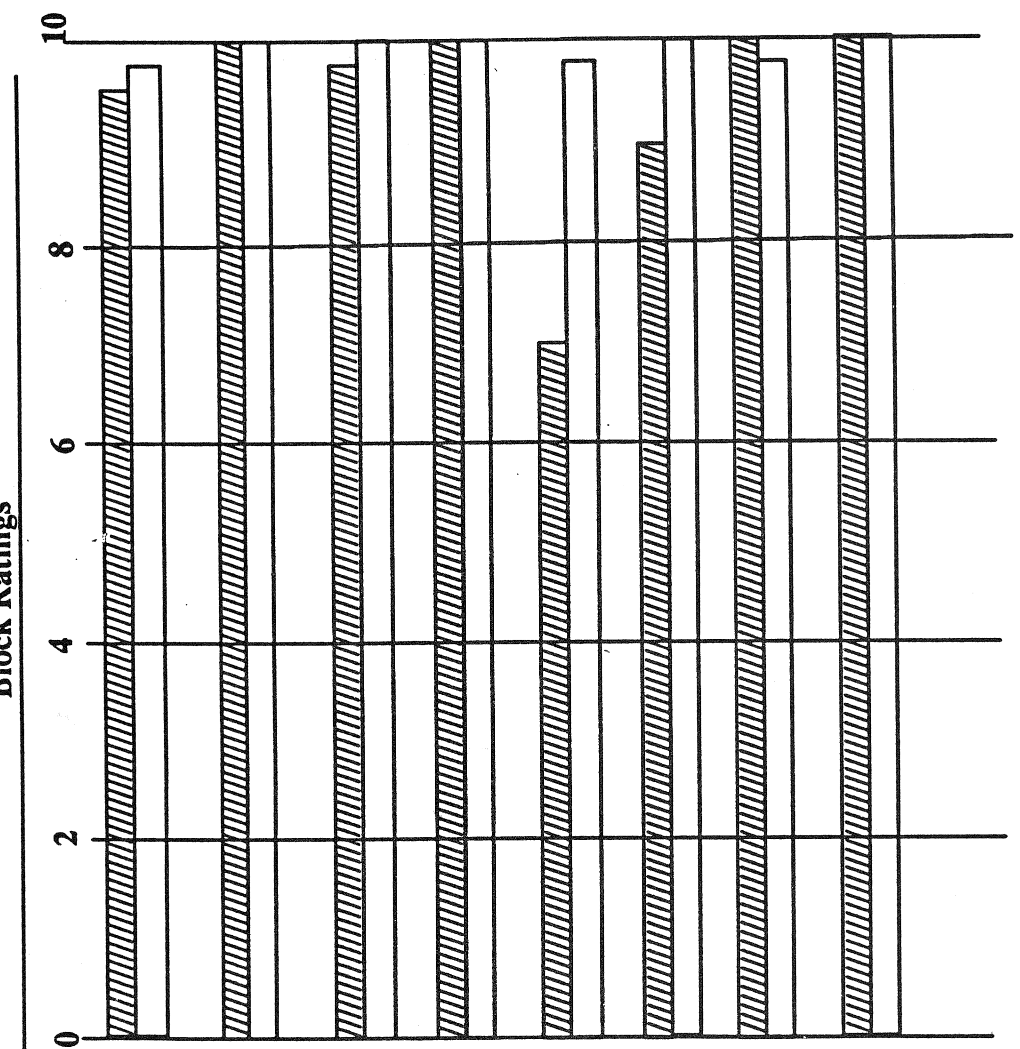
[1]Pressure treated AWPA MIO-77

[2]L = Leached

[3]Block Rating:
10 = Sound. Surface nibbles permitted.
9 = Light attack
8 = Moderate attack
4 = Heavy attack
0 = Failure

Termite (Reticulitermes flavipes) Control[1] with Pressure-Treated[2] Yellow Pine Blocks

