POTENTIAL OF UNMODIFIED AND COPPER-MODIFIED ALKYLAMMONIUM COMPOUNDS AS GROUNDLINE PRESERVATIVES

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ABSTRACT

Pinus radiata D.Don (radiata pine) and **Betula alba** L. (silver birch) sapwood stakes were exposed for periods of up to 12 months in a fungus cellar after treatment with various unmodified and copper-modified alkylammonium compounds. In general, dialkyldimethyl ammonium salts performed best, followed by benzalkonium chloride. Primary and tertiary amine salts failed to afford any significant protection from fungal attack. Amendment of treatment solutions with copper salts extended performance of all alkylammonium compounds. Results are discussed in conjunction with short-term field trials, and predictions of long-term field performance are attempted. It is concluded that quaternary ammonium compounds, and in particular dialkyldimethyl compounds, show considerable potential for protection of radiata pine in ground contact. This potential is further extended when treated solutions are modified by addition of cupric salts. None of the preservative formulations tested protected silver birch stakes from soft rot, although some performed as well as copper-chrome-arsenate preservative.

INTRODUCTION

In conjunction with the extensive laboratory test programme of alkylammonium compounds as wood preservatives (Butcher, 1979; Butcher and Drysdale, 1977; Butcher, Hedley and Drysdale, 1977; Butcher, Preston and Drysdale, 1977; Butcher *et al.,* 1978; Butcher and Preston, 1978; Cross, 1979; Preston and Butcher, 1978) trials were established both in the fungus cellar (Forest Research Institute, 1978) and in the field to determine their potential in groundline applications. The New Zealand Timber Preservation Authority approved commercial treatment of "above-ground" commodities of *Pinus radiata* D.Don (radiata pine) with alkylammonium compounds in 1978, but their use is unlikely to become widespread until approvals are granted for ground-contact commodities.

Field testing of treated stakes commenced $3\frac{1}{2}$ years ago (with benzalkonium chloride in pine) and since then over 1000 stakes, representing some 50 different alkylammonium compounds or formulations, have been installed. Tests in the fungus cellar started only 18 months ago, but comprehensive data have already been obtained on performance of 40 different treatments using a total of 700 test stakes. This paper is concerned with only a limited number of these tests, representing a range of alkylammonium compounds used with and without copper addition. Tests in the fungus cellar extended for periods of up to 12 months and can be regarded as long-term in this type of facility. To help place results in perspective, performance in the fungus-cellar was compared with performance in the field where all treatments were reproduced.

MATERIALS AND METHODS

Sapwood stakes of radiata pine and *Betula alba* L. (silver birch) comprised the test material. The stakes for exposure in the fungus cellar measured 180 × 25 × 12.5 mm whereas those for field testing in the Forest Research Institute (FRI) "graveyard" conformed to standard dimensions (500 × 50 × 25 mm) for IUFRO field test stakes. Treatment was by the Bethell process using a schedule of —85 kPa for 30 min followed by 700 kPa for 60-120 min; fungus cellar stakes had the shorter pressure period, and graveyard stakes the longer one. The range of alkylammonium compounds and formulations under discussion in this paper, together with their approximate retentions (based on analysed solution strengths, measured uptakes, and stake volumes) in radiata pine and silver birch, are presented in Table 1. There were five replicate stakes of each

TABLE 1—Retentions of alkylammonium compounds (active ingredient) and of copper-chrome-arsenate (commercial salt) in fungus cellar test stakes. Data for field test stakes referred to in the text are also included

Treatment	Calculated retention (kg/m^3) Fungus cellar stakes		Field stakes	
	Radiata pine	Silver birch	Radiata pine	Silver birch
Benzalkonium chloride	14	13	10.6	12.5
Octyldecyldimethyl ammonium chloride	8	7	5.6	5.8
	—	—	—	11.9
Didecyldimethyl ammonium chloride	13	12	—	—
Cocodimethylamine acetate	7	6	—	6.5
	12	11	11.6	11.0
Dodecylamine acetate	7	6	—	—
	12	11	—	—
Benzalkonium chloride : cupric chloride (4 : 1)*	15	13	11.0	11.2
Octyldecyldimethyl ammonium chloride : cupric chloride (2 : 1)*	7	7	5.6	6.0
Cocodimethylamine acetate : cupric acetate (4 : 1)*	—	—	5.8	6.1
	13	13	—	—
Copper-chrome-arsenate	6	—	—	—
	—	10	—	—

* These formulations contain cupric sulphate for treatment of field test stakes.

treatment for fungus cellar tests, and 10 replicates for field tests. After treatment, stakes were wrapped (by treatment sets) in polyethylene and stored for 2 weeks to allow preservative fixation. Stakes destined for fungus cellar exposure were then partially air-dried before being placed in continuous running water for 65 hours as a leaching procedure. Field test stakes were fully air-dried and were not subjected to a leaching schedule.

