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ABSTRACT

Evaluation of previously established field trials of internal remedial treatments continues to verify the excellent long-term protection afforded by these treatments. Field trials with gell encapsulated methylisothiocyanate (MITC) demonstrate that gelatin does not interfere with chemical release, nor is addition of supplemental moisture required for release.

Field trials have been established to evaluate several new formulations including Basamid plus copper, boron/fluoride rods, and boron rods. Field trials of gelled and pelletized metham sodium indicate that both formulations are moving well through Douglas-fir poles one year after treatment. Evaluations of a copper naphthenate/boron paste for internal treatment indicate that the formulation has moved a short distance from the point of application 3 years after treatment.

Boron rod field trials were not fully sampled for residual chemical level this past year; however, evaluation of cores removed from fused borate rod trials in New York indicate that some additional boron diffusion has occurred. Examination of treatment holes suggests that considerable amounts of the boron remain in rod form 2 years after application.

In laboratory studies, we have evaluated the use of metham sodium/basamid mixtures and have found that these formulations provide enhanced MITC production over longer periods than either of the components alone. Both formulations were solid, creating the potential for development of safer formulations which provide a rapid release with long term protection. Field trials of these systems will be established in the coming months.

Studies also continue with Basamid in an effort to enhance decomposition of this compound. Studies have shown that moisture addition has the most significant effect on decomposition followed by the presence of copper and increasing pH. Further studies on decomposition products are planned to better understand the activity of this molecule.

Examination of Douglas-fir timbers treated with metham sodium indicate that MITC levels are similar to those found in poles at similar times after treatment. The presence increased surface area on timbers apparently did not adversely affect diffusion or chemical loss.

Evaluation of the fungitoxicity of mixtures of MITC and carbon disulfide is underway in an effort better understand the activity of metham sodium. This compound decomposes to produce a wide array of volatile compounds with varying degrees of toxicity to fungi. Preliminary trials have shown the relatively low toxicity associated with carbon disulfide, a major decomposition product, particularly under acidic conditions. Trials with mixtures will begin shortly.

Efforts to develop a three dimensional model of MITC movement are continuing. The model has been evaluated on data collected from small blocks and efforts are underway to verify these results. In addition, full pole grids have been prepared to evaluate the effects of treatment hole geometry and orientation on fumigant movement.

Studies to identify alternative treatments for protecting western redcedar sapwood from decay are continuing. A variety chemicals have been shown to be effective 5 years after treatment; however, longer term trials of other formulations suggests that performance declines rapidly at longer time points. Field trials of remedial treatments for field drilled bolt holes continue to demonstrate the performance of diffusible boron and fluoride for preventing fungal attack. These trials will be evaluated again in the coming year.

Inspection of the above ground region of Douglas-fir poles in the Pacific Northwest have shown that many poles are colonized by decay fungi far above the groundline. Fungal incidence was greatest in poles near the coast, but decay fungi were also isolated from poles in drier climates. Sampling of additional poles is planned to provide a more detailed analysis of the risk of above ground decay in this region.

Efforts are also continuing to evaluate the performance of through-bored Douglas-fir poles to provide better data on the degree of preservative penetration required in the through-bored zone to achieve optimum performance. These trials have shown that most poles are well treated, but no decay has been detected in the through bored zone of poles with as little as 60 % of the through-bored zone treated. Efforts are also underway to evaluate penetration and retention of preservative in poles with various throughboring patterns.

Studies to identify optimum conditions for sterilization of air-seasoned Douglas-fir poles are continuing. These trials have evaluated pentachlorophenol in oil treatments. The results illustrate the value of long treatment cycles which incorporate Boulton-seasoning. The data from these trials will be used to construct heating curves for this treatment.

Trials of groundline preservative systems on Douglas-fir pole stubs continue to show that more recently developed formulations continue to move through the wood at rates which are similar to those found with older pentachlorophenol based systems. Trials in California on pine, Douglas-fir and western redcedar have provided similar results. Tests are now underway to establish thresholds for mixtures of groundline preservative formulations.

Copper naphthenate treated wood continues to perform well in both field and fungal cellar trials. Unweathered western redcedar stakes have tended to perform better than stakes which were weathered prior to treatment. These differences may reflect an increased permeability which enhances leaching.

ACKNOWLEDGEMENTS

The cooperative depends heavily upon the assistance of others in utilities, wood treatment facilities and allied disciplines to complete the outlined tasks. These contributions are essential for the success of the program and we gratefully acknowledge the numerous groups which have assisted us in the past year. We look forward to continued collaboration to enhance the performance of wood in utility systems.

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*Central Lincoln P.U.D.

*Empire State Electric Energy Research Corporation

New York State Electric and Gas Corporation

*Pacific Gas and Electric

* Pacific Power Corporation

* Puget Power

Portland General Electric Company

*Western Wood Preservers Institute

J. H. Baxter & Company

Koppers Company, Inc.

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Niedermeyer-Martin Company

Taylor Lumber and Treating Company

*CSI, Inc.

*ISK Biotech

*OSMOSE Wood Preserving Inc.

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*Asterisk denotes funding. All supplied poles, hardware, or other assistance.

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OBJECTIVE I DEVELOP SAFE ENVIRONMENTALLY ACCEPTABLE CHEMICALS FOR CONTROLLING INTERNAL DECAY OF WOOD POLES

The development of effective which specifications include adequate seasoning prior to treatment, methods for enhancing treatment around the decay susceptible groundline zone such as through-boring or kerfing, and a good posttreatment quality control program remain the primary methods for ensuring long pole Despite these precautions, service life. however, the treatment zones in some poles will be compromised, either during installation or as the pole seasons in service. permitting the entry of decay fungi or insects. The detection and control of this damage before significant losses in structural integrity occur poses a major challenge to electric utilities. The development of fumigants for remedial control of decay fungi in wood poles in the late 1960's ushered in an new era in effective pole management. Fumigants are widely used for arresting internal decay in utility poles, timbers, piling, and even live trees. As we approach the 25th Anniversary of the initial fumigant field trials, there is a continuing need for performance information on the existing systems as well as a need for safer systems for controlling wood decay. This Objective addresses both volatile and diffusible methods for arresting internal decay of wood poles.

A. EVALUATION OF PREVIOUSLY ESTABLISHED TESTS OF VOLATILE REMEDIAL INTERNAL TREATMENTS

Over the years, the Cooperative Pole Research Program has established field tests in Oregon, Washington, California and New York to evaluate the performance of various promising treatments (Table I-1). These tests are initially sampled on an annual basis to develop data on the performance of each treatment under field conditions. As the tests mature, they are sampled less frequently, but they provide important information on longevity of various treatments which can be used to develop retreatment schedules. At present 13 field tests are underway evaluating various remedial internal treatments (Table I-2).

1. <u>New York field test of</u> <u>encapsulated fumigants</u>: The field test comparing the performance of gelatin encapsulated methylisothiocyanate and Vorlex with metham sodium was established in 9 year old chromated copper arsenate treated poles in 1981 and was sampled in 1991. The field test was not sampled this past year, but will be sampled next year to provide 14 year data on the performance of this treatment.

2. <u>Treatment</u> of through-bored <u>Douglas-fir poles with gelatin encapsulated</u> <u>MITC or chloropicrin</u>: The Douglas-fir poles treated with gelatin encapsulated MITC or chloropicrin were scheduled to be sampled this past year, but an inspection could not be arranged. Attempts will be made to sample this test in the Fall.

Table I-1. Characteristics of remedial treatments being evaluated in Coop field tests.									
Trade Name(s)	Active Ingredient	Concentration (%)	Toxicity (LD ₅₀)	Sources					
Timber Fume (Chloropicrin)	Trichloronitromethane "	96%	205 mg/kg	Osmose Wood Preserving Inc. Great Lakes Chemical Co.					
Wood Fume	Sodium n-methyldithio- carbamate	32.1%	1700-1800 mg/kg	Osmose Wood Preserving Inc.					
ISK Fume	n			Chapman Chemicals Inc.					
Vorlex	20% methylisothiocyanate 80% chlorinated C ₃ hydrocarbons	99%	538 mg/kg	NorAm Chemical Co.					
MITC-FUME	methylisothiocyanate	96%	305 mg/kg	Osmose Wood Preserving Inc.					
Impel Rods	boron	99%		CSI Inc.					
Pole Saver Rods	sodium octaborate tetrahydrate	58.2%		Preschem Ltd.					
	sodium fluoride	24.3%							

Table I-2. Active field trials evaluating the performance of selected remedial treatments.							
Test Site	Chemicals Evaluated	Date Installed					
Peavy Arboretum	field drilled bolt hole treatments	1981					
Peavy Arboretum	cedar pole sprays	1981					
Dorena Tap (BPA)	encapsulated Chloropicrin	1982					
Hamburg Line (NYSEG)	encapsulated MITC	1982 1981					
Alderwood Tap, (BPA)	encapsulated MITC	1987 1984					
Peavy Arboretum	encapsulated MITC (MITC-fume)	1987 1988 acc					
Peavy Arboretum Francisco	Basamid " / K add	1988 - 1989 -					
Peavy Arboretum	copper naphthenate/boron	1989					
Peavy Arboretum	Impel Rods	1989					
Hilo, Hawaii (CSI)	Impel Rods	1990					
Central Lincoln (CLPUD)	Impel Rods	1990					
Peavy Arboretum	Gelled NaMDC	1992					
Pacific Power, Corvallis	Basamid	1993					
Peavy Arboretum	Boron/Fluoride Rods	1993					

Alderwood Tap

3. Above ground treatment with gelatin encapsulated or pelletized MITC: Douglas-fir poles treated in the zone below, $a_{\mathcal{D}}^{\mathcal{A}}$ an underbuilt distribution line in 1987 with gelatin encapsulated or pelletized MITC were not sampled this past year. Efforts will be made to arrange an inspection with utility personnel this Fall.

4. Effectiveness of glass encapsulated MITC in Douglas-fir or southern pine poles: While a significant amount of testing has been performed on the effectiveness of MITC as a wood fumigant, these studies were performed using pure molten MITC or MITC encapsulated in gelatin capsules. The development of glass encapsulated MITC in 1988 encouraged additional trials to determine if this formulation provided similar protection to wood poles in service. The vials were evaluated in two tests.

Laboratory trials: In an effort to establish the rate of MITC release from MITC-Fume® tubes. eighteen 25-cm diameter by 75-cm long Douglas-fir pole sections were end-coated with an elastomeric paint. Nine of these pole sections were then air-seasoned prior to treatment to a 25% moisture content 5.0 cm below the wood surface, and the remainder were treated while still green (MC>25%). Near the center of each pole section, a single hole, 1.9-cm diameter by 20.5-cm long, was drilled at a 45-degree angle, and an MITC-Fume[®] tube containing 30 g MITC was inserted, open-end down, in the hole. The holes were plugged with rubber stoppers, and sets of three pole sections from each of the moisture-content groups were placed in one of the following locations: a cold room (5°C), a hot wet room (30°C, 90% relative humidity), or outdoors at ambient temperature.

At periodic intervals, the MITC-Fume[®] tubes were removed from the treatment holes, weighed (nearest 0.01 g) to determine , the amount of chemical remaining, and returned to the holes. Several tubes whose weight indicated they had completely lost the MITC were extracted with 5.0 ml ethyl acetate. The extract was analyzed for residual MITC Varian content with а 3700 gas chromatograph equipped with a flame photometric detector and filters specifically for sulfur compounds. Residual MITC content was quantified by comparison with prepared standards.

Field trials: The efficacy of MITC-Fume® compared to metham-sodium was investigated as follows. Thirty-six Douglasfir and 36 loblolly pine pole sections (25 to 30 cm in diameter, 3.6 m long) were SY Ppa'es obtained locally. The poles were pressuretreated to a nominal retention of 6.4 kg/m³ with chromated copper arsenate (CCA) Type DF PolesC and then painted with an elastomeric paint chemonite to retard vapor loss. (Previous studies have + readed shown that MITC diffuses readily through CCA-treated wood and is better retained in wood treated with pentachlorophenol in P9 Type A oil). The poles were then set to a depth of 0.9 m at a site 16 km north of Corvallis, Oregon. This site receives approximately 112 cm of precipitation annually, mostly during the winter months.

Into each of six poles per wood species, a series of two, four, six, or eight holes, 1.9 cm in diameter and 20.5 cm long, was drilled at steep angles, beginning at groundline and spiraling upward at 120degree-by-15-cm intervals. One tube of MITC-Fume[®], containing approximately 30g 96% MITC, was inserted, open-end down, The holes were then into each hole. plugged with tight-fitting, preservativetreated wood dowels to retard fumigant loss. In addition to these sets of poles (which, depending on the number of holes drilled, received 60, 120, 180, or 240 g MITC), an

1988

CCA treated

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additional set of six poles of each species was treated with 500 ml metham-sodium equally distributed among three holes drilled as described for the MITC-Fume®-treated poles. A final set of six poles of each species, the control group, received no chemical treatment. The ability of MITC, applied as either MITC-Fume® or methamsodium, to diffuse through the poles and eliminate fungi was evaluated 6, 12, 24, 36 and 60 months after treatment. The evaluation included two types of fungal bioassays - dowel and closed tube - as well as fungal culturing and chemical analysis.

The dowel bioassays provided an approximate measure of the extent of fumigant diffusion through the test poles over the study period. To perform these bioassays, pressure-soaked western hemlock dowels were placed in moistened vermiculite in plastic bags with a semi-permeable patch. The bags were then sterilized (20 min. at 121°C). A 1% malt extract solution. inoculated 2 weeks earlier with Postia placenta, was then added to the vermiculite; the bags were sealed; and the dowels were incubated for at least 4 weeks or until the dowels were thoroughly colonized by the test fungus.

At 6, 12, 24, and 36 months after the test poles were treated with fumigant, the colonized dowels were inserted into sets of three 15-cm-deep holes, 120° apart, that had been drilled in the poles 0.0, 0.3, 0.9, and 1.5 m above the highest treatment hole. (Dowel bioassays were not conducted for sites between treatment holes because the high levels of fumigant expected in this zone would have made it difficult to resolve any treatment differences accurately.) These holes were then plugged with tight-fitting rubber stoppers to minimize fungal desiccation during the exposure period. Initially, dowels were exposed for a period of 6 months prior to removal; however, due to a low fungal survival rate in dowels in the untreated poles (presumably because of drying), the exposure period was reduced to 3 months in subsequent tests. Following removal from the test poles, the dowels were plated onto potato dextrose agar and observed for evidence of regrowth of the test fungus.

Closed-tube bioassays represent a slightly different approach to assessing fumigant distribution. With dowel bioassays, the test fungus is exposed to fumigant vapors diffusing through the wood over several months. With closedtube bioassays, the test fungus is exposed to all of the fumigant (both bound and vapor) in the wood in a short time (7 to 10 days). Previous studies have shown that closed-tube bioassays are very sensitive to low levels of fumigant.

In our study, closed-tube bioassays were performed 12, 24, 36 and 60 months after pole treatment by removing two 15cm-long increment cores, 180° apart, from each test pole 0.3 m below groundline, and sets of three increment cores of the same size, 120 degrees apart, from sites 0.0, 0.3, 0.9, and 1.5 m above the highest treatment hole. (Cores were not removed from sites between treatment holes because, as with the dowel bioassays, it was felt that the high levels of fumigant expected in this zone would prevent accurate resolution of any treatment differences.) The inner and outer 2.5-cm sections of each of the 14 cores were placed in separate tubes containing an actively growing culture of Postia placenta. The tubes were then sealed and incubated in an inverted position to allow fumigant vapors released from the core sections to come into contact with the test fungus. The rate of test fungus growth in the presence of fumigant-treated wood, compared to its growth rate in the absence of wood, provided a measure of the degree to which the treated wood inhibited fungal growth.

The middle section of each of the closed-tube bioassay cores was used for a culturing analysis. These sections were plated onto malt extract agar and, after 1 month of incubation at room temperature, were examined for evidence of fungal growth. If growth occurred, it was identified as either decay fungi (fungi with characteristics typical of basidiomycetes, a class of fungi containing many important wood decayers) or as nondecay fungi. No attempts to further identify the fungi were made.

For the chemical analysis of fumigant diffusion in the test poles, a second set of 15-cm-long increment cores was removed from each pole at locations adjacent to those sampled for the closed-tube bioassays. The outer and inner 2.5 cm of these cores were placed in separate test tubes containing 5.0 ml ethyl acetate. The tubes were stored for a minimum of 48 hours, and then, the extract was chromatographically analyzed as for the residual MITC in

the laboratory trials, to determine the MITC level in each wood section. The results were quantified by comparisons with analyses of solutions of known MITC content.

MITC-Fume® tubes over a 3.5-year period indicated that MITC was released most rapidly from tubes in poles exposed to hot humid conditions - in these conditions, complete release occurred within 1 year (Fig. I-1). Although tubes in poles exposed to ambient temperatures had not released all of their fumigant by the end of the 2-year period, the data for the 40% MC wood indicated a release period of about 3 years. MITC was released most slowly in poles exposed to cool conditions. A slow MITC release rate is not, in itself, a negative characteristic, provided a sufficient level of chemical is released to eliminate any fungi established in the wood - and previous studies have suggested that the levels required for fungitoxicity are fairly low.

Higher wood moisture content accelerated MITC release significantly only for ambient temperature exposures; and this effect continued throughout the 2-year period, even though the moisture content of the two groups of poles become equivalent within 6 months of pole treatment. These results suggest that MITC diffusion was negatively affected by the conditioning of the drier poles, which might have increased the degree of pit aspiration in those poles.

Gas-chromatographic analyses of extracts from empty tubes found only trace levels of MITC; although, the tubes did contain a coating of sulfur crystals left by the MITC decomposition. These trace levels should not pose a disposal risk, as they will volatize rapidly when tubes are removed from the treatment holes.

<u>Field Trials</u>: As mentioned, in the initial 6-month exposure period for the dowel bioassays, <u>Postia placenta</u> exhibited excellent survival in the untreated (control) southern pine poles; in contrast, survival in the control Douglas-fir poles was only half as high. This marked difference indicated

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Figure I-1. Rate of MITC release from MITC-Fume[®] tubes (as determined by residual weight of tubes) in Douglas-fir pole sections with initially different moisture contents, exposed for 3-1/2 years to cold, ambient, and hot/wet conditions.

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that moisture conditions were not uniformly suitable for survival of the test fungus across both wood species, and so the exposure period for the dowels was reduced to 3 months to decrease the possibility of fungal desiccation.

The <u>P</u>. <u>placenta</u> survival percentages for the dowel bioassays (Table I-3) indicate that in both wood species the MITC-Fume[®] and metham-sodium treatments were well distributed to 0.3 m above the highest treatment hole within 6 months of pole treatment. With the Douglas-fir poles, low survival percentages 0.9 m above the treatment hole suggest that the fumigants had reached this level by 6 months.

Dowel bioassay results generally must be viewed with caution, however, because external environmental conditions can affect both the degree of chemical diffusion and fungal survival in different For example, hot dry wood species. conditions increase fungal would desiccation. reducing survival rates. Something of this nature probably occurred for the southern pine poles in our study, as illustrated by the fact that 1 year after treatment, fungal survival in dowels in the untreated southern pine poles was extremely low as compared to that in the untreated Douglas-fir poles. For this reason, the fungal survival data for the fumigant-treated southern pine poles from 1 year onward is suspect and will not be discussed.

Fungal survival rates in MITC-Fume[®] treated Douglas-fir poles 1 year after treatment suggest that, as at the 6-month point, fungitoxic levels of MITC were present to 0.3 m above the highest treatment hole, but MITC levels 0.9 m above the highest treatment hole were insufficient to completely eliminate the test fungus. Fungal survival rates in metham-sodium treated Douglas-fir poles 1 year after treatment suggest that this fumigant no longer was producing fungitoxic levels of MITC. Metham-sodium must decompose to produce MITC. It is possible that by 1 year after treatment, the decomposition reactions had ceased and that most of the chemical had dissipated through the wood and was therefore less available for diffusion into the fungal-colonized dowels.

Dowel bioassays for the Douglas-fir poles 2 and 3 years after treatment produced results similar to those for the 6-month and 1-year bioassays; both of these later samplings indicated that fungitoxic levels of MITC continued to be present just above the highest treatment hole and that fungal survival rates increased with distance from this site. Our data suggest that MITC continues over time to diffuse from very high concentrations near treatment sites and to gradually lose its fungitoxic effects with distance from these sites.

Field Testing: Culturing of increment cores removed from both Douglas-fir and southern pine poles over the course of the study revealed that the incidence of decay fungi increased steadily in non-fumigant treated control Douglas-fir poles over the five year test period (Table I-4). This increased incidence may reflect a gradual spread of fungi which survived the initial treatment process, although it is difficult to confirm this finding. No decay fungi were isolated from the treated or untreated Southern pine poles, probably reflecting the relatively small amount of untreated wood available for fungal colonization in these well treated pole sections.

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36 mos. 11 6 20 7 6 54 7 83 Table I-3. Survival of Postia placenta in hem-fir dowels inserted in southern pine and Douglas-fir poles treated with MITC-Fume[®] or metham-sodium 6, 12, 24, or 36 24 mos. 75 75 100 100 87 83 33 50 12 +1.5 m 12 mos. **28** 33 78 28 67 12 6 11 33 30 mos. **5** 83 83 50 38 38 50 50 9 Fungal survival (%) at different vertical distances from treatment zone 202 N. M. M. 36 mos. 5 32 32 **6** 32 0 2 0 0 50 11 Stores C 24 mos. 40 56 82 82 67 70 25 14 33 33 61 +0.9 m 12 mos. higherdone 100 100 11 33 33 33 17 17 39 - 0 mos. 33 33 33 39 13 24 11515 9 Southern Pine 36 mos. 0010 52 9 Douglas-fir 00 00 90 24 mos. 8 8 33 0000 000 +0.3 m 100 12 mos. 6)0 6 0 11 0 0000 H mos. 5 27 5 16 33 0 9 <u>s s o o</u> 36 mos. 23 0 0000 00 0000 0.0 m mos. 24 8 2 08 0000 0000 Dosage 500 500 months prior to dowel insertion.* Chemical Treatment Metham-sodium Metham-sodium^e MITC-Fume^b MITC-Fume^b Control Control

"Wood dowels colonized by Postia placenta were inserted in sets of three holes, 120° apart, drilled in the poles at selected heights above the highest treatment hole. The dowels were removed after 3 or 6 months and cultured on malt agar/benomyl plates. ^bDosage in grams. ^oDosage in ml.

Anti-

							- no deriv		Sourse :					
			6 99 100		0(61)	0(50)	6(94) 0(53)	6(61)		0(22)	0(28)	0(53)	(55)0	
		E S	36 110		0(88)	0(52) 0(52)	0(94) 0(87)	0(83)		6(39). 10(29)	0(22)		0(0)	
			24		0(100)	(001) 0(100)	(001) 0(100)	0(100)	*	0(100) 0(100)	0(67)	10(80)	(mī)n	
			12		0(100)	0(100)	(001)0 0(100)	0(100)		0(100) 10(40)	(11)0	640	(ec)n	
		.9 m				(6£)0	0(56)	6(33) 7(53)	0(72)		6170 6110 6110	(11)0	7(53)	(<c)n< td=""></c)n<>
			36		0(83)	0(22)	0(33) 0(33)	0(89)		619 619	619	66	(00)07	
		0	24 100		(001)0	818	(00) 0(100)	0(100)		0(100) 7(100)	0(67)	10(80)	0(100)	
	() fung		12		(001)0	800	(100) 0(100)	0(100)		0(50) 0(64)	0(15)	10(50)	رمداه	
ham-sodiun	y (nondeca		648- 1048-		6(22)	0(33)	6(28) 0(33)	0(72)	v	0(11)	0(11)	0(33)		
ne® or met	ining deca	ε	36 TIOS.		(65)0	0(67)	0(38) 0(73)	0(83)		(0)0 (1)0	0(10)	13(3)	122/07	
MITC-Fun	f cores cont	0.3	24 mot.	tm Pine	0(100)	0(100)	0(100) 0(80)	0(100)	çlas-fir	0(50) 0(100)	0(67)	10(50)	1001)07	
catment with	Percentage o		12 moi.	Southe	0(100)	(00) (00) (00)	8 8 8 8 8 8 8	0(100)	Doug	0(33) 0(71)	0(58)	640		
tha after tr	-				0(17)	0(33)	9(8) 0(20)	0(20)		(8) (8) (8)	600		1.201	
nd 36 mor		E	36 104.		0(17)	0(14)	0(17) 0(40)	0(83)		(0)0 (0)0	800	10(50)	1	
oles 12, 24, a		0.0	24 mor.		(Q)	0(57)	0(0) 0(40)	0(100)		0(33) 0(29)	0(17) 0(17)	0(40)		
bouglas-fir p			12 mos.		0(67) 0(83)	0(30)	Q(50) Q(40)	0(100)		0(22) 0(29)	0(16) 0(29)	0(60)		
pine and D					0(30)	ନ୍ଦୁ	(n) (n) (n) (n) (n) (n) (n) (n) (n) (n)	873)		6) 8) 8)	6000	020		
n southern		-0.3 m°	36 TTOB.		0(67) 0(42)	6 (21)	0(28)	0(92)		0(42) 0(17)	(1)) (13)	0(40)		
rdecay fungi i			24 mos.		0(50)	0(28)	69 9	00(100)		00) 0(57)	0(50) 0(33)	0(60) 33(100)		
decay and nor			Dougo		60 120	180	240 260 260	•		120	180 240	. ⁵ 0		
Table I-4. Incidence of (Chemical Treatment		MITC-Fume ⁶⁴		Metham-sodium [®]	Control		MITC-Fume ^{®b}		Metham-sodium [*] Control		

"Cores were removed from selected locations at different vertical distances above and below the treatment site. The middle segment of cores was used for this analysis. "Values manysis an average of 15 total cores per dosage/position. Figures in parentheses represent non-decay fungi isolated from the same cores." "Twelves month data not taken for -0.3 m cores." "Dosage in grams

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Limited numbers of decay fungi were isolated from MITC and metham sodium treated Douglas-fir poles, particularly 1.5 m above the highest treatment hole. The incidence of decay fungi isolated was somewhat variable with time, suggesting that fungal colonization was not widespread within these zones.

