PERFORMANCE OF UNMODIFIED AND COPPER-MODIFIED ALKYLAMMONIUM-TREATED STAKES IN GROUND CONTACT

JEANETTE A. DRYSDALE

Forest Research Institute, New Zealand Forest Service,
Private Bag, Rotorua, New Zealand

(Received for publication 20 August 1982)

ABSTRACT

Pinus radiata D. Don sapwood stakes treated with two unmodified and two copper-modified alkylammonium compounds were examined during 4 years' exposure in the Whakarewarewa "graveyard". The stakes treated with benzalkonium chloride (10.6 kg/m^3) and dialkyldimethyl ammonium chloride (6.2 kg/m^3) have been colonised and attacked by brown-rot, soft-rot, and white-rot fungi. Stakes treated with these chemicals modified by the addition of a cupric salt were in better condition. The modified treatments partially controlled white rot but treated stakes remained susceptible to soft rot and an unsightly brown erosion. This erosion is thought to be caused by brown-rot fungi. Although none of the four treatments examined is suitable for approval as a groundline treatment, copper modification still offers potential for this end-use and further formulation studies are considered worthwhile.

INTRODUCTION

An extensive screening programme in search of new alternative permanent wood preservatives has been carried out at the Forest Research Institute (Butcher *et al.* 1977; Butcher & Preston 1978; Hedley *et al.* 1979). As a result one group of chemicals, commonly referred to as the alkylammonium compounds, has been approved by the New Zealand Timber Preservation Authority for the commercial treatment of *Pinus radiata* for use in low decay-hazard "above-ground" situations. This approval of specific alkylammonium compounds for use as wood preservatives has stimulated further research here and overseas (Cross 1979; French & Robinson 1981; Hedley *et al.* 1982; Preston & Chittenden 1982; Preston & Nicholas 1982; Ruddick 1981; Tillot & Coggins 1981).

After initial laboratory tests in which pure fungal cultures were used, stakes treated with a range of alkylammonium compounds were installed in a "fungus cellar" and in the Whakarewarewa "graveyard" in 1977 for testing in a high decay-hazard situation. Some 30 unmodified and copper-modified alkylammonium treatments were included in the graveyard alone to test for suitability as ground contact preservatives.

Certain alkylammonium compounds, in particular the tertiary amine salts, appeared satisfactory in laboratory tests using pure cultures but subsequently failed on exposure to unsterile soil in the fungus cellar. Nevertheless, preliminary fungus cellar and field results did indicate a few alkylammonium treatments, specifically the dialkyldimethyl ammonium salts, could have potential as groundline treatments for pine (Butcher *et al.* 1979). It was also observed that their field performance was enhanced by addition of a cupric salt to treating solutions.

At the time of the first fungus cellar trials it was noticed that alkylammonium-treated pine was prone to an unsightly superficial brown degrade. It was suggested, however, that this degrade would have little effect on the over-all service life (Butcher *et al.* 1979).

A study was undertaken to observe the development and types of decay in alkyl-ammonium-treated pine in ground contact in the field. Particular attention was paid to the brown superficial degrade which with time erodes away the surface of stakes. Soundness was assessed visually and microscopic examinations were made of both benzalkonium chloride and dialkyldimethyl ammonium chloride treatments with and without copper modification over a 4-year exposure period.

MATERIALS AND METHODS

Pinus radiata sapwood flat-sawn stakes measuring 500 × 50 × 25 mm were treated by the Bethell process (–85 kPa for 30 min followed by 700 kPa pressure for 120 min). The four treatments examined in this study were benzalkonium chloride 2% active ingredient with and without the addition of 0.5% cupric sulphate, and dialkyldimethyl ammonium chloride 1% active ingredient with and without 0.5% cupric sulphate. Ten stakes were treated with each solution. After treatment each set of stakes was wrapped in polythene and left 2 weeks to allow the preservative to fix. The stakes were then air-dried before installation in the Whakarewarewa graveyard.