The treated radiata pine and silver birch stakes assigned to the fungus cellar were placed at random (150-mm centres), and to half their length, in unsterile soil maintained at 28°C and a moisture content of the order of 45-55% (o.d. weight basis). Humidity was maintained at 85% R.H. The soil was of the same type as occurs in the FRI "graveyard". The fungus cellar has previously been described in some detail (Forest Research Institute, 1978). All stakes were inspected at 4-weekly intervals for the first 6 months of exposure, after which they were inspected at 3-monthly intervals. No test exceeded 12 months.

Field test stakes were installed in the FRI graveyard following well-established procedures. Almost all results for treated radiata pine stakes were based on assessment after 30 months of exposure, whereas treated silver birch stakes were assessed after 18 months of exposure; stakes were installed at different times.

The condition of all stakes was recorded according to the standard procedures of ASTM D1758-62.

RESULTS AND DISCUSSION

Results of 1 year's exposure of treated radiata pine stakes in the fungus cellar are presented in Table 2. Copper-chrome-arsenate (CCA), at a retention of 6 kg commercial salt/m^3 performed best. Stakes were free of infection for 9 months and displayed only minor, and localised, degrade after 12 months. Performance of the primary and tertiary amine salts was least satisfactory and their inability to control decay led to their removal from test after 6 months of exposure. The tertiary amine salt (cocodimethylamine acetate) was only slightly superior to the primary amine salt (dodecylamine acetate). Stakes treated with quaternary ammonium compounds appeared to hold an intermediate

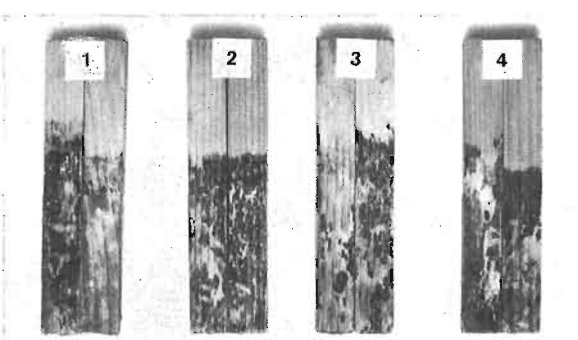
TABLE 2—Condition of radiata pine test stakes with unmodified alkylammonium compounds or copper-chrome-arsenate, after exposure in the fungus cellar for up to 12 months

Treatment	Retention (kg/m^3)	Mean soundness (%) with time (months) 1	2	3	4	5	6	9	12
Benzalkonium chloride	14	100	100	82	80	76	70	70	76
Octyldecyldimethyl ammonium chloride	8	100	96	92	88	82	78	75	72
Didecyldimethyl ammonium chloride	13	100	100	100	100	100	100	95	—
Cocodimethylamine acetate	7	70	62	54	52	51	42	—	—
	12	76	66	58	54	54	50	—	—
Dodecylamine acetate	7	72	50	32	30	26	30	—	—
	12	76	64	54	44	46	50	—	—
Copper-chrome-arsenate	6	100	100	100	100	100	100	100	98
Untreated	—	61	45	0					

position in terms of performance. Results indicated that the twin-chain quaternary ammonium compounds (octyldecyldimethyl ammonium chloride and didecyldimethyl ammonium chloride) were approximately twice as effective as benzalkonium chloride.

