

EFFICACY OF ACIDIC AND ALKALINE SOLUTIONS OF ALKYLAMMONIUM COMPOUNDS AS WOOD PRESERVATIVES

JOHN A. BUTCHER and JEANETTE DRYSDALE

Forest Research Institute, New Zealand Forest Service, Rotorua

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ABSTRACT

Solutions of alkylammonium compounds were modified by addition of various levels of acid (HCl) or alkali (Na_2CO_3). Solution concentrations were designed to provide sub-toxic retentions of the alkylammonium compounds in treated poplar or pine wood blocks. The effect of acid or alkali addition to treating solutions was determined through increase or decrease in decay after treated wood was incubated with test fungi (brown-rot, white-rot, and soft-rot). Addition of low levels of acid (0.025-0.1% w/w HCl) improved performance against basidiomycetes, and to a lesser extent soft-rot fungi. Addition of high levels of acid (1% w/w HCl) further improved soft-rot control, but resistance of treated wood to basidiomycete attack was reduced. Addition of alkali to treating solutions generally led to increased loss of wood substance when treated wood was exposed to fungal attack. Results are discussed in terms of the effect of acid and alkali on the fixation process and subsequent macro- and micro-distribution of alkylammonium compounds in wood.

INTRODUCTION

Recent investigations have demonstrated the efficacy of alkylammonium compounds in controlling basidiomycete and soft-rot attack of both hardwoods and softwoods. (Butcher, Preston and Drysdale, 1977; Butcher, Hedley and Drysdale, 1977; Butcher and Drysdale, 1977).

Preliminary work suggested that addition of acid or alkali to treating solutions of alkylammonium compounds affected their fixation and distribution in wood. The probable mechanism has been summarised by Rosen (1975). As the pH of aqueous solutions of cationic surfactants (i.e. alkylammonium compounds) is lowered, the surface of a charged, solid substrate (e.g. lignified cell walls) will become more positive through adsorption of protons. In consequence, there will be a decrease in the adsorption of the similarly charged alkylammonium cations. When the pH is raised, the converse is true and a greater adsorption of cations will occur.

Observation during preliminary work indicated that treatment with acidic solutions resulted in an even distribution of alkylammonium compounds through the wood, whereas treatment with alkaline solutions resulted in preferential adsorption in the surface layers of wood samples. Fungal assay of wood treated with acidic or alkaline

solutions of alkylammonium compounds suggested that acidic solutions were more effective against basidiomycetes, and alkaline solutions were more effective against soft-rot fungi. However, it is possible that these results more truly reflected differences in block preparation for decay tests. In tests with basidiomycetes, blocks were cut in half transversely after treatment to expose central zones of the wood to fungal attack. Veneers used for soft-rot tests were not re-cut after treatment. It is reasonable to assume that protection from basidiomycete attack was best when blocks were treated with acidic solution because this resulted in an even distribution of the alkylammonium compound throughout the wood. Conversely, treatment with alkaline solution was more effective against soft-rot fungi because of the preferential adsorption of alkylammonium compounds in peripheral zones of the wood where soft-rot attack first occurs.

The present work was undertaken to re-examine the effect on the decay resistance of treated wood of adding acid or alkali to the treatment solutions of alkylammonium compounds. The main aim was to gain information for improved biological performance through minor modification of treating solutions.

MATERIALS AND METHODS

Two bulk solutions of alkylammonium compounds were prepared, one containing 0.38% a.i. (active ingredient) Bioquat 501 — alkyl (64% C₁₂, 30% C₁₄, 6% C₁₆) dimethylbenzylammonium chloride, and the other 0.35% a.i. Bardac 20 — dialkyl (50% C₈C₁₀, 25% C₈C₈, 25% C₁₀C₁₀) dimethylammonium chloride. Concentrations were determined by chemical analysis following the procedure outlined by Butcher and Drysdale (1977). They were chosen to provide sub-toxic threshold retentions of both compounds in treated wood. Bulk solutions were modified, as below, to provide 14 solutions for treatment of test blocks.