After 2.5 years one representative stake from each treatment set was removed. A 10-mm-thick cross-section was cut from the groundline. This cross-section was recut into small blocks suitable for microtoming. Other stakes were examined non-destructively, thin sections being removed from outer surfaces with a razor blade. After 4 years only sections cut with a razor blade were examined. Both tangential and radial sections were cut from areas of discoloration or decay. Sections were stained with 0.2% trypan blue and examined by light microscopy. At both assessment times all the stakes were rated and each treatment was given a percentage soundness figure based on the ASTM Decay Grading system D1758-62.

RESULTS

The results of the visual assessment of soundness are listed in Table 1 and examples of the stakes are shown in Fig. 1. The dialkyldimethyl ammonium chloride was slightly better than the benzalkonium chloride treatment and at approximately half the retention of the latter. After 2.5 years the copper-modified dialkyldimethyl ammonium chloride was superior but the soundness rating dropped after 4 years to below that of the modified benzalkonium chloride.

Benzalkonium chloride (10.6 kg/m^3)

At the time of the first microscopic examination, after 2.5 years' service, there was evidence of colonisation by both basidiomycetes and soft-rot fungi. Soft-rot cavities were sparse but were observed at greater depths into the stake than the bore holes and erosion

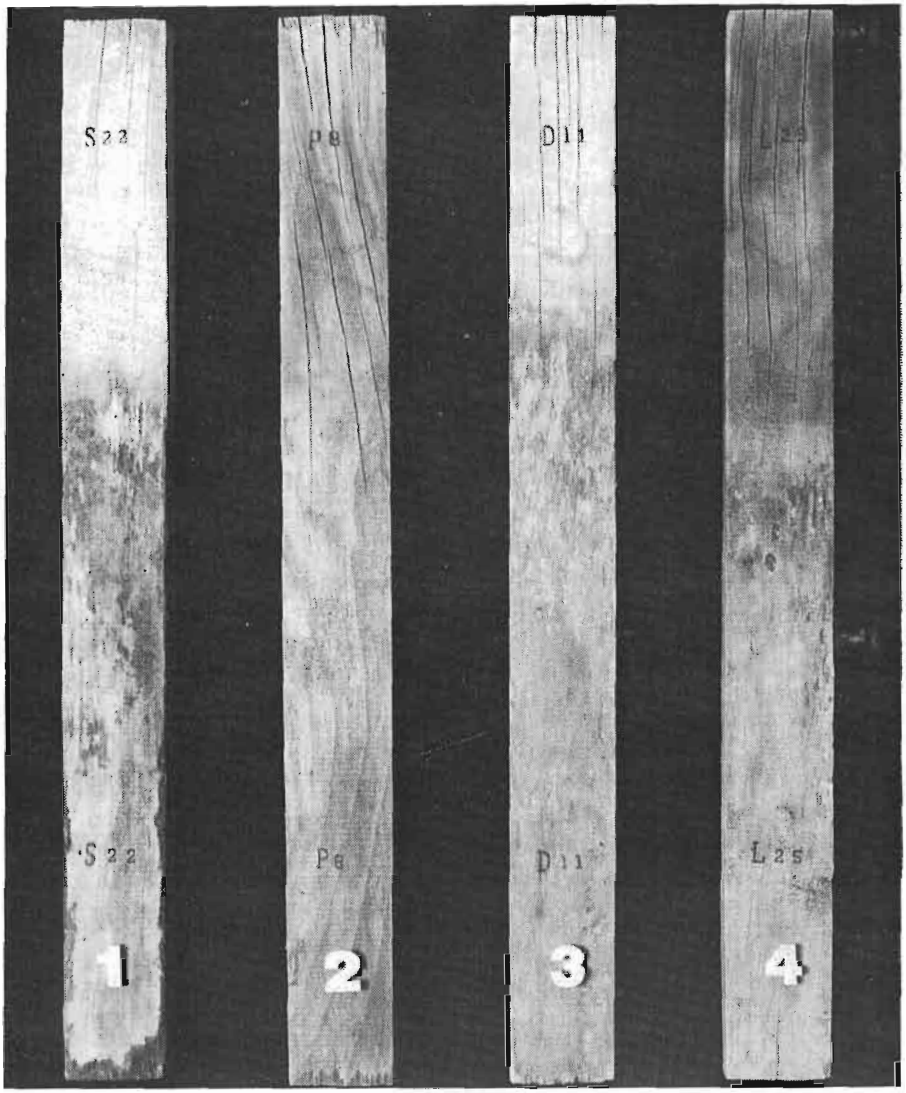