The isolation frequency of non-decay fungi was generally high in all poles, although the levels tended to be highest in southern pine poles. This species is typically colonized to a greater extent by microfungi. Many of these fungi are capable of producing soft rot attack, although their ability to cause soft rot in CCA treated southern pine or Douglas-fir heartwood is sharply limited. The effect of these fungi on fumigant effectiveness, however, remains poorly understood.

The cultural results suggest that limited invasion of the poles is occurring away from the fumigant treated zones, but the fumigant treated zone remains free of active fungal attack.

Closed tube bioassays of increment core segments indicated that most MITC-Fume treatments continued to inhibit the growth of the test fungus, although the levels of inhibition continue to decline (Table I-5). Levels of inhibition in the metham sodium treated samples continue to be generally lower than those found with MITC, illustrating the benefit of using pure instead of depending MITC on decomposition of metham sodium to MITC. Previous studies have shown that this conversion is somewhat inefficient in wood. Inhibition levels 0.9 m and 1.4 m above the highest treatment hole were generally low, suggesting that neither MITC or metham sodium were present at levels which would completely inhibit fungal colonization. These findings compare well with the presence of decay fungi in Douglas-fir poles in this zone, but do not agree with those for culturing from southern pine poles.

Chemical analysis of increment cores removed from the poles indicate that measurable MITC is present in all treatments on both wood species (Table I-6). Chemical levels remain highest in the treatment zone of the southern pine poles after both 36 and 60 months (Figures I-2, 3). The presence of higher MITC levels in this species in comparison with Douglas-fir is perplexing since previous reports suggest that fumigant treatment of pine provides a shorter protective period that found with Douglas-fir. Our results would suggest that MITC performance on pine should be at least similar to that found with Douglas-fir.

Fumigant levels continue to be slightly higher in the inner zone of the poles; however, the differences were sometimes slight. These results suggest that fumigant distribution has become more uniform with time due to diffusion from high to low concentrations within the wood.

Residual MITC concentrations in the treatment zone have continued to decline with time, but remain well above the levels required for protection against fungal colonization. MITC levels away from the treatment zone were generally low in all dosages, suggesting that the rate of MITC diffusion into these zones is relatively slow. While the toxicity levels of MITC at higher dosages have been studied, the effects of relatively low levels of MITC over a long period of time on fungal survival remain

		Months after	Fungal growth (as % of control) ^b										
Vertical			Southern pine						Douglas-fir				
distance from treatment	Core		MITC-Fume®				Metham- sodium	MITC-Fume®				Metham- sodium	
zone	tested ^c	treatment	60g	120g	180g	240g	500 ml	60g	120g	180g	240g	500 ml	
-0.3 m	outer	12	12	0	0	0	23	34	25	4	0	77	
	1	24	17	0	20	0	100	16	6	20	0	20	
		36 - 474	55	41	33	32	78	25	21	20	22	82	
		60-1271	74	99		79	73	90	79	74	91	80	
	inner	12	0	0	0	0	14	0	12	0	0	49	
		24	0		0	0	0	0	0	0	0	16	
		30	14		3	0	28		14	13	10	69	
0.0 m	outer	12	16	20	11		28		45	55	01	57	
0.0 m	outer	24	0	7	30	ő	100	16	0	0	0	10	
		36	38~	12	24	10	69	10	21	26	21	76	
		60	76 -	82	87	22	90	85	47	75	77	58	
	inner	12	0	0	0		Ó	o	0	0	0	0	
		24	0	0	Ō	o ·	0	Ō	10	Ő	ŏ	ō	
		36	13	3	7	3	5	8	2	1	0	82	
		60	47	53	36	1	26	73	46	66	47	46	
0.3 m	outer	12	80	0	21	41	63	65	32	4	0	67	
Į.	ļ	24	83	36	33	33	100	40	23	0	0	0	
х		36	51	25	28	27	67	24	19	15	7	91	
ĺ		60	79	96	85	68	89	94	91	74	69	48	
	inner	12	40	0	0	0	45	16	12	0	0	15	
		24	0	0	13	0	13	16	13	0	0	33	
		36	5	6	19	1	23	8	20	14	3	84	
		60	76	66	83	33	67	92	75	71	62	75	
0.9 m	outer	12	100	73	95	100	90	79	64	27	19	70	
		24	90	77	94	100	100	43	43	23	24	60	
		30	101	100	101	85	84	3/	31	29	13	83	
	inner	12	90	102	101	85	89	88	82	09	//	08	
	Inner	24	57	63	35	100	60	20	20	16		39	
		36	78	40	43	36	50	20	54	41	15	00	
	ł	60	89	00	89	79	86	70	103	80	82	70	
1.5 m	outer	12	100	100	100	100	100	63	100	62	48	86	
		24	97	100	100	100	87	53	47	60	100	100	
		36	88	91	89	85	93	74	71	72	86	92	
		60	98	99	108	90	98	93	102	93	90	54	
	inner	12	100	100	100	50	97	95	100	68	50	84	
	1	24	100	94	80	57	70	77	43	30	67	67	
		36	99	83	74	61	57	76	74	75	77	102	
		60	97	93	95	76	86	76	107	75	93	73	

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Cores were removed from selected locations at different vertical distances above and below the treatment site.

Values represent the growth of Postia placenta in tubes containing treated wood cores as a percentage of its growth in tubes to which wood cores were not added. complete inhibition (0% growth) represents fungitoxic chemical levels. Where outer represents 2.5 cm from pole surface and inner represents 12.5-15.0 cm from pole surface.

Table I-6. Ro 24, 36, and 6	Table I-6. Residual MITC content as measured by gas chromatographic analysis of increment cores in southern pine and Douglas-fir poles 6, 12, 24, 36, and 60 months after treatment with MITC-Fume® or metham-sodium.											
Vertical	Core	Months				MITC c	ontent (µg/ov	en-dried g	of wood) ^b			
distance from	segment tested ^e	after treat-			Southern	pine		Douglas-fir				
treatment zone		ment		MITC do	C-Fume® osage		Metham- sodium dosage		MITC-F dosag	ume® ge		Metham- sodium dosage
			60g	120g	180g	240g	500 ml	60g	12 0 g	180g	240g	. 500 ml
-0.3 m	Outer	12 24 36 60 12	105 125 30 14 369	179 306 31 70 1534	170 204 56 86 1282	320 185 163 61 1644	10 213 2 56 147	164 140 18 58 292	346 168 81 65 270	401 404 28 24 1327	439 273 55 18 441	- 15 2 6 143
		24 36 60	203 536 187	1996 368 120	2028 284 188	1754 277 854	535 257 212	132 186 68	154 219 58	2161 182 95	1240 127 36	44 26 26
0.0 m	Outer	12 24 36 60	93 127 138 10	147 120 62 107	169 426 176 92	275 140 62 235	95 18 1 15	119 219 61 99	485 200 59 36	280 192 51 44	1500 322 78 37	31 3 18 18
	Inner	12 24 36 60	2031 2054 675 137	2777 1798 673 131	2009 2033 736 330	3425 2381 1332 1085	1986 319 227 93	2525 1191 418 267	2879 1928 223 70	3745 1600 260 135	3985 1242 251 46	34 68 64 64
0.3 m	Outer	6 12 24 36 60	0 38 T 21 9	1 94 40 42 17	3 30 33 34 46	2 29 13 36 37	0 9 T 2 13	5 26 46 37 51	84 12 94 48 31	132 149 177 63 26	132 206 311 99 56	11 22 8 30 30
	Inner	6 12 24 36	1 239 285 77	14 316 353 139	12 212 322 91	6 184 281 135	2 96 54 19	132 128 256 92	296 349 459 142	534 1052 363 108	624 262 554 107	105 306 24 10
0.9 m	Outer	6 60 12 24 36	51 0 T T 1	48 0 12 T 4	47 0 13 T 6	112 0 10 T 5	10 0 0 T	29 0 34 84 26	29 2 94 60 40	48 0 25 40 17	30 0 34 72 20	21 10 T 4 10
	Inner	6 60 12 24 36	6 0 T T 2	6 0 12 T 12	5 0 9 T 12	14 0 T 46 8	9 0 0 7	21 2 24 149 34	30 115 198 117 26	18 4 26 92 28	28 2 31 165 48	10 102 49 8 15
1.5 m	Outer	6 60 12 24 36	8 0 0 0 0	7 0 0 0 T	15 0 0 0 T	15 0 0 2	8 0 0 0 T	12 0 5 T 3	22 0 T T 3	12 0 T T T	16 0 T 49 4	15 T 0 T 16
	Inner	6 60 12 24 36	7 0 0 0	24 0 0 0	3 0 0 T	11 0 0 0 2	7 0 0 0 T	9 0 T T 3	15 0 T T 6	7 0 T 3 7	16 0 21 120 2	16 0 T 14

*Cores were removed from selected locations at different vertical distances above and below the treatment site.

^bValues represent the growth of <u>Postia placenta</u> in tubes containing treated wood cores as a percentage of its growth in tubes to which wood cores were not added. complete inhibition (0% growth) represents fungitoxic chemical levels. ^cWhere outer represents 2.5 cm from pole surface and inner represents 12.5-15.0 cm from pole surface.

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Figure I-2. Residual MITC at selected locations in the inner zone of Douglas-fir and southern pine poles 3 years after treatment with 500 ml metham-sodium or 60-240 g MITC-Fume[®].



Figure I-3. Residual MITC at selected locations in the inner zone of Douglas-fir and Southern pine poles 5 years after treatment with 500 ml metham sodium or 60 to 240 g MITC-Fume.

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poorly understood. Thus, it is difficult to determine if the chemical levels present 0.9 and 1.5 m above the groundline will prevent fungal colonization. The presence of some decay fungi in this zone suggests that these relatively low levels are not adequate for this purpose.

At present, MITC loadings in the treated zones of all MITC-Fume treatments appear to be adequate for protection against fungal attack, while those associated with the 500 ml metham sodium treatment are generally lower. These poles will be resampled 7 years after treatment to track the decline in fumigant concentrations and the extent of fungal colonization. The current data has also been evaluated in comparison with the fumigant movement model under development.

5. <u>Treatment of Douglas-fir poles in</u> <u>California with MITC-FUME</u>: As a part of the evaluation of MITC-FUME, a second field trial was established in 1989 within the Pacific Gas & Electric system. Douglas-fir and ponderosa pine poles located near Half-Moon Bay and Belmont, Ca received 3 or 4 vials of MITC-FUME applied to downward sloping holes drilled in the poles beginning at the groundline and moving upward. The holes were plugged with tight fitting wooden dowels after treatment. Ten Douglasfirpoles received 3 vials, 10 received 4 vials and 10 ponderosa pine received 4 vials.

The extent of MITC movement from the vials was assessed 2, 4, and 5 years after treatment by removing 3 increment cores from three equidistant sites around the pole 0.3 nd 0.9 m above the groundline.

The inner and outer 25 mm within the untreated heartwood zone of the cores was then placed into glass tubes containing 5 ml of ethyl acetate which was used to extract any residual MITC from the wood. The extracts were then analyzed for residual MITC as described in Section IA-4. The residual wood from the core was then cultured on malt extract agar for the presence of decay fungi. No viable decay fungi grew from any of the core samples 2, 4 or 5 years after treatment, suggesting that the treatment remained effective 5 years after treatment.

MITC levels generally rose between 24 and 48 months in both pine and Douglasfir (Table I-7). Levels after 48 months were slight higher than those found with the Douglas-fir poles in the Corvallis site. Inset Examination of treatment holes 24 months After 60 monafter treatment indicated that residual MITC remained in most of the tubes examined 200% a 2cw. These results compare favorably with those $C_{175}^{+a^{1}5}$ found in small pole sections and suggest that te mained. MITC release from the treatment holes occurs relatively slowly. While this has some major advantages from the perspective of providing controlled release of fumigant into the wood, some utilities have expressed concern about the presence of concentrated fumigant in a treatment hole for many years Fumigant levels in the after treatment. wood declined in the outer zone in most cases between 4 and 5 years after treatment, but levels were more variable in the inner zone. The inner zone should be more stable

						Residual MITO	C (µg/g wood) [∗]					
				Half-M	oon Bay		Belmont					
	Dosage	Months in	0.3	3 m	0.	9 m	0.3	3 m	0.9) m		
Wood Species	(g)	Test	outer	inner	outer	inner	outer	inner	outer	inner		
Douglas-fir	90	24	30	81	0	\$ 10	56	138	89	*2		
		48	54-71	- 255 309	93/23	174 184	7	174	9	70		
		60	22	306	4-19	-114 99	24	146	0	12		
	120	24	60	938	3 5	165	8 6	124 /74	1	15		
		48	270	568	204	267	49	245	20	108		
		60	30	706	27	32-321	36	322 202	4	7262		
Ponderosa	120	76 24	63	13 0 210	61 19	80 25	89 89	80 ,184	8 X Z	3 6 8		
		48	8	69	14	20	10	28 51	9	39 64		
		60	84	92	¥Z	30	14 22	92 84	26	16-13		

Table I-7. Residual methylisothiocyanate in Douglas-fir and ponderosa pine utility poles 2, 4, and 5 years after treatment with 3 or 4 vials of MITC-Fume.

«Values represent means of 30 analyses per sampling site.

with regard to fumigant concentrations since it is more buffered against dramatic changes in temperature or moisture content and the reasons for this anomaly are, as yet unclear. MITC levels were also higher in the Douglas-fir poles. MITC levels in Douglasfir in the Corvallis field trials were generally lower than those found with southern pine. Ponderosa pine is normally considered to be equal in treatability with southern pine and the nature of the chemical retention and diffusion differences are unclear. Further monitoring of these poles is planned.

B. EVALUATE PREVIOUSLY ESTABLISHED TRIALS OF NON-VOLATILE REMEDIAL INTERNAL TREATMENTS

While we have concentrated heavily on the identification of more effective wood fumigants, we have also examined several non-volatile diffusible fungicides including boron and fluoride based systems. Both boron and fluoride have significant advantages in terms of safety and ease of application, but there is relatively little data on the diffusion of these compounds in western wood species.

1. <u>Ability of fused borate rods to</u> <u>diffuse through Douglas-fir heartwood</u>: Douglas-fir poles sections were treated with 2 % chromated copper arsenate by dipping, then stored under cover for 24

hours to permit fixation to occur. A 1.9 cm diameter hole was drilled through the pole 40 cm from the top and a single galvanized bolt was inserted into the hole. A second 20 cm long hole was drilled 15 cm above the bolt and 40 or 80 g of fused boron rod (1 or 2 rods) was added. The holes were plugged with tight fitting dowels and the poles were exposed out of ground contact at Corvallis, OR or Hilo, Hawaii. Poles were sampled one year after treatment by removing increment cores from sites above and below the treatment hole. The results indicated that very little boron had diffused into the wood over the first year of the test at either exposure site. Discussions suggested that the boron may have diffused completely out of the poles after the first year.

The poles at Corvallis were sampled this past winter by removing increment cores from sites above and below the sites for boron application. The cores were sprayed with the curcumin/ salicylic acid indicator and any boron penetration was measured. The cores were then divided into inner and outer zones and segments from a given location with a treatment group were combined prior to grinding to pass a 20 mesh screen. The ground wood was sent to CSI (Charlotte, NC) for analysis. We are currently awaiting the results, which will be reported in the next annual report.

2. <u>Performance of fused borate</u> rods in groundline treatments of Douglasfir poles in Owego, New York: As a part of the evaluations of fused boron rods as internal decay treatments, a second field trial of these materials was established at a site near Owego, NY. Douglas-fir poles were presampled by removing increment cores from sites near the groundline. These cores were cultured for the presence of decay fungi and the poles were segregated into 4 treatment groups of 6 poles each. Poles received 3 (120 g) or 6 (240 g) fused borate rods and either 0 or 150 ml of water at the time of treatment. The poles were sampled 16 months after treatment by removing increment cores from 3 sites around each pole 0, 0.3, and 0.9 m above the groundline. Analysis of these cores for the presence of boron indicated that little boron movement have occurred over the test period ('92 Annual Report, pages 25-27). This past winter, additional cores were removed by NYSE&G personnel from selected poles at sites located 150 mm above and 75 or 225 mm below the location of the rod application site. Cores were initially sprayed with the salicylic acid/curcumin indicator specific for boron. Cores were ground and extracted in hot water, then analyzed for boron using the Azomethine H method. The analysis of these cores is nearly complete and will be included in the next annual report.

3. Effect of Boracol and other glycol based materials on movement of boron from fused borate rods. While fused borate rods are increasingly employed by utilities for controlling internal decay of wood poles, our data suggests that the effectiveness of these treatments is questionable. Because of concerns about the effects of wood moisture on boron movement, we have proposed the establishment of an additional test which will include moisture measurements in poles as well as the inclusion of treatments to enhance boron diffusion. Laboratory trials: Douglas-fir heartwood blocks (38 by 88 by 150 mm long) will be pressure soaked with water to increase the moisture levels to between 80 and 130%. Blocks will then be aerated until their moisture levels equilibrate to 30 or 60%. An additional set of blocks will be equilibrated to 15% moisture content in a constant temperature room. As the blocks reach their desired moisture level, they will be dipped in molten paraffin to retain moisture. The blocks will then be stored at 5 C for 30 days to allow further equilibration of moisture.

A single treatment hole (15 mm by 50 mm long) hole will be drilled into the center of the tangential face of each block. Fused borate rod will be added to holes in 12 blocks to produce a boron acid equivalent of 6.0 kg/m^3 . Additional blocks will be treated with combinations of fused borate rod and 5 ml of Boracol 40. Boracol 20, Boracare, or Timbor (at equivalent BAE's) in ratios of 2:1 or 1:1 (rod: liquid) on a boric acid equivalent basis. Where necessary, the holes will be widened to accommodate additional chemical. Additional blocks will receive glycol plus boron rod to serve as controls. The holes will be plugged with tight fitting rubber stoppers and the blocks will be incubated at room temperature for 4, 8, or 12 weeks.

At each time point, four blocks per treatment (moisture content/chemical dosage) will be examined for boron distribution by cutting a series of 5 mm thick sections from each end of the block. Sections corresponding to 5 to 10, 20 to 25, 40 to 45 and 55 to 60 mm from each end of the block will be oven dried over night at 54 C, then sprayed with salicylic acid/curcumin extract to detect the presence of boron. Boron penetration will be assessed visually and photographs will be taken of wafers from each treatment group. The wafers will be segmented into an outer 8 mm zone around the circumference and an inner core. Each zone will then be ground (to pass a 20 mesh screen), extract and analyzed by ICP.

The results should provide a relative guide to the extent of boron diffusion under different moisture regimes in the presence or absence of additives.

Field trials: A series of 30 pole Douglas-fir pole sections (25 to 30 cm in diameter by 2.1 m long) have been installed at the Peavy Arboretum test site. One half of the poles will be equipped with overhead sprinklers and these poles will be subjected to a daily 2 hour watering period during the period between June and September to encourage higher internal moisture contents.

Three 20 mm diameter by 150 mm long holes will be drilled horizontally into the poles at three equidistant points around the pole 15 cm below groundline. Each hole will receive a single boron rod (12.5 mm in diameter) alone or combinations of boron rod and Boracol 40 or Timbor in water to produce an effective boric acid equivalent dosage of 150 g. The treatment holes will then be plugged with tight fitting plastic plugs.

The poles will be sampled for boron content annually by removing increment cores -300, 0, and 300 mm from the groundline from 3 equidistant sites around the pole in line with the original treatment holes. The cores will be divided into inner and outer halves and each core segment will be weighed. These cores will then be oven-dried and reweighed to determine wood moisture content at time of sampling. Cores from a given individual treatment and sampling location will be combined prior to being ground and analyzed as above.

In addition to the boron movement studies, the moisture distribution in each pole will be studied using Time Domain Reflectometry. In this procedure, the dielectric constants are monitored using parallel steel probes inserted into the wood. Previous studies suggest that this technique can provide reliable in situ moisture measurements. Since moisture is critical for boron diffusion, determining moisture profiles in poles nondestructively would provide important collaborating data. Selected poles will be equipped with sensors to depths of 25, 75, and 150 mm at groundline, 150 mm below groundline, 150 mm above groundline, and 300 mm above groundline. These sensors will be

monitored weekly initially, then monthly as conditions within the poles stabilize. We would plan to install sensors on one pole per treatment, but would consider additional poles if the technique proves useful. In the event the technique fails to produce reliable data, we would establish additional poles which would be destructively sampled for moisture levels by removing increment cores from the same locations as those described for the boron sampling. These cores would be divided into outer (sapwood), outer heartwood, and inner heartwood zones and each sample would be weighed in the field, oven dried (105 C for 24 hours) and reweighed to determined moisture content.

The results of these studies should provide data on the effects of moisture content on boron movement as well as information on seasonal moisture distribution in wood poles. The latter data may be especially useful for explaining the distribution differences found in many boron tests.

C. EVALUATE PROMISING NEW TREATMENTS UNDER FIELD CONDITIONS

1. Evaluate the efficacy of Basamid in Douglas-fir utility poles: In previous reports, we have described tests to evaluate the various additives for enhancing the decomposition of solid Basamid into MITC in wood. Last year, we established a field trial in which Douglas-fir poles which had been in service for 1 to 2 years were treated with 200 or 400 g of Basamid alone or amended with 1 % copper sulfate. The Basamid was applied to three steeply angled 17 mm diameter by 300 mm long holes drilled at equidistant points around the groundline beginning at groundline and moving upward at 150 mm intervals. The holes were plugged with tight fitting dowels. An additional set of poles was treated with 500 ml of liquid metham sodium to serve as a comparative control. Each treatment was replicated on 6 poles.

The poles were sampled one year after treatment by removing increment cores from equidistant points around the pole 150, 450 and 900 mm above the highest treatment hole. The outer, preservative treated shell was discarded and the inner and outer 25 mm of the remaining core were extracted in 5 ml ethyl acetate at room temperature for 48 hours prior to gas chromatographic analysis. The poles were sampled earlier this summer and the results will be reported in the next annual report.

2. Evaluate the efficacy of a fluoride/boron based internal remedial treatment: While we continue to develop solid fumigants such as basamid, a number of alternative diffusible treatments with potential for arresting internal decay in poles have also been commercialized. The sodium fluoride/boron rod formulation (24.3 % sodium fluoride/58.2 % disodium octaborate tetrahydrate) rod was developed and commercialized in Australia. We have installed 40 pentachlorophenol treated Douglas-fir poles (250-300 mm in diameter by 2.4 m long) drilled with one of four treatment patterns:

a. 3 holes beginning at groundline and moving upwards at 0.3 m height increments and spiraling around the pole at 120° intervals.

b. 3 holes beginning at groundline and moving upwards at 0.3 m height increments and spiraling around the pole at 90° intervals.

c. 6 holes beginning at groundline and moving upwards at 0.15 m height increments and spiraling around the pole at 120° intervals.

d. 6 holes beginning at groundline and moving upwards at 0.15 m height increments and spiraling around the pole at 90° intervals.

Each treatment hole received a single 23 g rod and was plugged with a tight fitting wood dowel. The poles were sampled one year after treatment by removing increment cores from sites 150 mm above and below the treatment zone as well as in the center of this zone. The outer, preservative treated shell was discarded and the remainder of the core was divided into equal sections corresponding to inner and outer zones. Cores from a given height within and individual treatment were combined and ground to pass a 20 mesh screen prior to analysis for boron using the Azomethine H-A2 method or for fluoride using AWPA Standard A5. The samples from these poles have been taken and the boron analysis is nearly completed. The results will be reported in the next annual report.

3. Evaluation of gelled and pelletized metham sodium in Douglas-fir poles: While metham sodium remains the most widely used fumigant owing to it low volatility and ease of handling, concerns about the use of liquid fumigants have encouraged a search for safer formulations of this fumigant. Previously, we have reported on the use of pure sodium nmethyldithiocarbamate as a wood fumigant, and while this chemical was effective, it is not commercially available. Several years ago, however, we examined two metham sodium formulations which were developed for applications in hot climates, where traditional liquid metham sodium volatilized too quickly to be effective as a soil fumigant. These formulations were based upon pelletizing and gelling the metham sodium. The gelled formulation contains 40 % by

weight of NaMDC, while the pelletized version contains 25 % by weight of this chemical. Preliminary laboratory trials indicated that this formulation was as effective as the conventional liquid metham sodium.

Field trials were then established in which 50 ACZA Douglas-fir poles (250 to 300 mm in diameter by 3.6 m long) were set to a depth of 0.6 m at the Peavy Arboretum test site. Three steeply angled 19 mm diameter by 225 mm long holes were drilled into the pole beginning 0.9 m above the groundline, moving upward in 150 mm increments and spiraling 120 degrees around the pole. The poles were treated with 100, 200, 300, or 750 g of gelled metham sodium applied using a large bore syringe or with 100, 200 or 300 g of 25 % pelletized metham sodium. An additional set of poles were treated with 750 g of 40 % gelled metham sodium 6 months after the initial trial was begun. All treatment holes were plugged with tight fitting wooden dowels to retard fumigant loss. Each treatment was replicated on 5 poles per treatment.

Funigant performance was assessed 6, 12, and 24 months after treatment by removing 3 increment cores from equidistant sites around the poles 0.3, 0.9, and 1.5 m above the highest treatment hole. The inner and outer 25 mm of each core were placed into 5 ml of ethyl acetate and stored for 48 hours at room temperature. The ethyl acetate was then examined for residual fumigant content using the gas chromatograph. The remainder of each core was then evaluated for residual fungitoxic fumigant levels using the closed tube bioassay with <u>Postia</u> <u>placenta</u> as the test fungus. Inhibition was assessed on the basis of the ability of the fungus to grow in the absence of wood.