1.	0.38% a.i. Bioquat 501	— unamended	pH 6.2
2.	"	+ 0.025% w/w HCl	pH 2.1
3.	"	+ 0.1% w/w HCl	pH 1.7
4.	"	+ 0.5% w/w HCl	pH 1.3
5.	"	+ 1.0% w/w HCl	pH 1.15
6.	"	+ 0.037% w/w Na ₂ CO ₃	pH 10.5
7.	"	+ 0.15% w/w Na ₂ CO ₃	pH 10.75
8.	"	+ 0.73% w/w Na ₂ CO ₃	pH 11.25
9.	"	+ 1.46% w/w Na ₂ CO ₃	pH 11.4
10.	0.35 a.i. Bardac 20	— unamended	pH 6.1
11.	"	+ 0.1% w/w HCl	pH 1.7
12.	"	+ 1.0% w/w HCl	pH 0.85
13.	"	+ 0.15% w/w Na ₂ CO ₃	pH 10.8
14.	"	+ 1.46% w/w Na ₂ CO ₃	pH 11.4

Each solution was used to treat 16 blocks (20 × 20 × 20 mm) of both *Pinus radiata* sapwood and *Populus robusta* sapwood by vacuum impregnation in the laboratory. Immediately after treatment, solution uptake was determined for subsequent calculation of chemical retentions. Blocks were then wrapped in polyethylene and stored for two weeks to allow fixation.

On completion of the fixation period all blocks were air dried. Three blocks of each wood species were removed from each treatment group for chemical analysis. The alkylammonium compound was extracted from wood (2.5-3.0 g of 20 mesh air-dry sawdust) by steeping in 100 ml of 1M alcoholic hydrochloric acid (Metcalf, 1960) for 12 hours; 2 ml aliquots of the extract were then titrated against standardised sodium lauryl sulphate (Butcher and Drysdale, 1977). The remaining blocks were then impregnated with deionized water and placed in 100 times their volume of deionized water to leach any unfixated chemical. Leaching solutions were agitated daily. The leachates from blocks treated with each of the 14 solutions were held for chemical analysis of alkylammonium compounds. Leached blocks were then air dried. One block of each wood species and each treatment group was then cut in half transversely. A 0.04% solution of bromophenol blue in 20% aqueous ethanol was then applied to the cut surfaces to determine distribution of the alkylammonium compounds. Treated wood stains blue, untreated wood stains purple.

The remaining 12 blocks of each wood species — treatment group combination were assigned to biological assay. Eight blocks were cut in half transversely to provide 16 "half-blocks" (20 × 20 × 9 mm) for basidiomycete tests. The remaining four blocks were cut transversely to provide three 20 × 20 × 6 mm blocks for soft-rot tests. Basidiomycete decay tests were carried out with *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. — CSIRO DFP 7520, and *Fomes gilvus* (Fr.) Lloyd — CSIRO DFP 2442, using a fungal exposure system which closely followed the ASTM D1413-61 solid-wood-block test method. Four test blocks were exposed in each of two jars for all fungus-wood treatment combinations. Soil jars were incubated at 27°C for 10 weeks. Soft-rot tests were carried out using an unsterile soil technique in which sterile wood blocks were buried in nursery soil moistened to 155% field capacity with deionized water. Six blocks were placed in each of two jars for all fungus-wood treatment combinations. Jars were incubated at 30°C for 10 weeks.

On completion of the incubation period, blocks were removed from soil jars, cleaned of adhering mycelium, reconditioned to 12% moisture content, and reweighed. Decay was expressed as a mean percentage loss of wood substance.

RESULTS

Quantitative and Qualitative Analyses

The mean retentions of alkylammonium compounds in blocks calculated from solution uptakes were 2.6 kg/m³ and 2.52 kg/m³ (a.i.) for Bioquat 501 in pine and poplar respectively. The values were slightly lower (2.42 kg/m³ and 2.36 kg/m³ a.i.) in wood treated with Bardac 20. Chemical analysis of alkylammonium compounds in unleached blocks first indicated no differences in retention between blocks treated with unamended or alkali modified solutions, but a gradual decrease in retention as blocks were treated with more acidic solutions. When analyses were repeated, the 12-h cold soak extraction in 1M alcoholic hydrochloric acid was followed by refluxing for 2 h. Subsequent analysis then detected similar amounts of alkylammonium compounds in blocks treated with unamended and acidic solutions.

No alkylammonium compounds were detected in any of the leachates, indicating that complete fixation had occurred.