FIG. 1—**Pinus radiata** stakes after 4 years' exposure. The four treatments were:
1 = Benzalkonium chloride (10.6 kg/m³)
2 = Benzalkonium chloride (11.3 kg/m³) plus cupric sulphate 4 : 1
3 = Dialkyldimethyl ammonium chloride (6.2 kg/m³)
4 = Dialkyldimethyl ammonium chloride (5.5 kg/m³) plus cupric sulphate 2 : 1.

of cell lumina indicative of colonisation by basidiomycete fungi. Only occasionally were pit membranes absent. Rays were colonised in advance of tracheids by large pigmented hyphae. Sometimes the hyphae observed in the tracheids were "mis-shapen" with bud-like projections along the hyphal length.

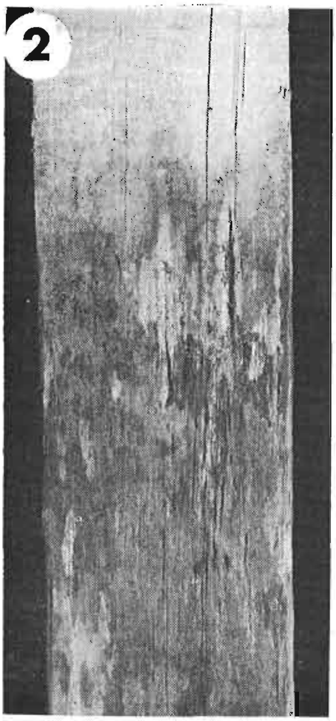
Eighteen months later all stakes were noticeably affected by white rot. On some stakes the white rot appeared as isolated pockets (Fig. 2) while on others the attack

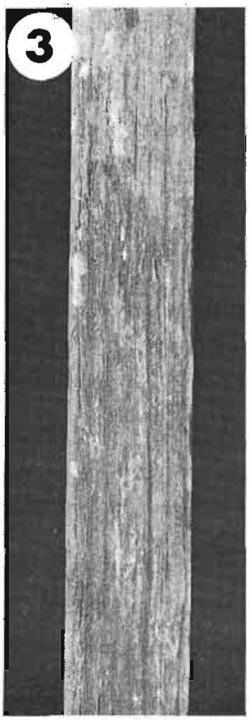
TABLE 1—Visual assessment of soundness of treated stakes after exposure in the graveyard

Treatment	Soundness (%)	
	2.5 years' exposure	4 years' exposure
Benzalkonium chloride (10.6 kg/m^3)	77	62
Benzalkonium chloride (11.3 kg/m^3) plus cupric sulphate 4 : 1	85	85
Dialkyldimethyl ammonium chloride (6.2 kg/m^3)	74	70
Dialkyldimethyl ammonium chloride (5.5 kg/m^3) plus cupric sulphate 2 : 1	92	73
Untreated control	32*	0†

* 4 stakes failed

† 10 stakes failed





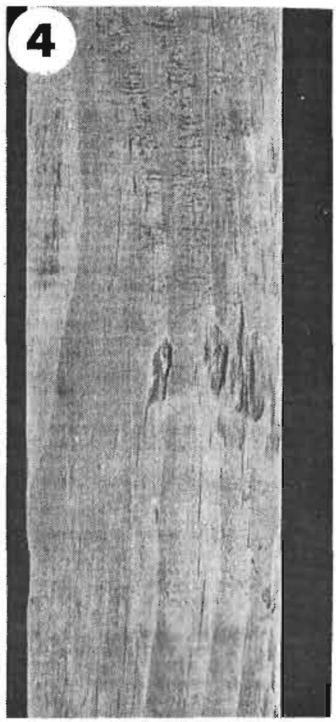


FIG. 2—Benzalkonium chloride (10.6 kg/m^3). Close-up of groundline showing fungal attack on a tangential face.