On completion of the 1-year exposure period, stakes were examined closely and it became apparent that ratings of condition for those treated with quaternary ammonium compounds did not reflect their true condition. Superficial appearance of stakes (Fig. 1) certainly seemed to justify the ratings, which led to many being judged 70% sound, but when stakes were cross-cut through infected zones the degrade was observed to be restricted to the surface leaving internal condition unchanged (Fig. 2). Microscopic examination of this surface degrade on stakes exposed for 12 months in the fungus cellar suggested that the extreme limit for fungal infection did not proceed beyond the fortieth tracheid from the surface (about 1 mm penetration). In many stakes, particularly those treated with dialkyldimethyl quaternary ammonium compounds, fungal infection was contained within the outer three or four tracheids. Degrade was caused mainly by soft-rot fungi, but some white rot was also involved. These observations strongly suggest that stakes treated with quarternary ammonium compounds should more correctly have been assessed as 98% sound after the 12 month exposure period. The improved performance reported for the high retention (13 kg active ingredient/m^3) of didecyldimethyl ammonium chloride over the low retention (8 kg/m^3) of octyldecyldimethyl ammonium chloride and benzalkonium chloride (14 kg/m^3) can be explained simply in terms of a reduction in the extent of this highly superficial degrade. It was of interest to note that the very small zones of degrade on CCA-treated (6 kg salt/m^3) stakes were of similar appearance to the more widespread degrade on stakes treated with quaternary ammonium compounds.

Results of exposure tests with silver birch are summarised in Fig. 3. Stakes were treated with nominal 2% solutions of each chemical or preservative. Retentions for all alkylammonium compounds were of the order of 12-14 kg active ingredient/m^3, whereas CCA retentions were slightly lower at 10 kg commercial salt/m^3. This test was run for only 9 months, but by that time the relative performance of the four



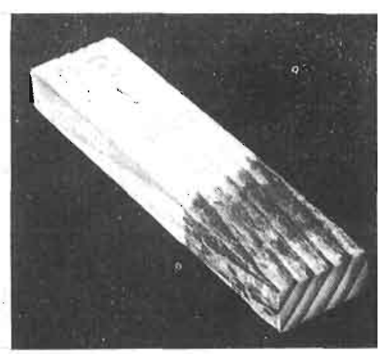


FIG. 1 (left)—Appearance of radiata pine stakes treated with quaternary ammonium compounds, after 12 months' exposure in the fungus cellar.

FIG. 2 (right)—Radiata pine stake treated with a quaternary ammonium compound, showing the highly superficial nature of the surface degrade. Internal condition remains unchanged after 12 months' fungus cellar exposure.

treatments could be clearly seen. Stakes treated with the tertiary amine salt had all failed within 3 months; untreated stakes had failed only 1 month earlier. Benzalkonium chloride performed better, with treated stakes failing at 9 months, but the dialkyldimethyl quaternary ammonium compound was performing as well as CCA after this time. However, neither of these last two treatments adequately protected silver birch from soft-rot attack.