Closed tube bioassays indicate that the residual fumigant levels have declined only slightly between 1 and 2 years after treatment in both the pelletized and gelled metham sodium treatments (Table I-8). These values compare favorably with those found with the 500 ml metham sodium treatment in the MITC-Fume trials and suggest that both of the modified metham sodium formulations will provide protection which is comparable to that found with the liquid formulation.

Gas chromatographic analyses of extracts of wood removed from the treated poles produced results which followed trends which were similar to those found 1 year after treatment. MITC levels 0.3 m above the treatment zone were generally low, but increased with increasing dosage (Table I-9). There appears to be relatively little difference in MITC levels between the inner and outer zones of the core, suggesting that the fumigant distribution had become relatively uniform near the original treatment zone. Fumigant levels 0.9 and 1.5 m above the treatment zone were extremely low and these results conflict with those from the closed tube bioassays, which showed substantial residual inhibition in this zone. The closed tube bioassay provides a relative measure of residual protection which is extremely sensitive to fumigant and which also reflect, to a limited extent, the presence of any volatile heartwood extractives.

Chemical levels in the pelletized metham sodium treated poles appeared to be slightly higher than those in treated

Table I-8. Degree of inhibition of <u>Postia placenta</u> in a closed tube bioassay of wood samples removed from selected heights of Douglas-fir poles 6, 12, or 24 months after treatment with gelled or pelletized metham sodium.										
		Fungal growth as % of control at selected sampling heights*								
		0.3 m			0.9 m		1.5 m			
Chemical	Dosage	6 mos.	12 mos.	24 mos.	6 mos.	12 mos.	24 mos.	6 mos	12 mos.	24 mos.
40% Gelled Metham sodium	100 200 300 500 750	48(46) 46(39) 17(24) 30(29) 37(12)	18(13) 15(11) 16(15) 15(13)	22(12) 13(12) 13(15) 15(12) 37(12)	62(46) 60(44) 39(38) 58(42) 29(11)	20(13) 14(11) 17(16) 23(12) -	20(12) 18(15) 17(16) 23(12) 19(11)	58(48) 41(41) 27(34) 36(43) 27(11)	21(14) 12(13) 13(14) 21(12) -	21(14) 12(13) 12(14) 21(12) 27(11)
25% Pelletized Metham sodium	100 200 300	29(37) 17(32) 50(45)	10(12) 12(12) 15(12)	10(12) 12(12) 15(12)	44(42) 37(41) 81(44)	23(13) 22(8) 20(10)	23(13) 22(8) 20(10)	20(39) 33(47) 37(52)	10(13) 15(9) 16(13)	10(13) 15(9) 16(13)

* Values represent means of 15 replicates while those in parentheses represent one standard deviation.

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Table I-9. Residual MITC levels in Douglas-fir poles for 6, 12,	or 24 months after treatment with gelled or pelletized metham.
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			MITC level (ug/g oven-dry wood) at selected sampling heights ⁴								
			0.3 m			0.9 m			1.5 m		
Chemical	Dosage (g)	Sampling zone	6 mos	12 mos	24 mos	6 mos	12 mos	24 mos	6 mos	12 mos	24 mos
40% Gelled		(mm)									
Metham sodium	100	0-25 50-75	1(3) 6(11)	1(2) 3(6)	1(2) 3(6)	1(2) 4(10)	0(0) 3(6)	0(0) 0(0)	0(0) 0(0)	0(0) 0(0)	0(0) 0(0)
	200	0-25	1(4)	0(0)	0(0)	1(3)	0(0)	0(0)	0(0)	0(0)	0(0) 0(0)
	300	50-75 0-25	3(8) 4(6)	3(5) 5(9)	5(5) 5(9)	0(0)	2(2) 0(0)	2(2) 0(0)	0(0)	0(0)	0(0) 0(0)
	500	50-75 0-25 50-75	17(30) 9(14) 12(5)	11(14) 18(19) 16(16)	11(14) 18(19) 16(16)	0(0) 3(5) 2(4)	1(3) 0(0) 0(0)	1(3) 0(0) 0(0)	0(0) 2(5) 0(0)	0(0) 0(0) 0(0)	0(0) 0(0) 0(0)
	750	0-25 50-75	9(12) 6(12)	- -	9(12) 6(12)	2(4) 0(0) 4(8)	-	0(0) 4(8)	1(1) 1(2)	- -	1(1) 1(2)
25% Pelletized											
Metham sodium	100	0-25 50-75	7(11) 4(5)	5(8) 4(5)	5(8) 4(5)	0(0) 0(0)	1(0) 0(0)	1(1) 0(0)	0(0) 0(0)	0(0) 0(0)	0(0) 0(0)
	200	0-25	20(21)	5(9)	5(9)	3(6)	1(2)	1(2)	0(0)	0(0)	0(0)
	300	0-25 50-75	0(0) 22(34)	6(13) 13(15)	6(13) 13(15)	2(4) 0(0) 3(5)	1(1) 0(0)	1(2) 1(1) 0(0)	0(0) 0(0) 5(10)	1(1) 0(0)	0(0) 1(1) 0(0)

* Values represent means of 15 replicates. Values in parentheses represent one standard deviation.

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to have higher residual chemical levels. However, the differences in residual fumigant concentration at this time may reflect a number of variables including a difference decomposition rate of the initial NaMDC to MITC. The differences in performance illustrate the need to adequately evaluate formulations of the same active ingredient prior to extensive field use. While both formulations produced MITC at levels which would effect fungal control in the treatment zone, the pelletized formulation should provide a longer protective period which might make it more attractive for field use. We plan to continue monitoring these treatments until the chemical levels and degree of fungal inhibition decline to the point where a retreatment would be recommended.

4. Evaluation of metham sodium for remedial treatment of large Douglas-fir timbers: In 1990, a Douglas-fir highway bridge located north of Salem, Oregon was treated with metham sodium. At the time, there was little data on the effectiveness of this chemical in large timbers. Sawn wood should have higher levels of exposed trachieds which might provide avenues for increased fumigant loss. As a result, fumigant performance might be expected to be reduced in these materials.

Metham sodium was applied through 19 mm diameter holes drilled at 1.2 m intervals along the timbers. One year after treatment, increment cores were removed from sites near the top and bottom edge 0.6 m from each treatment hole on 7 stringers. The outer, treated shell was discarded and the outer and inner 25 mm of the untreated zone were placed in ethyl acetate. The cores were extracted for 48 hours prior to GC analysis of the extracts. The remainder of each core was cultured on malt extract agar and observed for the presence of decay fungi, which served as a measure of the protection afforded by metham sodium treatment.

Fumigant levels in the bridge stringers declined slightly in most treatments between 2 and 3 years after treatment, reflecting the tendency of MITC to diffuse from the wood (Table I-10). Chemical levels varied widely between the outer and inner zones as well as from the top to bottom of the timbers; however, the differences were not consistent. The variations in fumigant levels may reflect the increased surface area exposed on the timbers, in comparison with poles. In addition, timbers would tend to have more exposed open fibers which would provide avenues for fumigant loss to the wood surface. As a result, chemical levels might be expected to vary more widely than in comparably treated poles. Despite the variations in MITC levels in the timbers, fumigant levels remain at levels which should prevent recolonization of the wood, particularly above the ground.

Culturing of increment cores indicated that no viable decay fungi were present in the timbers 2 or 3 years after metham sodium application (Table I-11). The results should be viewed with caution since only a small number of cores contained viable decay fungi 1 year after treatment and the wood was not sampled prior to treatment to determine initial levels of colonization; however, the absence of fungi suggests that fungitoxic levels of MITC remain in the wood.

determined by gas entonialographic analysis of early acease extracts of wood samples.								
		ug MITC/OD g wood						
			Inner		Outer			
Structure #	Stringer Position	1 year	2 years	3 years	1 year	2 years	3 years	
5	Тор	4.3	52.3	9.7	0.00	27.6	3.3	
	Bottom	59.7	34.7	31.1	24.5	112.4	84.1	
10	Тор	40.2	136.1	71.3	53.2	60.3	76.4	
	Bottom	75.8	114.9	43.0	39.9	59.4	116.3	
15	Тор	27.3	66.1	46.4	37.4	59.5	145.4	
	Bottom	16.0	99.7	17.8	24.3	112.9	43.4	
20	Тор	26.2	115.5	58.2	65.4	130.6	44.6	
	Bottom	82.7	42.6	67.7	23.2	19.9	163.1	
25	Тор	26.5	80.2	40.7	13.1	44.4	52.5	
	Bottom	33.4	83.3	86.0	65.5	95.4	32.1	
30	Тор	73.2	126.8	77.5	100.3	98.5	70.2	
	Bottom	83.6	40.8	83.3	75.8	63.7	49.3	
35	Тор	44.1	74.1	108.7	60.6	120.8	56.5	
	Bottom	14.0	75.1	19.2	9.2	42.4	8.8	
40	Тор	-	50.1	-	-	140.4	-	
	Bottom	-	92.1	-	-	56.7		
	Тор	34.5	87.7	58.9	47.1	85.3	64.1	
Average (Std.)	Bottom	52.3	72.9	49.7	37.5	70.4	71.0	

Table I-10. Residual MITC content in Douglas-fir bridge stringers one or two years after metham sodium treatment as determined by gas chromatographic analysis of ethyl acetate extracts of wood samples.

Table I-11. Levels of colonization by Douglas-fir timbers 1 to 3 years after application of metham sodium as measured by culturing increment cores.

		Cores With Decay Fungi (%) ^a					
Structure #	Stringer Position	1991	1992	1993			
5	Тор	0	0	0			
	Bottom	0	0	0			
10	Тор	0	0	0			
	Bottom	0	0	0			
15	Тор	17	0	0			
	Bottom	0	0	0			
20	Тор	0	0	0			
	Bottom	0	0	0			
25	Тор	17	0	0			
	Bottom	0	0	0			
30	Тор	0	0	0			
	Bottom	0	0	0			
35	Тор	17	0	0			
	Bottom	0	0	0			
Average	Top Bottom	0	0	. 0			

" Values represent means of 6 cores/treatment

The results suggest that application of fumigants to above ground timbers such as cross arms might be an effective method for arresting decay in these members, although the use of non-liquid formulations would be essential for this purpose.

1. <u>Distribution of chloropicrin in</u> <u>Douglas-fir poles 1 to 7 years after</u> <u>remedial treatment</u>: Fumigants are widely used in North America to arrest and prevent internal decay of large timbers and poles. Of the fumigants registered for wood application, chloropicrin remains among the most effective, providing more than 20 years of protection against renewed fungal attack. It is believed to have strong interactions with wood, although the nature of the interactions remains unclear.

While chloropicrin is widely used for treatment of uninhabited wood structures, there is relatively little data on the residual levels in wood. Such information has become increasingly important as utility companies assess the full effect of use and attempt to determine if residual chemicals pose a risk for disposal. Knowledge of residual chemical levels can also provide clues to the effective protective period for various treatments.

In this note, we describe an evaluation of residual chloropicrin in Douglas-fir poles 1 to 7 years after remedial treatment.

Creosote- and pentachlorophenol-treated Douglas-fir poles (belonging to Consumer's Power Inc., Corvallis, OR) that had been remedially treated by an inspection agency were randomly selected for study. The poles were primarily distribution and small transmission poles that had been in service as long as 30 years in the Willamette Valley of western Oregon.

Fifteen poles were sampled for each of four time intervals since fumigation: 1, 3, 5, and 7 years. All poles had been remedially treated with 250 ml of chloropicrin applied to three steeply sloping holes drilled in a spiral pattern starting near the groundline and moving upward 0.3 m around the pole 120 degrees. The holes had been plugged with tight-fitting wooden dowels immediately after treatment.

Poles were sampled by removing 150-mm-long increment cores from three locations 120 degrees apart at 0.3 and 0.9 m above the groundline. In general, samples were removed from the lower and upper regions of the fumigated zone. After the zone containing creosote or pentachlorophenol was discarded, the outer and inner 25-mm of each core were individually placed into screw-cap test tubes containing 5 ml of hexane and extracted for a minimum of 48 hours at room temperature. The core portions were then stored at 5°C until analysis.

The hexane extracts were analyzed with a Varian 3700 gas chromatograph equipped with a ⁶³Ni electron capture detector. Column conditions were as follows: injector temperature 60°C, column temperature 60°C, detector temperature 100 °C, and nitrogen carrier gas flow 35 ml/minute. Separation was achieved by means of a column (1.5-m long x 2-mm inner diameter) packed with Supelco-port 100/120 mesh coated with 20 percent SP-2100 and 0.1 percent Carbowax 1500 (Supelco, Inc. Bellfonte, PA).

Residual chloropicrin was detected in every pole sampled, although values varied widely within poles treated in a given year (Table I-12). The differences reflect the natural variation in the wood and the commercial treatment, which did not require precisely metered dosages in carefully spaced treatment holes. However, the results are those that most utility companies might expect to find in poles at the selected times since treatment.

Chloropicrin levels were generally highest in the lower regions of the fumigated zone, a trend also noted for western redcedar (8), because the downward sloping holes direct the chemical in that direction.

As expected, chloropicrin levels were also higher in the inner zones because the treatment holes directed fumigant toward the center of the pole. The levels varied more widely in the outer assay zone, possibly because the wood there is more affected by annual variations in weather. Not surprisingly, since fumigants normally diffuse from high to low concentration with time and eventually dissipate from the wood, the chloropicrin levels tended to decline with increasing time since treatment, although the rate of decrease was not linear. Previous studies of fumigant-treated southern pine utility poles have found chloropicrin levels that are approximately one-tenth of those found in the poles in this study after comparable time intervals. The difference probably reflects the different permeability of southern pine to chloropicrin. High residual chloropicrin levels were noted in a study of redcedar pole stubs 5 years after treatment, but since those poles were stored indoors, the levels may not be representative of those found in poles exposed outdoors.

The amount of chloropicrin required for preventing colonization by decay fungi in Douglas-fir heartwood remains poorly understood. Previous studies have noted little difference in attack patterns in chloropicrin-treated and control wafers under laboratory conditions. The variety of fungi isolated from Douglas-fir poles after chloropicrin treatment have included some that are considered antagonistic to conventional decay fungi. Very few basidiomycetes have been isolated from Douglas-fir poles even 20 years after treatment. No basidiomycetes were found in southern pine poles 7 years after chloropicrin treatment, although soft rot fungi had colonized much of the substrate. Soft rot fungi do not appear to be a significant problem with most Douglas-fir poles, although they are a prevalent mode of attack in Douglas-fir treated with pentachlorophenol by the Cellon process. Thus, the apparent resistance of soft rot fungi to chloropicrin does not appear to pose a challenge to the use of this treatment in Douglas-fir.

The results of this study confirm that marked levels of chloropicrin remain in Douglas-fir poles up to 7 years after treatment. At the current rate of loss, the fumigant should remain detectable for many more years, although the level at which wood protection is lost remains undetermined.

2. Effect of mixtures of methylisothiocyanate and carbon disulfide on survival of wood colonizing fungi: Fumigants are widely used in North America to arrest and prevent internal decay of electric utility poles and other large wood members in service. Of the fumigants used for this purpose, metham sodium (32.7% sodium nmethyldithiocarbamate) is the most commonly used chemical. This chemical is not highly fungitoxic, but decomposes in the presence of organic compounds to produce a variety of highly fungitoxic compounds including methylisothiocyanate (MITC). The toxicity of MITC to wood degrading fungi has been the subject of extensive study and its behavior under varying regimes is well-documented. Metham sodium decomposition in soil produces significant levels of MITC under a variety of conditions, although a variety of other decomposition products are possible. A number of studies suggest that MITC is a relatively minor component of metham sodium decomposition in wood, with substantial amounts of carbon disulfide and carbonyl sulfide being produced. While the latter two compounds can be fungitoxic, the levels required far exceed those produced by metham sodium decomposition. Furthermore, neither of these compounds has substantial interactions with the wood, and thus remain in the wood for only short periods after treatment. Despite these characteristics, metham sodium provides

good protection to wood poles over a 7 to 10 year period for Douglas-fir poles and 3 to 5 years for southern pine poles. This performance may reflect synergistic interactions with various decomposition products which enhance fungitoxicity of the treatment; however, there is little data to support this premise in wood. In this report, we describe the effects of carbon disulfide and MITC, alone or in combination, on survival of a variety of wood colonizing fungi in wood. Blocks colonized by 6 basidiomycetes and 1 ascomycete were prepared using modifications of a previously described procedure (Table I-13).

Ponderosa pine sapwood (*Pinus* ponderosa Laws) and Douglas-fir heartwood (*Pseudosuga menziesii* (Mirb) Franco) blocks (10 by 10 by 3 mm. long) were placed in autoclavable plastic bags equipped with a single breathable patch. Approximately 100 g of vermiculite (fine grain) and 700 ml of distilled water were added to the bags which were loosely sealed prior to autoclaving for 20 min at 120 C. The bags were then inoculated with a macerated hyphal/spore mixture of the respective fungus.

Basidiomycete inoculum was prepared by placing a small agar plug cut from the edge of an actively growing malt extract agar culture of the test fungus into a flask containing 50 ml of 1.8 % malt extract solution. The flasks were incubated at room temperature on a rotary shaker (80 rpm) for 7 to 14 days, then the mycelium was filtered, resuspended in sterile distilled water and blended for 10 seconds at approximately 11,000 rpm. The macerated mycelium mixture from a single flask was transferred to a squeezable
bottle and poured over the blocks in the plastic bags. The bags were heat sealed and incubated 20 to 30 days at 27 C. *Hormoconis resinae* was grown on 1.8% malt extract agar and the plates were flooded with sterile distilled water to dislodge conidia. The conidia were poured over the blocks in the same manner as the mycelial suspension. Colonization during the incubation period was periodically assessed by removing selected blocks from the bags and placing them on malt extract agar. Growth of the test

Table I-12.	Residual chloropicrin in Douglas-fir poles 1, 3, 5, and 7 years after remedia	1
treatment, a	shown by gas chromatographic analysis of wood extracts. ^a	

Distance above			Chloropicrin (u	g/g wood) at	
groundline (m)	Core Portion	1 year	3 years	5 years	7 years
0.3	Inner	5,905 (749)	4,834 (1,541)	2,897 (1,180)	2,255 (1,933
	Outer	1,910 (1,093)	1,188 (335)	998 (640)	469 (109)
0.9	Inner	2,276 (405)	2,752 (203)	819 (143)	865 (30)
	Outer	834 (183)	273 (42)	488 (46)	465 (83)

* Values represent the means of 45 replicates per treatment. Figures in parentheses represent one standard deviation.

^b Inner zone = the inner 25 mm of each core; outer zone = the first 25 mm inside the preservative-treated shell.

Table I-13. Fungi evaluated for sensitivity to car	bon disulfide and MITC.
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Name	Isolate #	Source
Antrodia carbonica (Overh.)Ryv&Gilbn.	L-8242-sp	FRL, Corvallis, OR
Postia placenta (Fr.) M. Lars & Lomb.	MAD	FPL, Madison, WI
Irpex lacteus (Fr.:Fr.) Fr.	FP-105915-sp	FPL, Madison WI
Trametes versicolor (L.:Fr.) Pilát.	A4CD-34	FRL, Corvallis, OR
Hormoconis resinae v. Arx & de Vries	P1600	SUNY College of Env. Sci. & For.
Gloeophyllum trabeum (Fr.) Murr.	MAD-617	FPL, Madison, WI
G. saepiarium (Fr.) Karst	S4UT	FRL, Corvallis, OR

fungus from the blocks was used as a measure of successful colonization.

The blocks were exposed to metham sodium decomposition products in a fumigation apparatus consisting of a series of five 40 ml wide mouth glass jars each capable of holding a different metham sodium decomposition product Fig. I-4). The jars were equipped with Teflon[•] lined caps to retard possible fumigant loss. Teflon[•] tubing (6 mm outer diameter) was

used to connect the jars so that different ratios of the selected fumigants could be introduced into the system. The five bottles were in turn connected to a single mixing vessel which was connected to a manifold which distributed the gas mixture to a series of twelve 135 ml glass jars. Each jar contained 10 blocks colonized by a single fungus. Flow from the fumigant jars to the mixing chamber was controlled using Teflon[®] lined control valves, while flow to individual fumigation chambers was controlled using glass restrictor tubes packed with Celite[®] (diatomaceous earth) to produce a flow of 15 ml fumigant laden air/minute. All gas flows were measured using a bubble flow meter. Fumigant concentrations were varied by increasing the flow of gas from a given fumigant component reservoir to the mixing vessel.

Air flowing through the apparatus was first humidified by bubbling through distilled water, then the air flowed over the jars containing the fumigant, through the mixing jars and finally into the jars containing the fungal colonized blocks. Fumigant flow rates were adjusted until the desired concentration of each gas was achieved, then the apparatus was allowed to operate for 24 hours prior to introduction of fungal colonized blocks.

Fumigant concentrations over the course of the trial were assessed by removing air samples from a site on the fumigation chamber in which a rubber serum cap had been inserted. For carbon disulfide, 5 ul of gas was injected into a Varian 3700 Gas Chromatograph equipped with a Flame photometric detector with filters specific for sulfur. The GC conditions were as follows: nitrogen flow rate 33.3 ml/minute; detector temperature 240 °C; injector temperature 150 °C and column temperature was at 40 °C. Separation was achieved using a 3 m long by 4 mm inner diameter column packed with 10 % Carbowax 20M on 80/100 Supelcoport (Supelco, Bellefonte, PA). For methylisothiocyanate, 200 ul air samples were injected. GC conditions were similar except that column temperature was increased to 110 °C.

The fumigant chamber was first employed to evaluate the fungitoxicity of 0.5, 3-4 and 8-9 mg of carbon disulfide per ul of air or 5, 10, and 18 ng MITC/ ml of air. The results from these trials indicated that 3 to 4 ng of carbon disulfide and 5 ng MITC were sublethal exposures rates and the effects of a mixture of these two gases at the sublethal level was then evaluated.

Fumigations were carried out over 10 day periods. Each day, one block colonized by each fungus species was removed from each chamber and aerated to permit the fumigant to dissipate. The aerated block was placed into a 36 ml stainless steel canister containing a stainless steel ball and 5 ml of sterile distilled water. The canister was shaken for 5 seconds using a Kleco[•] 4100 Pulverizer (Kleco Kenetic Manufacturing Co., Visalia, Ca). After maceration, the steel ball was removed using a magnetic stir bar wand, and the macerated wood suspension was diluted to 30 ml with additional distilled water. A 1.5 ml aliquot of the suspension was added to 10 ml of molten (45 °C) 1.8 % malt extract agar and the mixture was poured into a petri dish and allowed to solidify. Three plates were prepared from each macerated block. The plates were incubated at room temperature and the number of colonies which developed in each plate were counted. These results were compared with colony counts of similar blocks which were not exposed to the fumigants. The data were expressed as number of colony forming units to reflect the possibility that colonies could arise from both hyphal fragments and spores. The data were used to construct concentration x time (CT) curves to assess the amount of chemical necessary to kill each fungus at selected exposures.

The number of CFU's (colony forming units) varied widely between the fungal species, reflecting both the sensitivity of each species to the isolation procedures as well as the presence or absence and relative amounts of conidia or chlamydospores in the wood (Tables 2-4). Hormoconis resinae produced the largest number of CFU's reflecting the massive sporulation which is a common feature of this fungus. Irpex lacteus produced the smallest number of CFU's and showed the highest sensitivity to both fumigants. The absence of asexual spores or other special survival structures and the presence of thin to slightly thickened generative hyphae help explain the sensitivity of this fungus.

In addition to the variation between fungal species, CFU's in some nonfumigant exposed control blocks tended to decline slightly over the 10 day test period. This effect was more noticeable in *I. lacteus* than in any other species. Efforts were made to humidify the atmosphere by bubbling the air used in the test apparatus in distilled water before it passed over the blocks. Condensation was noted on the walls of the tubing along the line, indicating that moist air was reaching the blocks but signs of dryness appeared after 7 or 8 days. CFU declines in controls may reflect loss of viability due to drying during the exposure period, although declines did not always occur. For example, CFU's of *A. carbonica* growing on pine increased with time. Despite declines in some species, differences between control and chemically exposed samples were generally of a magnitude which permitted comparisons between the treatments.

Carbon disulfide: Fumigations with carbon disulfide appeared to stimulate the number of CFU's in most of the treatments between the first and fourth day of exposure. Increases in CFU's exceeding 350 % with *P. placenta* on Douglas-fir and pine were obtained.

The lowest level of carbon disulfide (500 ppm) had minimal effect on CFU's for all the species tested. As with the controls, CFU's for *G. saepiarium* and *H. resinae* exceeded 100% after ten days of fumigation. Many fungi produce thickwalled chlamydospores which are able to withstand long exposures under adverse environmental conditions or the presence of toxic substances. *Antrodia carbonica* produced large amounts of thick-walled chlamydospores while none were observed for *I. lacteus* which was less tolerant to the treatments does not produce chlamydosproes.

Some fungi growing under sulfurdeficient regimes have been shown to be more resistant and even stimulated when fumigated for two hours with MITC. Sulfur is necessary for fungal growth and reproduction. The ability of fungi to oxidize sulfur *in vitro* has long been recognized. Sulfur content in wood is generally less than 0.1% for species such as Douglas-fir and pine. It is possible that some fungi metabolize MITC or CS_2 to satisfy sulfur needs. These effects may help to explain the initial stimulation in CFU's observed in most of the species fumigated with CS_2 , although more refined studies of sulfur balance in fumigated fungi would be required to confirm this effect.

Differences in the number of CFU's between species reflect the ability to react to environmental changes, especially with regard to amount and types of resistant structures produced (Table I-14). For example, G. trabeum was characterized by high CFU's at the beginning of fumigation, but these levels declined rapidly with time, suggesting this species was very susceptible to fumigation under the conditions of this experiment. Both G. trabeum and G. saepiarium produce large amounts of thin-walled arthrospores, which may be less resistant to fumigation than chlamydospores. Trametes versicolor was also stimulated by fumigation, but the values obtained for this species were extremely variable.