FIG. 3—Benzalkonium chloride (10.6 kg/m^3). Brown superficial degrade on radial face.

FIG. 4—Benzalkonium chloride (11.3 kg/m^3) plus cupric sulphate. Erosion of a tangential face.

was evenly spread the full length of the surface below ground. Black, discoloured, soft-rotted areas were evident on most surfaces but brown-coloured surface degrade was patchy. In some stakes this degrade had developed into areas of obvious erosion (2–4 mm deep) with the radial longitudinal faces being worst affected (Fig. 3). Microscopic examination confirmed fungal attack. Pit membranes were almost entirely degraded or missing in areas of fungal degrade after 4 years.

Benzalkonium chloride (11.3 kg/m^3) plus cupric salt (4 : 1)

Stakes of this treatment appeared more sound than those treated with the unmodified benzalkonium chloride treatment. All stakes were colonised by soft-rot fungi, especially on the radial longitudinal faces. No damage to walls by basidiomycetes was observed. Ray tissue was colonised by large pigmented hyphae deep into the stakes.

After 4 years brown superficial degrade had developed. On some stakes it was restricted to the outer one or two tracheids while other stakes had isolated deeper areas of erosion (Fig. 4). Microscopic examination confirmed the colonisation and degrade by soft-rot and basidiomycete fungi. Bore holes and erosion channels in cell lumina were observed for the first time, indicating the presence of white-rot fungi.

Dialkyldimethyl ammonium chloride (6.2 kg/m^3)

All the stakes treated with this alkylammonium compound were visually more sound than those treated with benzalkonium chloride and at almost half the retention.

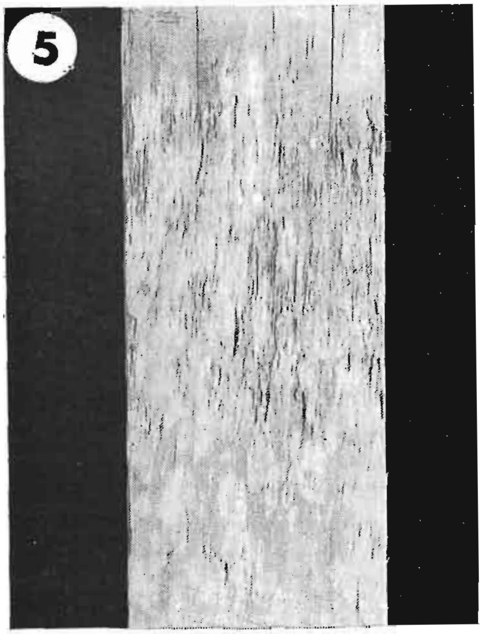
Microscopic examination revealed that, after 2.5 years in the graveyard, the outer 10 tracheids were usually heavily soft-rotted with occasional pockets of soft-rot cavities up to 25 tracheids deep. Some bore holes were seen on the outer surface but colonisation by basidiomycete fungi was not always observed. Basidiomycete decay did not penetrate as deeply as soft rot into the stake. As was seen in the benzalkonium treatments, large pigmented hyphae were present in the ray tissue penetrating to a depth of up to 50 tracheids. Very infrequently these hyphae branched to enter the tracheids adjoining the rays.