Preservative	Active (Ingredient)	Retention (pcf)
TBTO	0.3	0.09 - 0.09
TBTO	0.5	0.15 - 0.16
TBTO	0.75	0.25 - 0.24
TBTO	1.0	0.32 - 0.34
Polyphase	0.5	0.16 - 0.16
Polyphase	1.0	0.33 - 0.32
PCP	2.5	0.85 - 0.87
PCP	5.0	1.65 - 1.70
Control	0	0



Leached
Non-Leached

[1]AWPA Method M12 - 72

[2]Pressure - Treated AWPA M10 - 77

[3]Block Rating: 10 = Sound. Surface nibbles permitted
9 = Light attack
8 = Moderate attack
4 = Heavy attack
0 = Failure

TABLE 8

ABOVE GROUND FIELD EXPOSURE OF TREATED YELLOW PINE SAP WOOD

HARRISON STATE FOREST, MISSISSIPPI
6 MONTHS EXPOSURE

PRESERVATIVES	TREATING SOLUTION (% a.i.)	TERMITES	FUNGI STAIN	RO
TBTO	1.0	0	+	0
	0.75	0	+	0
	0.5	0	+	0
	0.3	0	+	0
TBTM/MMA	1.0	0	+	0
	0.75	0	+	0
	0.5	+	+	0
POLYPHASE	0.75	+0	+0	+0
	0.5	+	+0	+
PENTACHLOROPHENOL	5.0	0	0	0

