

# FUNGICIDAL EFFECTIVENESS OF VARIOUS SALTS OF A TERTIARY AMINE

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## ABSTRACT

Laboratory decay tests show that the fungicidal activity of alkylammonium compounds (AAC) used for the control of wood-decaying fungi can be markedly affected by changing the nature of the anion used.

Amine salts formed from weak acids (e.g. naphthenic acetic acid) show significantly greater effectiveness than those formed from strong acids (e.g. hydrochloric, hydrobromic acid). Enhanced fungicidal activity is ascribed to improved macro- and micro-distribution of the preservative due to a slowing in the rate of the ion-exchange fixation mechanism.

## INTRODUCTION

Studies by the Wood Preservation Section of the Forest Research Institute directed towards the development of new wood preservatives with desirable environmental, supply, and cost characteristics, have concentrated largely on the use of alkylammonium compounds (AAC) (Butcher, Preston, Hedley and Cross, 1977). The initial investigations centred on the use of benzalkonium compounds (Butcher, Preston and Drysdale, 1977; Butcher, Hedley and Drysdale, 1977) but emphasis has now shifted to the tertiary amine salts which are likely to be more cost effective than the benzalkoniums.

In a recent study (Butcher and Preston, 1978) trends in fungicidal activity through a series of tertiary amine acetates with varying alkyl chain length (i.e. changing the character of the cation) have been investigated. Effectiveness against soft rot in the hardwood (*Betula alba*) used was greatest with an alkyl chain length of C<sub>14</sub>, though others in the C<sub>12</sub> to C<sub>18</sub> range showed considerable activity against soft rot. In the basidiomycetes tests, fungicidal activity was fairly constant throughout the C<sub>12</sub> to C<sub>18</sub> range with a marked drop-off in effectiveness below these chain lengths.

Butcher and Drysdale (1978) have shown that modification of AAC treating solutions with acid or alkali can have a significant effect on the ability of the biocide to prevent decay. Addition of low levels of alkali were found to cause a marked decrease in fungitoxicity, while addition of acid had the opposite effect. It is assumed that the presence of excess hydroxide or hydronium ions is not altering the fungitoxicity of the chemical but rather is influencing the macro- and micro-distribution of the AAC within the wood structure. The presence of excess hydroxide ions in an AAC solution will

accelerate fixation, leading to high treatment levels in the peripheral zones of the wood, but only to low levels in the interior. Thus, in a cut-block test as performed in this study, high weight losses will occur through decay in the poorly treated interior. Conversely, the presence of acid will hinder fixation and allow AAC to be distributed evenly throughout the wood. Furthermore, the slower rate of fixation may allow greater penetration of the cell wall by the preservative and hence afford greater protection against soft rot.

The results of the study on acid- and alkali-modifications suggested that addition of low levels of acid could improve performance of AAC preservatives substantially. In practice, modification of treating solutions by adding acid could lead to problems of plant corrosion and solution strength control, and similar effects may possibly be achieved through the use of anions other than the chloride used in the earlier studies.

In considering trends relating to strengths of a series of acids, increase in acid strength implies a decrease in strength of the conjugate base of the acid. Conversely, lower acid strength implies a stronger conjugate base. Conjugate bases of weak acids can therefore be expected to produce tertiary amine salts of less ionic character than those produced by reacting a tertiary amine with a strong acid. Lowering the ionic character of the AAC should hinder fixation and permit a more even distribution of the preservative through the wood with improved micro-distribution through deeper penetration of the cell wall. It has been the object of this study to investigate whether such a trend does occur through a series of nine different acids combined with a selected tertiary amine.

### EXPERIMENTAL

Dodecyldimethylamine (as ADMA-2, from Ethyl Corporation) was treated with the following acids to give 0.067 M aqueous solutions (i.e. equivalent to 2% active ingredient (a.i.) dodecyldimethylamine acetate).

No anion (i.e. dodecyldimethylamine base in alcohol)

Acetic acid	Hydrobromic acid
Boric acid	Hydrochloric acid
Fluoroboric acid	Hydrofluoric acid
Formic acid	Naphthenic acid

The 2% a.i. stock solutions were sub-divided and diluted to give three treating solutions for each amine salt: 2%, 1% and 0.5% a.i.

Eight blocks (20 × 20 × 20 mm) of *Pinus radiata* sapwood and eight blocks (30 × 10 × 5 mm) of *Betula alba* sapwood were treated for each of the 27 solutions by a laboratory vacuum soak procedure. Individual retentions (kg/m<sup>3</sup>) were calculated from solution uptakes, solution concentrations, and mean block volumes. After treatment, all blocks were wrapped in polythene, by treatment groups, and held for two weeks at room temperature to allow fixation. They were then slowly air-dried, following which they were impregnated with deionized water and subjected to a standard leaching procedure for two weeks (blocks in 9 times their own volume of water which was changed every two days).