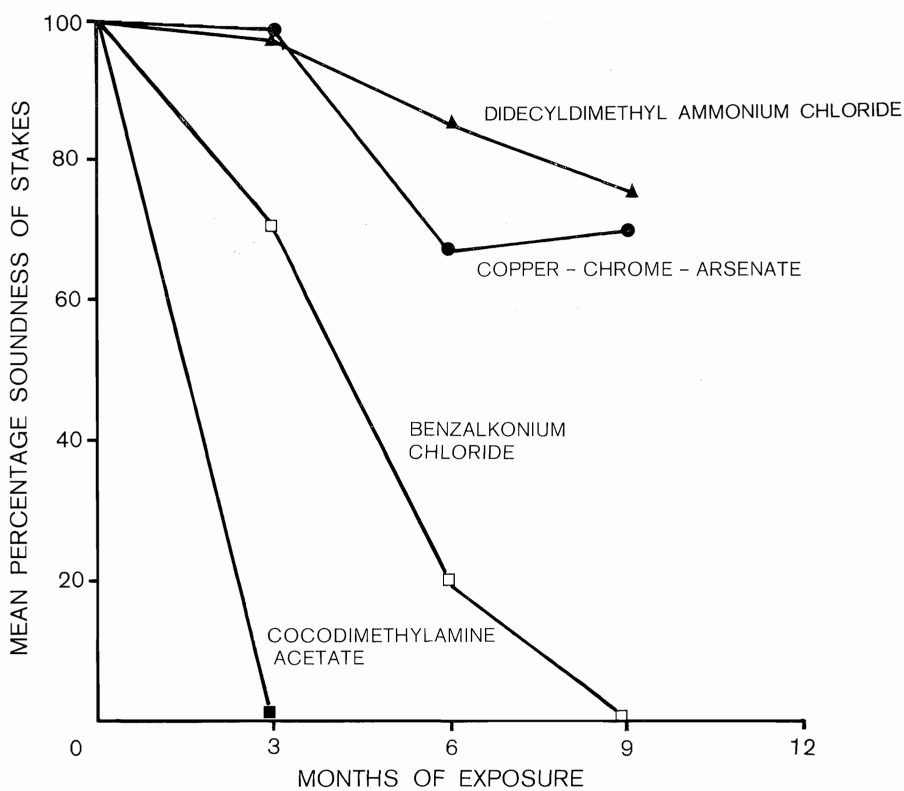


FIG. 3—Relative performance of cocodimethylamine acetate (11 kg/m^3), benzalkonium chloride (13 kg/m^3), didecyldimethyl ammonium chloride (12 kg/m^3), and copper-chrome-arsenate (10 kg/m^3) in silver birch stakes exposed for 9 months in the fungus cellar.

Tests with copper-modified alkylammonium compounds proved very interesting (Fig. 4). In all of them, the presence of copper greatly enhanced performance. Stakes treated with 3 kg cupric chloride/m^3 (the control for copper-modified quaternary ammonium chlorides) or with 3 kg cupric acetate/m^3 (the control for copper-modified tertiary amine acetates) all failed rapidly within the first 3 or 4 months of exposure. In radiata pine, copper-modified quaternary ammonium compounds tended to decrease the amount of superficial degrade on stakes whereas copper modification of the tertiary amine salt prevented onset of decay. The most marked effect of copper modification, however, was observed in treated silver birch stakes and was especially noteworthy with

