Three groups of experiments were performed to determine an effective procedure for controlling decay in southern pine (Pinus spp.) laminated timbers. (i) A decaying laminated arch of southern pine was treated with chloropicrin. Movement of the chemical vapor through the arch and its effect on the decay and nondecay fungal population were monitored. (ii) Fungitoxicity studies with three decay fungi isolated from the laminated arch were performed by exposing infected wooden wafers to fumigant concentrations for various lengths of time, and by monitoring fumigant concentration and death of fungi in treated wooden blocks over a 24-hour period. (iii) Vapor movement across gluelines and along the radial and longitudinal axes of southern pine blocks conditioned to a range of moisture contents was monitored.

Fungitoxic chloropicrin vapors diffused about 2 m from the treatment sites in the laminated arch over a 13-month period. A vapor wrap enclosing a portion of the arch limited escape of chloropicrin from
the wood and improved treatment. Diffusion along the length of the arch was much greater than that between laminates.

The minimum lethal dosages of chloropicrin determined in infected pine wafers ranged from 1.73 to 18.40 \( \mu g \) hrs/ml for *Gloeophyllum saepiarium* and from 13.44 to 15.00 \( \mu g \) hrs/ml for *Poria* sp., for 24 and 4 hour exposure periods respectively.

Chloropicrin concentration/time values in wood blocks were maximized at 30 to 60% wood moisture content indicating that treatment may be more effective at this moisture content range than at 8%. Movement radially through wood and across gluelines was severely limited when compared to longitudinal movement. The rate of chloropicrin diffusion through wood blocks decreased with increasing severity of incipient decay. Minimum lethal dosages of chloropicrin to decay fungi were higher in infected wood blocks than in infected wafers.

The findings of this research support the following recommendations: (i) Decay may be controlled by treatment with 0.5 cc of chloropicrin per square centimeter of cross sectional area at appropriately spaced intervals along the timber. (ii) Treatment sites should be spaced at about 2 m intervals along the decayed length of the timber for wood at about 8% moisture content. Treatment sites should be spaced closer together for wood of higher moisture contents. (iii) Treatment holes should contact all laminates. (iv) A vapor barrier should be employed to retain fumigant vapors in the timber.
Chloropicrin Movement and Fungitoxicity in Decaying Southern Pine Laminated Timbers

by

Barry Scott Goodell

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Redacted for privacy

Professor of Forest Products in charge of major

Redacted for privacy

Professor of Forest Products in charge of major

Redacted for privacy

Head of Department of Forest Products

Redacted for privacy

Dean of Graduate School

Date thesis is presented: August 3, 1979

Typed by Linda S. Crooks for Barry S. Goodell
THESIS COMMITTEE:

Redacted for privacy

Redacted for privacy

Redacted for privacy

Redacted for privacy
DEDICATED TO

My Mother
Inez G. Reinhold
and My Father
S. Maurice Goodell
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Laminated timbers are used extensively in structures such as bridges, warehouses, and recreational facilities designed to support heavy loads while providing unobstructed space below. They are also used frequently in churches, homes, and other modern construction where their unique esthetic and design properties are desirable. Because of inadequate construction codes, portions of untreated laminated timbers are frequently exposed to the weather, or are used under humid conditions in structures such as natatoriums, where moisture may condense on the wood. If checks, defects, or design features are present which provide places for moisture to collect, a suitable environment for fungal growth is created allowing decay fungi to become established in the wood.

The high incidence of decay in laminated timbers has prompted the American Institute of Timber Construction to recommend changes in construction codes to require pressure treatment of laminated timbers constructed of nondurable species exposed to direct precipitation and used as structurally supporting members \((3,4)\). Acceptance of the changes would greatly reduce the incidence of decay in exposed laminated timbers. However, it would not provide control for established decay of the wood.

In the past, there was no effective means of controlling decay of in-service laminated timbers. Conventional methods of treatment with
preservative paints, water soluble salts, or impregnated films and wraps (bandage treatments) proved ineffective and may have even aggravated the problem. Recently, however, volatile chemicals have been proven effective for controlling decay in transmission poles and pilings. In preliminary work, chloropicrin, a volatile fungicide used in agriculture, showed promise for controlling decay in a Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] laminated beam (13) but movement of the chemical vapor may have been restricted by glue lines and joints. More research is needed to develop the potential of this and other volatile toxicants in controlling decay in laminated timbers and other wood products.

To develop an effective procedure for controlling decay in laminated pine timbers, the following experiments were performed with chloropicrin:

(i) A decaying laminated arch of southern pine (*Pinus* spp.) was treated with chloropicrin. Movement of the chemical vapor through the arch and its effect on the decay and nondecay fungal populations were monitored.

(ii) Fungitoxicity studies with three decay fungi isolated from the laminated arch were performed by exposing infected wooden wafers to fumigant concentrations for various lengths of time, and by monitoring fumigant concentration and death of fungi in treated wooden blocks over a 24 hour period.

(iii) Vapor movement across gluelines and along the radial and longitudinal axes of southern pine blocks conditioned to a range of moisture contents was monitored.
LITERATURE REVIEW

There are many reports in the literature concerning the use of fumigants in controlling organisms ranging from rodents to bacteria. The fumigation of wood for the control of insects is well established (21, 31, 32) and was reported for termite control as early as 1911 by Mackie (22). Fumigation for control of wood decay fungi is a relatively recent development, however, and few reports exist on this subject. The earliest report that I found concerning the use of fumigants to control wood decay was in 1959 by Stabnikov (35). He reported that Coniophora puteans in wood flooring was killed by a 30 minute exposure to 30 g/m³ of chloropicrin. In later work, Partridge (30) determined that the oak wilt fungus Ceratocystis fagacearum in infected oak sections, 3-4" diameter x 8" long, was killed by a three day exposure to a saturated atmosphere of chloropicrin or methyl bromide vapors.