+ = Present
0 = Not-Present
+0 = Questionable

Table 9

Mold / Stain Growth on TBTO - Treated Southern Yellow Pine

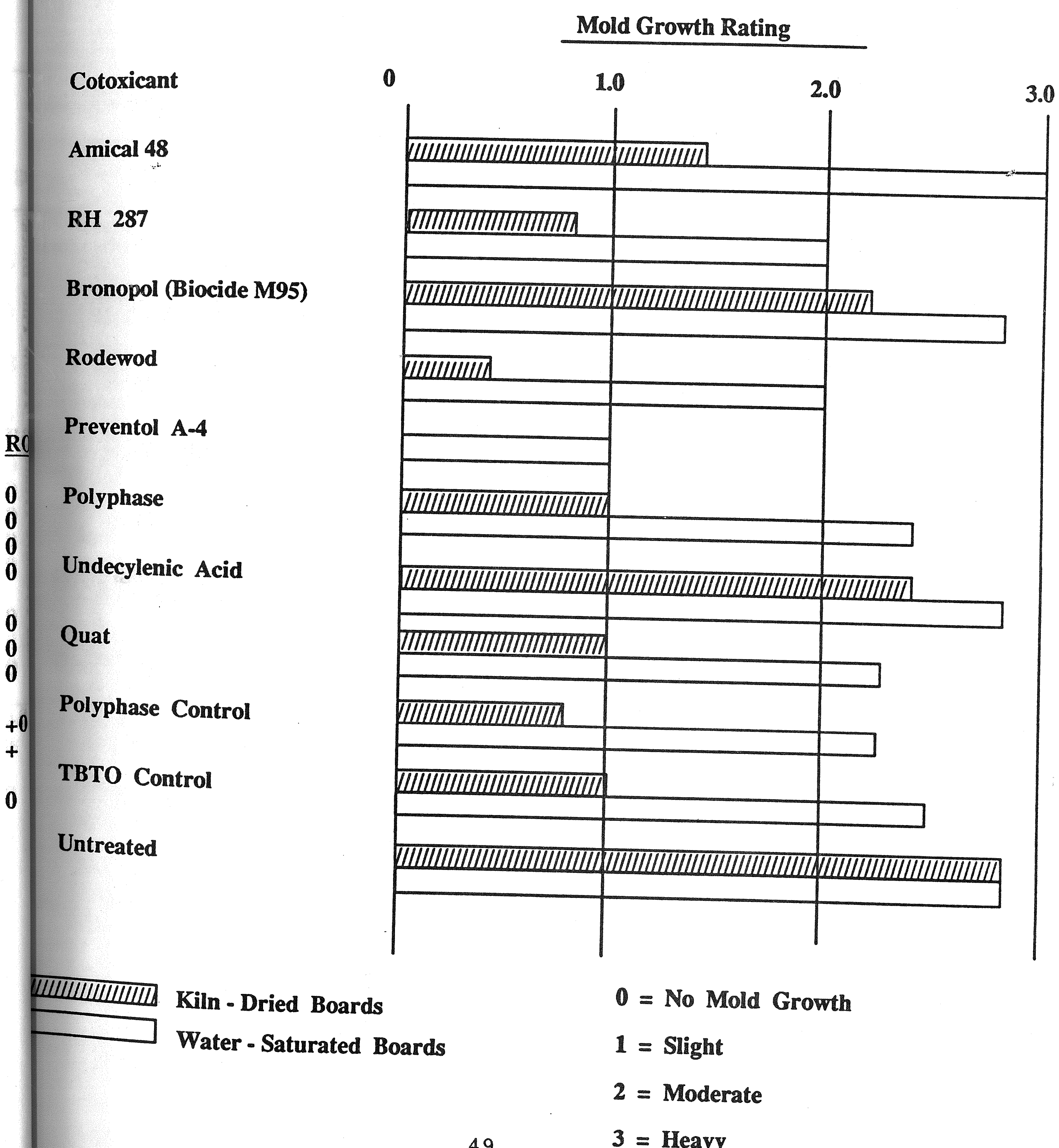


FIGURE 3

HANDLING CONSIDERATIONS FOR TBTO

EXPOSURE	RESPONSE
Eye Contact	Severe eye irritation
Skin Contact	Irritation / dermatitis
Inhalation	Irritation of upper respiratory tract; over exposure produces coughing, head ache and nausea[1]
Low Level Chronic Exposure	No known chronic effects

[1]ACGIH* TLV/8 hr day - 0.1 μg tin/m^3 of air

*American Conference of Governmental Industrial Hygienists

FIGURE 4

GUIDELINES FOR SAFE HANDLING

1. Protective equipment against skin and eye contact:

   a) Gloves, long sleeve shirt and impermeable apron.

   b) Chemical goggles or face mask.

2. Adequate ventilation to remove solvent vapors; respirators should be used where ventilation is inadequate.

3. Eye wash and showers should be readily available.

4. Good personal hygiene - discard contaminated garments.

5. Prompt thorough washing with soap and water after exposure to minimize or eliminate any potential dermal effects.

FIGURES

TABLES

1. van der Kerk, C.V.M. and Luijten, V.G.A., *J. Appl. Chem.*, Investigations on Organic Compounds, **4**, 314-9 (1954).

Snoeij, N.J., Penninks, A.H., and Seinen, W., *Environ. Res.*, Biological Activity of Organotin Compounds - An Overview, **44**, 335-353 (1987).

Cockcroft, R., *J. Inst. Wood Sci.*, Evaluating the Performance of Wood Preservatives Against Fungi, **6**, 2-8 (1974).

Evans, E.J. and Karpel, S., "Organotin Compounds in Modern Technology," Library 16 Elsevier Sci., Published 1985.

Blunden, S.J., Cusack, P.A., and Hill, R., "The Industrial Uses of Tin Chemicals," Royal Society of Chem., Pub. 1985.

Gitlitz, M.H., *J.Coat. Tech.*, Recent Developments in Marine Antifouling Coatings, **53**, 46-52 (1981).

King, S., *Tin and Its Uses*, Twenty Years of Tributyltin Compounds in Wood Preservation, **124** (1980).

Hill, R. and Killmeyer, A.J., "Chemical and Biological Investigations of Organotin Compounds as Wood Preservatives," Proceedings, AWPA Annual Meeting, Minn. (1988).