Increasing carbon disulfide levels to 3000 to 4000 ppm produced declines in CFU's for virtually all of the fungi tested, but this level was only toxic to *I. lacteus* on Ponderosa pine. Several other fungi experienced declines in CFU's which exceeded the controls, but none succumbed to this fumigant level.

Exposure to 8000 to 9000 ppm of carbon disulfide resulted in decreased CFU's for all of the fungi tested, although several species survived a 10 day exposure to this chemical level. Initial stimulation of CFU's were again noted for A. carbonica, P. placenta, or G. saepiarium on Douglas-fir or pine; and for I. lacteus and T. versicolor on pine. Very low levels of survival were noted with P. placenta on both pine or Douglas-fir, A. carbonica on pine, T. versicolor on pine or Douglas-fir and G. saepiarium on Douglas-fir upon prolonged exposure, suggesting that the fumigant might be effective upon even longer exposures. Drying of wood in the fumigation system in longer exposures would, however, cause a corresponding decrease in CFU's as a result of desiccation, obscuring potential fumigation effects. Several fungi, including A. carbonica on Douglas-fir, H. resinae on Douglas-fir or ponderosa pine, and G. saepiarium on ponderosa pine were relatively unaffected by exposure to 8000 -9000 ppm carbon disulfide. Antrodia carbonica is an important colonizer of Douglas-fir heartwood and the survival of this species in the presence of carbon disulfide would be a major drawback if this fumigant were the only decomposition product of metham sodium. Similarly, G. saepiarium is an important colonizer of untreated pine, although studies suggest that this species is not an important colonizer of preservative treated southern pine (Zabel et al, 1980). The survival of H. resinae at the highest carbon disulfide level is not surprising in the light of the well known tolerance of this species to a variety of biocides. This fungus was occasionally isolated from Douglas-fir poles, but was the most frequently isolated fungus from creosote-treated southern pine utility poles. The possible effects of this fungus on residual fumigant levels in wood are unclear. Hormoconis resinae is capable of utilizing creosote as a sole

carbon source but its ability to utilize carbon disulfide is unknown.

These results demonstrate that exposure of wood colonized by various decay and non-decay fungi to low levels of carbon disulfide reduces the numbers of CFU's in the wood but these levels were generally not lethal. Metham sodium is a relatively short lived treatment characterized by reinvasion of poles by decay fungi starting only 3 to 7 years after treatment. The limited residual time of NaMDC in the wood may permit survival of fungal propagules in zones where diffusion of decomposition products is limited. These zones might include wet pockets, knots or other wood defects. If decomposition conditions shift heavily towards production of carbon disulfide, selected fungi may survive as chlamydospores and later be able to germinate as conditions again become suitable for microbial growth.

Fungitoxicity of MITC: As expected, MITC had a more dramatic effect on the number of CFU's than carbon disulfide for all the species in the study (Table I-15). As with carbon disulfide, an initial stimulus of CFU's was noted during the first two days of fumigation, especially for the 5 and 10 ppm MITC treatments. In some cases, this effect was also noted for the 18 ppm treatment.

The lowest concentration tested (5 ppm) produced declines in CFU's for most species except for *A. carbonica* on Douglas-fir (Table I-15). High levels of CFU's were found with *P. placenta* on pine, and *T. versicolor* on both pine and Douglas-fir. *Trametes versicolor* showed a

significant increase in CFU's after the fifth or sixth day of exposure during this fumigation. This effect may reflect delayed stimulation under low fumigant concentrations, but the reasons for this lag in effect are unclear. Little or no fungal survival was found with I. lacteus on pine or Douglas-fir and both G. saepiarium and G. trabeum on pine or Douglas-fir. The presence of even limited surviving CFU's could be an important factor in wood "reinvasion" by fungi at points away from the fumigant application point were MITC levels might be expected to be low. The possibility of a surviving microflora in fumigated treated poles merits further study. Fungal recolonization of some wood species is often quite slow and the species present appear to differ from those found in non-fumigant treated wood. Survival structures of some fungi may play a major role in this process.

Exposures to 10 ppm MITC produced a faster decline on CFU's for all species (Table I-15). Irpex lacteus, G. trabeum and G. saepiarium growing on both pine and Douglas-fir showed rapid declines in CFU's until the seventh to ninth day when these species succumbed. Initial increases in CFU levels were also evident in most species during the first days of treatment as in carbon disulfide and 5 ppm MITC fumigations but the CFU's were much lower. Only A. carbonica and H. resinae survived a ten day exposure to 10 ppm MITC and even these species experienced marked CFU declines compared to the carbon disulfide and 5 ppm MITC treatments.

The highest rates of CFU decline were achieved with the 18 ppm MITC treatment. Only *A. carbonica* on Douglasfir and *H. resinae* on pine or Douglas-fir produced viable colonies after 10 days of fumigation, although CFU levels were only 1 % of those found with the untreated controls.

Fungitoxicity of the MITC - CS_2 mixture: Since both MITC and carbon disulfide are produced during NAMDC decomposition, these products may act synergistically to enhance fungal control. The initial results suggested that 5 ppm MITC and 3000-4000 ppm carbon disulfide produced CFU declines which while noticeable, were not lethal. These levels were subjected to further study in combination.

The CFU stimulus noted with MITC or carbon disulfide alone was absent in the mixture; however, sampling was performed every 24 hours and a stimulus earlier in the fumigation might be missed by our procedures. Mixtures of sublethal dosages of carbon disulfide and MITC were generally more fungitoxic than MITC alone at either 5 or 10 ppm for A. carbonica on Douglas-fir, P. placenta, I. lacteus, G. trabeum and T. versicolor (Table I-16). The latter fungus exhibited increased CFU's for the 5 ppm fumigation on both pine and Douglas-fir, but this effect was absent with the mixture. Fumigant mixtures did not appear to have a noticeable effect on the number of CFU's of H. resinae or G. saepiarium in comparison to 5 ppm MITC but the mixture was more effective than carbon disulfide alone at 3000 to 4000 ppm.

Concentration time estimates:

While air concentration of a chemical is a useful measure of fumigant exposure, fumigant studies are more often expressed as concentration x time or CT values. These values reflect the total dosage to which the fungus was exposed. The CT required to reduce colony forming units to 10% of the control, or CT₉₀ provides a useful measure of chemical effectiveness.

CxT curves for sublethal dosages of each chemical alone or in the mixture show that the log of survival declined more rapidly with the mixture than with either fumigant alone with most fungi (Figures I-5-11). The effects were more variable with <u>T</u>. <u>versicolor</u> and the relationship between CT and survival changed at lower CT values. These effects again reflect the initial stimulation of CFU's previously discussed.

CxT values necessary to kill 90% (CT_{90}) of the CFU's for the fumigant mixture were generally lower than those for either carbon disulfide or MITC alone for most species. For example CT values for the mixture against A. carbonica on Douglas-fir were 5 times lower than MITC alone and over 3 times lower than CS_2 alone. The CT_{90} for the mixture for P. placenta on Douglas-fir was nearly 3 times lower than MITC or CS_2 alone. In some instances, however, CT₉₀ values for the mixture were higher than those for the individual components. CT₉₀ values for the mixture against I. lacteus on pine were 1.5 times larger than CS_2 alone, that against P. placenta was equivalent to carbon disulfide and the CT_{90} for the mixture against H. resinae on pine or Douglas-fir was similar to that found for MITC. Finally the CT_{90} values for the mixture against G. saepiarium on Douglasfir or pine were higher than that for MITC.

CT₉₀ values also tended to be higher for Douglas-fir than ponderosa pine with the 3000-4000 ppm carbon disulfide treatment. Douglas-fir heartwood is less permeable than pine sapwood; however, this effect was not evident at higher CS₂ levels (8000-9000), with MITC alone or the CS₂/MITC mixture. Douglas-fir permeability to MITC is largely influenced by wood moisture content. Very low MITC concentrations, which may not be toxic to inactive decay fungi in dry wood, become fungitoxic in wet wood. Increased susceptibility of A. carbonica to MITC in wet wood may be important in determining long-term wood protection, since fungal growth and active decay will only occur in wood above fiber saturation point. In the present study, moisture content in wood was maintained above the fiber saturation point which may help to explain the excellent fungitoxicity of the fumigants despite the low MITC concentrations employed.

The results from the present study suggest a synergism between MITC and carbon disulfide which enhances metham sodium fungitoxicity. This synergism, if present between other metham sodium decomposition products, may help to explain the relatively strong performance of this fumigant in wood.

The interactive effects of MITC and CS_2 suggest that the fungicidal action of metham sodium in wood is far more complex than previous thought. While synergistic activity among biocides is well documented, the possibility that the various metham sodium decomposition products can interact to enhance performance helps to explain the higher activity of this fumigant in wood. The results also suggest that interactions may occur among the other decomposition products. Metham sodium decomposes to over 14 possible compounds. Of these, only MITC and CS_2 have been studied in wood. Further studies using other volatile decomposition products such as methylamine and hydrogen sulfide may provide important clues concerning the factors which maximize fungitoxicity of this fumigant in wood and could be used to enhance decomposition to produce the compounds which are most likely to effect fungal control.

3. Effect of Wood Moisture Content on Diffusion of Boron Based Biocides Through Western Hemlock and Douglasfir Lumber: While there are a wide array of chemicals which can arrest fungal growth, many are less suitable for application in areas where people may come in contact with the treated wood. Some utilities have turned to the application of boron-based fungicides to the decaying wood. These formulations are based upon sodium octaborate tetrahydrate with or without varying levels of glycols. The glycols are presumed to enhance boron movement into dryer wood. As an alternative, some applicators employ fused borate rods which are applied to holes drilled into the wood.

Boron has a number of attractive properties including low mammalian toxicity, solubility in water-based formulation, and, most importantly, the ability to diffuse into wood along moisture gradients.

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s.ª	esinae	Pine		100 163	153 158	148	145	151 160 160		100	127	<u>1</u>	91	80 76	688		100 70	26 4	41 38	34	31	21 19		
of controls	Н. г	D-fir		100 96	101	104	122	126 1143 127		100	86	2 8 2	91	88	80 80 80		100 74 75	57	22	57	7 6 F	46 33		
s-fir as a %	sicolor	Pine		100 230	195 183	233	183	226 182 278		100	130	183	122	144	2 69 E		100 225	1/1	- 294 168	328	14	24 16		
or Dougla:	T. ver	D-fir		100 286	257 373	212	225 225	328 333 317		100	255	57	107	54 54	28 88 8		100 40	42 25	6 Y	202	5 % -	5 1		
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for seven sl	beum	Pine	ulfide	100 93	136	103	81 140	88 5 02	n disulfide	100	291	800	31	37	19	n disulfide	32 32	107	121	30	16	3		
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ility to prod	centa	Pine		100 152	174 144	130	172	117 133 156		8	194	180	62 52	17	4 60 64		100 370	152	22	16	0 60	0		
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sicolor	Pine		100 44 78 81 127 127 130 301 534 534 534		100 211 88 16 51 22 29 29 29 29 29 20 20 12 12 20 0		100 334 197 72 47 21 10 0 0 0	0
T. ver	D-fir		100 139 112 112 100 199 143 143 143 143 143		100 100 82 82 65 76 53 32 55 55 55		100 157 124 99 10 10 10 0 0	0
iarium	Pine		1 0 0 3 3 5 6 4 1 1 0 0 1 1 0 0 1 1 0 0 1 1 0 0 1 1 0 0 1 1 0 0 1 1 0 0 1 1 0		100 138 77 7 1 1 1 0 0 0		100 255 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0
G. saer	D-fir		100 270 293 113 113 113 113 113		100 193 123 241 21 20 0 0 0		100 552 0 0 0 0 0 1 255 0 0 0 0 0 0 1 255 0 0 0 0 0 0 1 255 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0
beum	Pine	ITC	100 114 112 125 112 112 1100 112 114	ITC	100 126 112 11 11 11 11 100 100 100 100 100 100	ITC	100 103 117 117 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0
G. tra	D-fir	500 ppm. M	100 124 124 125 126 126 126 124 100	10 ppm. M	100 84 93 3 6 0 0 0 0 0 0 0 0	18 ppm. M	100 216 1222 3 3 0 0 0	0
teus	Pine		100 127 53 53 33 22 22 22 22 22 22		100 661 17 17 0 0 0 0 0		100 4 4 6 4 6 4 6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0
I. lac	D-fir		100 146 111 111 111 111 111 111 111 111 111		100 120 337 337 337 30 11 1 1 0 0		100 59 15 15 15 100 0 0 0	0
centa	Pine		100 329 80 80 83 83 83 83 83 83 83 83 83 83 83 83 83		100 93 111 111 52 52 52 52 52 52 52 52 52 52 52 52 52		100 108 36 0 0 6 4 8 6 0 0 0 0 6 4 8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0
P. pla	D-fir		100 222 228 2328 232 232		100 82 92 113 66 68 68 68 68 68 68 7 7 7 7		100 255 0 0 1 3 9 22 0 0 0 1 1 3 9 22 0 0 0 0 1 1 3 9 22 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0
arbonica	D-fir							the overage
A. c			100 95 83 83 83 83 83 83 83 84 84 84 84 82 83 82 83 82 83 83 83 83 83 83 83 83 83 83 83 83 83		100 118 118 118 110 56 71 72 72 72 72 72		100 100 112 4 18 18 18 10 10 10 10 10 10 10 10 10 10 10 10 10	0
i	Time (days)		0 8 4 3 2 2 1 0 10		01126480280100		0-100400080	10 Ualues rer

Table I-16. E orming units (ffect of fumigation v CFU's) as a % of c	with a mixture controls. ^{a)}	of 5 ppm A	AITC and 3	000-4000 pp	m CS ₂ on th	he ability of	seven specie	s of fungi on]	pine or Dougi	as-fir to prod	ice colony	
Time	A. carbonica	P. plac	centa	I. lat	cteus	G. tra	ıbeum	G. sae	piarium	T. ven	sicolor	H. re	sinae
(days)	D-fir	D-fir	Pine	D-fir	Pine	D-fir	Pine	D-fir	Pine	D-fir	Pine	D-fir	Pine
0	100	100	100	100	100	100	100	100	100	100	100	100	100
1	48	94	6 6	49	75	23	41	73	103	50	80	98	103
7	47	68	69	35	64	18	7	49	37	56	113	81	103
3	39	43	57	10	69	~	3	40	59	44	153	84	86
4	28	51	66	3	9 <u>0</u>	9	0	28	49	43	222	73	71
S	18	45	42	•	36	0	0	31	44	52	141	59	61
9	27	15	22	•	7	1	0	34	31	56	109	57	54
7	32	7	19	•	1	1	0	28	34	161	188	36	44
8	27	2	9	•	•	0	0	26	15	. 79	91	21	25
6	20	2	7	•	0	0	0	14	S	131	74	80	6
10	12	2	0	0	0	0	0	10	0	162	18	4	4

*) Values represent the average of 3 replicates.

Table I-17. Concentration x Time (CT) values necessary to kill 90% of the propagules for seven species of fungi exposed to carbon disulfide, MITC or a CS2/MITC mixture. Values in parenthesis represent the number of days necessary to reach 90% kill.

			CT ₉₀ value	s (x10 ⁶)				
		CS:	2		MITC		Mi	xture
Fungus	Wood Species	3000-4000 ppm	8000-9000 ppm	5 ppm	10 ppm	18 ppm	CS2	MITC
A. carbonica	Douglas-fir	3172.18 (42)	3496.59 (19)	6.72 (62)	7.47 (35)	1.99 (5)	941.81	1.35 (2.5)
P. placenta	Douglas-fir	1544.08 (20)	1722.21 (9)	1.95 (18)	1.99 (9)	1.3 (3.3)	496.16	0.71 (6.6)
	pine	551.29 (7)	1192.71 (6.5)	2.21 (20.5)	1.81 (8.4)	1.67 (4.3)	525.97	0.75 (7)
I. lacteus	Douglas-fir	489.423 (6.5)	779.69 (4)	0.83 (7.7)	1.10 (5)	1.16 (3)	208.07	0.33 (3)
	pine	253.19 (3)	798.18 (4)	7.85 (72)	1.05 (5)	1.12 (3)	391.24	0.56 (5)
G. trabeum	Douglas-fir	5337.48 (70)	1769.55 (9.7)	0.61 (5.6)	1.01 (5)	1.17 (3)	211.11	0.30 (3)
	pine	764.19 (10)	1374.04 (7.5)	0.57 (5)	1.06 (5)	1.31 (3.4)	167.41	0.07 (2)
G. sacpiarium	Douglas-fir	3725.8 (49)	1237.33 (7)	0.69 (6)	1.03 (5)	0.96 (2.5)	841.99	4.20 (11)
	pine	2257.54 (30)	2916.02 (16)	0.54 (5)	0.83 (4)	0.82 (2)	570.64	0.82 (7.5)
T. versicolor	Douglas-fir	2312.71 (30)	1669.89 (9)	-4.38	2.60 (12)	1.93 (5)	-1155.80	-1.64
	pine	2010.45 (27)	3140. <i>5</i> 7 (17)	-8.15	1.44 (6.7)	1.93 (5)	2299.13	3.28 (30)
H. resinae	Douglas-fir	7484.86 (100)	4872.45 (26)	1.03 (9.5)	1.60 (7.4)	1.98 (5)	739.16	1.06 (10)
	pine	2818.80 (37)	2538.99 (14)	1.03 (9.5)	1.49 (7)	1.83 (4.7)	759.71	1.09 (10)









Fig. I-5. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *A. carbonica*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).

Comparison for P. placenta on D-fir survival fumigated with three different fumigants



Fig. I-6. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *P. placenta*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).

Comparison for *I. lacteus* on D-fir survival fumigated with three different fumigants



Fig. I-7. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *I. lacteus*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).





⁺ C2 3000-1000 pen * KITC 5 ppm O C2/MITC Mexture

Fig. I-8. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *G. trabeum*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).







Fig. I-9. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *T. versicolor*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).





Comparison for *G. saepiarium* on D-fir survival fumigated with three different fumigants

Fig. I-10. Effect of sublethal dosages of CS_2 and MITC along with $CS_2/MITC$ mixture on survival of *G. saepiarium*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).



Comparison for H. resince on D-fir survival fumigated with three different fumigants

Fig. I-11. Effect of sublethal dosages of CS_2 and MITC along with CS_2 /MITC mixture on survival of *H. resinae*. The Y axis represents the logarithm of survival and both X axis represent the product of concentration multiplied by time for MITC (lower axis) and carbon disulfide (upper axis).

⁺ C2 3000-1000 ppc * KTC 5 ppc O C2/KTC Kithere

Boron diffusion is particularly sensitive to wood moisture content. Since moisture levels in wood may vary quite widely delivering effective boron loadings deep into decaying wood may represent a significant challenge. Boron glycol diffuses for limited distances into southern pine joists, but effective levels were only present within 6.5 mm of the wood surface. Similarly, 4 to 8 mm of penetration has been noted into Pinus sylvestris after 3 months, depending on the storage conditions. While 25 to 50 mm of penetration in scots pine timbers 35 months was noted after application of Boracol 20 Rh (a boron/glycol formulation). Penetration did not change appreciably between 14 and 35 months. While these studies suggest that boron and boron/glycol are capable of significant movement in some species, there is relatively little data on the ability of these formulation to diffuse through wood species from the western U.S. In this report, we describe studies of 3 boron formulations on Douglas-fir and western hemlock.

Dry Douglas-fir and western hemlock lumber (37.5 mm by 87.5 mm by 2.4 m long) was obtained from the Willamette Valley in Western Oregon. The lumber was cut into 150 mm long blocks and a 90 mm long by 40 wide 2 mm deep well was cut into the wide face of each block. The blocks were then oven dried at 54 C for 24 hours prior to being weighed (nearest 0.1 g). The blocks were then pressure soaked with water by drawing a 15 minute vacuum (88 KPa), then raising the pressure to 880 KPa and holding for 1 hour. The pressure was released then the blocks were blotted dry and weighed to determine initial moisture

content. The blocks were then aerated at room temperature (23 to 25 C) until their weights indicated that they were at 20, 35, or 50 % moisture content. These levels were selected as representative of those found in many buildings. As blocks reached the desired moisture level, an adhesive-backed paper label was placed over the well and the blocks were dipped in molten paraffin to retard further moisture loss. The label was intended to prevent wax from blocking flow in the wood exposed in the well. The blocks were then stored for an additional 6 weeks at 23 C to permit equilibration of moisture within the wood.

The blocks were treated with boron by removing the paper label from the indented area and applying a weighed amount of each formulation into the well. Blocks received 11.3 g of Timbor (disodium octaborate tetrahydrate), 10.6 g of Diffusol (boron salts plus 2-n-octyl-4isothiazolin-3-one in various thickeners), or 11.5 g of Boracare (40.6 % disodium octaborate tetrahydrate plus 11.9 % polyethylene glycol and 47.5 % monoethylene glycol). Timbor was diluted to produce a 20 % BAE solution, Diffusol was diluted to produce a 20 % BAE solution, and Boracare was diluted to produce a 23 % BAE solution. The blocks were then incubated in plastic bags at room temperature (23-25 C) for 1, 2, or 3 months. At each time point, 3 blocks per treatment condition were sampled.

A single 40 mm thick section was cut from one end of the block. This section contained approximately 10 mm of the well zone. These sections were ovendried (105 C) overnight, then sprayed with an indicator for the presence of boron as described in AWPA Standard A3-91. The presence a red color served as an indicator for boron. Boron penetration was measured in the zone directly beneath the treatment well and averaged for the cross section. Initial boron measurements suggested complete penetration of boron in all treatments. The tests were performed again by slicing a 5 mm thick section from the remaining sample and respraying with the boron indicator. The zone beneath the treatment well was then segregated into zones corresponding to 0 to 5, 5, to 10 and 10 to 20 mm below the wood surface. Samples from each zone for the 3 blocks per treatment were combined and ground to pass a 20 mesh screen prior to analysis for residual boron content using the Azomethine-H method as described in AWPA Standard A2-92. The results were calculated on % boric acid equivalent basis (% BAE) for all treatments.

BORON PENETRATION: Boron penetration, as shown by the indicator, was virtually complete below the well on all specimens but those in the 20 % moisture content treatment even one month after treatment. These results differ markedly from those reported previously. To ensure that the penetration measurements were the result of boron diffusion and not carry over from the sawing, a fresh surface was exposed in the dry blocks and this surface was sprayed with the indicator. Boron penetration was far shallower in many specimens. These results more closely agree with those previously reported and highlight the need for caution when using very sensitive chemical indicators on freshly-cut wet wood.

Boron penetration appeared to be slightly better in Douglas-fir blocks (Table I-8). Douglas-fir is generally considered to be less permeable than western hemlock and previous studies of boron diffusion have shown western hemlock to be more receptive to diffusion than Douglas-fir. As expected, boron penetration was greatest in the 35 and 50 % MC wood, illustrating the benefits of having free water present in the material at the time of treatment. Boron diffusion appeared to be most consistent in blocks treated with Boracare, although boron penetration in blocks treated with Timbor was consistently higher in the 50 % MC blocks of both wood species. These results suggest that non-amended boron solutions alone will penetrate into very wet wood, but are of lesser value when moisture contents are more variable. The presence of glycol appears to markedly improve distribution of boron in drier wood. The thickening agents present in Diffusol had a more variable effect on both wood species at all 3 moisture levels and further studies would be required to more clearly define the value of thickeners in this system.

While the results of penetration measurements suggest that Boracare was associated with improved penetration in drier wood, while Timbor produced better treatment of wet wood, the results must be viewed with some caution. The boron indicator is relatively sensitive to boron (approximately 0.1 to 0.15 % BAE), detecting boron at levels below those required for fungal control. As a result, the presence of boron may provide a false positive for fungal control in an infested structure. BORON RETENTION: Chemical analysis revealed that most of the residual boron present was less than 5 mm from the wood surface, even in samples with a moisture content of 50 % (Table I-18, 19). Boron levels within the outer 5 mm of all but one treatment (Timbor after 1 month on 50 % MC Douglas-fir) were above the level considered necessary for protection against wood decay fungi. Boron levels in the two inner assay zones were negligible for most samples, suggesting that the boron treatments were primarily topical surface treatments.

Effect of formulation on residual boron levels: As noted, boron penetration was relatively shallow for all treatments and species. Boron concentrations of the treatment solutions were similar for the 3 formulations, suggesting that residual boron levels should also be similar at the conclusion of the trial. However, this was not the case and boron levels varied widely among the three treatments. Interestingly, boron levels in Douglas-fir were highest in the 20 % MC Timbor treatment 2 or 3 months after treatment. This chemical was also associated with the highest variation in boron levels among the moisture contents and treatment times, suggesting that minor variations in wood characteristics could markedly affect diffusion. Both Boracare and Diffusol contain additives which are presumed to enhance boron diffusion, but our results suggest that these additives provided little additional value from the standpoint of maximizing boron entry beyond the outer 5 mm of the wood. Diffusol did, however, appear to produce more uniform retentions over the course of the study, particularly at the lowest MC level.

Boron levels in western hemlock blocks treated with each of the 3 formulations were consistently higher than those found with Douglas-fir, but levels among the various formulations again varied. This trend was indirect contrast with that found with the indicator and again highlight the need for chemical analysis instead of indicator based measurements when assessing boron diffusion. Boron levels above 3 % BAE were found in 4 of 9 Diffusol treatments, 7 of 9 Boracare treatments, and 7 of 9 Timbor treatments. Boron levels tended to fluctuate within treatments, for example all three 50 % MC treatments were above 3 % BAE for Boracare and Timbor, but below that level for Diffusol. Boron levels in Timbor treatments were initially low in 20 and 35 % MC blocks after 1 month, but rose to levels comparable to those found in the 50 % MC blocks in the second and third month. Boron levels in the 20 % MC Boracare treatment were also initially low, but rose more slowly over the second month in comparison with Timbor.

