# TOXICITY OF TERTIARY AMINE ACETATES AGAINST BASIDIOMYCETES AND SOFT-ROT FUNGI

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ABSTRACT

The acetate salts of seven tertiary amines, which provided a series of increasing alkyl chain length from $C_8$ to $C_{18}$, were screened for fungicidal effectiveness against basidiomycetes and soft-rot fungi in pine and birch timber respectively. Dodecyldimethylamine acetate was the most effective against basidiomycetes (toxic threshold 1.6-3.2 kg/m$^3$). Tetradecyldimethylamine acetate was the most effective against soft-rot fungi, but some decay (mean loss of wood substance 3.1%) occurred at 6 kg/m$^3$, the highest level tested. Decreasing alkyl chain lengths (below $C_{12}$,) greatly reduced effectiveness whereas increasing alkyl chain length (above $C_{14}$) caused only a gradual reduction in fungitoxicity.

## INTRODUCTION

Butcher, Preston and Drsydale (1977) screened nineteen quaternary ammonium compounds and various salts of three tertiary amines for effectiveness in controlling decay of *Pinus radiata* sapwood caused by three basidiomycete fungi. It was concluded that salts of dimethyllaurylamine (referred to in this paper as dodecyldimethylamine) were the most effective fungicides, and that alkylammonium compounds in general showed good potential as wood preservatives. Subsequent tests (Butcher, Hedley and Drysdale, 1977) compared performance of a quaternary ammonium compound (lauryldimethylbenzyl ammonium chloride) and copper-chrome-arsenate in hardwoods and softwoods exposed to decay from both basidiomycetes and soft-rot fungi. Although the quaternary ammonium compound performed well, similar trials with a tertiary amine chloride proved disappointing in terms of soft-rot control; poor performance was thought to be due to formulation problems. For this reason, work with tertiary amine salts was temporarily discontinued and the major research effort given to quaternary ammonium compounds (Butcher, 1978; Butcher and Drysdale, 1977; 1978a; Butcher *et al.*, 1978; Cross, 1979).

Recently, a detailed examination of the potential of tertiary amine salts as wood preservatives was undertaken because if preliminary results of effectiveness against basidiomycetes could be confirmed and effectiveness at relatively low wood retentions against soft-rot fungi established, they were likely to be amongst the most cost-effective of the alkylammonium compounds. This paper outlines the results of trials to establish effectiveness of a series of tertiary amine salts against basidiomycetes and soft-rot fungi.

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## MATERIALS AND METHODS

The acetate salts of seven tertiary amines were prepared by adding the following amounts of the tertiary amine and acetic acid to 1960 g of deionised water.

| | | | |
|---|---|---|---|
| Octyldimethylamine | 28.94 g | + acetic acid | 11.06 g |
| Decyldimethylamine | 30.21 g | + acetic acid | 9.79 g |
| Dodecyldimethylamine | 31.21 g | + acetic acid | 8.79 g |
| Cocodimethylamine | 31.55 g | + acetic acid | 8.45 g |
| Tetradecyldimethylamine | 32.03 g | + acetic acid | 7.97 g |
| Hexadecyldimethylamine | 32.71 g | + acetic acid | 7.29 g |
| Soyadimethylamine | 33.18 g | + acetic acid | 6.82 g |

The amine acetates so formed represent a series of increasing alkyl chain lengths from $C_8$ to $C_{18}$. Cocodimethylamine acetate contained alkyl chains of varying length (7% $C_8$, 6.5% $C_{10}$, 53% $C_{12}$, 19% $C_{14}$, 8.5% $C_{16}$, 1% $C_{18}$, 5% $C_{18}^{1}$) as did the soyadimethylamine acetate (1% $C_{14}$, 24% $C_{16}$, 1.0% $C_{16}^{1}$, 10% $C_{18}$, 49% $C_{18}^{1}$, 15% $C_{18}^{11}$). The trivial names derive from the original vegetable oil source.