In the late 1960s, Hand and Lindgren (18) of the Bonneville Power Administration reported that agricultural fumigants applied internally to Douglas-fir transmission poles diffused as a gas through the wood and eliminated decay fungi in the poles. Later work at Oregon State University by Graham and Corden further developed the use of fumigants in Douglas-fir transmission poles (14, 15, 16) and in laminated timbers (13). The commercial use of these chemicals to control internal decay in transmission poles and laminated timbers by commercial engineering and pole inspection companies is now well established. Research is needed, however, to determine how fumigants move through
wood in situ and in what concentrations they are effective against decay fungi so that they may be used more efficiently.

Fumigant Treatment of Laminated Timbers

Factors which must be considered in the application of fumigants to untreated laminated timbers which do not come into play in pressure-treated transmission poles include:

(i) Presence of gluelines and finger joints.
(ii) Absence of an exterior preservative pressure-treated shell.
(iii) Proximity of the timbers to or enclosure in inhabited structures.

Additional factors previously investigated (8, 14, 26) for fumigant treatment of decayed wood in general include:

(i) Diffusion of fumigant vapors with respect to time and dosage in wood of various moisture contents and temperatures.
(ii) Specific fungitoxicity of fumigant vapors to decay fungi.

These factors are reviewed in greater detail in the following sections.

Diffusion of Fumigants

Theory

The application of fumigants to wood involves treatment with a quantity (initial dose) of the chemical which is gradually depleted until none remains, as the fumigant vapors diffuse into untreated wood and into the surrounding environment. For this reason there is never a constant amount of fumigant vapor passing through a particular
point in the treated region and Ficks second law for non-steady-state diffusion (12) in one dimension applies. Illustrated this appears as:

$$\left(\frac{\partial^2 c}{\partial t^2}\right)_{x} = D \left(\frac{\partial^2 c}{\partial x^2}\right)$$

where

$$\left(\frac{\partial^2 c}{\partial t^2}\right)_{x} = \text{rate of change in concentration with time}$$

$$D = \text{average diffusion coefficient for fumigant movement}$$

$$\left(\frac{\partial^2 c}{\partial x^2}\right) = \text{partial differential for concentration moving along a known distance X. Solving this equation provides a pattern of the change in concentration with time.}$$

Wood is a porous medium and various interactions between fumigants, the wood, and the moisture in wood may occur (38). In these respects wood is similar to soil and the mathematical models developed to account for diffusion of chemicals through soils (11, 12, 23) apply to wood as well. Factors needing consideration in the modification of Ficks law for non-steady-state diffusion include: (i) the porous structures of wood, (ii) sorbtion by wood, (iii) fumigant solubility in wood moisture, and (iv) decomposition. Illustrated, these modifications of Ficks second diffusion model (12) appear as:

$$\frac{\partial c}{\partial t} = \frac{D}{\theta + BK_{(sorp)} + (\theta_w/\theta)K_{(sol)}} \left(\frac{\partial^2 c}{\partial x^2}\right) - \left(\frac{\partial c}{\partial t}\right)_{(\text{decomp})}$$

where

$$\theta = \text{fraction of open pore space along a wood face}$$

$$BK_{(sorp)} = \text{constant factor representing the amount of fumigant sorbed by wood components}$$

$$\left(\theta_w/\theta\right)K_{(sol)} = \text{constant factor representing the amount of fumigant which goes into solution}$$

$$\frac{\partial c}{\partial t(\text{decomp})} = \text{rate of decomposition of the fumigant in wood}$$
Since the rate of decomposition is not dependent on the diffusion rate of the fumigant it may be subtracted from the right hand side of the equation. The reversible sorption and solution terms are dependent on the chemical diffusion rate and this is shown by their relation to the diffusion coefficient and the partial derivative in the equation.

With the present state of technology most of these factors would be difficult to estimate in wood; therefore, theoretical diffusion coefficients are usually calculated using Fick's second law without the modifications. These modifications are important however when considering diffusion of fumigants in wood as they may have an additional effect on fungitoxicity.

**Permeability of Wood to Gases**

**Pressure permeability.** The permeability of pine species sapwood along the three orthogonal axes is known to be relatively high in comparison to other softwood species (20). Research on gas permeability in heartwood and sapwood of southern pine has been reported by many researchers (7, 20, 41, 42). Choong and Fogg (20) reported that the air permeability ratio for southern pine sapwood in the longitudinal, radial and tangential (LRT) directions was 7,167:38:1 respectively. In later work (7) these researchers found the LRT ratios to be much smaller, with mean values of 69:19:1 in a young shortleaf pine tree (*Pinus echinata* Mill.) and 10:3:1 in wood from a mature shortleaf pine. The authors cite other studies that reported wide variation in permeability for other species, attributing the
differences to sample size, testing technique, and the inherent variability of wood.

Fumigant penetration may be reduced in heartwood of pine species since bordered pits are usually aspirated and extractives may block the bordered pits of the tracheids (20). Differences in air permeability of pine sapwood and heartwood were reported to be approximately 55 to 1 longitudinally and 5 to 1 in the transverse direction (20). Research on shortleaf pines (7) showed the average longitudinal sapwood/heartwood permeability ratio to be less than 10. Other researchers (41, 42) with pine obtained sapwood/heartwood permeability ratios from 9 to 1178.

Southern pine laminated timbers are likely to contain some pith or juvenile wood which could also affect the penetration of fumigants. Air permeability was lowest in wood near the pith in a mature shortleaf pine (7); presumably this would be juvenile wood. Wood from a 10 year old shortleaf pine which the authors (7) assumed to be all juvenile wood showed no difference in permeability with increasing distance from the pith. This wood was about six times more permeable in the longitudinal and radial directions than was sapwood and corewood from the mature tree.