Effect of Wood Species on Diffusion: Boron levels were consistently higher in western hemlock samples, reflecting the higher permeability of this species. Previous diffusion trials of similar western hemlock and Douglas-fir with Timbor produced similar results. In general, however, boron levels in the outer surface of both species were adequate for protecting wood in that zone from fungal attack, but it is difficult to determine how these levels relate to control of termites or other insects. Active fungal infestations deeper in the wood would be unaffected by the boron levels present. Effect of moisture content on boron level: Moisture content of the wood at time of treatment had variable effects on subsequent boron levels. For example, boron levels in 20 % MC Douglas-fir blocks treated with Timbor were among the highest measured for this species, while levels in the 50 % MC blocks treated with the same chemical were among the lowest. The reasons for this anomaly are unclear. Moisture content of Douglas-fir appeared to have minimal effects on treatments with Diffusol and had more variable effects on Boracare.

Moisture content of western hemlock also produced effects on residual boron levels. Boron diffusion of both Boracare and Timbor at lower MC levels (20 and 35 % MC) appeared to be more gradual, as shown by an increasing amount of residual boron between 1 and 3 months. Boron levels in Diffusol treated 20 % MC western hemlock appeared to decline between 1 and 2 months, although this trend probably reflects slight variations in wood blocks used since boron levels again rose between 2 and 3 months. In all instances, however, boron levels in the outer assay zone were above those required for fungal protection. In many cases, some boron was detected within the second and third assay zone, but the results were somewhat inconsistent. For example, boron was detectable in the middle assay zone in Timbor treated 50 % MC western hemlock blocks at levels which would approach those required for fungal protection, while those found in Boracare or Diffusol treated blocks were well below those levels. These results suggest that none of the topically applied boron treatments provided consistent protection deep within the wood, even

when the moisture content was above that typically considered to be necessary for diffusion.

The results suggest that all 3 boron formulations were capable of diffusing for short distances through Douglas-fir and western hemlock lumber at moisture contents typically found in decaying wood. The inability of these chemicals to rapidly diffuse throughout wood within a short period of time poses a major challenge to utilities interested in controlling active fungal attack. Our results suggest that these formulations will arrest decay near the point of application, but their effects on fungi deeper in the wood are uncertain. As a result, topical application of boron should be considered as a supplemental treatment which could prevent renewed fungal attack but will not control existing fungal protection, while those found in Boracare or Diffusol treated blocks were well below those levels. These results suggest that none of the topically applied boron treatments provided consistent protection deep within the wood, even when the moisture content was above that typically considered to be necessary for diffusion.

The results suggest that all 3 boron formulations were capable of diffusing for short distances through Douglas-fir and western hemlock lumber at moisture contents typically found in decaying wood.

Table I-18. R 50 % MC 1,	tesidual boron c 2, or 3 months	ontent of select	ed depths in Do with Timbor, B	uglas-fir blocks oracare or Diffu	at 20, 35, or isol.
			Resi	dual Boron (% I	BAE) ^a
		Incubation		Assay Zone (mm	1)
Chemical	Wood MC (%)	Time (months)	0-5 mm	5-10 mm	10-20 mm
Timbor	20	1 2	1.12(0.95) 6.53(1.18)	0.01(0.01) 0.02(0.01)	0.03(0.00) 0.02(0.01)
	35	3	4.51 (-) 2.08(1.20)	0.03(-) 0.02(0.01)	0.03(-) 0.03(0.02)
		23	3.52(2.47) 1.75(0.96)	1.81(2.49) 0.08(0.08)	0.05(0.03) 0.03(0.01)
	50		0.17(0.19) 1.66(0.84)	0.06(0.02) 0.03(0.02)	0.05(0.01) 0.03(0.01
7	20	3	1.46(0.22)	0.05(0.02)	0.05(0.03)
Boracare	20	1 2 2	0.60(0.39) 2.47(2.04)	$\begin{array}{c} 0.03(0.01) \\ 0.03(0.01) \\ 0.02(0.01) \end{array}$	0.05(0.02) 0.04(0.01)
	35		0.61(0.39)	0.03(0.01) 0.07(0.03)	0.02(0.00) 0.09(0.08)
	50	3	1.34(0.37) 2.08(1.63)	0.12(0.13) 0.09(0.03)	0.12(0.12) 0.03(0.01)
	50	2 3	$\begin{array}{c} 1.20(0.60) \\ 2.05(0.16) \\ 1.65(0.23) \end{array}$	0.05(0.01) 0.05(0.02) 0.05(0.01)	0.03(0.02) 0.07(0.03) 0.03(0.01)
Diffusol	20	1	2.28(2.28)	0.03(0.00)	0.03(0.01)
	25	3	2.82(0.45)	0.01(0.01) 0.02(0.00)	0.02(0.01) 0.03(0.01)
	35	1 2 2	0.96(0.82) 2.66(0.79)	0.06(0.02) 0.07(0.03)	0.05(0.01) 0.05(0.02
	50	3 1 2	2.46(0.11) 1.79(1.51)	0.03(0.01) 0.53(0.69)	0.04(0.02) 0.03(0.00)
		3	1.73(0.83)	0.02(0.00)	0.02(0.01)
^a Values repre standard devia	sent means of 3 ation. Untreated	replicates, whi wood containe	le figures in pa d 0.02 % BAE	rentheses represe boron.	ent one

Table I-19. H 35, or 50 % I	tesidual boron c MC 1, 2, or 3 n	ontent of select	ed depths in we tment with Tin	stern hemlock b ibor, Boracare o	locks at 20, or Diffusol.
			Resi	dual Boron (% 1	BAE) ^a
		Incubation		Assay Zone (mn	n)
Chemical	Wood MC (%)	Time (months)	0-5 mm	5-10 mm	10-20 mm
Timbor	20	1 2	2.75(1.66) 6.27(1.55)	0.02(0.01) 0.05(0.04)	0.03(0.01) 0.09(0.06)
	35	3 1	5.10(0.12) 1.85(2.55)	0.05(0.02) 0.09(0.08)	0.20(0.16) 0.06(0.06)
		23	4.56(4.52)	0.13(0.00)	0.06(0.04)
	50	1	3.97(1.53)	0.65(0.64)	0.08(0.02)
		3	5.83(1.54)	0.42(0.32)	0.05(0.03)
Boracare	20	1 2	1.55(1.27) 2.58(1.96)	0.11(0.06) 0.31(0.39)	0.03(0.00) 0.19(0.24)
	35	3 1	6.30(0.83) 2.18(0.88)	0.17(0.15) 0.13(0.06)	0.09(0.06) 0.03(0.02)
		23	4.90(2.43) 6.82(0.90)	0.11(0.10) 0.28(0.21)	0.03(0.01) 0.04(0.03)
	50	1 2 3	3.56(2.53) 3.16(0.50) 4.13(1.16)	0.27(0.34) 0.18(0.07) 0.12(0.07)	0.11(0.09) 0.03(0.00) 0.02(0.01)
Diffusol	20	1 2	5.33(0.99) 2.05(1.25)	0.02(0.01) 1.08(1.48)	0.01(0.01) 0.06(0.03)
	35	3	3.35(0.13) 2.82(0.53) 5.25(1.16)	0.02(0.01)	0.02(0.01) 0.04(0.01)
	50	3	4.08(0.57)	0.17(0.01) 0.10(0.02)	0.03(0.00)
	50	1 2 3	2.35(1.07) 1.36(1.18) 1.49(0.12)	0.17(0.07) 0.33(0.24) 0.32(0.10)	0.05(0.02) 0.06(0.07) 0.18(0.11)
* Values repression standard devia	esent means of 3 ation. Untreated	replicates, whi wood contained	le figures in pa d 0.02 % BAE	rentheses repres	ent one

The inability of these chemicals to rapidly diffuse throughout wood within a short period of time poses a major challenge to utilities interested in controlling active fungal attack. Our results suggest that these formulations will arrest decay near the point of application, but their effects

4. Decomposition of basamid in douglasfir heartwood: laboratory studies of a potential wood fumigant: Wood utility poles are routinely pressure-treated with preservatives to protect them against biological deterioration. However, many pole species, such as Douglas-fir, in western North America contain a high proportion of heartwood, which is largely impermeable to liquid penetration. Although the heartwood of Douglas-fir is impervious to liquids, it is permeable to gases. Several volatile agricultural chemicals have been added as liquids to the interior of poles via downward-sloping holes, where they vaporize and move through the wood as gases to kill established decay fungi. Poles remedially treated in this manner have been found to be free of decay fungi up to 14 years after treatment. Sodium N-methyldithiocarbamate (NaMDC), Vorlex (20% methylisothio-cyanate, 80% chlorinated C-3 hydrocarbons), chloropicrin (96% trichloronitro-methane), and MITC-Fume [97% solid methylisothiocyanate (MITC)] are the only fumigants registered with the U.S. Environmental Protection Agency for wood application. However, three of these chemicals are applied as liquids, creating potential hazards in safety and

on fungi deeper in the wood are uncertain. As a result, topical application of boron should be considered as a supplemental treatment which could prevent renewed fungal attack but will not control existing infestations.

handling. MITC-Fume[•], a solid at room temperature, has proven highly effective as a wood fumigant; however, it is also very volatile, expensive, and not yet widely used.

Alternatives to the currently registered chemicals are crystalline solids that decompose to produce volatile fungitoxic byproducts. One such chemical is Basamid (United Agricultural Products, Greeley, CO), a soil sterilant. Because Basamid is a solid, it is not as readily absorbed through the skin as are liquids, and it is more easily stored and recovered in the event of a spill.

Chemically, Basamid is a heterocyclic ring containing carbon, nitrogen, sulfur, and hydrogen (Fig. I-12). It was first prepared in 1897 by Delepine, who reacted carbon disulfide with trimethyltrimethylene triimine. The actual structure of the compound was later shown as 3,5-dimethyltetrahydro-1,3,5,2Hthiadiazine-2-thione (CAS Registry No. 533-74-4). More recently, it has been prepared commercially by reacting carbon disulfide with methylamine and caustic soda.



Fig. 1-12. The chemical structure of Basamid.

Basamid decomposes slowly in wood and has successfully controlled decay fungi there after long exposures. Such slow decomposition could be useful if the chemical were applied before decay had to be eradicated. However, in pure form Basamid does not decompose rapidly enough to diffuse and kill actively growing decay fungi in wood. To be effective there, a chemical must be able to eliminate an actively growing fungal colony within 6 to 12 months after application.

Under dry conditions and ambient temperatures, Basamid is stable and not

biologically active. Effectiveness against target organisms depends on the decomposition products formed and the rate at which they are released. Among the decomposition products reported are MITC, methylamine, hydrogen sulfide, and formaldehyde. Acid hydrolysis also yields carbon disulfide. MITC is considered to be the most important volatile toxicant produced and has received the most attention in Basamid evaluations. MITC production is dependent on several environmental conditions including moisture, temperature, pH, and the presence of trace metals.

The relative ratios of decomposition products formed from Basamid are also pH-dependent. Acidic media hydrolyze Basamid to carbon disulfide, formaldehyde, and methylamine. Under neutral or basic conditions, the reaction shifts toward the production of MITC and hydrogen sulfide along with formaldehyde and methylamine. MITC is produced at a greater rate at pH 10 than at pH 4 or 7. In soils, MITC production increased with pH up to 6.5, but then decreased up to pH 7.7. In one of the first tests of Basamid in wood, alkaline buffers (pH 10 and 12) greatly enhanced MITC production and fungal control in wood blocks.

Decomposition of some dithiocarbamates can be enhanced by the addition of certain metals. For instance, NaMDC decomposition increases in the presence of copper, manganese, iron, and zinc. Very low levels of cupric sulfate synergistically decrease acetate respiration of yeast while simultaneously increasing the production of MITC from Basamid. Soil minerals may actually catalyze the primary step in Basamid decomposition.

While there have been several studies of Basamid decomposition in soil, little information exists on how additives affect Basamid decomposition in wood. This paper describes tests designed to determine the effect of moisture and temperature as well as selected additives on the decomposition of Basamid in Douglas-fir heartwood. After an initial screening, two additives were selected for further study of their effects on both the rate of decomposition and the balance of decomposition products. Initial screening of additives: Several powdered additives were tested for their ability to enhance the decomposition of Basamid to MITC. On the basis of the weight of Basamid used, the following percentages of metals or other substances were added: 0.5, 1, 5, and 10% copper sulfate; 1% copper chloride; 1% manganese sulfate; 1% magnesium sulfate; and 5% of a buffer powder consisting of sodium phosphate (di and tri basic) formulated to reach pH 12 when mixed with 100 ml of water.

Douglas-fir heartwood was ground to pass a 3-mm screen. It was then adjusted to 30% moisture content (MC) in all tests except the ones in which only the buffer powder was added to it; in those cases it was adjusted to MC's of 12, 30, or 60%. In each test, 3 g (based on ovendry wt) of sawdust were placed in each of three 40-ml glass vials and lightly tamped. In each of the three vials, 120 mg of Basamid amended with the test additive were placed on top of the sawdust in an evenly distributed layer and covered with an additional 3 g of lightly tamped sawdust. All vials were then tightly capped with a Teflon-lined silicone septum and stored at 23°C.

Basamid decomposition was determined 1, 3, 5, 7, 10, and 14 days after treatment by removing an air sample through the septum of each vial with a gas-tight syringe. Those sample volumes (<250 ml) provided enough air for detection of MITC without creating a significant negative pressure within the vial. The samples were injected into a Varian 3700 gas chromatograph equipped with a flame photometric detector operating at the following conditions: injector temperature, 150°C; oven temperature, 100°C; detector temperature, 240°C; nitrogen carrier flow rate, 30 ml/minute; column, 10% Carbowax 20M on 80/100 Supelcoport (Supelco, Inc., Bellefonte, PA). MITC concentrations were quantified by comparison with injections of known amounts of MITC dissolved in ethyl acetate.

Effect of additives on

decomposition: On the basis of the initial screening, tests were run to determine the effects of wood and of promising additives on the rate and efficiency of Basamid decomposition into MITC and other products including primary amines and carbon disulfide. Glass vials (40-ml) equipped with Teflon-lined silicone septa were again employed. Each vial received 100 mg of Basamid either alone or amended. Three vials received 2 drops of water. Three vials received 50 mg of Douglas-fir heartwood sawdust ground to pass a 20-mesh screen and adjusted to an MC of 9%. Another three vials received 50 mg of sawdust to which 2 drops of water had been added. The following additives were tested without sawdust, each in three vials: 5 mg of buffer powder (with and without 2 drops of water), 2 drops of buffer solution at pH 12, 2 drops of NaOH in water at pH 12, 2.5 mg of copper sulfate (with and without 2 drops of water), and 2 drops of 1N acetic acid. All vials were stored at room temperature (20-24°C) for the duration of the experiment.

After 4, 24, and 48 hours, two headspace samples were removed through the septum of each vial with a gas-tight syringe. Each sample was injected into one of two Varian 3700 gas chromatographs. The chromatagraph used for amine analysis operated at the following conditions: injector temperature, 200°C; oven temperature, 75°C; flame ionization detector temperature, 240°C; column, 6 feet long by 2 mm inner diameter, glass, packed with 4% Carbowax 20M on 0.8% KOH 60/80 Carbopack B (Supelco, Inc.); nitrogen carrier flow rate, 30 ml/minute. The chromatograph used for sulfur analysis operated as follows: injector temperature, 150°C; oven temperature, 100°C; flame photometric detector temperature, 240°C; column, 6 feet long by 2 mm inner diameter, glass, packed with 10% Carbowax 20M on 80/100 Supelcoport (Supelco, Inc.); nitrogen carrier flow rate, 30 ml/minute. Standard amine solutions were made with distilled water as the solvent; MITC and carbon disulfide solutions were made in ethyl acetate. Concentrations of all detected compounds were determined by comparison with appropriate standards.

Effects of buffer and copper on decomposition: Tests were run in the presence of wood to determine the decomposition products of Basamid either alone or amended with 5% buffer powder or 1% copper sulfate or both, with the powdered additives being measured as percentages of the weight of Basamid used; the additives were mixed thoroughly before treatment. For each test, 120 mg of Basamid with or without additive(s) were placed in an evenly distributed layer in each of three 40-ml vials and covered with 1 g (based on ovendry wt) of sawdust that had been adjusted to an MC of 6 or 30%. A fine-meshed plastic screen was then placed on top of the sawdust, and an additional 2 g (based on ovendry wt) of sawdust adjusted to the same MC were placed on top of the screen. Each vial was sealed with a cap containing a Teflon-lined silicone septum and stored at 5°, 23°, and 32°C for up to 30 days. Control vials containing either sawdust but no chemicals or chemicals but no sawdust were assembled in sets of three to detect the volatile components from untreated wood and the stability of Basamid with additives in the absence of moisture.

Two air samples were removed from each vial after 5, 10, 20, and 30 days. One of these samples was injected into a Varian 3700 gas chromatograph and analyzed for sulfur-containing compounds as described above. The other sample was injected into a second Varian 3700 gas chromatograph and analyzed for non-sulfur compounds by a flame ionization detector. Operating conditions were the same as described above except for the following: column temperature, 110°C; column, 4% Carbowax 20M on 0.8% KOH 60/80 Carbopack B (Supelco, Inc.).

<u>Statistical analysis</u>: All tests were subjected to a repeated-measures analysis of variance (ANOVA) with an alpha level of 0.05 (SAS Institute, Inc., Cary, North Carolina). This analysis was chosen because each specimen was sampled several times over the test period. The statistical procedure included time as an independent variable, thus eliminating the error associated with it from the error sum of squares.

Initial screening of additives: Moisture greatly enhanced the decomposition of Basamid to MITC (Fig. I-13). No MITC was detected in any vial containing wood at 12% MC. MITC production from Basamid was significantly greater in wood at 60% MC than in wood at 30% MC. As in previous results, using a buffer powder also enhanced MITC production, although the resulting levels were still quite low. It is possible that much of the released MITC was bound to the wood, although no effort was made to confirm this possibility.

MITC production from Basamid was significantly greater with either copper sulfate (Cu^{+2}) or copper chloride (Cu^{+1}) than with manganese or magnesium. Copper chloride produced significantly higher MITC levels than did copper sulfate. MITC production also increased significantly as the amount of added copper increased. These results confirm field tests with Basamid amended with various additives. In those tests, copper sulfate with the same buffer powder used here outperformed other additives in elevating MITC production in Basamid-treated Douglas-fir poles over a 2-year period. The initial screening in the present tests also indicated that copper warranted further study: copper sulfate was chosen because the results could be more directly compared with previously established field tests in which this additive was used.

<u>Effects of additives on</u> <u>decomposition</u>: Unamended Basamid did not decompose into detectable volatiles during the test period (Table I-20), an indication that the chemical was very



Figure I-13. MITC levels at selected times in the headspaces of sealed vials containing Douglas-fir heartwood at various MC's as well as Basamid either unamended or amended with a buffer powder.

stable when kept dry at room temperature. Wood at 9% MC also had no effect on decomposition. However, adding water to unamended Basamid or to Basamid plus wood had a significant effect on MITC production. Decomposition into MITC when wood plus water were added to Basamid did not increase significantly over that obtained when only water was added to Basamid, indicating that wood was not a major catalyst in this reaction. However, when wood plus water were added to Basamid, levels of carbon disulfide increased dramatically over those when only water was added.

It should be noted that there were two overlapping sulfur peaks on the chromatograms, one being carbon disulfide (retention time ca. 0.41 minute) and the other being unidentified (retention time ca. 0.36 minute). The unidentified peak, probably either carbonyl sulfide or hydrogen sulfide, often overshadowed carbon disulfide, preventing the peak of the latter from being integrated. Further experiments will be needed to fully separate, identify, and quantify the more volatile sulfur-containing compounds.

The effect of pH-altering additives on MITC production was evident, but moisture appeared to be necessary for this increase. NaOH solution at pH 12 was more effective than the buffer solution at pH 12 from powder, indicating that the phosphate compounds in the powder may have reduced its effect as a catalyst. Acetic acid also increased MITC production, but to a lesser degree than did the additives at a higher pH.

In addition, acetic acid enhanced the production of carbon disulfide—to

levels similar to those induced by wood plus water. This similarity was not surprising as Douglas-fir heartwood has a pH almost as low as does acetic acid. However, the effects of pH on decomposition are poorly understood.

Copper sulfate clearly affected MITC production more than did any other additive tested. The addition of water was not necessary to induce this reaction but significantly enhanced the effect. Conversely, copper sulfate induced no carbon disulfide until water was added. Chromatograms indicated that an unidentified sulfur compound was produced in the absence of water and that the presence of water shifted the production of early-eluting sulfur compounds exclusively to carbon disulfide.

Surprisingly, neither mono- nor di-methylamine was detected in these tests, even when high levels of carbon disulfide were produced. When carbon disulfide is removed from the Basamid molecule (presumably as sulfur from position 1 and carbon along with its double-bonded sulfur from position 2), the only remaining atoms are carbon, nitrogen, and hydrogen. It seems likely that at least some amine component would be produced in detectable quantities from this residue. Because this was not the case, further tests are needed to determine the fate of the nitrogen-containing residues.

Effects of buffer and copper on decomposition: Analyses for both methylamine and dimethylamine in the headspaces of the test vials were inconclusive. If present, these compounds were below the limits of detection. There were, however, several unidentified compounds produced in small quantities in the tests conducted at higher MC's and temperatures. The presence of copper sulfate resulted in MITC production from Basamid even in the absence of wood or added moisture. Thus, in field applications it may be necessary to delay mixing this additive with Basamid until just before treatment in order to prevent premature decomposition of the fumigant.

Both MITC and carbon disulfide were identified in the headspaces of the test vials. As in the screening tests, higher MC's resulted in increased MITC production regardless of the temperature or additive used (Fig. I-14). Higher temperatures also enhanced MITC production, as has been previously noted with metham sodium. Similar trends were noted for carbon disulfide production (Fig. I-15), although these levels were much higher than those found for MITC. In most treatments, levels for both compounds were decreasing after 30 days. This decline may have resulted from various decomposition products recombining into non-volatile compounds or from loss from the vials.

Both buffer powder and copper sulfate affected decomposition in the same way as in the initial screening tests. Although trends in MITC production were nearly the same regardless of whether buffer powder was added to Basamid, the levels with the buffer were much higher. Addition of copper also enhanced production, but the effects were delayed and the levels of MITC did not decline as rapidly as in those treatments without copper. Once again, these results paralleled those in Basamid field tests. Combining the buffer and copper sulfate boosted both initial and long-term MITC production, especially at 30% MC and 32°C. In some tests, carbon disulfide production was also increased by the addition of buffer powder or copper sulfate; however, the proportion of carbon disulfide to MITC was not as great when copper sulfate was added.

One goal of this research was to identify additives that will enhance Basamid decomposition to effective fungicides. These fungicides must interact with wood and not immediately volatilize, leaving the wood unprotected. One way to measure the efficiency with which Basamid decomposes to form MITC, the most important fungitoxic product, is to determine the ratio of carbon disulfide to MITC formed. While copper increased carbon disulfide levels slightly, it increased MITC levels markedly, often causing the ratio of carbon disulfide to MITC to decrease by an order of magnitude. These decreases were statistically significant, especially when both additives were used in tandem.

There are two possible pathways for MITC production through cleavage of the Basamid ring. One involves the same carbon atom involved in the evolution of carbon disulfide, perhaps explaining why the latter's production rate falls when that of MITC rises. Although carbon disulfide is fungitoxic, it is less effective than MITC and volatilizes rapidly, providing no residual protection to wood. MITC, conversely, has been shown to remain in and to protect wood for long periods. Thus, it is crucial that both the decomposition products and their rates of breakdown be controlled if Basamid is to serve as a fungitoxicant in wood.

Raising the temperature and moisture content enhanced Basamid decomposition, as did adding buffer powder. The latter, however, greatly favored the production of carbon disulfide over that of MITC. Copper sulfate, on the other hand, enhanced the production of MITC from Basamid while reducing the evolution of carbon disulfide. This was especially true when buffer powder was added to the copper sulfate.

Basamid was unstable in the presence of copper sulfate, even without added moisture. Thus, in field applications it will be necessary to keep this additive separate from the fumigant until just before treatment. Although

amines are potential products of Basamid decomposition, none were detected in these studies; consequently, their possible role in the process remains unknown.

This study indicates that Basamid amended with appropriate additives produces significantly higher levels of MITC in Douglas-fir heartwood than does Basamid alone. Field tests with wood poles have shown that Basamid amended with additives produces moderate levels of MITC that protect against internal decay for at least 3 years. Further laboratory and field trials with this chemical should produce an internal treatment that is both safe to apply and lastingly effective.

Table I-20. MITC and CS_2 concentrations over a 48 hour period in the headspaces of vials containing 100 mg of Basamid amended with selected additives.

		Conc	entration (ng/ml of ai	r) of	
		MITC			CS ₂	
Additives	4 hr	24 hr	48 hr	4 hr	24 hr	48 hr
None	0	0	0	0	0	0
Water	0	410	236	0	Т	0
Wood	0	0	0	0.	0	0
Wood plus water	79	324	292	63	345	
Buffer powder	5	6	0	0	0	0
Buffer powder + water	108	421	334	2	14	0
Buffer solution at pH 12	4	64	340	242	2	5
(from powder)						
NaOH solution at pH 12	324	546	299	. 3	1	0
Copper sulfate	539	306	108	0	0	0
Copper sulfate + water	2895	705	270	323	1091	850
Acetic acid	223	193	90	288	537	373

T = trace

Table I-21. Volatile and residual chemicals produced from 100 mg Basamid alone or amended with copper sulfate as determined by a purge and trap method with 95% ethanol.

