Dialkyldimethylammonium Halides as Wood Preservatives

A.F. PRESTON, Institute of Wood Research, Michigan Technological University,
Houghton, MI 49931

ABSTRACT

Laboratory decay tests using brown, white and soft rot fungi on wood treated with a series of dialkyldimethylammonium halides show that maximum fungitoxicity is exhibited by compounds with alkyl chains of 10 and 12 carbon atoms. Both the cation and the anion appear to influence effectiveness with bromide salts showing greater activity values than chloride analogs. The anion presumably influences effectiveness through distribution, fixation, and availability of the compounds rather than directly by changes in fungitoxicity. Monobromination of one of the alkyl chains caused a decrease in fungitoxicity, though the alkyl chain length–fungitoxicity relationship was the same as for the unsubstituted series of compounds. Addition of certain copper or organic biocides to alkylammonium compound formulations increased activity, particularly against soft rot. While this result is a significant advance, the complex relationships involved in such formulations will demand considerable further research in respect of efficacy, fixation, leaching, treatability, and environmental aspects before such a product could be commercialized.

INTRODUCTION

Over the last 10 years environmental, supply, and economic pressures have led to increased research directed towards the development of new wood preservatives (1). Numerous chemicals have been tested but few commercialized. Ammoniacal copper-fatty acids, tributyltin oxide, and furmecyclox are among the few new products now used in some countries, and use of these is restricted to the protection of wood products above ground (2). Many biocides which have shown promise in laboratory studies have performed poorly in subsequent ground contact field tests (3).

Among the potential alternatives to presently used wood preservatives, a group comprised of long-chain quaternary ammonium compounds and tertiary amine salts, collectively referred to as alkyl ammonium compounds (AAC), has perhaps the greatest potential for development into waterborne wood treatment systems (4). Considerable research has been devoted to establishing the efficacy of AAC against decay and insects, and the extensive initial developments in New Zealand (5,6) have led to further research in a number of countries (7-11).

The data published till now shows that AAC are highly effective preservatives in wood when tested in laboratory situations and in field tests above ground (12,13), and AAC of the benzalkonium chloride type have been approved and commercialized in New Zealand for protection of wood products used above ground (14). In the early laboratory screening studies, it appeared that the various generic types of AAC were similar in their response to wood decay fungi (15), and supply and cost considerations in New Zealand led to research there being directed towards utilization of benzalkonium chlorides and tertiary amine salts for in ground use (16,17). However, in subsequent field tests with these two classes of compounds, the initial promise of the laboratory studies faded with the occurrence of premature failures, particularly with tertiary amine salts (18).

The other two major classes of AAC, however, show the greatest potential for commercial application in the USA. The alkyltrimethylammonium salts are highly active against termites (9) and as antisapstain chemicals (19), and are being developed for these specialized uses while, for the protection of wood products, the dialkyldimethylammonium salts have exhibited superior performance overall to the other AAC in both laboratory and field tests (7). Although dialkyldimethylammonium compounds have performed well in field tests using southern yellow pine (3) and radiata pine (1) as substrate, in other studies with ponderosa pine (10), Scots pine and spruce (9), poor performance occurred. The reasons for the variable field performance have not yet been established, but may be due to problems which have occurred in the treatment of certain species with AAC (20).

The generally excellent results we have obtained in this institute with didecyldimethylammonium salts gave rise to this current investigation into the relative effectiveness of a series of dialkyldimethylammonium salts against representatives of the three main wood decay types—namely brown, white, and soft rot. Ditoro (21) and Dadekian (22) have shown that marked differences exist in bactericidal activity between dialkyldimethylammonium chlorides as the chain lengths vary from 8 to 12 carbon atoms, and that replacement of a methyl group with a larger substituent also affects activity. The results of this study will enable optimization of future research through concentration of effort on selected dialkldimethylammonium salts that have the greatest potential for formulation as in-ground preservatives.