**Diffusion.** The diffusion coefficients for helium and air through the heartwood of some Japanese softwoods and hardwoods along the orthogonal axes are reported by Yokota (45). Elers (9) and Tarkow et al. (40) reported on diffusion through western United States softwoods. The range of longitudinal to transverse gas diffusion ratios in these studies was between 50 and 1,500, averaging around 100.
Fumigant Diffusion in Wood

Diffusion of fumigants through wood should be similar to that in soils where more rapid diffusion is expected when the pore size is increased, moisture in the soil is decreased, and temperature is increased (23). Diffusion of fumigants is also affected by sorption and solution (previous section) which vary with the substrate and may differ greatly from what is found in soils.

Diffusion coefficients for chloropicrin in Douglas-fir were determined over a range of temperatures by Cooper (8). At 21°C, longitudinal diffusion coefficients ranged from 2.76 to 1.55 cm²/sec x 10⁶ and in the transverse direction from 0.10 to 0.20 cm²/sec x 10⁶. The longitudinal/transverse diffusion ratios ranging from 8 to 28 were less than those reported for other woods and gases (9, 40, 45).

Most of the research concerning the control of wood decay with fumigants has been done with Douglas-fir. Research with fumigants in creosoted southern pine transmission poles, initiated by Graham and Corden (14) is now continuing at the State University of New York (46). More rapid diffusion of chloropicrin would be expected in pine sapwood than in Douglas-fir sapwood because the sapwood of pine is more permeable to gases in both the longitudinal and transverse directions.

Diffusion in Wood of Higher Moisture Content

For decay fungi to grow and decay wood, the moisture content must be above 20% and is frequently much higher. For this reason it is important to understand how the moisture content of wood affects the movement and retention of fumigants.
Stamm (37) stated that gases insoluble in water pass through green wood, above fiber-saturation, with great difficulty because the gas has to displace free water in the capillary paths. Previous work (36) also determined that with increasing moisture content the gas permeability of wood decreases because of capillary condensation which reduces the effective pore size that the gas must pass through. This would suggest that with moisture contents of 30% or higher the movement of chloropicrin in wood may be limited. Work by Graham and Corden (15), however, suggests that in woods of 20 to 44% moisture content control of decay fungi is better than in wood with higher or lower moisture content. No explanation for this phenomenon was given by the authors but it is possible that the diffusion rate of chloropicrin was regulated by the moisture in wood, with the optimum diffusion rate for decay control occurring in wood of 20 to 44% moisture content.

Diffusion Across Gluelines

Fumigant control of decay in laminated timbers may be severely limited if gluelines or finger joints inhibit the movement of the vapor into untreated laminates. The adhesive typically used to bond the laminates of these timbers is a phenol-resorcinol mix suitable for exterior use.

Cooper (8) found that phenol-resorcinol coated wood specimens with a total surface area of 234 cm² adsorbed approximately 2.75 g of chloropicrin after 20 days. Compared with other sealants that Cooper tested, this was a relatively small amount adsorbed and indicates that
a phenol-resorcinol coating is a good barrier to diffusion of chloropicrin vapors. Although Cooper did not report the thickness of his block coatings, gluelines are normally much thinner than coatings and fumigant penetration of a thin phenol-resorcinol glueline may be appreciable. Godfrey (10), determining the relative penetrability of several chemical vapors through various adhesive films found that an adhesive labeled "Golden Ground Glue" was relatively impenetrable and another adhesive labeled "U.S. Government Waterproof Glue" was relatively more penetrable to chloropicrin vapors.

The penetrability of gluelines in Douglas-fir plywood by liquid preservatives has been investigated by Miller and Currier (24). They found that phenol-resorcinol gluelines with high resin solids content were significantly more resistant to penetration of creosote and copper sulfate solutions applied under pressure than were phenol-resorcinol gluelines of low solids content. A comparison of the permeability of these gluelines to wood permeability was not made but would be expected to be much less. Earlier work presented in a review by Truax et al. (43) also showed that the gluelines in laminated timbers could prevent penetration during pressure treatment with liquid preservatives. Gas permeability of gluelines in wood has not been previously reported on but the research cited above suggests that it would be limited at best. Since small cracks might be expected to develop in gluelines with aging and the shrinkage and swelling of wood the permeability of gluelines to chloropicrin may increase with increasing service life of a laminated timber.
Vapor Barriers

Polyethylene and plastic films, compacted soil, and water saturated soil layers have been used to contain fumigant vapors in soils to obtain more effective treatment against microorganisms (23). A vapor barrier enclosing a treated laminated timber would also be expected to contain the fumigant vapors within the wood and improve treatment.

Graham and Corden (16) found that the effectiveness of chloropicrin treatment in wood blocks sealed in plastic containers was greater than that of treated blocks in open containers. Graham (13) also discovered that chloropicrin escaped readily through the decayed wood in a laminated timber, lessening the effectiveness of the treatment.

Vapor barrier paints used to retard movement of water vapor through painted surfaces are commercially available (34) and could perhaps be used as a vapor barrier to contain fumigants in laminated timbers. The disadvantages of using vapor barrier paints to coat laminated timbers are that (i) paint will not seal large checks or holes in the timbers and (ii) paints are not easily removed after treatment which may cause excessive amounts of moisture to be retained in the wood.

Polyethylene sheet vapor wraps may provide a more effective means to contain fumigant vapors in a large timber because a wrap can be used to seal all or part of the timber and may be easily removed following treatment. Previous research (8) on the rate of release of chloropicrin vapors from polyethylene vials showed that polyethylene is
somewhat permeable to chloropicrin vapors but that it can be used to restrict diffusion of this chemical.