Total % Recovered	82.3 97.5 89.9 97.6 97.6
Residual Basamid (mg)	81.0 97.5 89.5 93.0 97.1
Residual CS ₂ (ng)	509 509 0 0 5999
Residual MITC (mg)	0.3705 0.1347 0.1484 0.1484 0.0421 0.0115 1.4312
Volatiles (% Total)	0.91 0.20 0.26 0.43 0.53 3.38
Volatile CS ₂ (mg)	0.02224 0.0000 0.0000 0.0010 0.0004 0.0193
Volatile MITC (mg)	0.8087 0.2002 0.2629 0.4299 0.5369 3.3594
Added CuSO ₄	^, , , + + +
Sample	ф мог ж е

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Fig. I-14. MITC levels over a 30-day period in the headspaces of sealed vials containing Douglas-fir heartwood that had been conditioned at 6% or 30% MC, treated with Basamid either (A) alone or amended with (B) buffer powder, (C) copper sulfate, or (D) both buffer powder and copper sulfate, and stored at 5°, 23°, or 32°C.


Fig. I-15. CS_2 levels over a 30-day period in the headspaces of sealed vials containing Douglas-fir heartwood that had been conditioned at 6% or 30% MC, treated with Basamid either (A) alone or amended with (B) buffer powder, (C) copper sulfate, or (D) both buffer powder and copper sulfate, and stored at 5°, 23°, or 32°C.

5. <u>Basamid treatment of douglas-fir</u> <u>heartwood: analysis of volatile and residual</u> <u>chemicals</u>: Basamid[™](3,5-dimethyl-1,3,5,2H-tetrahydrothiadiazine-2-thion e) is a commonly used soil sterilant that has shown promise as a wood fumigant. Basamid must decompose from its pure form to become an effective fungicide. Methylisothio-cyanate (MITC) is considered the most important volatile compound formed from this catalysis. However, other decomposition products reported in soil include methylamine, hydrogen sulfide, and formaldehyde.

Previous tests for determining fungitoxic decomposition products produced when Basamid is in contact with Douglas-fir heartwood have been incomplete in that not all of the expected products were detected. In addition, the levels of compounds detected in closed chambers decreased over time, suggesting that volatile products were escaping from the vials or were reacting within the wood. This made it necessary to design tests that would purge and trap all volatile decomposition products before they could escape the test apparatus. It was also of interest to determine the amount of residual Basamid within the wood at the end of the test period. The following tests were performed to determine the cumulative concentrations of volatile decomposition products produced from Basamid in Douglas-fir heartwood and to determine residual chemical levels in the wood.

The chemical collection method was modelled after those previously used

to study various fungicides in soil by solvent scrubbing of air that had been slowly passed through glass cylinders packed with Basamid-treated sawdust. Chemical analyses of the solvent allowed identification and quantification of trapped volatile decomposition products.

Chemical collection assembly: Douglas-fir heartwood was ground to pass a 3-mm screen and adjusted to 30% MC by adding an appropriate amount of distilled water and allowing it to equilibrate for at least 48 hours at 5 C. A 1.75-g (oven-dry basis) aliquot of this wood was packed into a glass column (11 cm long X 1.6 cm diameter) and lightly tamped with a wooden dowel. A plastic screen was placed on top of the wood to separate it from the chemical treatment. Approximately 0.125 g (oven-dry basis) of wood was placed on top of the screen and tamped before an evenly distributed layer of Basamid was added. The chemical layer was then covered with an additional 0.125 g of wood. The entire assembly was tamped with the wooden dowel, resulting in 5 linear cm of wood in the glass column (Fig. I-16).

The columns received 100 mg Basamid or Basamid amended with $CuSO_4$ (1% as copper per weight of Basamid). Control columns with no chemical treatment were also tested to determine whether the wood alone would produce volatile products that might be trapped in the solvent and interfere with analyses. Three replicates per treatment were used. Air was passed through the glass columns at a rate of 10–20 ml per minute. Before passing through the columns, the air was humidified by bubbling through distilled water to prevent desiccation of the wood. The effluent air stream from each column was bubbled through three consecutive solvent traps, each containing 30 ml of 95% ethanol. Ethanol was chosen as a solvent because of the solubility properties of the majority of compounds expected to be produced. The ethanol in each trap was completely exchanged after 1, 2, 3, 5, and 7 days, and then every 3 days through day 28.

Volatile chemical analyses: The trapping solvents were analyzed by injecting 5 ml of each into one of two Varian Model 3700 gas chromatographs equipped for sulfur or amine analysis as described by Forsyth and Morrell (in preparation), except that an oven temperature program was required to completely separate all compounds. These programs were as follows: (1) sulfur compounds-40 C for 2 minutes, then increasing at 80 C per minute to 120 C for 2 minutes, and (2) amines-50 C for 2 minutes, then increasing at 80 C per minute to 150 C for 4 minutes. Compounds detected were quantified by comparisons with chromatograms of injected standards.

Residue analyses: After 28 days, the packed glass columns were disassembled and analyzed for Basamid and decomposition product residues. The 1.75-g portion of wood on the downstream side of the plastic screen was extracted in 95% ethanol for 48 hours at room temperature. The extract was then analyzed for volatile decomposition products as described above. The extracted wood was oven-dried at 100 C overnight and ground to pass a 30-mesh screen before being analyzed for total carbon, nitrogen, and sulfur.

The remaining 0.25 g of wood containing the Basamid layer was analyzed for Basamid residue by using a modification of a previously described method. The wood and chemical were placed in a test tube and extracted with 20 ml of dichloromethane for 10 minutes on a rotary shaker. The extract was then filtered through a 0.45-mm syringe filter and analyzed with a Shimadzu LC6A high performance liquid chromatograph. Analysis conditions were as follows: liquid phase-95% dichloromethane : 5% hexane; flow rate-3.5 ml per minute; column-Nucleosil 100 silica 5 micron (250 mm long X 4.6 mm inner diameter) (Alltech Associates, Inc., Deerfield, IL); UV detector-280 nm; injection volume-10 ml. Basamid residues were quantified by comparison with chromatograms of injected Basamid standards in dichloromethane. Percent recoveries were calculated by spiking 0.25 g of the same Douglas-fir wood with measured amounts of Basamid and comparing chromatograms with those of Basamid with no wood.

<u>Volatile chemicals</u>: MITC was always produced in higher amounts when Basamid was amended with $CuSO_4$ (Fig. I-17), confirming the results of previous tests. These production rates, however, were higher only during the first 7 days. After this time, rates were comparable for the two treatments. For instance, total MITC production between 7 and 28 days from Basamid alone was 216 mg; production from the copper- amended treatment was 238 mg, a difference of only 22 mg. This similarity indicated that although copper effectively catalyzed an initial burst of MITC production from Basamid, it played no significant role in prolonged production. After 28 days, the total production of MITC in the air effluent of the copper-amended treatment was approximately twice that of the Basamid alone treatment. Similar trends have been observed in Basamid-treated soil, although the MITC production levels were higher. This difference was probably due to the complete mixing of the chemical with the soil in a water suspension as well as the more reactive nature of soil. Higher initial rates of MITC production in earlier soil studies may have been caused by early catalytic effects of soil minerals.

Only one specimen treated with Basamid alone produced carbon disulfide, and then only at one time point. Carbon disulfide was produced from copper-amended Basamid at very low levels and was detected only during the first 3 days of the test, reflecting the early production of MITC (Fig. I-17).

It should be noted that one glass column assembly from each treatment was excluded from the final calculations because of water condensation inside the air lines and glass columns, an event that further illustrates the effect of moisture on Basamid decomposition. Figure 2 includes data from these water-contaminated columns and clearly shows the immediate catalytic effect of water on Basamid. <u>Residues</u>: MITC residues in the extracted wood averaged 141.5 mg for Basamid alone and 26.8 mg for Basamid amended with copper (Table I-21). This distribution was unexpected because total production of volatile MITC was far greater in copper- amended samples. Carbon disulfide residues for both treatments were very low.

Recoveries in the Basamid-spiked wood samples ranged from 95.7% to 100.9% (data not shown). These values were much higher than the previously reported recovery of 82.2%. Lower recovery rates probably were due to the added sample cleanup and concentration required in soil samples, resulting in loss of chemical.

Residual Basamid levels were quite high for both treatments, 93.5 mg for Basamid alone and 95.05 mg for copper-amended Basamid (Table I-21). These levels indicate a large reservoir of Basamid remaining that can provide long-term MITC release. Total carbon, nitrogen, and sulfur were similar for all samples following extraction and were not above expected background levels.

Copper sulfate catalyzed an increase in production of volatile MITC from Basamid, confirming previous tests. This increase was confined to the first few days following treatment, however; during later measurements, rates for non-amended and amended Basamid were similar. This suggests that copper sulfate boosts MITC production to levels necessary for fungal control soon after treatment. Accidental contamination by



Compressed Air

Fig. I-16. Purge-and-trap system used to collect volatile decomposition products from Basamid or Basamid amended with copper sulfate over a 28-day period.



Fig. I-17. Average cumulative production of (a) MITC and (b) CS_2 from 100 mg of Basamid or Basamid amended with copper sulfate in Douglas-fir heartwood at 30% MC as determined by purging and trapping in 95% ethanol over a 28-day period. Values that include water-contaminated samples are averages of all three samples in the treatment, including one in which water condensed.

		Ма	ximum MITC Co	ncentration (μ g/cc	air)
Distance from		End Convect (cr	ion Coefficient n/hr)	Radial Diffusi (cm	on Coefficient ² /hr)
Treatment Zone (cm)	Radial Position	83,340	83.34	0.0372	3.72
-30 cm	outer	0.80	0.80	0.89	1.17
	inner	3.58	3.60	8.01	1.33
at treatment hole	outer	1.35	1.35	1.25	1. 79
	inner	4.72	4.70	10.33	2.15
+30 cm	outer	0.77	0.77	0.92	0.86
	inner	2.70	2.70	7.36	0.86
+90	outer	0.30	0.30	0.54	0.25
	inner	1.21	1.20	4.29	0.30
+150	outer	0.13	0.13	0.32	0.08
	inner	0.53	0.53	2.52	0.09

Table I-24. Effect of convection coefficient or radial diffusion coefficient on MITC levels in a Douglas-fir pole 1 year after treatment with 60 g of MITC distributed in 2 holes as predicted by a computer simulation.

water had an immediate catalytic effect on Basamid. High Basamid residues remaining in the wood at the end of the test suggest that this chemical decomposes slowly enough to provide a long-lasting reservoir of chemical for future MITC release. This effect has been observed in field trials with Basamid supplemented with various additives.

6. Effect of voids on movement of chloropicrin or methylisothiocyanate through Douglas-fir heartwood: The study of the effects of voids on fumigant movement was not sampled in the 7th year. We anticipate sampling these poles near the end of this summer and will include the results in the next annual report.

7. Develop a model which predicts fumigant movement through wood poles under varying conditions: For the past five years we have been developing a computer model which predicts fumigant movement through wood poles. Last year, we reported on a preliminary effort to model MITC movement through douglasfir poles using the rate of MITC release from the MITC-Fume treated vials. The model uses ANSYS, a finite element model program to predict fumigant movement using previously developed sorption/desorption coefficients and diffusion coefficient. The model divides the pole into a series of segments for this purpose and calculates the rate of fumigant diffusion among the segments of the grid

over time. Our preliminary results were comparable to the levels present in the poles 6 or 12 months after fumigant application.

This past year, we executed the model over a one year period using 2 to 8 treatment holes and varying several parameters within the model to determine which variables most affected diffusion and subsequent MITC distribution. The model output can be delivered in plots showing gradients of fumigants at selected locations or as Tables showing maximum and minimum concentrations at a given height.

The results indicated that MITC distribution around the treatment hole reached a steady state within one year after application (Figures I-18, 19). Chemical levels were slightly higher at the upper edge of the treatment zone than 30 cm below this zone then declined sharply with increasing distance from the treatment zone. The use of an increased number of treatment holes (i.e. more MITC) resulted in increased fumigant levels 30 to 90 cm away from the treatment zone, but the relationship was not linear nor did increased dosage improve chemical levels 150 cm away from the treatment zone (Table I-22). These results imply that increasing the dosage in a relatively small treatment zone may have a diminishing effect on fungal control, while spreading the dosage over a larger area of the pole may be more effective for this purpose.

The initial model was run using a mainframe computer for which we had minimal priority within the university system. The finding that the model reached a steady state within one year permitted us to use a PC version of the model which ran more quickly. As a result, we explored the sensitivity of various model parameters.

While the model employs figures developed from previous laboratory studies, it is as yet unclear which factors most affect fumigant movement in the model. For this reason, we varied the convection coefficient from 0.001 to 1.00 while holding radial, tangential and longitudinal coefficients at 0.001489, 0.001245, and 0.435 cm^2/hr for heartwood and 0.002435, 0.002435, and 0.695 cm²/hr for sapwood and using a flux of 9.049 ug/hr/cm². This value is particularly important with the model since higher convection coefficient values at the ends of the pole would increase the rate of fumigant loss. The results indicate that decreasing the convection coefficient dramatically affected the performance of the model, resulting in a doubling in subsequent fumigant concentration as the coefficient was varied between 1 and 0.001 cm/hr (Table I-23). As in the initial model run, chemical levels declined away from the treatment zone, but the declines were not as sharp. Increasing the convection coefficient should speed movement through the wood, ultimately resulting in more uniform fumigant distribution, but also reducing the amount of fumigant nearest the treatment hole. Decreasing the convection coefficient should retain chemical within the wood, thereby increasing chemical levels at a given position.

The effects of convection coefficient and radial diffusion coefficient on subsequent fumigant distribution were further investigated by varying the

convection coefficient from 83.34 to 83,340 cm/hr. A thousand fold increase in convection coefficient had virtually no effect on MITC levels one year after fumigant application (Table I-24). These results suggest that there is a point of diminished sensitivity to convection coefficient values at a given series of diffusion coefficients. Similarly, there was little effect on MITC levels when the radial diffusion coefficient was varied from 0.0372 to 3.72 cm²/hr while the convection coefficient was held constant at 83.34 cm/hr (Table I-24). These results suggest that initially the rate of fumigant loss from the wood plays the most significant role in fumigant distribution, while the diffusion rate over these longer time periods has a less substantial role. Over shorter period, however, the diffusion coefficients should become more critical.

We are presently running the model over a 5 year period using the mainframe. If the results indicate that the model continues to reach a steady state within one year, we plan to continue to explore the sensitivity of the model to various treatment parameters.



Figure I-18. MITC concentrations at selected heights in a Douglas-fir pole 6 months after treatment with 60 g of MITC distributed between 2 treatment holes as predicted by a finite element model a) 30 cm below groundline, b) at the highest treatment hole, c) 30 cm above the highest treatment hole, d) 90 cm above that hole, and e) 150 cm above that point.



Figure I-19. MITC concentrations at selected heights in a Douglas-fir pole 12 months after treatment with 60 g of MITC distributed between 2 treatment holes as predicted by a finite element model a) 30 cm below groundline, b) at the highest treatment hole, c) 30 cm above the highest treatment hole, d) 90 cm above that hole, and e) 150 cm above that point.



Figure I-20. Effect of number of treatment holes on distribution of MITC in a Douglas-fir pole 12 months after treatment with 60 to 240 g of MITC distributed between a) 2 holes, b) 4 holes, c) 6 holes, or d) 8 holes as predicted by a finite element model.



Figure I-21. Effect of number of treatment holes on MITC distribution 30 cm below groundline in a Douglas-fir pole 12 months after treatment as predicted using a finite element model with a) 2 treatment holes, b) 4 treatment holes, c) 6 treatment holes, or d) 8 treatment holes.



Figure I-22. Effect of number of treatment holes on MITC distribution at the highest treatment hole in a Douglas-fir pole 12 months after treatment as predicted using a finite element model with a) 2 treatment holes, b) 4 treatment holes, c) 6 treatment holes, or d) 8 treatment holes.



Figure I-23. Effect of number of treatment holes on MITC distribution 30 cm above the highest treatment hole in a Douglas-fir pole 12 months after treatment as predicted using a finite element model with a) 2 treatment holes, b) 4 treatment holes, c) 6 treatment holes, or d) 8 treatment holes.

		М	laximum MITC co	ncentration (μ /cc :	air)
Distance from Treatment Zone (cm)	Radial Position	Two Holes	Four Holes	Six Holes	Eight Holes
· -30	outer	0.80	1.16	1.37	1.55
	inner	3.60	5.21	6.15	6.98
at highest	outer	1.35	1.92	2.26	2.60
treatment	inner	4.70	7.66	9.03	10.37
	outer	0.77	0.92	1.12	1.30
+30	inner	2.70	3.69	4.49	5.18
	outer	0.30	0.40	0.49	0.53
+90	inner	1.20	1.58	1.96	1.84
	outer	0.13	0.16	0.09	0.05
+150	inner	0.53	0.57	0.51	0.05

[']Table I-23. Effect of number of treatment holes on fumigant concentrations in a Douglas-fir pole 1 year after treatment with MITC^a

Table I-24. Effect of low convection coefficient values on MITC concentrations in a Douglas-fir pole one year after treatment with 60 g. of MITC equally distributed in 2 treatment holes as predicted by a finite element model.

		Maximum	MITC Concentration	(ug/cc air)
Distance from		Con	vection coefficient (cn	n/hr)
treatment zone (cm)	Radial Position	1.00	0.24	0.001
-30	outer	190	192	306
	inner	856	863	1260
0	outer	320	321	405
	inner	1119	1122	1337
+30	outer	185	185	257
	inner	647	649	936
+90	outer	76	77	128
4	inner	306	307	436
+150	outer	35	35	74
	inner	139	140	239

^a Radial, tangential and longitudinal diffusion coefficients were 0.001489, 0.001245 and 0.435 cm²/hr for heartwood and 0.002435, 0.002435, and 0.695 for sapwood, respectively.

OBJECTIVE II

IDENTIFY ENVIRONMENTALLY ACCEPTABLE CHEMICALS FOR PROTECTING WESTERN REDCEDAR SAPWOOD AND FIELD DRILLED BOLT HOLES

A. PROTECTION OF SAPWOOD EXPOSED ABOVE GROUND IN BUTT-TREATED WESTERN REDCEDAR POLES.

Western redcedar remains among our most durable pole species and many utilities preferentially purchase this species. The sapwood of western redcedar, like that of wood species, has little natural durability. Many utilities continue to use butt-treated western redcedar in the belief that the risk of decay above this zone is small. Even in drier climates, cedar sapwood eventually weathers and decays and its presence on the surface poses a considerable risk to line personnel who must climb these poles. For many years, pentachlorophenol on diesel oil was applied at 10 to 20 year intervals to these poles to retard the decay

process, but concerns about the use of penta in this application led to a substitution of copper naphthenate and a search for safer chemicals for this purpose.

Last year, we reported on the results of small and full scale field trials of a variety of potential alternative biocides for protecting western redcedar. These trials identified a number of promising alternatives. No additional research was performed under this section in the past year and we are awaiting the availability of field test poles within the Bonneville Power Administration system to provide a final evaluation of these chemicals.

B. EVALUATE TREATMENTS FOR PREVENTING DECAY IN FIELD- DRILLED BOLT HOLES

Proper specification of preservative treated wood includes an effort to make all cuts and holes prior to treatment to ensure that the envelop of treatment remains intact, but this is not always possible with poles. As a result, many holes are made in poles during installation or during maintenance. Installation of cable is a major contributor to the need for field drilling. The exposure of untreated wood in the field damaged area can permit the entry of moisture, fungi and insects, leading to reduced service life. The extent of the decay problem in field drilled bolt holes is difficult to determine; however, we estimate that 10 to 20 percent of field drilled poles eventually develop decay in this zone leading to weakened connectors and, ultimately, failure under extreme loads.

The American Wood Preservers' Association standards recommend that field damage to treated wood be treated by topical application of copper naphthenate, pentachlorophenol or creosote, but many lineman dislike these oily chemicals and do not apply them. It is expensive to check for application, making it even less likely that such treatments will be applied.

The introduction of decay avenues in poles is incongruous with the efforts of utilities to increase pole service life and enhance reliability. These concerns should create a need for an enhanced field treatment system which lacks the drawbacks of the existing oilborne formulations.

In 1981, a series of Douglas-fir poles were treated with pentachlorophenol in P9 Type A oil, then a series of 8 holes 2.5 cm in diameter were drilled into the poles beginning 60 cm above the groundline and extending upward at 45 cm intervals to within 45 cm of the top. The holes were treated with 10% pentachlorophenol in diesel oil, powdered ammonium bifluoride (ABF), powdered disodium octaborate tetrahydrate (Boron), or 40% boron in ethylene glycol (Boracol). Each treatment was replicated on 8 holes in each of 4 poles, while holes in an additional 8 poles were left untreated to serve as control. An addition of 4 poles received no chemical treatment, but chemically impregnated washers containing 37.1% sodium fluoride, 12.5% potassium dichromate, 8.5% sodium pentachlorophenate, 1% sodium tetrachlorophenate, and 11% creosote were used to attach bolts to the holes. Metal gain plates were inserted in one half of the holes on each pole and plastic gain plates were used on the remainder.

The poles have been sampled annually by removing increment cores from sites directly below each bolt hole gain plate on one side of the pole and from above the washer in the opposite site. The cores were cultured on malt extract agar and any fungi growing from the wood were examined for characteristics typical of basidiomycetes, a group of fungi containing many important wood degraders.

Colonization levels in the Patox washers continue to be elevated, reflecting the inability of this treatment to move to the point where fungal attack is occurring (Table II-1). These levels exceeded those found with the controls and indicate that Patox, while an effective fungicide, is not suitable for impregnating washers to prevent bolt hole decay.

As in previous years, the diffusible treatments (ABF, boron, and boracol) continue to have the lowest levels of fungal infestation (Table II-1), reflecting the ability of these chemicals to move through the wood as checks open, thereby providing improved protection. Boron and fluoride are both capable of considerable movement through Douglas-fir heartwood, but this diffusion has not yet resulted in depletion of preservative to the point where protection against fungal attack has been compromised to the extent that occurred with penta. The presence of fungal colonization in both the ABF and boracol treatment suggested that the effectiveness of these treatments is declining. Despite these declines, the diffusibles have outperformed the oilborne penta control and merit consideration for field treating bolt holes. These chemicals are less toxic and do not have the oily characteristics typical of penta and its more recent replacement, copper naphthenate. As a result, field application

by line personnel, particularly those not directly affiliated with the owner of the pole is more likely. These poles will continue to be sampled to determine the point when the diffusibles no longer afford protection to the poles.

Table II-1. Basidiomycetes and other fungi found in preservative-treated Douglas-fir poles 6 to 10 years after bolt holes were drilled and treated in the field, as shown by cultures from increment cores.

					ł	ercentag	ge of co	res cont	aining.					
	Basidiomycetes						Other Fungi							
Field Treatment	6 yr	7 yr	8 yr	9 yr	10 yr	11 yr	12 yr	6 yr	7 yr	8 yr	9 yr	10 yr	11 yr	12 yr
Ammonium bifluoride (n=32)	0	2	0	2	2	2	2'	5	2	16	42	9	47	39
Boracol [®] 40 (n=32)	0	2	0	0	·3	0	3	18	27	33	66	16	70	42
Patox ^{Φ} washer n=32	5	5	8	14	13	11	8	12	22	31	66	27	55	45
Pentachlorophenol (n=32)	2	2	8	5	6	5	6	25	17	25	51	25	80	61
Timbor [®] (n=32)	0	0	0	2	2	2	Ó	11	25	25	37	14	75	39
Control (n=64)	3	9	17	9	8	11	3	30	26	46	70	33	86	55

OBJECTIVE III

A. INCIDENCE OF DECAY ABOVE THE GROUNDLINE IN DOUGLAS-FIR POLES IN THE PACIFIC NORTHWEST

Douglas-fir from the coastal regions of the western United States has a thin, treatable sapwood shell surrounding a difficult-to-treat heartwood core. Post-treatment checking of poles in service often leads to the development of internal decay at the groundline, a problem well documented across the United States. The problem of internal decay has led many utility companies to regular inspections that include application of volatile fumigants.

Many utility companies now also specify through-boring, radial drilling, or kerfing at the groundline either to improve treatment or to control checking in this zone. The combination of good initial specifications coupled with vigilant inspection and maintenance has minimized the risk of decay at the groundline, thereby markedly extending the service life of poles.

Recently, however, utility companies seeking to further extend the service lives of older poles have become concerned about the incidence of decay above the groundline. In principle, such decay should be less frequent and slower to develop than that at groundline, largely because aboveground positions would have lower moisture levels, a lower inoculum potential, and a harsher environment for spore germination and colony establishment. Nevertheless, many utility companies are finding increasing levels of aboveground decay.

In this report, we describe a survey conducted in Oregon and Washington to define the incidence of both visible decay and fungal colonization in the aboveground zone of Douglas-fir poles ranging from 0 to 40 years old.

Four hundred and ninety Douglas-fir poles owned by the Bonneville Power Administration (BPA) were selected for study. The poles were located in five regions: Oregon coast, Washington coast, Puget Sound, southwest Washington/Willamette Valley, and eastern Oregon (Fig. III-1). These regions were arbitrarily defined but differ in precipitation and decay hazard above ground. Powerlines suitable for sampling were identified within each region; because of differing patterns of construction by BPA, equal numbers of poles of a given age were not present in all regions.

Each selected pole was examined for visible evidence of damage and then sampled by removing two 15-cm-long increment cores 120° apart at each of three heights: 1.5, 3.0, and 4.5 m above the groundline. (Sampling was done from ladders, on which 4.5 m was the maximum safe height.) The poles were left unsampled at the groundline because BPA specifies through-boring prior to preservative treatment, resulting in virtually 100 percent treatment of this



Figure III-1. Regions in Oregon and Washington from which poles were sampled to determine the prevalence of aboveground decay.

area. On each core, the depth of preservative penetration was noted, then this zone was discarded. The presence of decay along the core was recorded, and the core was placed in a plastic drinking straw, which was stapled shut and stored on ice. The sampling hole was then probed with a shell-depth indicator, the presence of any voids was recorded, and the hole was plugged with a tight-fitting wood dowel.