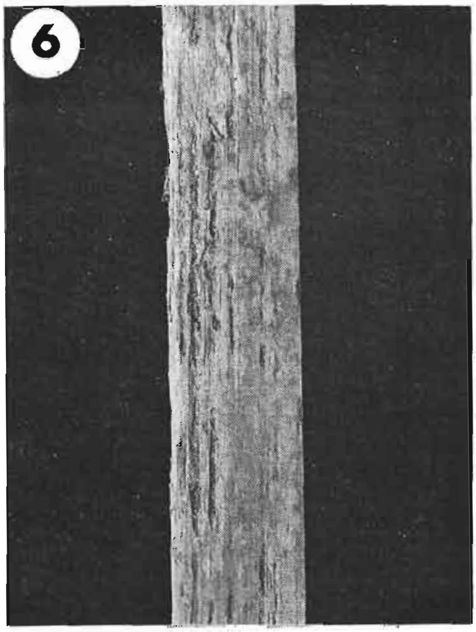
After 4 years the entire below-ground half of the stakes had been affected by fungi. At the groundline the outer 2 mm was severely decayed and eroded. When outer "soft" areas were scraped, soft rot was exposed underneath. Microscopic examination confirmed colonisation by soft-rot and basidiomycete fungi. Since the first microscopic examination, colonisation by white-rot fungi had increased. Figure 5 shows the groundline region of one stake; the white-rot attack is patchy but the erosion is obvious. The radial longitudinal faces were particularly eroded by fungal action (Fig. 6).

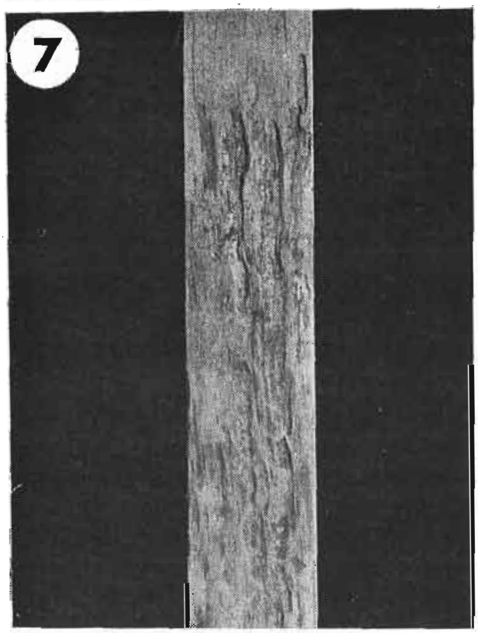
Dialkyldimethyl ammonium chloride (5.5 kg/m^3) plus cupric salt (2 : 1)

Two and a half years after installation in the graveyard these stakes looked sound. Microscopic examination confirmed the effectiveness of this treatment. Some soft-rot cavities were observed but these were sparse and restricted to the outer two tracheids.

At the second assessment 18 months later, the stakes were severely affected by surface erosion – particularly of the earlywood on the radial longitudinal faces (Fig. 7).







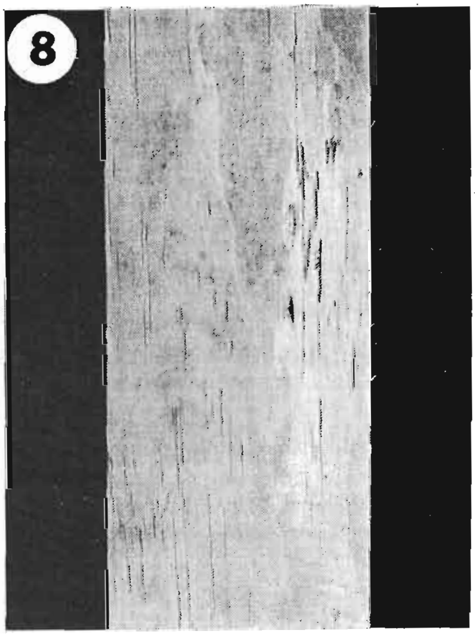


FIG. 5—Dialkyldimethyl ammonium chloride (6.2 kg/m^3). Erosion and patchy white rot on a tangential face.