**Fungitoxicity of Chloropicrin**

Fumigants have been used to destroy soilborne organisms in agriculture since the late 1800s (23) and extensive research has been conducted over the last 70 years concerning the application rates needed for pest control in agricultural soils under various environmental conditions. Two early reports by Wensley (44) and Stark (39) are worth noting because attempts to quantify lethal dosages of fumigants to soilborne fungi were made. Stark immersed several soil fungi in chloropicrin-water solutions for 24 hours and obtained lethal dosages ranging from $1/486,000 \text{g/cc } H_2O$ to $1/2000 \text{g/cc } H_2O$. His technique appears questionable though since chloropicrin is relatively insoluble in water and from a practical standpoint the toxicity of fumigant solutions is much less important than that of fumigant vapors. Wensley treated cultures of soil fungi sealed in 20 gm dilution bottles with various quantities of methyl bromide and ethylene dibromide. He found that concentrations of 0.1 ml and 0.2 ml per bottle of the liquid fumigants, respectively, were toxic to the fungi. Lethal vapor concentrations of the fumigants in the bottles were not reported.

Other early reports were concerned with application rates to soils and other substrates and lethal dosages to the organisms were not reported.
The technique for determining lethal dosages of fumigant vapors to microorganisms is somewhat more involved than with conventional pesticides in liquid or solid form because in addition to the dosage factor, the length of exposure to the microorganism must be considered when calculating lethal dosages. Because fumigant vapors must be contained in the treated substrate to be effective and the treatment can be applied for varied lengths of time, a concentration/time (CT) value is used to express the lethal dose of fumigant. The lethal CT value is obtained by multiplying the lethal concentration by the length of time necessary to effect death to the organism. If the dosage rate over time varies, as in unsteady-state diffusion, integral calculus can be applied (12) to determine the area under the dosage/time curve. This value should represent the same lethal exposure as the lethal CT value calculated by multiplying a steady-state dosage (constant dosage rate) by the appropriate exposure period.

Ideally the lethal CT value would be constant over time for any particular organism and fumigant; however, susceptibility of different organisms varies with the exposure period and dosage so that the lethal CT value may increase or decrease as these parameters vary (25, 27).

Although the CT concept has been used in insect fumigation studies for some time (19, 21, 27), only recently have the lethal dosages for fungi been reported using the lethal CT value as a measure of toxicity. Quantitative fungitoxicity of fumigants has been studied by Cooper (8) working with chloropicrin in Douglas-fir and Munnecke et al. (25) working with methyl bromide to control fungi.
in agricultural soils and in culture. Cooper found that the lethal doses of chloropicrin vapors to *Poria placenta* ranged from 20 to 100 mg/hr per liter under laboratory conditions. Munnecke *et al.* found that lethal dosages of methyl bromide ranged from 63 to 1,335 ml-hrs per liter for a variety of soilborne fungi. This later research group believed that their work was the first quantitative fungitoxicity data to be reported for methyl bromide where the gas concentration was monitored throughout the experiment.
MATERIALS AND METHODS

Southern Pine Laminated Arch

A 20-laminate, 13 x 65 x 406 cm section of a southern pine laminated arch was obtained from a manufacturer in Missouri where it had been stored outdoors and had started to decay. A treatment plan was formulated to obtain information on: (i) the effectiveness of a vapor wrap in containing fumigant vapors in wood, (ii) the effects of glueline, finger joints and grain orientation on the diffusion of chloropicrin in the timber, and (iii) the overall effectiveness of these factors in eliminating decay fungi in the wood.

Preparation and Treatment

The arch was prepared by removing 100 increment cores from sites indicated in Figure 1. Cores were cultured for fungi on malt/benomyl* agar to discourage nonhymenomycete growth and increase the isolation of decay fungi. Fourteen coreholes in the upper and lower seven laminates near the center of the arch were enlarged to accept 25 ml of 98% pure liquid chloropicrin. The inner six laminates were left untreated and the core holes sealed with cork and paraffin. This treatment design allowed individual laminates to be treated providing an opportunity to observe the longitudinal movement of chloropicrin in several laminates and the transverse movement through wood and gluelines.

*Malt extract agar with 10 ppm benomyl solution added.
Figure 1. Southern pine laminated arch. Treatment sites - ▲, Monitoring sites - •, Fungus assay sites - O, Electrical resistance monitoring sites - △.
Alternately numbered core sites located 30, 90 and 150 cm (A, B and C sites, respectively) to the right of the treatment zone in Figure 1 were fitted with rubber serum stoppers for withdrawal of gas samples used in the analysis. Core sites in laminates 2, 6, 10, 14 and 18, located 99 and 198 cm (D and E sites, respectively) to the left of the treatment sites were also fitted with serum stoppers while laminates 3, 7, 11, 15 and 19 were fitted with electrical resistance* sensors designed to quantitatively measure amounts of organic gases (Figure 2). All unused increment core sites or additional holes were sealed with cork and paraffin.

Prior to treatment a 15 cm zone around the treatment sites was sealed with paraffin to prevent leakage of liquid chloropicrin from checks or small holes. The arch was turned on its side and 25 ml of chloropicrin was poured into each treatment hole. The holes were sealed with tight fitting wooden dowels and then coated with paraffin. After righting the arch to the position it would remain throughout monitoring (Figure 2) the upper 10 laminates were wrapped with a 4 mil polyethylene sheet which was stapled securely into place (Figure 3).

Monitoring

Gas samples were removed from each sampling site in the arch at daily intervals for the first two weeks and at increasing time intervals thereafter. Each 1 cc sample was removed with a gas tight syringe and injected into a Varian Aerograph series 1200 gas chromatograph with

Figure 2. Serum stopper and adsistor in laminates 17 and 18, E sites in the southern pine laminated arch.
Figure 3. Portion of the southern pine laminated arch after treatment.
a flame ionization detector. Operating conditions for the chromatograph were: 122 cm X 3 mm o.d. stainless steel column packed with 14% \( \beta,\beta' \)-oxydipropionitrile (w/w) on a 100-120 mesh Gaschrome Q solid support; helium flow rate 24 cc/min; column temperature 65°C; injection port and detector temperatures 125° and 140°C respectively. A strip chart recorder was used to collect the data. Peak areas were manually integrated using a Hewlett Packard 9825A computer with a 9864A digitizer. The gas chromatograph was calibrated daily using a series of chloropicrin standard solutions. In conventional quantitative GLC analysis, where diffusion of the chemical being monitored is not a factor, an internal standard is usually added to the sample so that a fixed proportion of the standard and the chemical would be present in all samples analyzed. If the injection quantities were not changed throughout the analysis the response peak of the standard would remain constant and a comparison of the standard/sample peak response ratios would be used to detect sampling and detector response errors. An internal standard could not be used in my analysis, however, because chloropicrin would diffuse through wood at a different rate than a standard, resulting in an altered standard/sample response ratio at different monitoring sites.