The increment cores were later removed from the straws and lightly flamed to eliminate any surface contaminants. They were then placed on the surface of 1.8 percent malt agar in petri dishes and incubated for 30 days at room temperature (20°-24°C). Fungi growing from the cores were then examined for characteristics typical of basidiomycetes, a group of fungi including many important wood decayers.

The results were tabulated on the basis of pole age, sampling height, region and location, and the presence of one or more voids per pole.

When the data for all regions, age classes, and sampling heights were combined, 19 percent of all poles sampled contained decay fungi (Table III-1).

Effect of pole age: Among poles in service for 1 to 10 years, 8 percent yielded active decay fungi; however, because the sample size in this age class was only 12 poles (Table III-1), only a single isolation was involved. The latter was from 4.5 m above ground, suggesting that fungal invasion occurs rapidly and at some height. Alternatively, a fungus may have invaded the pole during seasoning before treatment; however, BPA requires a 48-hour Boulton seasoning cycle for wood poles, a period far exceeding that required to kill established decay fungi.

The incidence of decay increased dramatically in the next higher age class-to 20 percent among 11- to 20-year-old poles, an increase suggesting that there was a steady fungal invasion of these poles. Unlike the more recently installed poles, in this age class the incidence of decay fungi was slightly higher at the lowest sampling point. Similar levels of decay were found among poles 21 to 30 years old and those 31 to 40 years old. This leveling out of decay incidence may have resulted from either of two possibilities: there was a limited number of locations where wood along checks was at the fiber saturation point and thus conducive to fungal growth, or in some regions BPA, as it often does, may have removed poles with minor decay pockets, an action that would make the incidence of decay appear lower than it actually was. The nature of our sampling design made it impossible to determine which of these possibilities materialized; however, a general leveling in incidence of advanced decay with time has also been noted in studies made at the groundline and may indicate that not all poles are uniformly susceptible to internal decay.

Effect of height above groundline: Among poles from the various regions, there was no consistent trend in the incidence of decay fungi at the three sampling heights (Table III-2). The absence of an apparent height effect is particularly important because it highlights the need to inspect poles thoroughly at several heights for internal decay, thereby adding considerably to the cost of aboveground inspections in high-risk areas.

Effect of region: The incidence of fungal isolations from poles varied widely among locations within a given region, reflecting both differing pole ages and differing microclimates (Table III-2). Isolation levels were highest from poles around Puget Sound and along the Washington coast. These regions receive copious amounts of wind-driven rain, which would create ideal conditions for both germination of spores and growth of mycelium through wood above the ground.

Slightly fewer poles (17%) in the southwest Washington/Willamette Valley region contained decay fungi than did those around Puget Sound and along the Washington coast, a reflection of the slightly lower levels of precipitation and decreased frequency of wind-driven rain in this central region.

Poles along the Oregon coast had far less fungal colonization than did those in other regions west of the Cascade Mountains. This finding is puzzling in light of the perception by local utility companies that aboveground decay poses a major maintenance problem. However, poles from one location (Florence) were nearly all less than 10 years old, and those from another (Reedsport) were less than 20 years old (Table III-3). The incidence of decay fungi from the remaining two locations along the Oregon coast approached that found in other regions and probably more closely typifies the levels to be expected in this region.

Although the presence of decay fungi above ground in poles west of the

Cascades was expected, such presence in poles east of these mountains was surprising. The location sampled in eastern Oregon (Redmond) receives less than 250 mm of precipitation per year, primarily as snow. The summers are hot and dry, and the winters are cold with occasional precipitation. An initial sample of 50 poles revealed that 10 percent of them contained at least one viable decay fungus. When an additional 56 poles were sampled to verify the original results, the levels of fungal isolations were similar. Of the 106 poles sampled in all, 5 contained visible decay pockets, indicating that conditions for decay occur in these poles (Table III-4). The decay pockets may have resulted from fungi that colonized the wood over many years as conditions became suitable for spore germination or from fungi that colonized more recently and will eventually die as stored nutrients are depleted.

The poles in this region were almost all over 30 years old. Prior to 1963, BPA specifications limited the time a pole could be heated during pressure treatment. However, many decay fungi invade Douglas-fir poles as they air-dry prior to treatment. Although these fungi have little effect on wood properties prior to treatment, their survival throughout a treatment cycle is of some concern. The heat limitation imposed at that time by BPA markedly increased the likelihood that fungi established during the cutting and air-drying of the poles would survive the treatment cycle and cause early failures. Some of these fungi may still survive in poles 30 or more years after treatment, although determining the origin of the specific isolates would be impossible.

Incidence of voids above ground: Because of a sampling error, the presence or absence of aboveground voids was recorded for only 377 of the 490 poles. Of these poles, 21 (6%) contained 1 void, while 39 (11%) contained 2 or more voids (Table III-4). Among these 377 poles, about half of those from which viable decay fungi were isolated contained voids. This ratio implies that infestations in these poles are actively progressing to the visible stages of decay, although the periods involved appear to be relatively long. The highest incidences of voids were in poles around Puget Sound, suggesting that the rates of decay were highest in this region. However, the poles sampled in this region were among the oldest and, therefore, might be expected to have more visible evidence of decay. The incidence of aboveground voids in the other locations was generally lower than the 15 to 20 percent typically noted at the groundlines of Douglas-fir poles subjected to a first inspection.

Although conditions for development of decay fungi were clearly present above ground, wood closer to the ground is more likely to be above the fiber saturation point for longer periods each year and should decay more readily. The Pacific Northwest typically has very wet winters but receives little precipitation in summer. As a result, seasonal moisture levels in wood above ground can vary widely and might limit the decay rate. Thus, even with similar frequencies of fungal inoculation along the entire length of the pole, visible decay should be more prevalent at the groundline where the soil can provide a more stable moisture regime. In fact, cultural tests by Graham of wood removed from the groundline of

Douglas-fir poles suggest that the levels of infestation there are far higher than those found in aboveground zones in the current study.

Significance of aboveground decay: The significance of aboveground decay is difficult to assess. In through-bored poles from which decay fungi are excluded at the groundline, the presence of aboveground decay could ultimately develop into a serious problem. Although only 10 percent of the sampled poles less than 30 years old contained visible decay, the presence of weaker poles in a system poses a potential hazard, particularly under high wind or ice loading. And from a financial standpoint, detecting the presence of voids above ground would be both costly and time-consuming. Furthermore, current inspection methods can only detect advanced decay; consequently, incipient infestations could go undetected for many years until they caused serious damage. As utility companies extend the expected lives of their pole systems far beyond the 30 to 40 years originally envisioned, such concerns must be addressed. Instituting aboveground inspections 25 to 30 years after pole installation may become necessary in some regions.

The options for control of aboveground decay are limited. Liquid fumigants are widely used to control groundline decay and some, such as metham sodium, can be applied above ground, but the risks of spills during such application are markedly increased. One fumigant, MITC-Fume, is a solid that can be safely applied above ground, but its cost is higher than that of other fumigants. Water-borne diffusibles have also been proposed for aboveground applications, but preliminary field data suggest that the rates of diffusion from such applications are far slower than generally predicted.

Decay fungi are apparently prevalent in the aboveground zones of Douglas-fir poles in the Pacific Northwest, having been isolated from 19 percent of the poles sampled in Washington and Oregon. These findings make it incumbent on utility companies to begin aboveground inspection of poles older than 25 to 30 years and to consider alternatives for controlling detected fungi before they cause significant damage.

TABLE III-1.—Incidence of decay fungi at selected heights above ground in sampled Douglas-fir poles in service for up to 40 years in the Pacific Northwest.

Years in with	No. of	% cores with	th decay at indic	ated heights	% poles
service fungi	poles sampled	1. 5 m	3.0 m	4.5 m	with decay
0-10 11-20	12 120	0 8	05	4 5	8 20
21-30 31-40 Total or avg.	78 280 490	9 7 7	4 6 5	3 6 5	21 18 19

TABLE III-2.—Incidence of decay fungi at selected heights above ground in sampled Douglas-fir poles exposed in five regions of the Pacific Northwest.

Region and Nearby City	No. of	ated heights	% Poles with decay		
	sampled	1.5 m	3.0m	4.5 M	fungi
Oregon coast					
Coos Bay	23	7	4	· 6	26
Florence	10	0	0	3	10
Reedsport	11	0	0	3	9
Tillamook	49	6	5	2	18
Total or avg.	93	5	4	3	20
Washington coast					
Long Beach	77	8	5	6	28
Puget Sound					
Olympia	34	7	5	4	21
Snohomish	54	10	9	10	31
Total or avg.	88	8	7	8	27
SW Washington/Willamette Valley					
Chehalis	48	3	2	1	19
Corvallis	49	5	1	1	16
Eugene	29	2	6	1	14
Total or avg.	126	4	3	1	17
Eastern Oregon					
Redmond	106	1	1	1	10

TABLE III-3. Incidence of decay fungi above ground in sampled Douglas-fir poles in service for up to 40-years in five regions of the Pacific Northwest.

Region				Years	in Service			
and Nearby	H	0	11	-20	21-	30	-11	40
City	No. of poles sampled	% poles with decay fungi	No. of poles sampled	% poles with decay fungi	No. of poles sampled	% poles with decay fungi	No. of poles sampled	% poles with decay fungi
Oregon coast Coos Bay Florence	00	0	00	0	13 0	31 0	10	20 0
Reedsport Tillamook		00	23 8	13	0 6	33 0	23	0 17
Washington coast Long Beach	1	0	31	48	31	9	11	24
Puget Sound Olympia Snohomish	00	00	00	00	0 %	0 04	34 49	31
SW Washington/Willamette Valley Chehalis	0	0	0	0	84	19	0	0
Corvallis Bugene	00	00	18 10	11 20	е 0	33 0	28 19	19 11
Eastern Oregon Redmond	0	0	0	0	7	0	99	10

Region and nearby city*	No. of poles sampled	No. of poles with one void ^b	No. of poles with more than one void ^b	% poles containing voids
Washington coast				
Long Beach	77	1	2	3
Puget Sound				
Olympia	34	7	15	44
Snohomish	54	5	11	20
SW Washington/Willamette Valley				
Chehalis	48	1	2	4
Eugene	29	2	4	14
Eastern Oregon				
Redmond	106	5	5	5
Total or avg.	348	21	39	11

TABLE III-4. Incidence of voids above ground in sampled Douglas-fir poles in various regions in the Pacific Northwest.

"Only the regions and cities in which voids were recorded are listed.

^bThe presence of voids in both cores from a given height above groundline was counted as a single void.



B. THROUGH BORING OF POLES FOR IMPROVING TREATMENT: DISTRIBUTION OF PRESERVATIVE AND EFFECT ON PERFORMANCE

Wood poles of most species provide excellent performance when they are properly treated with preservatives using pressure processes. Some species, however, are more difficult to treat owing to the presence of only a shallow band of easily treated sapwood surrounding a difficult to treat core of heartwood. Poles of these species, which include Douglasfir, spruce, larch and scots pine, are often treated while the heartwood is still wet (above the fiber saturation point) and tend to develop checks near the groundline as they season in service. These checks often extend beyond the depth of the original treatment, permitting the entry of decay fungi into the untreated, heartwood zone, thereby creating maintenance problems and decreasing service life.

Internal decay can be arrested by internal application of fumigants at regular intervals, however, it is far more cost effective to prevent the entry of decay fungi through pretreatment processing procedures. Four techniques have evolved for improving the performance of wood poles: kerfing, deep incising, radial drilling, and through boring. Kerfing does not improve the depth of treatment, but it reduces the development of deep checks in the groundline zone, thereby minimizing the risk of internal decay. A variety of studies have clearly demonstrated the benefits of kerfing, but this technique is not widely used. Deep incising in the groundline zone to depths of 50 to 75 mm is used to a limited extent to produce a deeper treated shell surrounding the untreated heartwood core. Radial drilling

uses a series of holes in a diamond shaped pattern drilled around the poles to depths ranging from 65 to 125 mm from the wood surface. The result is a well treated shell to the depth of the drill holes. Through boring takes this process a step further by drilling a series of holes completely through the pole. This process creates the potential for complete treatment of the groundline region of the pole, thereby eliminating the risk of decay in this zone.

Of the four processes for minimizing the risk of internal decay prior to installation, through boring is the most widely used, probably owing to the ease of use and the minimal effects on strength (<5% less in bending for transmission size poles). Most utilities use variations of two patterns developed by Bonneville Power Administration (Vancouver, WA)(BPA) and Portland General Electric Corp. (Portland, OR)(PGE) (Figure III-2). These specifications vary slightly in pattern, but both appear to be adequate for achieving complete treatment of the wood. As a result, most specifications require that 100% of the wood in the through bored zone be treated with preservatives.

There is, however, some controversy concerning the requirement for complete treatment of the through bored zone. While complete treatment is desirable, the presence of small skips or gaps in an otherwise heavily treated zone seems unlikely to cause significant risk of decay. There is little data on the effects of



Figure III-2. Patterns used by a.) Bonneville Power Administration or b.) Portland General Electric for through boring of Douglas-fir poles at the groundline prior to treatment.

skips or gaps on performance of poles, nor is there an extensive data base on the distribution of preservative around through bored zones. In this report, we describe the distribution of preservative around poles receiving four through boring patterns as well as the performance of through-bored poles with differing degrees of preservative penetration.

Distribution of preservative in the through bored zone of Douglas-fir poles: Twenty- four 3.0-m long kiln dried (initial average moisture content 21 % at 50 mm) Douglas-fir pole sections (approximately 300 mm in diameter) were drilled with one of four patterns. These patterns were the original BPA and PGE specifications as well as modifications of each pattern which increased the distance between holes (Figure III-3). The goal of the study was the development of acceptable patterns for full-length through boring of poles prior to treatment. Each pattern was replicated on 6 pole sections.

The poles were treated with pentachlorophenol in P9 Type A oil to a retention of 9.6 kg/m³ in the outer 25 mm assay zone using a modified empty cell process. The treatment consisted of an initial conditioning-in-oil period of 14 hours at 88 C, an initial pressure of 224 kPa, introduction of the preservative, and a application of 880 kPa for 2.5 hours. The poles were then subjected to a 4 hour expansion bath at 99 C and a 1 hour final 88 kPa vacuum.

Following treatment, preservative penetration and retention were measured by removing increment cores from three regions: parallel to the boring and midway between two adjacent holes in a longitudinal plane (core 2), offset radially from the original sample site by 25 mm (core 1), and perpendicular to the original boring and midway between two adjacent holes in the longitudinal direction (core 3) (Figure III-3). Four cores were removed from each region per pole section and each core was divided into six 25 mm long segments. Respective segments from the same region of a given pole stub were combined, ground to pass a 20 mesh screen, oven-dried for 1 hour at 100 C, weighed (nearest 0.1 g) and analyzed for residual penta content using an ASOMA 8620 x-ray fluorescence analyzer (Asoma Instruments Inc., Austin, TX).

Preservative penetration in the through bored zone and its relationship with the presence of internal decay in Douglas-fir poles: Douglas-fir pole sections in both the PGE and BPA system were selected for sampling. The poles were located in Western Oregon and Washington and had been in service for 3 to 25 years. Most poles were treated with either pentachlorophenol or creosote, but 21 poles were treated with copper naphthenate.

Each pole was sampled by removing one to three 150 mm long increment cores from zones located parallel to and equidistant between two through bore holes near the groundline. The cores were examined for preservative penetration and any skips in penetration were noted. Preservative penetration was generally easily measured, but cores with light penetration or wet wood were allowed to dry overnight before being measured. Penetration along the core length was categorized from 0 to 100% of the core in the following classifications:



Figure III-3. Alternative patterns a.) Modified PGE or b.) Modified BPA used to through bore Douglas-fir poles prior to treatment. Core locations indicate sites where increment cores were removed after treatment to measure preservative penetration and retention.

100%, 90-99%, 70-89%, and 60-69% of the core penetrated. For the purpose of this study, rings were considered penetrated even when only the latewood was treated. No cores were found to be less than 60 % penetrated.

A total of 137 poles were sampled, 25 in the PGE system and 112 in the BPA system.

Distribution of preservative in the through bored zone of Douglas-fir poles: All but two of the 288 cores removed for preservative assay were completely penetrated with pentachlorophenol. Two cores, one from the modified BPA pattern and one from the modified PGE pattern had 86 and 89 % penetration, respectively. The results illustrate the excellent treatment produced within the through bored zone with all four boring patterns.

Pentachlorophenol retentions in the cores generally exceeded the 9.6 kg/m³ required in the 6 to 25 mm assay zone for Douglas-fir poles under AWPA Standard C4 (Table III-5). Retentions generally declined inward from the surface, although levels 125 to 150 mm from the surface still approached or exceeded those required in the outer assay zone for pole treatment. Gradients inward tended to be shallower than those found with non-through-bored holes, reflecting the benefits of having increased the amount of end-grain exposed to preservative treatment.

Sampling orientation had a variable effect on retention results. Cores removed from locations directly between 2 holes (core 2) tended to have slightly higher retentions than those removed from sites 25 mm away from this site (core 1), although there were exceptions to this trend. Cores from directly in line would be expected to have higher retentions since they would be more likely to be affected by end-grain penetration. Cores removed from sites perpendicular to the throughbored holes tended to have retentions similar to those found for the in-line samples, except with the modified BPA pattern. The reasons for this discrepancy are unclear. Cores removed perpendicularly from through bored holes would be expected to have high retentions since there would be multiple exposure of transverse faces to preservative flow.

The four through boring patterns produced slightly different preservative distributions, although the effects were not consistent among the various patterns tests. For example, the BPA and modified BPA patterns had similar retentions in core 1, but the modified pattern had lower retentions at both cores 2 and 3. The modified pattern spread the distance between holes to reduce potential strength effects and this increased distance apparently affected treatment gradients with little effect on the degree of preservative penetration. Interestingly, there was little consistent difference in preservative retention between the PGE and modified PGE patterns. This lack of effect may reflect the tendency for the PGE pattern to spread the holes to a greater extent than the BPA pattern.

The results suggest that all of the through bored patterns produced preservative distributions and retentions which would completely protect the through-bored zone. Further studies are planned to evaluate the effect of these patterns on strength.

			Retent	ion (Kg/m³)ª	
Sample zone ^b	Assay Depth (mm)	BPA	Modified BPA	PGE	Modified PGE
in-line	0-25	18.39 (4.69)	16.83 (4.46)	16.40 (3.44)	16.37 (5.07)
	25-50	15.59 (4.59)	11.91 (3.87)	14.61 (3.74)	12.54 (3.78)
	50-75	12.78 (5.46)	10.53 (4.40)	13.82 (4.78)	9.90 (3.08)
	75-100	12.29 (4.96)	9.80 (4.14)	13.49 (4.27)	9.52 (2.46)
	100-125	11.20 (5.03)	8.72 (5.57)	13.50 (2.19)	10.84 (4.70)
	125-150	9.06 (4.37)	8.07 (5.15)	12.21 (2.64)	12.18 (4.51)
off-set	0-25	17.15 (4.63)	15.50 (2.01)	16.14 (3.82)	15.45 (4.87)
	25-50	14.99 (4.40)	10.24 (4.17)	14.91 (3.33)	12.53 (4.48)
	50-75	12.78 (4.89)	7.36 (4.07)	13.30 (3.66)	9.76 (3.58)
	75-100	9.50 (4.49)	5.61 (4.75)	12.59 (3.55)	9.63 (2.94)
	100-125	8.90 (3.05)	4.98 (3.54)	11.46 (3.59)	8.78 (2.71)
	125-150	9.07 (2.61)	7.86 (1.33)	12.48 (3.39)	9.05 (3.98)
erpendicular	0-25	16.81 (4.67)	16.03 (3.60)	15.97 (2.78)	15.00 (5.83)
	25-50	13.19 (4.23)	13.76 (2.76)	13.07 (3.58)	14.30 (3.96)
	50-75	13.14 (6.88)	10.94 (4.17)	13.97 (3.30)	11.17 (1.87)
	75-100	8.00 (2.00)	10.61 (3.68)	11.42 (3.94)	10.14 (2.47)
	100-125	10.46 (4.41)	7.69 (4.47)	14.11 (4.75)	12.11 (2.87)
	125-150	9.85 (1.99)	5.22 (1.53)	12.78 (2.98)	11.83 (4.19)
combined	0-25	17.45 (4.71)	16.12 (3.55)	16.18 (3.38)	15.61 (5.30)
	25-50	14.59 (4.53)	11.97 (3.93)	14.19 (3.65)	13.12 (4.17)
	50-75	12.89 (5.80)	9.61 (4.51)	13.70 (3.98)	10.28 (3.00)
	75-100	9.93 (4.41)	8.67 (4.75)	12.50 (4.02)	9.76 (2.65)
	100-125	10.19 (4.35)	7.13 (4.87)	11.52 (5.36)	10.58 (3.80)
	125-150	8.32 (3.88)	6.18 (4.30)	11.14 (4.88)	10.34 (5.00)

1 able III-5. Effect of through-boring pattern on pentachlorophenol retention at selected depths from the surface of Douglas-fir poles.

^a Values represent means of 6 replicates/per core pattern. Values in parenthesis represent one standard deviation. Combined core samples represent 18 replicates/treatment.

^b Core sample identifications are as follows: in line: directly between 2 longitudinally oriented bore holes, offset: 25mm offset from 2 longitudinally oriented holes, and perpendicular: cores taken perpendicular to the orientation of the through bore holes.

Preservative penetration in the through bored zone and its relationship with internal decay in Douglas-fir poles: Poles sampled ranged from 3 to 25 years of age. Most were in the Long Beach area along the Washington coast where the poles were subjected to a high hazard of internal decay development. Preservative penetration varied from 60 to 100% in the 272 cores examined (Table III-6). Nearly 95 % of the cores examined were 90 to 100% penetrated, indicating that the through boring process had produced a well-treated zone around the groundline. The remaining cores had penetration values ranging from 60 to 89%. The effects of gaps or skips in a through-bored pole on the development of internal decay in the groundline zone are difficult to predict. In principal, any untreated wood should be susceptible to decay; however, it is likely that most of the gaps present in through-bored poles are surrounded by preservative treated wood. If these poles were treated to the same degree as those in the first portion of this study, then any treatment gaps would be surrounded by wood containing high levels of preservative. Thus, the risk of decay in a gap is likely to be quite low given the small probability that a spore or hypha of a decay fungus will be able to penetrate the treated zone to reach the untreated wood. None of the poles examined in the current study had any evidence of decay in the untreated locations in the through bored zone. The absence of visible decay fungi suggests that specifications which require 100% penetration of the throughbored zone may be excessive. The numbers of cores with penetration values below 90% in the current study, however, make it difficult to determine what an appropriate penetration minimum might be

for preventing internal decay in the through-bored zone and further inspections would be required for this purpose.

Through boring markedly improves penetration of preservative in Douglas-fir poles, although the modifications explored suggest that further refinement of through boring patterns to maximize preservative distribution while minimizing strength effects is feasible. The field inspections also suggest that, while most through bored poles are thoroughly treated in the bored zone, poles with incomplete penetration also remain free of internal decay in this zone. Further inspections are recommended to more fully delineate the point where incomplete penetration adversely affects performance.

					_	_	_	_	_		_	_
ng patterns.	% ange	100%	100	97	84	84	80	100	100	100	100	84
rough-bori	vith a given	%66-06	0	1	4	8	10	0	0	0	0	0
ving two th	of cores w servative pe	%68-0L	0	2	9	8	10	0.	0	0	0	80
poles receiv	% pre	%69-09	0	0	6	0	0	0	0	0	0	8
Douglas-fir		# of cores	45	102	50	12	10	9	2	9	14	25
ed zone of]		# of poles	15	51	25	6	5	3	1	3	7	21
e through-bore		Pole Age (yrs)	4	25	18	21	19	18	1	10	6	3
sgree of treatment in the		Geographic Location	Junction City, OR		Long Beach, WA	Salem, OR						Cottage Grove, OR
Table III-6. Relative de		Initial Treatment	Creosote		Pentachlorophenol							Copper Naphthenate
OBJECTIVE IV

EVALUATE THE POTENTIAL FOR DECAY DEVELOPMENT DURING AIR-SEASONING AND IDENTIFY CONTROL STRATEGIES

The exposure of freshly peeled poles to remove moisture markedly increases the likelihood that fungi will colonize the wood prior to preservative treatment. In previous reports, we have determined the levels of fungal colonization in Douglas-fir poles following varying periods of air-seasoning in the Pacific Northwest, identified treatments for limiting the colonization of air-seasoning poles, and evaluated the relative heating rates during the various processes used to treat Douglas-fir poles.

A. IDENTIFY METHODS FOR PREVENTING OR ELIMINATING FUNGI WHICH COLONIZE DOUGLAS-FIR POLES DURING AIR-SEASONING

1. Internal temperature development in Douglas-fir poles during kiln drying: While most poles in the Pacific Northwest continue to be airseasoned or Boultonized prior to preservative treatment an increasing number of treaters are exploring the use of kiln drying to season the outer shell prior to treatment. While kiln drying is energy intensive, it offers the advantage of reducing inventory needs and decreasing response times to an order. While kiln cycles to dry poles are typically long, they are also relatively mild in order to limit the risk of excessive check development. As a result, there was some concern that these treatments might not be adequate for sterilizing the wood. To answer these questions, we evaluated internal temperature development in 6 kiln charges in a commercial facility at Ridgefield, Washington as well as a seventh charge in our smaller kiln. The methods and results were described previously (93 Annual Report, pages 64-67). Over the pat year, we have explored methods for using this

data to predict heating requirements for Douglas-fir poles under varying drying conditions in cooperation with Dr. Keith Levien of the Department of Chemical Engineering. The data for rate of temperature increase in the earlier kiln runs (Figure IV-1) was used in conjunction with moisture loss to prepare heating curves for the time required for poles of various diameters to reach 67° C, the temperature considered to be required for sterilization of wood colonized by decay fungi. The data were also used to explore the feasibility of reducing the kiln schedule to produce equivalent drying and sterilization.