When leaching had been completed the blocks were redried. Four pine blocks were cut in half transversely to provide eight 20 × 20 × 9 mm blocks for basidiomycete

TABLE 1—Results of bioassay (% mean weight loss of wood samples) after treatment with ADMA-2 salts at three concentrations

	Anion*	Treating solution (% a.i.)		
		0.5	1.0	2.0
Substrate:	No anion	14.6	0.5	0.0
<b>Pinus radiata</b>	Naphthenate	9.7	1.5	1.3
	Acetate	2.2	1.6	0.9
	Formate	6.0	0.8	1.2
Test fungus:	Fluoride	10.1	1.5	0.9
<b>Gloeophyllum trabeum</b>	Chloride	5.1	2.5	1.4
	Bromide	4.3	2.2	1.2
	Borate	44.9	47.5	3.9
	Fluoroborate	20.2	12.6	10.2
Substrate:	No anion	22.0	2.1	1.7
<b>Pinus radiata</b>	Naphthenate	14.4	1.2	1.7
	Acetate	10.2	6.0	2.1
	Formate**	5.9	1.5	8.0
Test:	Fluoride	21.8	18.4	2.1
Unsterile soil	Chloride	16.6	13.1	3.3
	Bromide	22.2	24.6	19.2
	Borate	46.6	53.9	23.9
	Fluoroborate	55.5	41.1	21.7
Substrate:	No anion	17.2	21.4	22.3
<b>Betula alba</b>	Naphthenate	28.7	14.7	11.0
	Acetate	18.3	19.6	13.1
	Formate	34.6	12.6	13.1
Test:	Fluoride	39.9	33.8	18.0
Unsterile soil	Chloride	35.1	33.6	24.7
	Bromide	30.8	30.2	23.2
	Borate	30.3	31.1	16.9
	Fluoroborate	36.3	33.5	37.3

\* In order of increasing acid strength. For peculiarities of borate and fluoroborate see text

\*\* Results considered to be anomalous

tests, and the remaining four were cut transversely to provide twelve 20 × 20 × 6 mm blocks for soft-rot tests. The birch blocks were not re-cut. All blocks were conditioned to 12% e.m.c., and weighed before sterilisation by exposure to vapour of 1,2-epoxy-propane.

The basidiomycete decay test followed closely the ASTM D1413-61 standard method and used *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. as test organism. Four blocks were placed in each of two soil jars for each treatment group. They were incubated at 27°C for 10 weeks.

Soft-rot tests were carried out using an unsterile soil procedure — soil moistened to 150% field capacity. In tests with pine, three blocks were placed in each of four

jars for each treatment group. In tests with birch there were two replicate jars containing four blocks. Jars were incubated at 30°C for 10 weeks.

On completion of the incubation period, all blocks were removed from jars, cleaned, and then reconditioned to 12% e.m.c. and reweighed. Decay was expressed as a mean percentage loss of wood substance.

## RESULTS AND DISCUSSION

The results of the three bioassay tests (Table 1) show that distinct trends have emerged as regards the fungicidal effectiveness of a series of amine salts formed from acids with differing acid strengths. However, it is notable that the salts formed from boric and fluoroboric acid do not fit in with the trends apparent for other acids. Salts formed from the boric acids appeared to promote brown rot attack and this factor has overridden any other fungicidal effect these two salts may have had.

In the pure culture basidiomycetes test using *Gloeophyllum trabeum* no significant trend could be seen in relating fungicidal effectiveness to strength of the conjugate acid of the anion used. Except for the borate and fluoroborate salts, all of the amine salts exhibited control at 1% a.i. treating solution, though only the acetate salt gave control at 0.5% a.i. The variability of the results at 0.5% a.i. suggests that, in this test, the dodecyldimethylamine salts were close to the toxic threshold at this level of treatment.

The unsterile soil test using treated *Pinus radiata* as substrate showed a trend of increasing fungicidal activity against soft rot with decreasing strength of the conjugate acid of the anion used. The trend can be ascribed to improvement in the macro- and micro-distribution of the preservative when the ionic character of the amine salt is lessened. This occurs through a decrease in the rate of the ion exchange fixation mechanism allowing a more even distribution of the preservative. Such an effect would be more apparent with soft rot fungi than basidiomycetes as attack by soft rot is predominantly within the less accessible cell wall zones rather than at the lumen surface and thus improvements in micro-distribution would be more important in the control of this type of organism.

Salts of the tertiary amine (dodecyldimethylamine) were not expected to give control of soft rot in the hardwood-unsterile soil test and this proved to be so. However, as in the softwood-unsterile soil test, with the exception of the treatment with no anion, the same general trend of increasing effectiveness against soft rot with decreasing strength of the conjugate acid of the anion was observed. Further studies will be necessary to determine the most effective combinations of anion and tertiary amine in order to achieve control of soft rot in hardwood at a commercially acceptable level. In this regard future development should centre on salts formed from tertiary amines in which the alkyl residues are predominantly C<sub>14</sub>, and weak organic acids.

## CONCLUSIONS

Improvement in performance of tertiary amine salts against wood decaying fungi can be achieved through the use of anions having a weaker conjugate acid than that of the chloride anion. The effects of changing the anion portion of the salt are most marked in control of soft rot. The improvement can be attributed to better macro- and micro-distribution of the preservative through a decreased rate of fixation with the less

ionic amine salts formed from the weaker acids.

While AAC are, in general, more effective against basidiomycete fungi than against soft rot, control of the latter in softwoods can be readily achieved with these chemicals. Our studies show that while the amine salt used in the current study provides little better protection of hardwood from soft rot than copper-chrome-arsenate (CCA) preservatives, there is considerable leeway for manipulation of AAC formulations and indications are that soft rot control in hardwoods will be possible at a commercially acceptable level.

Further improvements in the performance of amine salts against soft rot can be expected if the anions which appear the most effective from this present study are used in combination with amines containing alkyl chain distributions of greater fungitoxicity than the dodecyldimethylamine used here.

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