Changes in resistance readings in the ten adsistors were monitored at regular intervals. Chromatographic and adsistor monitoring was terminated after 24 weeks.
Additional Analyses

Fifty-nine weeks after treatment, increment cores were removed from sites adjacent to the initial fungus assay sites and cultured for fungi on malt/benomyl agar to determine the effects of the treatment on the decay population in the arch. A 2 cm section from the center of each increment core was also tested to determine the relative amounts of fungistatic vapors present using the "closed tube assay" developed by Scheffer and Graham (33). Individual core segments were sealed in a 13 mm diameter x 100 mm long glass vial with a growing culture of *Poria carbonica*. After 10 days the growth of the fungus on nutrient agar was measured and compared to the growth of controls (Figure 4).

Moisture content in the arch was monitored with a resistance moisture meter before and 13 months after treatment.

Fungitoxicity of Chloropicrin in Infected Wooden Wafers

Preparation and Treatment

Southern pine wafers, 0.5 mm thick and 5 mm square were cut with end grain exposed along two of the 0.5 x 5 mm surfaces and equal amounts of early wood and late wood in each wafer. The wafers were inoculated as follows: Prior to each test 125 wafers were soaked in tap water, drained, and autoclaved for 20 minutes. After cooling, the wafers were divided into three groups and aseptically transferred to the mycelial surface of one-month old agar cultures of three decay fungi isolated from the laminated arch. Following a seven day
Figure 4. Closed tube assay. The concentrations of fungitoxic vapors increased from left to right inhibiting the growth of the decay fungus *Poria carbonica* on nutrient agar.
incubation, the wafers were removed from culture and excess agar and mycelium scraped from their surfaces. Five wafers from each culture were speared with sharpened wire hooks and placed on a special rack inside 2.5 liter desiccators (Figure 5). An angled glass plate connected to a magnetic stir bar was placed in each desiccator to facilitate air circulation and the desiccators were sealed with a ventable lid. Preliminary tests showed that after an initial equilibration period the concentration of chloropicrin could be maintained in the sealed desiccators for a period of at least one week.

Injections of liquid chloropicrin were made through the vent in the desiccator lid which was sealed with a rubber serum stopper. Immediately following injection the stir bar/glass plate "fan" was started rotating by placing the desiccator on a magnetic stirrer (Figure 6). Air circulation was continued until all liquid chloropicrin had evaporated and the vapor concentration, determined by gas liquid chromatographic analysis of vapor samples withdrawn through the serum stopper in the lid, had come to equilibrium (usually 15-20 minutes). A Hewlett-Packard 5750 research gas chromatograph with flame ionization detector was used for the analysis. Operating conditions were: 91.5 cm x 3 mm o.d. stainless steel column packed with 3% OV-17 on a Gaschrome Q solid support; helium flow rate 25 cc/min; column temperature 75°C; injection port and detector temperatures, 129° and 163°C, respectively. Since some of the chemical was adsorbed on the glass surface of the desiccators the vapor concentration could not be calculated from the injection volume. Therefore, a calibration curve was prepared to provide an estimate of
Figure 5. Positioning of infected wafers in desiccators.
Figure 6. Infected wafers sealed in desiccator with magnetically operated "fan."
the injection quantities needed to effect a certain vapor concentration in the desiccators.

**Fungal Assay**

Following exposure periods of 4, 8, 12, 18 or 24 hours the desiccators were vented and allowed to air for three to four hours. The wafers were removed from the desiccator, flamed lightly to destroy surface contaminants and aseptically transferred to malt/benomyl nutrient agar for culture of decay fungi. The cultures were observed frequently for three to four weeks.

The test was repeated for each fungus at each exposure period with a range of vapor concentrations until the minimum lethal dosage, the concentration at which no decay fungi could be isolated from the wafers, was determined for each case.

**Wood Block Experiments**

Four hundred and five 2.5 x 2.5 x 20.5 cm southern pine blocks were selected with a density range between 0.57 and 0.65 g/cc at 8% moisture content, and two to four growth rings per cm with the longitudinal axes of the wood extending the length of the block. Thirty five additional blocks of the same dimensions were selected with the radial axes of the wood extending the length of the block and the physiological pith of the tree centered from the ends of the blocks. The longitudinal blocks were used in experiments concerning longitudinal movement at three moisture contents, fungitoxicity, and
movement across gluelines; and the radial blocks in the radial movement experiment.

In all of these experiments a Hewlett-Packard 5750 flame ionization research gas chromatograph was used for analysis of gas samples removed from the blocks. Operating conditions for the gas chromatograph were as follows: 122 cm x 3 mm o.d. Teflon column packed with 7% Carbowax 20 M (w/w) on a Chromosorb WHP solid support; helium flow rate, 25 cc/min; column temperature, 82°C; injection port and detector temperatures, 135° and 170°C, respectively. A Hewlett-Packard 3370B integrator was used to determine peak areas.

Longitudinal Movement at Three Moisture Contents

One hundred and five blocks were side coated with two layers of a phenol-resorcinol resin. After curing excess resin was sanded from the end grain of the blocks and three 12 mm diameter x 22 mm long holes located at the center and 21 mm from the ends were bored into the tangential face of each block. The blocks were divided into three groups of 35 for preparation and conditioning as follows:

Group 1 (8% MC blocks). Stored at ambient laboratory conditions. Moisture content range from 7.5 to 9.0%.