FIG. 6—Dialkyldimethyl ammonium chloride (6.2 kg/m^3). Erosion of a radial face.

FIG. 7—Dialkyldimethyl ammonium chloride (5.5 kg/m^3) plus cupric sulphate. Erosion of a radial face.

FIG. 8—Dialkyldimethyl ammonium chloride (5.5 kg/m^3) plus cupric sulphate. Pockets of white rot on a tangential face.

Several stakes had actinomycete-like fungi growing on the outer surface. The development of small areas of white rot (Fig. 8) was confirmed microscopically. However, soft-rot cavities were found even deeper into the stakes beneath the white rot. Pits were degraded in the outer tracheids only in areas of obvious decay.

This treatment deteriorated quickly in the interval between the 2.5-year and 4-year assessments. Surface erosion was the predominant type of degrade, soft-rot activity continued, and white rot started to develop.

DISCUSSION

The soundness ratings in Table 1 are a visual assessment of performance whereas the microscopic examination identified the type(s) and depth of fungal attack. Although benzalkonium chloride and dialkyldimethyl ammonium chloride treatments were both being attacked by a range of fungal types, they were not equally susceptible. The benzalkonium chloride treatment was susceptible to attack by predominantly white-rot and soft-rot fungi. The brown superficial degrade was less severe. However, dialkyldimethyl ammonium chloride was more susceptible to the brown superficial degrade and soft rot. Pockets of white-rot attack were confirmed only after 4 years' service in the graveyard.

The addition of a cupric salt to both alkylammonium compounds enhanced performance by limiting the depth of attack and initially the type of fungal degrade. At the time of the first assessment almost all white-rot attack had been prevented by the copper modification and the soft-rot attack had been restricted. After 4 years in the graveyard the area of fungal degrade was still being restricted but there were no longer any differences between modified and unmodified treatments in the type of degrade.

In this study particular attention was given to the areas of brown superficial degrade which with time developed into erosion of the surface. This degrade which was first observed on alkylammonium-treated stakes in the fungus cellar (Butcher *et al.* 1979) makes the wood very brittle and flaky when dry and difficult to section. Many of these sections when examined microscopically either were found to be colonised by several types of fungi or appeared to have no fungi present. Figure 9 shows the typical appearance of this brown degrade under the microscope when only the outer one or two tracheids are affected. Similar sections viewed under polarised light had lost birefringence, indicating an altered cellulose structure in the cell walls. Also, at higher magnifications the cell walls were seen to be of an uneven thickness. This is the end effect likely to have resulted from the enzymic action of brown-rot fungi.

In laboratory tests with pure cultures, brown-rot fungi were found to be more tolerant than white-rot fungi to *P. radiata* treated with either benzalkonium chloride or dialkyldimethyl ammonium chloride (Butcher & Drysdale 1977). As white rot has been confirmed in the treated pine stakes then brown rot could be expected to be present too.

Macroscopic and microscopic evidence has confirmed the presence of three types of degrade – soft rot, white rot, and brown rot – at retentions of alkylammonium compound which exceed the toxic thresholds established by laboratory tests (Butcher *et al.* 1977).