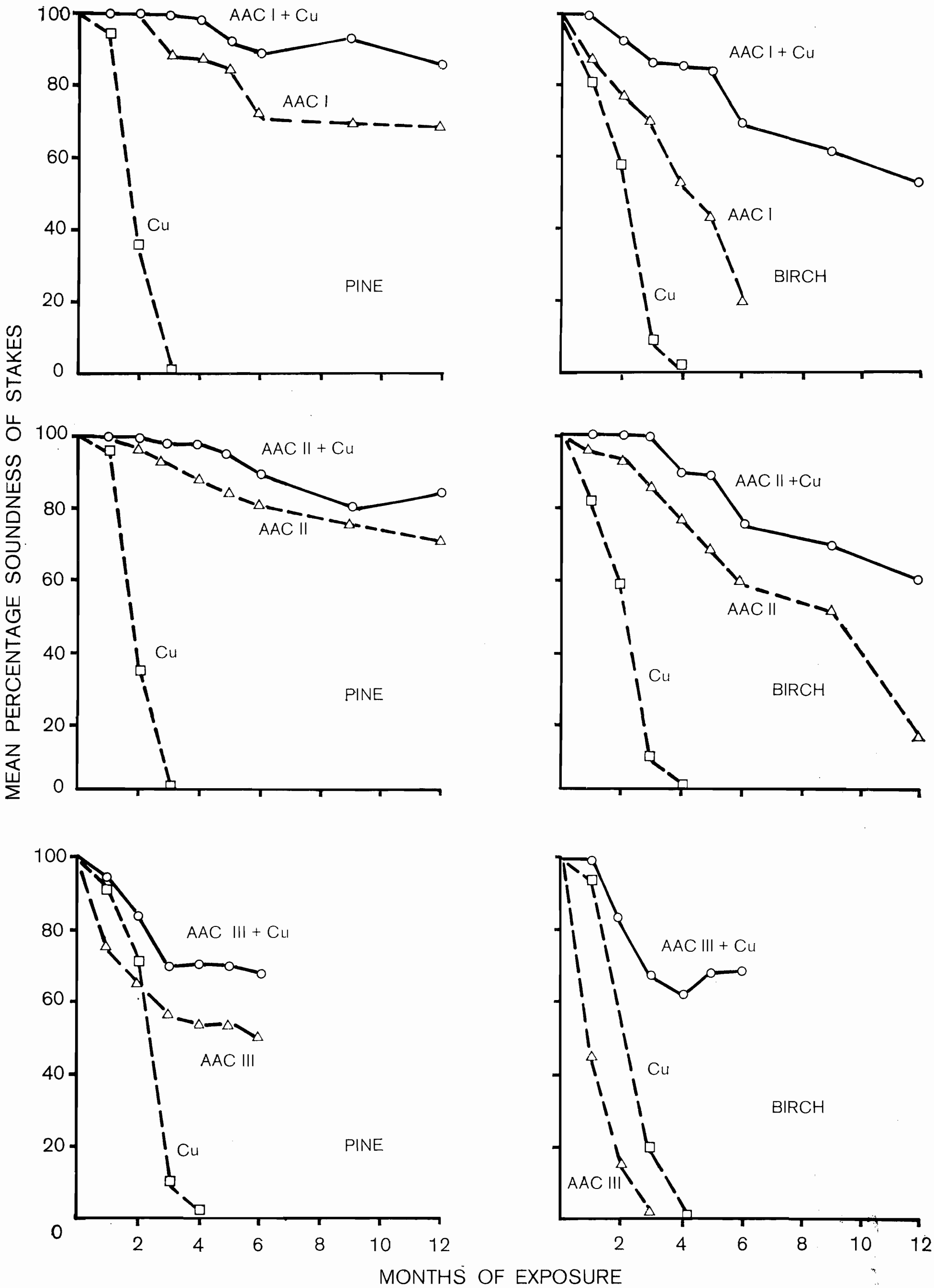
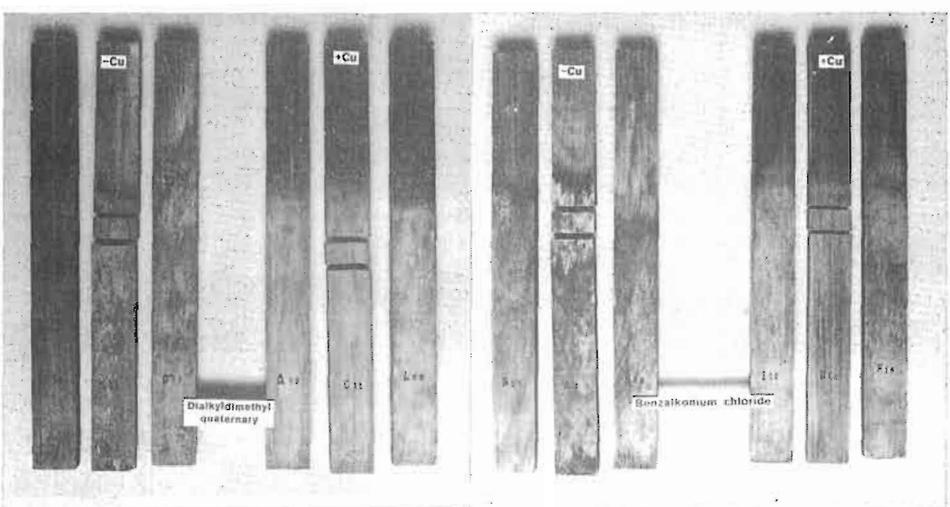


FIG. 4—Relative performance of unmodified and copper-modified alkylammonium compounds in radiata pine and silver birch stakes during 12 months' exposure in the fungus cellar. AAC I = benzalkonium chloride; AAC II = octyldecyldimethyl ammonium chloride; AAC III = cocodimethylamine acetate. For individual retentions consult Table 1.

the tertiary amine salt (AAC III); when used unmodified, stakes failed in 3 months (more quickly than those treated with cupric acetate alone) but with copper addition the silver birch stakes were still 65% sound after 6 months. Best performance was shown by stakes treated with octyldecyldimethyl ammonium chloride (AAC II) + cupric chloride to retentions of 7 kg/m^3. These stakes were rated as about 60% sound after 12 months which compares favourably with the rating of 69% which was assigned to CCA (10 kg/m^3) after the same period.

One of the most interesting features of this work was the failure of the tertiary amine acetate for ground-contact protection. Butcher and Preston (1978) reported good potential for this type of compound on the basis of detailed laboratory tests using three basidiomycetes and a natural flora of soft-rot fungi in unsterile soil for bioassay. Obviously, some factor not encountered in laboratory testing was of major importance in fungus cellar tests. Current work involving stake tests with a series of tertiary amine acetates of increasing alkyl chain length (C_{12}, C_{12} + C_{14}, C_{12} + C_{14} + C_{16}, C_{14} + C_{16}) and three distinct cocodimethylamine acetate formulations confirm the poor performance in natural soil contact both in the fungus cellar and the field. The reason for this lack of activity is not known, but it is the subject of investigation at the present time since it highlights the problems of using conventional laboratory test procedures for assessing potential of chemicals as wood preservatives. No such problems existed with quaternary ammonium compounds where relative performance between different formulations was similar in laboratory, fungus cellar, and field test.