METHODS

Each of the test compounds was diluted with water to provide solutions of appropriate strength. Five sapwood blocks per retention level of each of southern pine (*Pinus* spp.) (19 X 19 X 19 mm), aspen (*Populus tremuloides*) (19 X 19 X 19 mm) and paper birch (*Betula papyrifera*) (30 X 10 X 5 mm) were treated by vacuum-pressure impregnation for decay tests with brown, white, and soft rot, respectively. After treatment, uptakes of treating solutions were measured. Retention (kg ai/m^3 wood) calculated from uptakes and treating solution strengths were in the order of 0.75, 1.5, 3.0, 6.0 and 12.0 kg/m^3 for treating solution strengths of 0.125, 0.24, 0.5, 1.0, and 2.0% ai.

Immediately after treatment, the blocks were placed in polyethylene bags for one week to allow fixation. They were then air-dried and subjected to leaching by vacuum-pressure impregnation in 9 times their volume of deionized water. The water was changed after 24 hr and then every 48 hr for 2 weeks. After completion of the leaching cycle the blocks were air-dried, conditioned to 12% mc, weighed and sterilized before being exposed to fungal attack.

Three decay systems were used—the brown rot fungus, *Gloeophyllum trabeum* (Pers. ex Fr.), Karsten (ATCC

TABLE I

Percentage Weight Loss of Dialkyldimethylammonium Halide-Treated Blocks Exposed to Brown, White and Soft Rot Fungi

No.	Chemical	Alkyl chain length	Nominal retention (kg/m^3)	*Gloeophyllum trabeum*	*Irpex lacteus*	Unsterile soil
1	Dioctyldimethyl ammonium chloride	C_8C_8	0.75	36.0	67.6	–
			1.5	27.8	71.4	–
			3.0	17.3	64.4	12.6
			6.0	7.4	50.1	13.8
			12.0	–	–	12.6
2	Octyldecyldimethyl ammonium chloride	C_8C_{10}	0.75	23.2	68.8	–
			1.5	10.1	59.4	–
			3.0	0.9	24.2	12.7
			6.0	0.2	8.3	11.9
			12.0	–	–	11.0
3	Butyltetradecyldimethyl ammonium chloride	C_4C_{14}	0.75	17.1	63.2	–
			1.5	3.6	58.8	–
			3.0	0.3	58.9	8.9
			6.0	0.1	40.9	7.8
			12.0	–	–	9.5
4	Octyldodecyldimethyl ammonium chloride	C_8C_{12}	0.75	9.6	62.7	–
			1.5	2.9	56.5	–
			3.0	0.2	48.0	12.6
			6.0	0.0	8.2	11.6
			12.0	–	–	–
5	Didecyldimethyl ammonium chloride	$C_{10}C_{10}$	0.75	12.8	69.2	–
			1.5	6.7	62.3	–
			3.0	1.0	38.3	13.4
			6.0	0.3	4.4	13.2
			12.0	–	–	7.6
6	Didecyldimethyl ammonium bromide	$C_{10}C_{10}$	0.75	15.1	55.5	–
			1.5	1.1	26.4	–
			3.0	0.0	0.0	13.0
			6.0	0.0	0.0	10.1
			12.0	–	–	7.4
7	Decyldodecyldimethyl ammonium bromide	$C_{10}C_{12}$	0.75	26.3	57.1	–
			1.5	3.8	9.9	10.2
			3.0	0.1	0.3	7.8
			6.0	0.2	0.0	5.2
			12.0	–	–	0.4
8	Decyltetradecyldimethyl ammonium bromide	$C_{10}C_{14}$	0.125	23.6	56.2	–
			0.25	8.6	45.7	–
			0.5	5.9	14.6	7.3
			1.0	0.2	0.1	5.9
			2.0	–	–	0.0
9	Dialkyldimethyl ammonium chloride	$C_{12,14}C_{12,14}$	0.19	16.2	42.8	–
			0.38	3.7	27.5	–
			0.75	0.1	0.0	11.3
			1.5	0.2	0.0	8.4
			3.0	–	–	8.0

11539), the white rot fungus, *Irpex lacteus* Fr. (ATCC 11539) (*Polyporous tulipferae*), and unsterile soil. For the basidiomycete fungi, the exposure system used closely followed the ASTM D1413 soil-wood block test, with the exception that blocks exposed to the white rot were buried in the soil below the surface feeder strips. Jars were incubated at 27 C for 12 weeks.