Group 2 (30% MC blocks). Submerged in tap water for 40 minutes. Blocks were weighed before and after submersion to obtain an estimate of gross moisture content. The average moisture content before soaking was 8% and this figure was used in calculating the approximate oven-dry weight of each block. Moisture content of soaked blocks was calculated using the calculated oven-dry weight. To obtain the 30% MC the
blocks were slowly dried and weighed daily until the gross moisture content reached 30%. Blocks were then tightly wrapped in aluminum foil and conditioned for approximately 50 days in an attempt to provide an even moisture gradient within the blocks.

Group 3 (60% MC blocks). Submerged in tap water for 15 minutes followed by a 30 psi vacuum applied for 30 minutes.

Cracks which developed in the resin coatings of some soaked blocks did not appear to affect the concentration of chloropicrin vapors moving through the blocks and were ignored. The average weight change in the blocks following boring and resin coating was determined by weighing the blocks before and after these procedures and taken into account when determining the moisture content by weight.

Following conditioning of the blocks, each of the three holes was fitted with a rubber serum stopper. All moisture content groups were divided into smaller groups of five blocks each and the 30% and 60% moisture content blocks were placed on racks in ventilated humidity chambers (10 x 26 x 30 cm plastic boxes with one cm of water in the bottom). The 8% moisture content blocks were maintained at ambient laboratory conditions.

The six sets of blocks from each moisture content group were treated with 0, 10, 25, 50, 75, 100 or 125 μl of chloropicrin by injection through the serum stopper into the center hole in each block. Concentration of chloropicrin vapors at the monitoring sites was recorded after 8 and 24 hours and at increasing time intervals thereafter until the fourth week following treatment.
Humidity chambers were water misted daily to help maintain high moisture levels in the blocks. The moisture content of all blocks was determined after the fourth week.

Radial Movement

Thirty-five radially sawn blocks were side coated with two layers of phenol-resorcinol resin. After curing the blocks were bored and fitted with serum stoppers as reported in the previous section except that the holes were bored into the transverse face of the blocks. All blocks were conditioned to approximately 8% moisture content at ambient laboratory conditions prior to treatment.

The blocks were divided into sets of five and treated and monitored as reported in the previous section (Figure 7).

Longitudinal Movement and Fungitoxicity in Decayed Blocks

Ninety blocks were autoclaved for 30 minutes at 20 psi and 125°C. The blocks were cooled and submerged in sterile distilled water for 35 minutes to raise the moisture content of the wood to a level favorable for the growth of decay fungi. Inoculation of the blocks with decay fungi proceeded as follows: Four-week-old cultures of the three decay fungi isolated from the laminated arch were cut into 2.5 x 2.5 cm agar squares and transferred to the endgrain surfaces of the blocks, one inoculum species per group of 30 blocks. The inoculum squares were then covered with water-saturated autoclaved wooden wafers (Figure 8) and secured to the agar and block with rubber bands. Inoculated blocks were placed in alcohol-wiped humidity chambers and
Figure 7. Sequence showing the preparation of the radial movement blocks for treatment. From foreground to background: uncoated, coated and cut to size, bored, fitted with serum stoppers and treated with chloropicrin.
Figure 8. Inoculation of southern pine blocks.
incubated for 37 days at 27°C. Following incubation the blocks were dried in a laminar-flow air bench until their exterior surfaces were dry, and then further conditioned in a non-sterile environment to 8% moisture content. After drying the blocks were coated with two layers of phenol-resorcinol resin. Coatings on some blocks cracked severely and were recoated until all cracks were sealed. End wafers and agar residues were removed from the blocks following resin cure and excess resin on the end grain of the blocks was sanded off.

Blocks were bored and fitted with serum stoppers as in the previous sections except only one monitoring hole was made, leaving one end of the block unbored. Monitoring of chloropicrin concentrations was done after 4, 8, 12, 18 and 24 hours.

Procedures similar to these have been used previously (13, 14, 15) in bioassays of inoculated Douglas-fir blocks treated with various agricultural fumigants.

Immediately following the last monitoring period, two 5 mm wafers were cut from the unbored ends of the blocks; the outer wafers discarded and the inner wafers aired on a laboratory bench for three hours. Following aeration four 5-mm square blocks were cut from the center of each wafer, lightly flamed and plated in malt/benomyl agar. Growth from the blocks was observed after one, two and four weeks.

Movement Across Gluelines

Seventy laminated beams 2.5 x 7.5 x 20.5 cm long were constructed with a phenol-resorcinol resin from the Borden Chemical Company using three standard sized blocks per beam. Thirty-five beams were
constructed following the manufacturers specifications for adhesive spread and assembly time; the remaining beams prepared with less adhesive spread than suggested by the manufacturer (Table 1). After gluing, the beams were side coated with two layers of resin. Four treatment and monitoring holes were bored into side faces of the beams (Figure 9) and serum stoppers were fitted to the holes as in previous sections.

Normal and thin-glueline beams were divided into groups of five for injection through the centermost treatment holes with 0, 10, 25, 50, 75, 100 or 125 ml of chloropicrin. Chloropicrin vapors which diffused across gluelines into the two untreated laminates in each beam were monitored after 8 and 24 hours and at increasing time intervals thereafter until the fourth week.

**Analysis of Data**

Data storage, plotting, and statistics were done on the Hewlett-Packard 9825A computer. Three-dimensional plots of the southern pine arch data were done on the OS-3 computer systems at Oregon State University using public domain program SURF-6.
### TABLE 1. GLUING SPECIFICATIONS FOR LAMINATED BEAMS USED IN FUMIGANT MOVEMENT EXPERIMENTS.