It is premature to discuss in detail the early results of our extensive field trials of alkylammonium compounds. However, it is of some value to compare performance in fungus cellar and field of those treatments under discussion in this paper. Hedley (1980) considered that there was up to a 12-fold increase of decay rate in the fungus cellar compared with the field once decay had become established. For this reason, conditions of field stakes after 18 and 30 months' exposure are presented together with condition of fungus cellar stakes after 2 or 3 months which assumes a 10 times increase in decay rate (Table 3). Results for benzalkonium chloride, copper-modified formulations of quaternary ammonium compounds, and copper-chrome-arsenate comply well with this assumed relationship. Stakes treated with cocodimethylamine acetate formulations, and the untreated controls, decayed much faster in the fungus cellar. However, none of the treated stakes performed well in the field, and the fungus cellar results tended only to highlight this lack of performance. On the other hand, both radiata pine and silver birch stakes treated with octyldecyldimethyl ammonium chloride indicated better performance in the fungus cellar than in the field. Examination of selected field test stakes displaying the worst condition within each set gave clear evidence, when cut through infected zones (Fig. 5), that ratings of stakes treated with octyldecyldimethyl ammonium chloride were unusually harsh compared with those of other treatments. Radiata pine stakes treated with octyldecyldimethyl ammonium chloride were rated as 81% sound, yet they lacked any sign of fungal degrade when examined in cross-section and were essentially of similar appearance to those treated with copper-modified formulations which were rated between 94% and 97% sound (Fig. 6). In addition, this rating of 81% sound suggests that stakes were of similar condition to those treated with benzalkonium chloride (80% sound), but in that case obvious decay was present to a depth of 1.5 mm. A similar situation existed with silver birch stakes. The problem has arisen simply because too much importance has been attached to stake appearance and ratings tend to reflect surface area affected by superficial degrade rather than actual condition of stakes. Thus, the true condition of field test stakes treated with octyldecyldimethyl ammonium chloride is much closer to that recorded for fungus cellar stakes than first indicated. The above situation has been discussed in some detail because the highly superficial nature of the degrade on stakes treated with quaternary ammonium compounds had not previously been encountered, and field assessments using conventional inspection techniques obviously can lead to erroneous conclusions regarding stake condition.



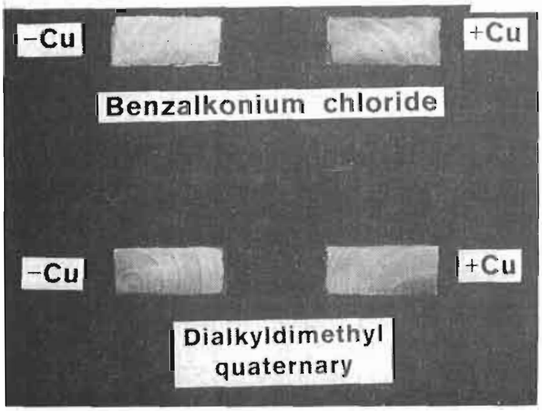


FIG. 5 (above)—External condition of radiata pine field test stakes showing where a stake was cross-cut for assessment of internal condition.

FIG. 6 (left)—Internal condition of radiata pine test stakes after 2½ years' field exposure.

Hedley (1980) compared fungus cellar and field performance of radiata pine stakes treated to various retentions of 12 different preservatives. For all preservatives except zinc-chrome-arsenate, performance in the fungus cellar predicted worse performance in the field than actually occurred when 1 month's fungus cellar exposure was equated

TABLE 3—Condition of field test stakes (after 18 or 30 months' exposure) compared with conditon of fungus cellar stakes (after 2 or 3 months' exposure)