In the unsterile soil test procedure, two 200-mL jars each containing three blocks were prepared for each treatment group and one untreated control. Blocks were buried ca. 15 mm below the surface of unsterile soil moistened to 150% of field capacity with deionized water. Jars were incubated at 27 C for 8 weeks.

On completion of the incubation period, blocks were cleaned of adhering mycelia and/or soil, conditioned to 12% mc, and weighed. Mean percent loss of wood substance was calculated for each set of blocks.

RESULTS AND DISCUSSION

The results shown in Table I clearly demonstrate a marked structure-activity relationship between alkyl chain length and fungitoxicity of dialkyldimethylammonium halides to the three fungal types tested. Dioctyldimethylammonium chloride (no. 1) exhibited low activity against all the fungi, with the octyldecyl (no. 2), butyltetradecyl (no. 3), and octyldodecyl (no. 4) compounds showing increasing activity against one or more of the fungi as the total carbon atoms in the molecules increased to the optimum of 22 or 24. However, while AAC with alkyl chain lengths of 10 and/or 12 carbon atoms constitute the most active group of compounds, optimum fungitoxicity was not restricted to one compound, but varied somewhat depending on the fungal type under test. One of the didecyl compounds (no. 6) was the most effective against brown rot (*G. trabeum*), while decyldodecyldimethylammonium bromide (no. 7) was at least as active as the didecyl compound against the white rot (*C. versicolor*) and markedly superior in the unsterile soil soft rot test. Interestingly, the C10,C14 compound, decyltetradecyldimethylammonium bromide (no. 8), was as active as the C10,C12 (no. 7) analog in the soft rot test but was less toxic to the basidiomycete fungi.

TABLE II

Percentage Weight Loss of Alkyl-ω-bromodecyldimethylammonium Bromide-Treated Blocks Exposed to Brown and White Rot Fungi

No.	Chemical	Alkyl chain length	Nominal retention (kg/m^3)	Weight loss (%) *Gloeophyllum trabeum*	*Irpex lacteus*
10	Octylbromodecyldimethyl ammonium bromide	C_8C_{10} Br	0.75	24.1	61.2
			1.5	27.4	62.3
			3.0	5.5	26.6
			6.0	0.0	1.4
11	Decylbromodecyldimethyl ammonium bromide	$C_{10}C_{10}$ Br	0.75	37.6	60.8
			1.5	14.4	52.3
			3.0	2.7	3.9
			6.0	0.4	0.3
12	Dodecylbromodecyldimethyl ammonium bromide	$C_{12}C_{10}$ Br	0.75	23.4	42.1
			1.5	20.3	41.4
			3.0	7.2	0.9
			6.0	0.8	0.2
13	Tetradecylbromodecyldimethyl ammonium bromide	$C_{14}C_{10}$ Br	0.75	41.1	62.6
			1.5	25.9	48.5
			3.0	12.4	5.6
			6.0	4.0	0.3

TABLE III

Percentage Weight Loss of Treated Blocks Exposed to Brown, White, and Soft Rot Fungi