<table>
<thead>
<tr>
<th></th>
<th>&quot;Normal Thickness&quot; Gluelines</th>
<th>&quot;Thin&quot; Gluelines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive</td>
<td>Cascophen LT-75, FM-260 (Borden Chemical Company)</td>
<td></td>
</tr>
<tr>
<td>Adhesive Spread</td>
<td>100 lbs/1000 ft² G.L. (2.5 gm/block surface)</td>
<td>23 lbs/1000 ft² G.L. (0.6 gm/block surface)</td>
</tr>
<tr>
<td>Open Assembly Time</td>
<td>20 minutes</td>
<td></td>
</tr>
<tr>
<td>Closed Assembly Time</td>
<td>45 minutes</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>21°-24°C</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>125 ± 10 psi</td>
<td></td>
</tr>
<tr>
<td>Press Time</td>
<td>6 hrs</td>
<td></td>
</tr>
</tbody>
</table>
Figure 9. Small laminated beams. From left to right: uncoated; bonded, coated and bored; fitted with serum stoppers.
RESULTS AND DISCUSSION

Southern Pine Laminated Arch

Chloropicrin Movement

GLC analysis showed that chloropicrin vapors moved through the arch in a 'wave' pattern with the highest concentrations monitored at the A sites, 30 cm from the treatment zone (Figure 10). A distinct peak in vapor concentration was noted in the A sites after seven weeks. This peak was not as accentuated in the other monitoring sites further from the treatment zone (Figures 11, 12, 13, 14) but maximum concentrations at these sites occurred between the fourth and the tenth week after treatment. Concentrations of chloropicrin were higher in sound wood than in severely decayed wood.

Volatile pine resins at three monitoring sites produced a massive response on the gas chromatograph strip chart recorder which eclipsed the smaller chloropicrin response peak. Data from these sites were not used in the analysis.

Adsistors were not effective in determining chloropicrin concentrations at the levels present in the arch.

Effects of the Vapor Wrap. In almost all cases the concentration of chloropicrin vapors was greater in the wrapped than in the unwrapped section of the arch (Figures 10-14). This indicates that the vapor barrier limited the escape of fumigant vapors from the wood and provided a reservoir of fumigant vapors capable of diffusing into wood.
Figure 10. Three dimensional view of the change in chloropicrin concentration at the "A" site laminates over time. (For "A" site location, see insert.) Shaded area represents the vapor-wrapped portion of the arch. Treated laminates are represented by underlined labels. Reference points in µg/ml.
Figure 11. Three dimensional view of the change in chloropicrin concentrations at the "B" site laminates over time. (For "B" site location, see insert.) Labelling follows Figure 10.
Figure 12. Three dimensional view of the change in chloropicrin concentrations at the "C" site laminates over time. (For "C" site location, see insert.) Labelling follows Figure 10.
Figure 13. Three dimensional view of the change in chloropicrin concentrations at the "D" site laminates over time. (For "D" site location, see insert.) Labelling follows Figure 10.
Figure 14. Three dimensional view of the change in chloropicrin concentrations at the "E" site laminates over time. (For "E" site location, see insert.) Labelling follows Figure 10.
at sites remote from the treatment zone. Chloropicrin was detected in all wrapped laminates after one week. In severely decayed areas, such as the unwrapped section of the C sites, 150 cm from the treatment zone, no chloropicrin was detected after 24 weeks. The largest peak occurred in an unwrapped portion of the arch (laminate 16 in the A sites) but was probably caused by a defect such as an internal check in the wood which allowed greater quantities of chloropicrin to move to that site.

**Treated versus Untreated Laminates.** Chloropicrin concentrations were noticeably less in untreated laminates than in treated laminates at distances up to 90 cm from the treatment zone (sites A and B). Beyond that distance the differences in vapor concentration in treated and untreated laminates were eclipsed by the effects of the vapor wrap. In general, vapor movement across laminates was much less than longitudinal movement in the wood.

**Assays**

**Isolation of Fungi.** Decay fungi isolated from the arch on malt/benomyl agar were identified from descriptions by Nobles (29). Three decay fungi were isolated: *Gloeophyllum saepiarium* (Wulf. ex Fr.) Karst., *Schizophyllum commune* Fries, and an unidentified species of *Poria*. The later fungus keyed out to *Poria placenta* but was unlike laboratory isolates of that fungus, being a less aggressive decayer and having a more appressed fungal mat.

Typical nondecay fungi isolated from the arch were identified from descriptions by Barnett and Hunter (5) and Barron (6), and
included species of *Penicillium*, *Paecilomyces*, *Aureobasidium*, and *Epicoccum*.

**Effects of Treatment on Decay Fungi.** Decay fungi were isolated frequently from all areas of the arch prior to treatment. Thirteen months after treatment the frequency of isolation from all wrapped areas of the arch was greatly reduced whereas in the unwrapped section isolation frequency was noticeably reduced only at the A and D sites (Figure 15). Both of these sites were located in relatively sound wood within 100 cm from the treatment zones.

Comparing the frequency that decay fungi were isolated from treated and untreated laminates, no noticeable differences were observed. Since very few decay fungi were isolated from the wrapped section of the arch, treatment of all laminates may not be necessary when a vapor wrap is employed. However, *S. commune* was isolated from the treatment zone only three laminates (9 cm) from a treatment site in the unwrapped section of the arch (Figure 15, treatment sites) suggesting that treatment of every laminate is necessary if a vapor barrier is not employed.