Timber	Treatment	Field exposure			Fungus cellar		
		kg/m³	Months	% sound	kg/m³	Months	% sound
Radiata pine	Benzalkonium chloride	10.6	30	80	14	3	82
	Octyldecyldimethyl ammonium chloride	5.6	30	81	8	3	92
	Cocodimethylamine acetate	11.6	18	74	12	2	66
	Benzalkonium chloride : cupric salt (4 : 1)	11.0	30	94	15	3	98
	Octyldecyldimethyl ammonium chloride : cupric salt (2: 1)	5.6	30	97	7	3	98
	Untreated	—	30	53	—	3	0
Silver birch	Benzalkonium chloride	12.5	18	78	13	2	78
	Octyldecyldimethyl ammonium chloride	5.8	18	74	7	2	94
		11.9	18	78	13	2	98
	Cocodimethylamine acetate	6.5	18	50	6	2	10
		11.0	18	64	11	2	34
	Benzalkonium chloride : cupric salt (4 : 1)	11.2	18	86	13	2	90
	Octyldecyldimethyl ammonium chloride : cupric salt (2 : 1)	6.0	18	96	7	2	100
	Cocodimethylamine acetate : cupric salt (4 : 1)	6.1	18	84	—	—	—
		—	—	—	13	2	80
	Untreated	—	18	60	—	2	45
Radiata pine	Copper-chrome-arsenate	5.7	72	93	6	9	100
Silver birch	Copper-chrome arsenate	9.6	72	75	10	9	70

to 1 year's field exposure. Stakes treated to two retentions of zinc-chrome-arsenate (5.4 and 14.2 kg salt/m^3 wood) had ratings in the field which were about 25% lower than fungus cellar values.

The question now arises as to whether a prediction of probable field performance can be made on the basis of fungus cellar tests. This is important in a developmental research programme where the time required for field testing is unacceptable (field testing should be reserved for confirmatory tests). Current knowledge from the short programme of fungus cellar tests at the Forest Research Institute suggests that:

(1) The rate of decay in the fungus cellar proceeds at approximately 10 times the speed at which it occurs in the field;

(2) Estimates of field performance based on this ratio tend to be under-estimates because the lag phase before decay establishment is often absent in fungus cellar test (Hedley, 1980);

(3) Over-estimation of field performance can occur, but in the one instance quoted (zinc-chrome-arsenate) it was felt that laboratory leaching had not fully reproduced loss of available zinc which occurs in the field (Hedley, 1980).

When considering performance of alkylammonium compounds in radiata pine, there was a general tendency to downgrade condition of stakes treated with quaternary ammonium compounds because of fairly extensive, but highly superficial, surface degrade. Ratings for amine salts in radiata pine, and for all alkylammonium formulations in silver birch were more accurate because decay had become well-established.

From the above discussion, and from the data at hand, a reasonable prediction of field performance can be made on the assumptions that the fungus cellar accelerates decay by a factor of 10 times and that with alkylammonium preservatives, this relationship holds true with time. On this basis, the following broad predictions of service life of test stakes in the field can be made:

(1) Unmodified amine salts should protect radiata pine stakes for only about 5 years, and silver birch stakes for 3 years.

(2) Benzalkonium chloride (12-14 kg/m^3) and dialkyldimethyl quaternary ammonium compounds (6-8 kg/m^3) should protect radiata pine stakes for up to 15 years. Higher retentions (13 kg/m^3) of dialkyldimethyl quaternary ammonium compounds should give service life of up to 20 years. In silver birch, performance will be more limited and service life of stakes treated to 12 kg/m^3 with a dialkyldimethyl quaternary ammonium compound is unlikely to exceed 10-15 years.

(3) Assuming that copper in modified solutions remains well fixed, performance of stakes treated with copper-modified formulations of quaternary ammonium compounds should be further extended.

CONCLUSIONS

This work is taken to indicate that quaternary ammonium compounds, particularly dialkyldimethyl ammonium salts, show considerable potential for groundline protection of radiata pine timber. Modification of treatment solutions with copper salts greatly enhances performance and extends this potential which now awaits confirmation by long-term field testing. Predictions of probable service life in the field should be regarded only as indicative, and are interpreted simply as showing that certain alkylammonium compounds are worthy of further work to establish an acceptable formulation for groundline use.

Two major problems deserve immediate and close attention. The first concerns the surface degrade on treated radiata pine stakes which makes them unsightly without apparently influencing performance. The second, and more important, is that amendment of treating solutions with copper salts leads to chemical instability of the treating solution and serious risk of corrosion of metals contacting treated wood. For these reasons it is doubtful whether simple addition of copper salts will provide a commercially acceptable formulation. Current research seeks more stable formulations and the use of other additives which extend performance without introducing any problematical side effects.

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