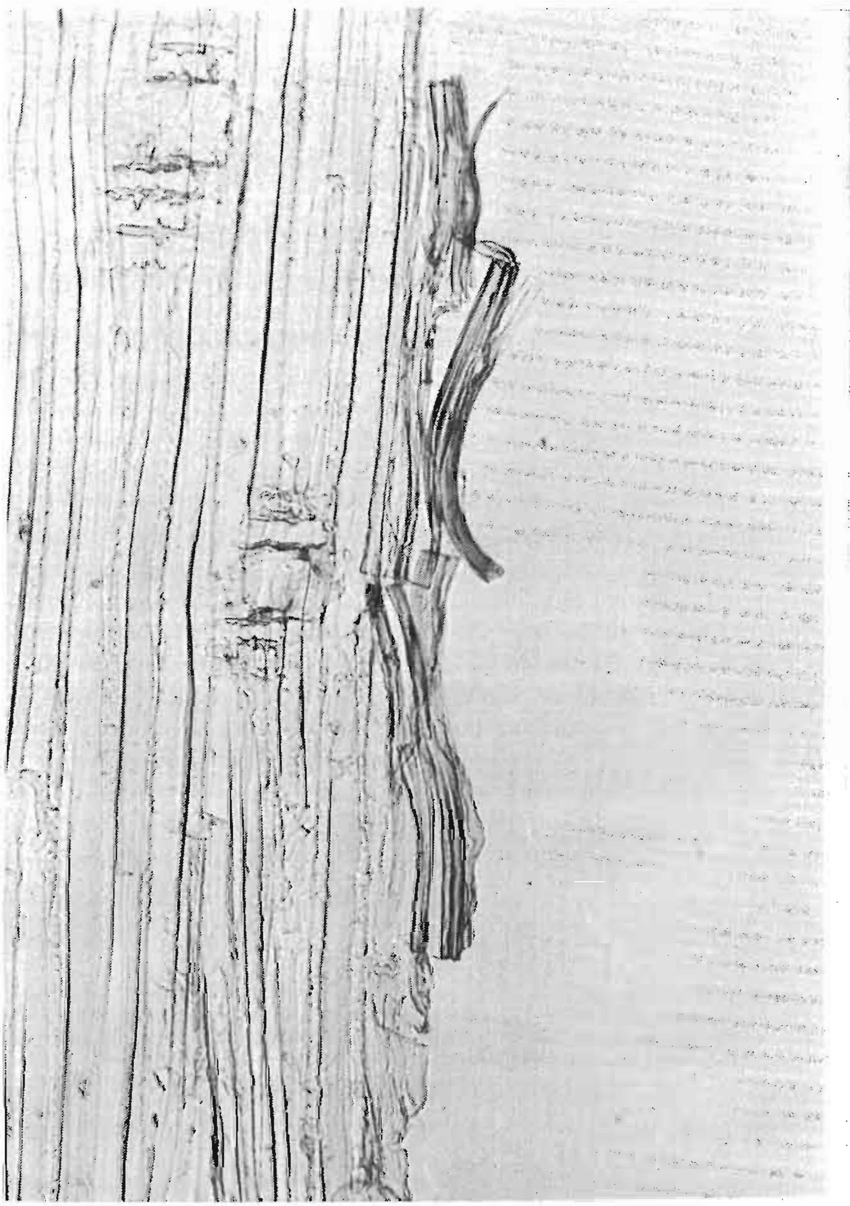


FIG. 9—Appearance of the superficial brown degrade on a stake treated with dialkyldimethyl ammonium chloride (6.2 kg/m^3). (× 150)

Therefore it follows that either the alkylammonium compound is being detoxified or leached out of the stakes or that all the fungi colonising the treated stakes are tolerant to both alkylammonium compounds with and without copper amendment.

A subsequent study on the fixation and leaching of benzalkonium chloride from treated stakes has shown how the retention in the outer 2 mm can be depleted by

20–40% (Drysdale 1983). If this is occurring when treated stakes are in ground contact then retentions on the outer surface will eventually become sub-threshold thereby allowing colonisation by fungi. This may well be the explanation for the initial appearance of brown-rot attack as a very superficial degrade affecting only the outer one or two tracheids. Assuming there is a continuation of the leaching stress, then in time less-tolerant fungi (e.g., the white-rot fungi) will be able to colonise the stakes and the depth of decay will gradually increase. This assumption fits the pattern of attack observed in the stakes examined in this study.