Spot tests, using the bromophenol blue indicator to detect the presence of alkylammonium compounds on the freshly cut transverse faces of "halved" blocks clearly demarcated treated and untreated zones. In pine blocks treated with unamended solutions, a positive reaction for alkylammonium compounds was present across the entire cross section but the characteristic blue coloration was very marked in latewood bands and indistinct in earlywood. This distribution pattern is typical of blocks treated to sub-threshold loadings of these compounds. All acidic solutions resulted in an apparently uniform blue coloration of both latewood and earlywood. There was some suggestion of less intense coloration in peripheral zones of blocks treated with quaternary ammonium compounds plus 1.0% w/w HCl. In contrast, all blocks treated with alkaline solutions showed positive reaction for quaternary ammonium compounds only in the peripheral zones of wood.

In general, poplar blocks were of similar appearance to pine blocks. The only difference noted between the two wood species was that poplar blocks treated with unamended solutions were indistinguishable from those treated with acidic solutions. There were no apparent differences between treatments with Bioquat 501 or Bardac 20.

Biological Tests

The concentrations of Bioquat 501 and Bardac 20 treating solutions were chosen to provide sub-threshold retentions of the active ingredients (approximately 2.5 kg/m³) in treated wood. Thus, some wood loss through decay was expected in all blocks treated with unamended solutions. The effect on biological performance of adding acid or alkali to treating solutions could therefore be determined by an increase or decrease in percentage loss of wood substance.

Results of decay exposure tests are shown in Fig. 1. In all cases, addition of acid to treating solutions improved biological performance of Bioquat 501 and Bardac 20 in both poplar and pine. The two wood species responded in a similar manner to all 14 treating solutions, except that losses of wood substance tended to be greater in poplar blocks.

Losses of wood substance from basidiomycete attack were least in those blocks treated with solutions amended with the lowest levels of acid (i.e. 0.025% or 0.1% w/w HCl). As acid addition was increased there was some increase in wood loss. This was most marked in blocks exposed with *G. trabeum*. In contrast, blocks exposed to soft-rot infection in unsterile soils showed progressive decrease in wood loss as acid levels increased.

Additions of alkali to solutions of alkylammonium compounds generally resulted in greater losses of wood substance in treated blocks than occurred when they were treated with unamended solutions.

DISCUSSION

The importance of this work has been to show how simple modification of treating solutions may influence the distribution of alkylammonium compounds in wood, with consequent increase or decrease in preservative efficacy. Such simple modifications are not possible with copper-chrome-arsenate preservatives — for example addition of acid overcomes problems of copper screening in treatment of N.Z. podocarp species, but fixation of chromium is adversely affected (FRI, unpubl.).