The 2% (w/w) stock solutions were diluted with deionised water to provide 0.1, 0.25, 0.5 and 1.0% (w/w) solutions for block treatments. Twelve *Pinus radiata* sapwood blocks (20 × 20 × 20 mm) and eight *Betula alba* sapwood blocks (30 × 10 × 5 mm) were treated for each solution using a laboratory vacuum-soak procedure. Individual block retentions (kg/m$^3$) were estimated from solution uptakes, solution concentrations, and mean block volumes.

After treatment, blocks were wrapped in polythene and held for two weeks at room temperature to allow fixation. They were then slowly air-dried, following which they were impregnated with deionised water and subjected to leaching. The leaching procedure comprised placing blocks, by treatment groups, into 9x their own volume of deionised water which was changed every second day for two weeks. After leaching, blocks were air-dried. The *P. radiata* blocks were cut in half transversely to provide 20 × 20 × 9 mm blocks for basidiomycete exposure tests. The *B. alba* blocks assigned to soft-rot tests were not re-cut. All blocks were then conditioned to 12% e.m.c., weighed, and sterilised by exposure with vapor of 1,2-epoxypropane.

The fungal exposure system used for basidiomycete tests closely followed the ASTM D1413-61 standard method, with the exception that blocks were partially buried in soil either side of a narrow feeder strip of untreated *P. radiata* sapwood. The test fungi used were *Gloeophyllum trabeum* (Pers. ex Fr.) Murr (CSIRO DFP 7520), *Poria placenta* (Fr.) Cke (CSIRO DFP 7522), and *Fomes gilvus* (Fr.) Lloyd (CSIRO DFP 2442). Two soil jars, each containing four replicate blocks, were prepared for all treatment/fungus combinations. Jars were incubated at 27°C for 10 weeks.

An unsterile soil procedure was used for soft-rot tests with *B. alba.* Two jars, each containing four replicate blocks, were prepared for each treatment group. Blocks were buried approximately 5 cm below the surface of an unsterile nursery soil moistened to 150% of field capacity with deionised water. Jars were incubated at 30°C for 10 weeks.

On completion of the incubation period, blocks were removed from the jars, cleaned, reconditioned to 12% e.m.c., and reweighed. Decay was expressed as a mean percentage loss of wood substance. The toxic threshold was taken as lying between that retention of the tertiary amine acetate which prevented decay (mean loss of wood substance less than 2%), and the next lowest retention.

## RESULTS AND DISCUSSION

### *Block Treatment*

The mean retentions in blocks of *P. radiata* and *B. alba* after treatment with the four solution strengths of each tertiary amine acetate are presented in Table 1.

All blocks treated came close to their theoretical maximum uptake. The slightly lower retentions in *B. alba* were a result of the slightly higher basic density of this species compared with *P. radiata.* The estimated retentions are those immediately following treatment and do not take account of any losses suffered during the leaching schedule. However, loss of an alkylammonium compound by leaching treated wood in deionised water is likely to be negligible at retentions up to 6 kg/m$^3$ (Butcher *et al.,* 1978).

### *Basidiomycete Tests*

Results of basidiomycete decay tests are presented in Table 2 to illustrate the effect of alkyl chain length of tertiary amine acetates on their toxicity to decay fungi. In general, the results show low toxicity at an alkyl chain length of $C_8$ (octyldimethylamine acetate), increased toxicity at $C_{10}$ (decyldimethylamine acetate), and greatest toxicity at $C_{12}$ (dodecyldimethylamine acetate). There was slightly less activity at $C_{14}$ (cocodimethylamine and tetradecyldimethylamine acetates) and a further reduction at $C_{16}$ (hexadecyldimethylamine acetate) and $C_{18}$ (soyadimethylamine acetate).