The predictions of time to reach 67° C varied from 105 to 144 hours for poles ranging from 15 to 40 cm in diameter. Sterilization would not be achieved in larger poles using the kiln schedule employed in our study. As a result, kiln drying alone may be inadequate for eliminating fungi established deep within larger poles. However, some judgement must be used in these cases since we have

also generally found that fungi are absent from poles which did not reach the temperature required for sterilization. We plan to explore the effect of varying kiln schedule on sterilization over the coming year.

Attempts to shorten kiln schedules while producing pole sterilization indicated that the kiln cycle employed for our study could be shorted markedly without adversely affecting sterilization. However, this finding does take into account the potential effects of shortened kiln cycles on pole quality. Kiln drying of poles is an intuitive process which is largely developed for individual kilns. Our preliminary examination of kiln schedules suggests that there is considerable room for optimization to reduce drying costs while producing sterilization and maintaining pole quality. We plan to continue these studies over the coming year.



Figure IV-1. Internal temperature development during kiln drying of Douglas-fir poles in 6 different kiln cycles.



Figure IV-2. Internal temperature development and changes in wood moisture content in Douglas-fir poles during kiln drying in an experimental kiln.



Figure IV-3. Effect of pole radius on time required for a Douglas-fir pole to reach $67 \degree C$ at the pith during kiln drying.





Figure IV-4. Effect of decreased kiln drying times on time required to reach 67° C in a Douglas-fir pole at an initial kiln temperature of 55.5 ° C.

OBJECTIVE V

EVALUATE THE EFFICACY OF GROUNDLINE PRESERVATIVE SYSTEMS FOR WESTERN WOOD SPECIES

The treatment of wood with preservatives provides an excellent barrier against fungal attack; however, even this barrier eventually declines in some wood species. Rather than allow preservative treated wood poles to slowly decline, many utilities have opted to apply supplemental preservatives to the surface of the wood at periodic intervals. These treatments contained a variety of biocides including sodium dichromate, creosote, pentachlorophenol, and sodium fluoride. These materials were highly effective, but the decision to list many of these preservatives as restricted use pesticides led many utilities to seek alternative materials for protecting the surface of their poles. While many of the new external preservative systems contained biocides which had been employed for protecting wood in other applications, there was little data documenting the effectiveness of these systems for the new application. The following tests were established to help utilities make more informed decisions on the use of the alternative systems.

A. PERFORMANCE OF MODIFIED SYSTEMS ON DOUGLAS-FIR POLES IN CORVALLIS, OREGON

Douglas-fir pole sections (25 to 30 cm in diameter by 1.8 m long) were seasoned for 6 months, then treated with one of the following formulations:

CUNAP WRAP (CSI Inc.) containing 2.0 % copper naphthenate (as Cu) on an absorbent pad.

CuRap 20 (ISK Biotech) a paste containing 18.16 % amine based copper naphthenate and 40 % sodium tetraborate decahydrate

COP-R-NAP (Osmose Wood Preserving Inc.) a paste containing 19.25 % copper naphthenate.

CRP 82631 (Osmose Wood Preserving Inc.) a paste containing 19.25 % copper naphthenate and 45 % sodium fluoride.

Pole Nu 15-15 (ISK Biotech) a grease containing 12.9 % pentachlorophenol 15 % creosote, and 1.5 % chlorinated phenols.

Pole Nu (ISK Biotech) a grease containing 10.2 % pentachlorophenol.

The latter two systems were included to provide comparisons between new formulations and those used previously for this purpose.

The pastes were applied according to manufacturer's directions. All but the self-contained CUNAP Wrap were covered with polyethylene wrap prior to being set in the ground to a depth of 45 cm at the Peavy Arboretum test site. The tops were then capped with roofing felt to retard decay above the groundline.

The Peavy test site receives an average of 105 cm of rainfall per year, with 81 % of the precipitation falling between October and March. Average monthly temperatures range from 3.9 to 11.7 C during that same period. Temperatures outside that period rarely exceed 30 C or fall below 0 C. The soil is an Olympic silty-clay and is slightly acidic (pH 5.4). During the winter months, the water table at the test site rise to within 15 cm of the soil surface. Over the course of the study, however, the site has experienced below average rainfalls.

Preservative performance has been assessed 18, 30, 42 and 54 months after treatment by removing either increment cores or 1 cm diameter plugs from 3 equidistant sites around each pole section 15 cm below the groundline. Plugs were initially employed, however, it became difficult to obtain solid plugs as the poles became wetter and increment cores were substituted. The samples were cut into segments corresponding to 0 to 4, 4 to 10, 10 to 16, and 16 to 25 mm from the wood surface. Segments from the same zone for a given pole were combined and the wood was ground to pass a 20 mesh screen. The wood was then analyzed for copper or pentachlorophenol using an Asoma 8620 X-ray fluorescence analyzer (XRF). Borate analysis was performed using the Azomethine H method as previously described ('92 Annual Report, page 73). Fluoride analyses were performed on a blind sample basis by R. Ziobro, (Osmose Wood Preserving Inc.) using AWPA Standard A2 Method 7.

Untreated control poles have now largely failed due to a combination of surface and internal decay. Treated poles remain sound, but the surfaces have begun to soften. This attack reflects the dependence solely on the remedial surface treatment for protection.

Levels of preservative in all of the formulations continue to steadily decline 54 months after chemical application (Table V-1). Penta levels in the outer zone of both Pol-Nu formulations continue to remain well above the threshold for fungal growth. Although these levels are declining slightly further into the wood, the presence of sufficient chemical near the surface of the wood is of primary importance for these formulations.

Levels of copper near the surface of three of the four copper naphthenate containing formulations declined markedly over the past year. Copper levels in CUNAP, Cop-R-Nap, and CuRap 20 declined 29, 60, and 27 %, respectively. Declines in residual copper further into the wood of poles treated with these formulations were more variable. Copper levels in the remaining formulation declined by only 8 % in the same time period. While the levels of copper in all Table V-1. Chemical content at selected depths from the wood surface of Douglas-fir posts 18, 30, 42 or 54 months after treatment with selected ornundline handage systems

		۵	16-25 mm					0.35 0.55 0.52		, ,	
		1 Fluoride	10-16 mm	wt/wt)	• •		1 1	0.55 0.81 0.57			
		Sodiun	4-10 mm	· %)		1 1		1.21 1.23 0.71	1 1		
			0-4 mm			1 1	1 1	2.38 2.38 1.32	t 1	1 1	
			16-25 тт		1 1	1 1	0.51 0.23 0.17 0.08		1 1	1 1	
		Jron	10-16 mm	BAE)		1 1	0.87 0.28 0.26 0.11		1 1	1 1	
		ğ	4-10 mm	%)	• •	1 1	1.41 0.27 0.22 0.10			1 1	
			0-4 mm		• •	1 1	1.75 0.27 0.15 0.12				
	Chemical Level	PENTA	16-25 mm			1 I	1.4		0.16 0.16 0.16 0.16 0	0.16 0.16 0.16 0.16 0	
			10-16 mm	g/m³)			• •		0.48 0.32 0.32 0.06	0.80 0.64 0.32 0.32	
	Average		4-10 mm	(K	• •	1 1	1 1	4 1	1.44 0.96 0.80 0.80	2.56 1.76 1.44 1.28	
			0-4 mm						3.36 2.40 1.60 1.76	6.24 4.32 2.72 3.04	
.01112			16-25 mm		0.32 0.16 0.48 0.31	0 0 0 0.15	000	0.16 0.16 0.32 0.11			
160 of a		pper	10-16 mm		0.80 0.64 0.96 0.61	0.32 0.32 0.32 0.30	0.16 0.16 0.16 0.06	0.48 0.32 0.48 0.24			
		Col	4-10 mm		1.60 1.28 1.76 1.01	0.64 0.64 0.64 0.52	0.80 0.48 0.48 0.34	1.12 0.64 0.96 0.70	1 1	1 1	
			0-4 mm	(^e m ³)	2.56 1.60 2.24 1.61	2.72 2.24 2.40 1.45	3.36 2.40 2.88 2.10	3.84 2.88 2.88 2.65			
min Bio			Exposure Period (Mos)	(kg/	18 30 54	18 30 42 54	18 30 42 54	18 30 42 54	18 30 42	18 30 42	wood surface
	-		Chemical Treatment		cunap ^I W Farp	Cop-R-Rap	CuRap 20	COP-R-PLASTIC	Pol-Nu 15-15	Pol-Nu	t De distance (mm) from

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four treatments remain above the threshold for protection of wood, sharp declines in retentions over short periods are a cause for concern and these poles will continue to be monitored for residual chemical levels. The copper declines are particularly important in the CUNAP and Cop-R-Rap formulations since these systems lack a co-biocide to provide supplemental protection to the wood.

Boron levels in the CuRap 20 poles have now declined to the point where they are only slightly above background boron levels. While it is possible that some of this boron has migrated further into the poles where it may provide supplemental protection against internal decay, it provides little protection against renewed fungal attack new the surface. The absence of boron in the wood to act as a co-biocide, coupled with the declining copper levels suggest that the performance of this treatment will differ little from that of the 2 formulations which contain only copper naphthenate.

Analysis of fluoride in the Cop-R-Plastic treated poles has not yet been completed. These results will be provided in next the next Annual Report.

The results continue to show that the modified formulations have moved through the wood at rates which are comparable to those found with the earlier penta based systems. The value of boron in groundline wrap systems remains questionable, as shown by the marked declines in the levels of this chemical with time due to its sensitivity to moisture.

These trials will continue to be samples to better quantify the point when retreatment with these systems is advisable.

B. PERFORMANCE OF MODIFIED EXTERNAL PRESERVATIVE SYSTEMS ON DOUGLAS-FIR, PONDEROSA PINE AND WESTERN REDCEDAR POLES IN MERCED, CA

While the results of the Oregon field trials indicate that the modified external preservative systems performed comparably to the existing formulations in a wet site, on a thin sapwood species, some potential users questioned the validity of the data under drier conditions with other wood species. for this reason, a second field trial was established in California using three of the commercial formulations on active utility poles. Douglas-fir, western redcedar and ponderosa pine poles in a Pacific Gas and Electric Co. line located near Merced, CA was sampled by removing increment cores from three sites around the groundline. These cores were ground to pass a 20 mesh screen prior to analysis for residual penta content by XRF and segregated into 3 groups of nine poles per wood species so that each group had an approximately similar distribution of preservative retentions. The poles were then treated with CUNAP wrap (CSI Inc.), CuRap 20 (ISK Biotech) or Patox II (Osmose Wood Preserving, Inc.). The composition of the former two systems was described in Section A. Patox II contains 70.3 % sodium fluoride. Wraps were applied from a zone extending 8 cm above the ground to 45 cm below the groundline and soil was replaced around the poles.

The poles were sampled one and two years after treatment by removing increment cores from sites 15 cm below the groundline in one third of the poles in a given treatment group. These cores were divided into zones corresponding to 0-4, 4-10, 10-16, and 16-25 mm from the wood surface and zones from a given pole were combined prior to grinding to pass a 20 mesh screen. The wood was then analyzed for copper, boron or fluoride content as described in Section A.

Residual levels of the various external preservatives continue to decline in most treatments, although there were small increases in some species. These differences may reflect the need to remove samples from different points around the poles at various times

Copper levels in both the Cunap Wrap and CuRap 20 have declined between 2 and 3 years after treatment (Figure V-1). Copper levels in the outer 4 mm zone of the CuRap treated poles remain well above 1 kg/m³ (as Cu) in all three species. Levels remain highest in ponderosa pine, followed by western redcedar and Douglas-fir. Copper levels in the CuRap treated poles fall dramatically 10 mm from the surface, suggesting that the amine copper lacks the mobility of the oil based material. Copper levels in the outer zone of Cunap Wrap poles were highest in the Douglas-fir poles followed by ponderosa pine and western redcedar. Copper levels in the pine poles have a nearly flat gradient from 0 to 25 mm from the surface, reflecting the higher permeability of the wood of this species. Copper levels in western redcedar poles were near the threshold for copper naphthenate and declined sharply from the surface. The reasons for the decreased chemical levels in the western redcedar poles is unknown. While the heartwood of this species is impermeable to liquids, the sapwood is quite treatable, as evidenced by the copper levels found in the CuRap treated poles. Interestingly, copper levels in the Cunap wrap in this test are markedly lower than those from the Corvallis site even though the Corvallis site was installed nearly 18 months earlier, while those in the CuRap 20 treated poles are lower near the surface, but more than double those in the next zone inward. these differences illustrate the need to carefully consider conditions within individual utilities when evaluating new formulations.

Fluoride levels in the poles have now declined to levels below 2 %, although levels in the outer zone of the ponderosa pine poles rose from 1 to near 2 % between 2 and 3 years (Figure V-2). The reasons for the increases in ponderosa pine are not clear, although they may reflect sampling variations between the years. Fluoride levels were highest in ponderosa pine followed by western redcedar and Douglas-fir. Chemical levels declined to the greatest extent in western redcedar between 1 and 3 years, but these levels were still above those found with Douglas-fir.

Boron levels in CuRap 20 treated poles have declined sharply between 2 and 3 years. Boron levels were lowest in Douglas-fir poles with little differences in levels from the inner to outer zones. Boron levels in ponderosa pine, while higher than those in Douglas-fir, followed a negative gradient from the outer to inner zones and this gradient suggests that boron has been depleted from the surface of the wraps. Future samples should show a continued depletion of boron in this zone. Boron levels in western redcedar had declined between 1 and 3 years but these levels remained higher than those found with either of the other two species.

The results indicate that the three external preservative systems are moving well through the three would species. As expected from the data from the Corvallis site, boron levels are declining to the point where this chemical will have little influence on external wood protection, while copper levels remain well above the threshold for wood protection in most cases. These poles will continue to be sampled to determine when levels of residual copper, born or fluoride decline below the thresholds for those chemicals. These data, coupled with information being developed on the protective effects of low levels of these chemicals on protection of wood against fungal attack in soil contact will be used to develop retreatment schedule recommendations for the various formulations.

C. THRESHOLDS OF SELECTED EXTERNAL GROUNDLINE PRESERVATIVE COMPONENTS AGAINST SOIL INHABITING MICROORGANISMS

While a well treated pole provides excellent protection against the agents of deterioration, some wood species require supplemental protection as the wood ages and preservative is lost from the surface. For many years, combinations of pentachlorophenol and creosote in pastelike formations were applied to the below ground surfaces and protected from direct soil contact with coated wraps. These formulations were extensively studied and provided excellent protection to the wood surface, but both penta and creosote are now restricted-use pesticides and can only be applied by applicators licensed by the appropriate state regulatory bodies. For many utilities, the prospect of using restricted-use pesticides for remedial treatment was considered an unnecessary

burden with regard to linemen training. As a result, chemical companies developed alternative formulations containing combinations of copper napthenate, sodium fluoride or boron. Preliminary laboratory and field tests suggest that these formulations move through the wood at levels and rates which are consistent with creosote or penta-based systems (Objective V-A.B): however there is little data outlining the levels of chemical required to provide supplemental protection in soil contact. Such data will be essential for designing treatment schedules which ensure that adequate levels of chemical remain in the wood. In this report, we describe tests to determine the thresholds against fungal attack in soil contact for several remedial treatment systems.



Figure V-1. Copper retentions at selected depths in the below ground portion of Douglas-fir, ponderosa pine and western redcedar pole sections one to three years after treatment with CUNAP wrap or CuRap 20.



Figure V-2. Boron and fluoride levels present in the below ground zones of Douglas-fir, ponderosa pine or western redcedar poles one to three years after treatment with CuRap 20 or Patox II.

Because of difficulties with weight losses at the higher chemical loadings, these results should be considered extremely preliminary.

Ponderosa pine (Pinus ponderosa L.) sapwood cubes (1 cm^3) were cut from kiln-dried boards. The cubes were oven dried (54 C) for 24 hours and weighed. The blocks were then treated with amine based copper naphthenate, oil-borne copper naphthenate, sodium fluoride, or sodium decaborate octohydrate or combinations of these chemicals to produce a range of retentions typical of those which might be found in a remedially treated pole in service (Table V-2). Blocks were immersed in a solution of the respective chemical and a 20 minute vacuum was drawn over the wood. The vacuum was released and the process was repeated. The blocks were then blotted to remove excess preservative prior to being oven dried (54 C) and reweighed. Blocks receiving more than one chemical received those chemicals in 2 separate vacuum treatments. Each treatment was replicated on 8 blocks and all blocks were then sterilized by exposure to 2.5 mrads from a cobalt-60 source.

The treated blocks were evaluated for decay resistance using a modified soil burial test. Briefly; forest soil was placed in 113 ml glass jars to a depth of 25 mm and a single block was added to each jar. An additional 25 mm layer of soil was Added along with enough water to raise the soil moisture content to 80 to 100% of field capacity. The jars were loosely capped and incubated for 6 months at 32 C. Water was added periodically to maintain moisture levels. At the end of the treatment period, the blocks were scraped clean of any adhering mycelium prior to oven-drying (54 C) and reweighing to determine weight loss over the exposure period. Selected blocks from each treatment regime were then subjected to chemical analysis to determine residual preservative retentions. These blocks were ground to pass a 30 mesh screen. Copper naphthenate treated blocks were assayed using an ASOMA 8620 x-ray fluorescence analyzer (ASOMA Instruments, Austin, TX). Boron was determined using the carminic acid/azomethine H method, while fluoride was determined using AWPA Standard A5.

While copper levels appeared to be close to the target retentions at the end of the decay period, levels of boron and fluoride were generally low (Tables V-3, 4). The loss of the water soluble components is not surprising.

Weight losses associated with the treatments varied widely and in some cases followed a negative dose-response curve. We are currently investigating the nature of these variations and plan to retest portions of the experiment. We plan to complete the new trials in January and will present the result in the next annual report.

Table V	7-2.	Chemical	treatments	evaluated	for	protecting	ponderosa	pine	sapwood	in a	soil	burial	decay	tests.
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Chemical	Sources	Target Retention (% wt)
Sodium fluoride	Osmose Wood Preserving, Buffalo, NY	0.1, 0.15, 0.30, 0.60
oil-borne copper naphthenate	Osmose Wood Preserving, Buffalo, NY	0.02, 0.04, 0.08, 0.16, 0.32, 0.96
oil-borne copper naphthenate	CSI, Seattle, WA	0.02, 0.04, 0.08, 0.16, 0.32
amine-based copper naphthenate	ISK Biotech, Memphis, TN	0.02, 0.04, 0.08, 0.16, 0.32
sodium tetraborate decahydrate	ISK Biotech, Memphis, TN	0.02, 0.04, 0.8, 1.6

	Residual Retention (kg/m ³)												
			Boron target (kg/m ³)										
Copper	0		1.12		2.24		4.64		9.12				
Target (kg/m ³)	Copper	Boron	Copper	Boron	Copper	Boron	Copper	Boron	Copper	Boron			
0.32 0.64 1.28 2.40 4.80 15.20	- 0.83 1.68 1.55 3.42 11.23		- 0.48 0.69 1.26 1.52 3.20 11.39	0.36 0.13 0.16 0.12 0.15 0.09 0.12	- 0.61 0.56 0.94 1.47 3.17 10.56	0.65 0.31 0.23 0.25 0.30 0.25 0.23	- 0.38 0.99 0.83 1.71 3.47 11.95	0.73 0.58 0.44 0.42 0.49 0.44 0.36	- 0.38 0.48 0.83 1.89 3.02 12.30	1.55 1.17 1.05 0.86 0.89 1.08 0.73			

Table V	7-3 .	Residual 1	oadings	of an	nine copp	er and	boron	in pone	derosa	pine	blocks	treated	with	selected
wood pi	reser	vatives an	d expose	ed to	biological	lattack	in a 6	month	soil b	urial	test.			

Table V-4. Residual loadings of copper and fluoride in ponderosa pine blocks treated with copper naphthenate and sodium fluoride and exposed to biological attack for 6 months in a soil burial test.

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		Chemical Retention by Analysis (kg/m ³)												
Copper		Fluoride Target Retention (kg/m ³)												
Target (kg/m ³)	0		1.12		2.24		4.64		9.	12				
0 0.32 0.64 1.28 2.56 5.12 15.36	- 0.45 0.62 1.10 2.82 7.07 19.73	-	- 0.38 0.78 1.36 3.68 6.50 20.11		- 0.42 0.74 1.33 3.34 6.32 20.46		- 0.38 0.66 1.20 2.82 6.05 20.14		- 0.40 0.69 1.04 3.09 7.10 21.07					

OBJECTIVE VI

PERFORMANCE OF COPPER NAPHTHENATE TREATED WESTERN WOOD SPECIES

A. DECAY RESISTANCE OF COPPER NAPHTHENATE TREATED WESTERN REDCEDAR SAPWOOD IN A FUNGUS CELLAR

Western redcedar remains a preferred species by many utilities owing to it naturally durable heartwood. The sapwood of this species, however, must be treated to provide adequate performance. While pentachlorophenol and creosote remain the primary biocides used to treat western redcedar, a number of utilities have considered converting to copper naphthenate. This chemical has a lower toxicity and is not a restricted use preservative. While copper naphthenate has been commercially used for wood protection for many years, there is little data on its performance in western redcedar. The prospects for using this chemical were explored in the following trials.

Western redcedar sapwood stakes (12.5 by 25 by 150 mm long) were cut from either freshly sawn boards or from the above ground, untreated portion of poles which had been in service for a approximately 15 years. The stakes were conditioned to a stable moisture content, then treated with copper naphthenate in diesel oil to produce retentions of 0.8, 1.6, 2.4 3.2, and 4.0 kg/m³ (as copper). Ten stakes of each wood type were treated to each target retention.

The stakes have been exposed at 28 C and 80 % relative humidity in forest loam soil. The soil is watered regularly, but is allowed to cycle between wet

and dry to simulate natural decay conditions. The stakes have been assessed on a regular basis for degree of decay on a scale from 0 (failed) to 10 (sound).

Stake ratings after 52 months of exposure indicate that the condition of stakes which were weathered prior to treatment continue to decline more rapidly than non-weather stakes (Table VI-1). It is likely that microbial action on the pits in the weathered stakes rendered these samples more susceptible to depletion of preservative, thereby reducing their service life. This effect is particularly acute at the lower retentions and suggests that the economics of retreatment of poles to extend service life should be carefully evaluated.

Unweathered stakes continue to perform well at all retentions, although there are some variations among the treatment levels. Treatment of stakes with diesel continues to provide protection which is equivalent to that produced with the highest retentions on weathered stakes. The results indicate that copper naphthenate treatment of western redcedar sapwood at the levels currently specified in the American Wood Preservers' Association for both pressure (1.92 kg/m³) and thermal treatments (2.4 kg/m³) should provide adequate protection to this species. The stakes will continue to be evaluated on an annual basis.

B. EVALUATION OF COPPER NAPHTHENATE TREATED DOUGLAS-FIR POLES IN SERVICE

As a part of our evaluations of copper naphthenate treatments, we have cooperated with suppliers of this chemicals and utilities purchasing poles treated with this chemical to monitor the performance of copper naphthenate treated poles in service. This past year, we inspected 22 Douglas-fir poles located south of Eugene, Oregon in the BPA system. The poles were samples by removing increment cores within the through-bored zone and measuring the degree of preservative penetration. The presence of any treatment skips were noted. In addition, increment cores were removed from sites 0.9 and 1.5 m above the groundline. These cores were placed in plastic drinking straws which were returned to the laboratory for culturing on malt extract agar. Any fungi growing from the cores were examined for characteristics typical of basidiomycetes, a class of fungi containing many important wood decayers.

Eighteen of 22 cores removed from the through bored zone were completely penetrated by preservative, illustrating the enhanced treatment afforded by through boring. The four cores not completely treated were penetrated 53, 62, 72, and 89 % respectively. As noted earlier, the significance of untreated zones in the through-bored region remain unclear and these poles will continue to be monitored over time to assess the effects of skips on performance.

Culturing of cores removed from the poles revealed that 1 of 44 cores contained a decay fungus. The fungus was identified as <u>Stereum sanguinolentum</u>, a common inhabitant of Douglas-fir poles in air-seasoning yards. The presence of this fungus in treated poles is surprising given its sensitivity to elevated temperatures. As these poles are resampled, special attention will be given to detecting the continued presence of this fungus. At present, the remainder of the poles remain free of decay fungi, although 16 of 44 cores contained non-decay fungi.

We plan to continue sampling these poles to ensure that copper naphthenate poles perform similarly to poles treated with pentachlorophenol or creosote.

		Weathered Samples							New Samples				
Target Retention ¹		Average Decay Rating ²							Avera	ige Decay	Rating ²		
(kg/m)	Actual Retention (kg/m ³)	6 mos	14 mos	26 mos	40 mos	52 mos	Actual Retention (kg/m ³)	6 mos	14 mos	26 mos	40 mos	52 mos	
control diesel 0.8 1.6 2.4 3.2 4.0	- - 1.6 1.4 2.1 2.7 4.0	4.7 8.5 9.0 9.5 9.6 9.6 9.9	0.9 6.8 8.0 8.9 9.2 9.1 9.2	0.4 5.3 7.5 8.8 9.1 9.0 9.1	0.1 3.8 6.9 9.0 8.6 8.8 9.1	0 3.4 5.7 8.0 8.2 8.1 8.7	- 0.6 1.3 1.9 2.6 3.4	6.6 9.9 10.0 10.0 10.0 10.0 10.0	3.2 8.4 9.6 9.4 9.4 9.2 9.5	1.3 8.0 9.4 9.3 9.4 9.2 9.4	1.1 8.6 9.5 9.2 9.2 9.0 9.4	1.1 8.4 9.6 9.4 9.3 8.9 9.3	

Table VI-1.	Condition of western redcedar sapwo	od stakes treated to	selected ret	etentions with a	copper naphther	nate in diesel o	il and e	exposed in
a soil bed for	6 to 52 months.							

¹ Retentions measured as kg/m³ (as copper) ² Values represent averages of 10 replicates pretreatment, where 0 signifies completely destroyed and 10 signifies no fungal attack.