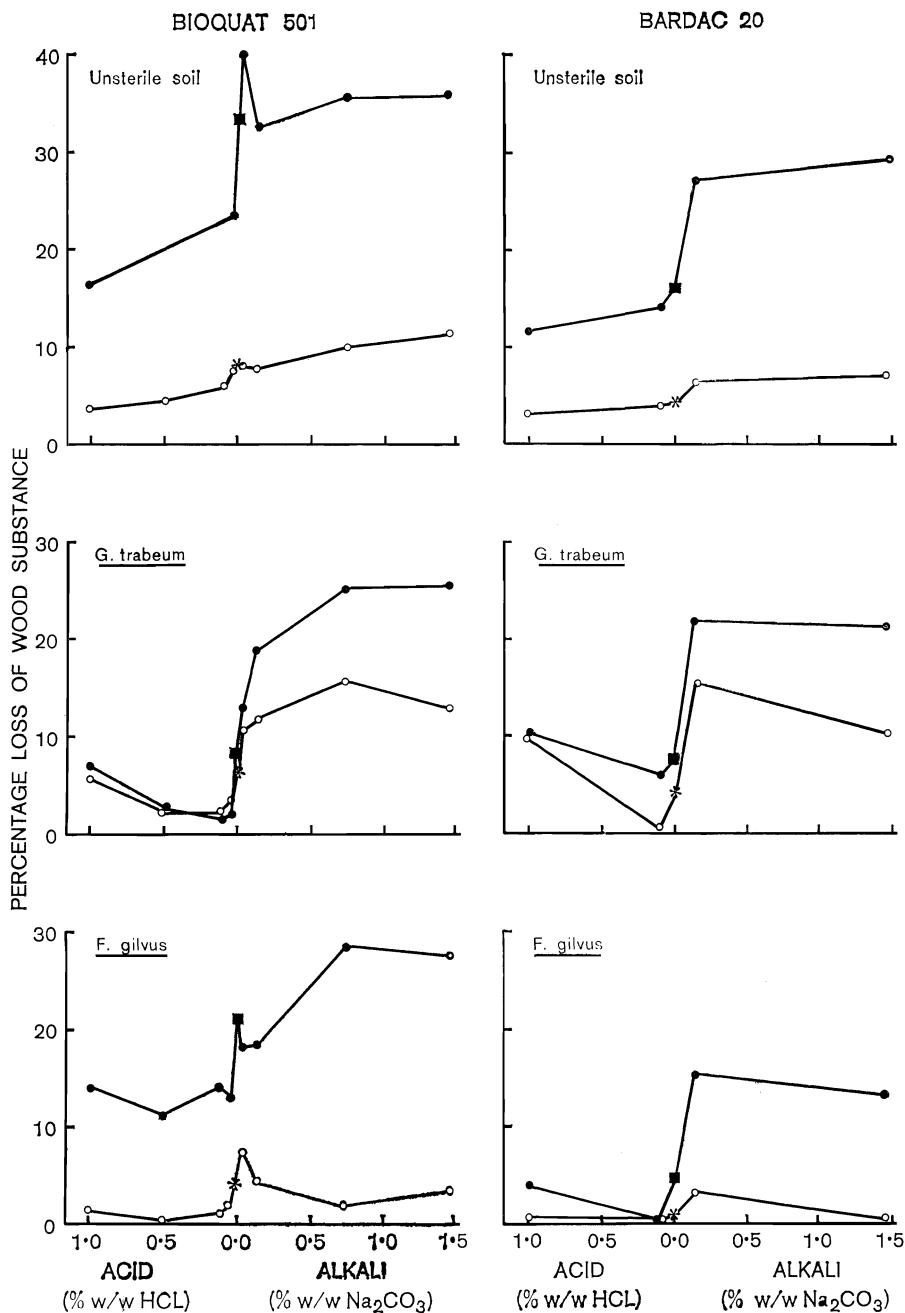


FIG. 1—Losses of wood substance in pine (open circles) and poplar (closed circles) blocks treated with 0.38% a.i. Bioquat 501 and 0.35% a.i. Bardac 20 alone, or when amended with various levels of acid or alkali, after exposure to test fungi. Values for unamended solution highlighted by square on poplar trace and star on pine trace.

The mechanism for improved preservative efficacy under acidic treating conditions may be explained in terms of the model outlined by Rosen (1975). At low levels of acid addition to treating solutions, the added protons compete with alkylammonium cations for fixation sites and prevent their preferential adsorption by the first cell walls contacted during the liquid uptake phase of preservative treatment. This resulted in a uniform distribution of the alkylammonium compound throughout the wood (as shown by spot tests on cross-cut transverse faces of blocks) and improved effectiveness against basidiomycetes. As the addition of acid to treating solutions increased, more protons were present to compete for fixation sites. It is likely that this resulted in a decrease in cation exchange in wall layers adjacent to cell lumens, and a greater penetration of cell walls as "free" alkylammonium cations were adsorbed on the less readily available fixation sites within the S2 layer. This explanation is supported by biological evidence, for soft-rot control improved in all timbers as acid levels in treating solutions increased. At the same time, control of basidiomycete attack was reduced. These results support the general view that cell wall loadings of a toxicant are most efficacious against soft-rot fungi, and lumen surface deposits against basidiomycetes.

When wood was treated with highly acidic solutions, the difficulty experienced in quantitative extraction of alkylammonium compounds by simple steeping of sawdust in alcoholic hydrochloric acid, also suggests that location of these compounds was markedly different from that obtained with the other treating solutions. It is reasonable to assume that a more severe extraction procedure (2-h reflux) was required to remove alkylammonium cations from the more inaccessible (inner) regions of the cell wall.

The probable effect of adding alkali to treating solutions is the removal of protons from the wood substance, creating negative sites which will aid adsorption of alkylammonium cations. The result of treating with such solutions was the preferential uptake and fixation of quaternary ammonium cations in peripheral zones of the wood. This led to increased losses of wood substance during fungal exposure as all blocks were first cross-cut to expose central (untreated) zones.

This work should not be regarded as a recommendation of commercial feasibility for improving biological effectiveness through adding acid to treating solutions — problems of plant corrosion may occur, for example. However, it does illustrate how performance may readily be improved by partially impeding the cation exchange fixation process. White (1970) discusses the effect of solution temperature, pH, and inorganic salt content on adsorption of alkylammonium compounds by cellulosic materials. Thus, similar effects to those obtained by acid amendment of treating solutions may be achieved through manipulation of other factors.

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