TABLE 1—Mean retentions (kg/m$^3$) in **P. radiata** and **B. alba** blocks after treatment with four solution strengths of seven tertiary amine acetates

| | Treating solution strength (% w/w) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **P. radiata** | | | | **B. alba** | | | |
| Amine Salt | 0.1 | 0.25 | 0.5 | 1.0 | 0.1 | 0.25 | 0.5 | 1.0 |
| Octyldimethylamine acetate | 0.6 | 1.5 | 3.1 | 6.2 | 0.5 | 1.4 | 2.7 | 5.4 |
| Decyldimethylamine acetate | 0.6 | 1.6 | 3.0 | 6.1 | 0.6 | 1.4 | 2.7 | 5.6 |
| Dodecyldimethylamine acetate | 0.6 | 1.6 | 3.2 | 6.3 | 0.6 | 1.4 | 2.7 | 5.5 |
| Cocodimethylamine acetate | 0.6 | 1.6 | 3.1 | 6.0 | 0.6 | 1.4 | 2.9 | 5.4 |
| Tetradecyldimethylamine acetate | 0.6 | 1.6 | 3.1 | 5.7 | 0.6 | 1.3 | 2.8 | 5.8 |
| Hexadecyldimethylamine acetate | 0.7 | 1.4 | 3.0 | 6.1 | 0.6 | 1.4 | 2.7 | 5.1 |
| Soyadimethylamine acetate | 0.6 | 1.5 | 3.2 | 5.8 | 0.6 | 1.3 | 2.7 | 5.7 |

For practical purposes, the effect of alkyl chain length on toxicity need only be considered for the most tolerant test fungus, namely *G. trabeum.* When this is done, the following order of effectiveness can be given to alkyl chain length: $C_{12} > C_{14} = C_{16} = C_{18} > C_{10} > C_8$.

In preliminary screening trials with salts of three tertiary amines (Butcher, Preston and Drysdale, 1977) dodecyldimethylamine (referred to as dimethyllauryl amine) was more effective than tetradecyldimethylamine (referred to as dimethylmyristylamine), and the same toxic thresholds were established as in the present test.

TABLE 2—Effect of alkyl chain length of tertiary amine acetates on toxicity to three basidiomycetes

| Amine Salt | Alkyl chain length | Toxic threshold (kg/m³) *G. trabeum* | *P. placenta* | *F. gilvus* |
|---|---|---|---|---|
| Octyldimethylamine acetate | $C_8$ | 6.2 | 6.2 | 1.5-3.1 |
| Decyldimethylamine acetate | $C_{10}$ | 3.0-6.1 | 0.6-1.6 | ca. 1.6* |
| Dodecyldimethylamine acetate | $C_{12}$ | 1.6-3.2 | 0.6-1.6 | 0.6-1.6 |
| Cocodimethylamine acetate | $C_{12-14}$ | ca. 3.1* | 0.6-1.6 | 0.6-1.6 |
| Tetradecyldimethylamine acetate | $C_{14}$ | ca. 3.1* | 0.6-1.6 | 0.6-1.6 |
| Hexadecyldimethylamine acetate | $C_{16}$ | ca. 3.0* | ca. 1.4* | 0.7-1.4 |
| Soyadimethylamine acetate | $C_{18}$ | ca. 3.2* | ca. 1.5* | 0.6-1.5 |

* Maximum loss of weight in any block not exceeding 3%.

### *Soft-rot Tests*

None of the tertiary amine acetates completely controlled soft-rot of birch in the unsterile soil test. The length of the alkyl chain was again shown to be important in respect to fungitoxicity (Fig. 1). Tetradecyldimethylamine acetate was the most active of the compounds tested. At a retention of less than 6 kg/m³, mean loss of wood substance was reduced to 3.1% (range 2.0-4.3). Effectiveness of tertiary amine acetates against soft-rot fungi was reduced as alkyl chain lengths became shorter ($C_{12}$ downwards). Increasing chain length ($C_{16}$ and $C_{18}$) also caused a reduction in effectiveness, but this was less marked.

It is well established that soft-rot of hardwoods is difficult to control with commercial preservatives such as copper-chrome-arsenate (CCA). The toxic threshold of CCA salts in *Betula alba* wood, for example, is about 25 kg/m³ (Butcher and Drysdale, 1978b). Initial soft-rot tests with a quaternary ammonium compound (lauryldimethylbenzyl ammonium chloride) showed it to be very effective in controlling soft-rot caused by pure cultures of *Chaetomium globosum* Kunze or *Humicola* sp. (toxic threshold not greater than 5 kg/m³), but to give only partial soft-rot control in unsterile soil tests (Butcher, Hedley and Drysdale, 1977).