Hoft, T., *J. Inst. Wood Sci.*, Review of Literature Concerning the Evaluation of Organotin Compounds for Preservations of Wood, **4**, 19-28 (1969).

Crowe, A.J., Hill, R., Smith, P.J., and Cox, T.R.G., *Int. J. Wood Pres.*, Laboratory Evaluations of Tributyltin Compounds as Wood Preservatives, Vol. 1, No. 3, 119-124 (1979).

Hill, R., Chapman, A.H., Samual, A., Manners, K., and Morton G., *Int. Biodeterior.*, Biological and Chemical Observations on the Early Fungal Colonization of TBTO Treated Swedish Redwood Stakes, Vol. 21, No. 2 (1985).

Cserjesi, A.J. and Johnson, E.L., *For. Prod. J.*, Mold and Sapstain Control: Laboratory and Field Tests of 44 Fungicidal Formulations, Vol. 32, No. 10 (1982)

Unligil, H.H., *For. Prod. J.*, Prevention of Fungal Stain on Pine Lumber - Laboratory Screening Tests with Fungicides, Tech. Note, (Jan. 1976).

Imsgard, F.J., Jensen, B., Plum, H., and Landsiedel, H., Stability and Performance of Some Modern Fungicides Used in Wood Preservation, Proceedings, Record Ann. Conv. BWPA, 47-54 (1955).

Richardson, B.A., Organotin Wood Preservatives Activity and Safety in Relation to Structure, Proceedings presented at AWPA Annual Meeting (1988).

16. Carter, F.L., and Beal, H., *Int. J. Wood Pres.,* Termite Responses to Susceptible Pine Wood Treated with Antitermitic Extracts, Vol. 2, No. 4 (1982).

17. Schweinfurth, H., Tributyltin Compounds in Wood Preservatives; An Update of Health and Safety Aspects., Proceedings, BWPA Annual Convention, Cambridge, 30 June - 3 July (1987).

18. Morgan, J.W.W. and Purslow, D.F., Volatile Losses of Wood Preservatives, Proceedings, BWPA Annual Convention (1973).

19. Manners, K.B. and Morton, L.H., *Mater. Org.,* Bioassay of the Inactivation of TBTO by Above Ambient Temperatures, 21 (3), 191-202 (1986).

20. Sutter, H. and Carey, J.K., *Int. Biodeterior.,* Bioassay to Determine Detoxification of Tri-n-butyltin oxide by Species of Phialophora, 22 (3), 195-200 (1986).

21. Jermer, J. Edlund, M., Henningsson, B., Chemical and Biological Investigations of Double-Vacuum Treated Windows after 5 Years Service. Document No: IRG/WP/3419 (1987).

22. Blunden, S.J. and Hill, R., The Compatability of Tributyltin Fungicides and Synthetic Pyrethroid Insecticides as Wood Preservatives, Document No: IRG/WP/3414 (1987).

23. Edlund, M. and Bjorn, H., Chemical and Biological Studies on Organotin Treated and Painted Wood Stakes after Outdoor Exposure, Document No: IRG/WP/3419 (1987).

TOXIC LIMITS FOR TBTO* AGAINST WOOD BORING BEETLES BY LARVAL TRANSFER TESTS BS3651/DIN 52163 CEN 38/U4

PRESERVATIVE	TOXIC LIMITS Kg/M^3	
	ANOBIUM PUNCTATUM	HYLOTRUPES BAJULUS
TBTO* (in an organic solvent)	1.39 - 2.93[1]	0.16 - 0.65[2]

Baker, J.M. and Taylor, J.M. "The Toxicity of Tributyltin Oxide to Wood Boring Beetles, Lyctus brunneas Steph. and Anobium punctatum Deg." Ann. Appl. Biol. 60.181-190 (1957).

Houtinstituut Tno Report H-66-198 (1963) and Report H-67-38 (1967).