Tillot & Coggins (1981) reported poor performance of *Pinus sylvestris* L., *Picea abies* (L.) Karst. (spruce), and *Acer pseudoplatanus* L. (sycamore) stakes treated with tertiary amine salts and dialkyldimethyl ammonium chloride (from 3 to 15 kg/m^3) after 1 year in the field. Spruce stakes were less effectively protected than pine or sycamore stakes. The addition of copper to one tertiary amine improved performance. Dialkyldimethyl ammonium chloride was marginally better than all the other formulations but there was a suggestion of uneven treatment. Ruddick (1981) observed similar uneven treatment of *Pinus ponderosa* C. Lawson stakes treated to 6.5 kg/m^3 with dialkyldimethyl ammonium chloride. After 3 years' service these stakes were not performing as well as laboratory tests had indicated they should (Ruddick 1982). Butcher *et al.* (1979) predicted that benzalkonium chloride (12–14 kg/m^3) and dialkyldimethyl ammonium chloride (6–8 kg/m^3) should protect pine for up to 15 years. Tertiary amine salts were not considered satisfactory. From the current observations and in view of the results from subsequent leaching studies this was an optimistic forecast. Certainly copper-modified treatments were superior but they were not completely free of fungal degrade. Also, as was pointed out by Butcher *et al.* (1979), a simple addition of copper salts to alkylammonium solutions is not necessarily a practical solution as this leads to chemical instability of treating solutions and risk of corrosion. Improved formulations may overcome this problem and at the same time increase the efficacy of the preservative.

REFERENCES

BUTCHER, J. A.; DRYSDALE, J. A. 1977: Relative tolerance of seven wood-destroying basidiomycetes to quaternary ammonium compounds and copper-chrome-arsenate preservative. **Material und Organismen 12(4):** 271–7.

BUTCHER, J. A.; PRESTON, A. F. 1978: Toxicity of tertiary amine acetates against basidiomycetes and soft-rot fungi. **New Zealand Journal of Forestry Science 8:** 397–402.

BUTCHER, J. A.; PRESTON, A. F.; DRYSDALE, J. 1977: Initial screening trials of some quaternary ammonium compounds and amine salts as wood preservatives. **Forest Products Journal 27(7):** 19–22.

——— 1979: Potential of unmodified and copper-modified alkylammonium compounds as groundline preservatives. **New Zealand Journal of Forestry Science 9:** 348–58.

CROSS, D. J. 1979: Alkylammonium compounds as insecticidal wood preservatives. **Material und Organismen 14(2):** 105–16.

DRYSDALE, J. 1983: A technique for measuring preservative loss or redistribution during leaching. **International Research Group on Wood Preservation Document No. IRG/WP/2199.**

FRENCH, J. R. J.; ROBINSON, P. J. 1981: A rapid field assessment of insecticide-treated wood against termites. 20th Forest Products Research Conference, Vol. 2. C.S.I.R.O., Australia.

HEDLEY, M. E.; TSUNODA, K.; NISHIMOTO, K. 1982: Evaluation of alkylammonium compounds for use as low toxicity wood preservatives in Japan. **Wood Research 68:** 37–46.

HEDLEY, M. E.; PRESTON, A. F.; CROSS, D. J.; BUTCHER, J. A. 1979: Screening of selected agricultural and industrial chemicals as wood preservatives. **International Biodeterioration Bulletin 15(1):** 9–18.

PRESTON, A. F.; CHITTENDEN, C. M. 1982: Alkylammonium compounds as above-ground wood preservatives. **New Zealand Journal of Forestry Science 12:** 102–6.

PRESTON, A. F.; NICHOLAS, D. D. 1982: Efficacy of a series of alkylammonium compounds against wood decay and termites. **Wood and Fiber 14(1):** 37–42.

RUDDICK, J. N. R. 1981: Testing alkylammonium compounds. **International Research Group on Wood Preservation Document No. IRG/WP/2152.**

——— 1982: Calculation of performance index of Bardac 20 (an alkylammonium compound) evaluated in a field stake test. **International Research Group on Wood Preservation Document No. IRG/WP/3206.**

TILLOT, R. J.; COGGINS, C. R. 1981: Non-arsenical preservatives – a review of performance and properties. **Proceedings British Wood Preservers' Association Annual Convention 1981:** 32–46.