The present results indicate that specific tertiary amine acetates offer improved control of soft-rot compared with laurydimethylbenzylammonium chloride and CCA. However, it must be noted that although soft-rot attack was very restricted in blocks treated to about 6 kg/m³ with tetradecyldimethylamine acetate, the severity of attack where it occurred, remained high.

Complete control of soft-rot may possibly be achieved by treating wood to higher retentions (e.g. 10 kg/m³) of the preservative. Recent work has also shown that some minor modifications to treating solutions (Butcher and Drysdale, 1978a), and the use of tertiary amine salts of lower ionic character (Preston and Butcher, 1978), enhances soft-rot control presumably because fixation of alkylammonium compounds in wood is slowed down and greater cell wall penetration is achieved. Thus, improved performance

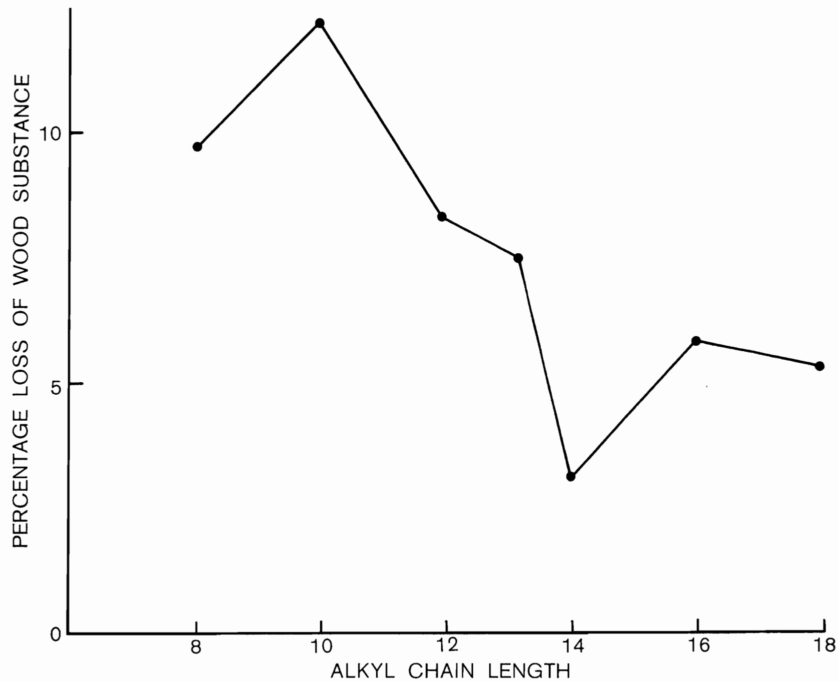


FIG. 1—Effect of alkyl chain length of tertiary amine acetates on protection of treated **Betula alba** sapwood against soft-rot fungi.

may be obtained by means other than simple increase of treating solution strengths; an important consideration where cost effectiveness of treatment is involved.

## CONCLUSIONS

Dodecyldimethylamine acetate was most effective against basidiomycetes, whereas tetradecyldimethylamine acetate was most effective against soft-rot fungi. In theory, this suggests that dodecyldimethylamine acetate should be used for protection of wood exposed above-ground where the decay hazard is primarily caused by basidiomycetes. Similarly, tetradecyldimethylamine acetate shows good potential for protection of wood exposed in ground contact where the decay hazard also involves soft-rot fungi. In practice, factors other than the intrinsic toxicity of the chemical must be considered, and one of the most important is chemical cost. It is highly probable that the mixtures of tertiary amine acetates made from the natural-product-based cocodimethylamine and soyadimethylamine will be most cost effective. If this is so, their cost effectiveness may be improved further by reference to the influence of alkyl chain length on fungal toxicity. For example, cocodimethylamine acetate should be formulated to contain a minimum of alkyl chains of $C_{10}$ and below to attain greatest fungicidal toxicity. Formulations with the highest percentage of $C_{14}$ alkyl chains will be most suitable for protection of wood in ground contact.

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