No.	Chemical	Alkyl chain length	Nominal retention (kg/m^3)	*Gloeophyllum trabeum*	*Irpex lacteus*	Unsterile soil
14	Didecyldimethyl ammonium chloride plus copper chloride		0.75 + 0.075	9.2	61.8	–
			1.5 + 0.15	4.8	57.5	–
			3.0 + 0.3	0.0	9.3	13.8
			3.0 + 0.6	0.0	1.1	10.4
			6.0 + 1.2	–	–	7.2
15	Didecyldimethyl ammonium chloride plus organic additive		0.75 + 0.075	8.4	66.1	–
			1.5 + 0.15	0.2	65.2	–
			3.0 + 0.3	0.0	47.3	4.4
			3.0 + 0.6	0.0	38.6	0.1
			6.0 + 1.2	–	–	0.0
16	Alkyldimethylbenzyl ammonium chloride	$C_{12,14}$	0.75	67.9	24.2	–
			1.5	65.6	10.2	–
			3.0	62.6	1.3	13.7
			6.0	37.3	0.6	11.7
			12.0	–	–	10.5
17	Alkyldimethyl ammonium acetate	$C_{12,14}$	0.75	56.3	64.1	–
			1.5	51.2	62.5	–
			3.0	46.2	70.6	14.3
			6.0	27.8	66.0	13.5
			12.0	–	–	10.4
18	Didecylmethyl ammonium acetate	$C_{10,10}$	0.75	53.0	64.2	–
			1.5	47.0	63.2	–
			3.0	28.9	50.4	12.6
			6.0	10.9	15.4	12.6
			12.0	–	–	11.3
19	Chromated copper arsenate (oxide basis)		0.75	32.5	14.7	–
			1.5	7.5	0.0	–
			3.0	1.5	0.0	6.5
			6.0	0.0	0.0	0.7
			12.0	–	–	0.2
Controls			0.0	55.2	60.4	12.3

The influence of alkyl chain lengths of the cation on fungitoxicity was blurred somewhat by the influence of the anion. Didecyldimethylammonium bromide (no. 6) was more active than its chloride analog (no. 5) against the white rot fungus. However, this superiority was minimal in the case of brown rot and was not apparent in the soft rot test.

The relationship between alkyl chain length and fungitoxicity established in this study is very similar to that found by Angele (23) and Dadekian (22) in their studies of the bactericidal properties of this class of compounds.

The structure-activity relationships with respect to alkyl chain lengths established in the initial test were also found in a study of four ω-brominated dialkyldimethylammonium bromides (Table II). In this series, the bromodecyldecyl (no. 11) and bromodecyldodecyl (no. 12) compounds were the most active, the former being of slightly higher activity against the brown rot fungus, while the bromodecyldodecyl compound was superior in the control of the white rot fungus *I. lacteus*. Although the relationship of alkyl chain lengths to fungitoxicity of these monobrominated AAC is identical to that of the unsubstituted analogs, bromination of the carbon chain lead to diminished fungitoxicity relative to the unsubstituted analogs.

The laboratory results obtained from modification of didecyldimethylammonium chloride treating solution by the addition of copper chloride (no. 14) (see Table III) reflect the field test results, where improvement to AAC performance is imparted by the addition of copper salts, especially when hardwood stakes are exposed to a high soft-rot hazard (3,6,11). In another approach to increasing AAC effectiveness, addition of an organic fungicide to an AAC treatment solution–formulation no. 16–gave a substantial increase in effectiveness against brown rot and, more significantly, also in the unsterile soil soft-rot test. Field testing with these systems is in progress.

Confirming results from earlier studies (7), the benzalkonium compound (no. 16) and the monoalkyl tertiary amine salt (no. 17) exhibited low antifungal activity, particularly against soft rot and *G. trabeum*, though the benzalkonium salt was moderately active against white rot. While the didecyl amine salt (no. 18) exhibited greater fungitoxicity than the monoalkyl compound (no. 17), it was significantly less active against any of the fungal types than its quaternized didecyl analogs (nos. 5 and 6) discussed above. Chromated copper arsenate (no. 19) was more active than the unmodified AAC against the white rot fungus and in the soft rot test but was less active against *G. trabeum*. This result reflects those obtained to date in field tests with these preservatives where unmodified AAC are outperformed by CCA treatment (3) through the occurrence of shallow surface degradation of the outer zones of test stakes below ground. This surface phenomenon has been ascribed to differential desorption and adsorption of AAC and CCA preservatives in the periphery of the wood (11) and further research centered on identifying the fixation mechanism(s) of AAC to wood, be it an ion exchange or a sorption process, should facilitate formulation modifications which will overcome the erosion.

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