**Closed Tube Assay.** Twelve months after treatment this assay showed that fungistatic concentrations of chloropicrin vapors were present 90 cm from the treatment sites in most unwrapped laminates and up to 150 cm from the treatment sites in some of the wrapped laminates (Figure 16). These results compare well to those from the decay fungi assay and the GLC monitoring. The data indicate that chloropicrin did not move in appreciable amounts into the unwrapped decayed area of the
Figure 15. Distribution of decay fungi in the southern pine laminated arch. Decay fungi present before treatment (left of assay sites), and thirteen months after treatment (right of assay sites).

\[ g = \text{Gloeophyllum saepiarium}, \quad p = \text{Poria sp.}, \quad s = \text{Schizophyllum commune} \]
Figure 16. Closed tube and decay population assays in the southern pine laminated arch thirteen months after treatment. Decay fungi present thirteen months after treatment (left of assay sites). 

g= Gloeophyllum saepiarium, p= Poria sp., s= Schizophyllum commune

Growth of Poria placenta in mm., after 10 days (right of assay sites). Control growth after 10 days= 28mm.
C sites and that, in general, the concentration of chloropicrin was higher in the wrapped section of the arch.

**Moisture Content.** Moisture content in the arch before treatment ranged from 8 to 18% with most readings at about 14% MC. Thirteen months after treatment the moisture content ranged from 8.5 to 13% in the wrapped portion of the arch and from less than 7 to 9% in the unwrapped portion. No effects on chloropicrin movement or fungitoxicity were attributed to the differences in moisture content in this study.

**Fungitoxicity in Infected Wooden Wafers**

The classic method of determining the toxic level of a chemical to fungi is to expose fungal spores to various concentrations of the toxicant and calculate the percentage of spore germination after treatment. With my experimental design it was impossible to count the number of vegetative mycelial cells in each wafer which remained viable after treatment. Since the number of viable cells in a wafer from which fungi were cultured could not be determined, the minimum lethal dosage (MLD) is reported (Table 2) rather than the ED<sub>90</sub> or ED<sub>50</sub> figures used more commonly in the literature. The MLD value is a more useful term from a practical standpoint because it corresponds to the chloropicrin vapor concentration required to stop decay in a timber.

The MLD values in this experiment were calculated by averaging the lowest chloropicrin dosage which prevented fungal growth from the wafers, and the next lowest dosage, for a number of replicate tests.
<table>
<thead>
<tr>
<th>Hours Exposure</th>
<th>Fungus</th>
<th>Minimum Lethal Dosage of Chloropicrin (µg/ml)</th>
<th>Lethal CT Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>G. saepiarium</td>
<td>0.064</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>Poria sp.</td>
<td>0.61</td>
<td>14.64</td>
</tr>
<tr>
<td>16</td>
<td>G. saepiarium</td>
<td>0.106, 0.125, 0.131*</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>Poria sp.</td>
<td>0.55, 0.77</td>
<td>10.56</td>
</tr>
<tr>
<td>12</td>
<td>G. saepiarium</td>
<td>0.86, 0.90</td>
<td>10.56</td>
</tr>
<tr>
<td></td>
<td>Poria sp.</td>
<td>1.39</td>
<td>16.68</td>
</tr>
<tr>
<td>8</td>
<td>G. saepiarium</td>
<td>1.70</td>
<td>13.60</td>
</tr>
<tr>
<td></td>
<td>Poria sp.</td>
<td>1.77, 1.95, 2.26</td>
<td>15.95</td>
</tr>
<tr>
<td>4</td>
<td>G. saepiarium</td>
<td>2.95, 3.62</td>
<td>13.14</td>
</tr>
<tr>
<td></td>
<td>Poria sp.</td>
<td>2.94</td>
<td>11.76</td>
</tr>
</tbody>
</table>

*More than one value is given where replicate tests did not agree on one lethal concentration for that exposure period. Replicate values were averaged to calculate the lethal CT factors.*
More than one MLD value was used in the data analysis when replicate tests did not agree on a single value for a particular exposure period.

The lethal chloropicrin dosages and exposure periods for *G. saepiarium* and *Poria* sp. are plotted in Figures 17 and 18 respectively. Both the concentration and time axes of these two graphs are scaled logarithmically which results in linear data plots for both fungi. The expected lethal CT values for *G. saepiarium* and *Poria* sp. can be calculated using the dosage and time coordinates from the two regressions. Representative values are listed in Table 3.

Poor growth of *S. commune* from untreated control and treated wafers prevented determination of the lethal CT values for this fungus. Although preliminary tests showed that a one week incubation period was enough to infect the wafers, *S. commune* is a relatively weak decay fungus and may have needed longer to adequately infect all the wafers used in these tests.

Theoretically the lethal CT values should remain constant throughout the exposure range.* The lethal CT values for *Poria* sp. follow this theory in that the lethal CT range is small between the four and 24 hour test limits. *G. saepiarium*, however, is apparently more susceptible to chloropicrin after longer exposure periods and therefore does not support the theory.

*Except at the extremes of the time exposure range this should hold true (11). Presumably I did not test over these extremes.
Figure 17. Minimum lethal dosages of chloropicrin to Gloeophyllum saepiarium over time.
Figure 18. Minimum lethal dosages of chloropicrin to Poria sp. over time.
<table>
<thead>
<tr>
<th>Hours Exposure</th>
<th>Gloeophyllum saepiarium</th>
<th>Poria sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MLD (µg/ml)</td>
<td>Lethal CT Factor</td>
</tr>
<tr>
<td>24</td>
<td>0.072</td>
<td>1.73</td>
</tr>
<tr>
<td>20</td>
<td>0.11</td>
<td>2.20</td>
</tr>
<tr>
<td>15</td>
<td>0.22</td>
<td>3.30</td>
</tr>
<tr>
<td>10</td>
<td>0.56</td>
<td>5.60</td>
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<tr>
<td>5</td>
<td>2.75</td>
<td>13.75</td>
</tr>
<tr>
<td>4</td>
<td>4.60</td>
<td>18.40</td>
</tr>
</tbody>
</table>
Wood Block Experiments

Longitudinal Movement at Three Moisture Contents

The moisture contents (MC) of the three groups of blocks, four weeks after treatment, were as follows:

Group 1 (8% MC blocks). MC ranged from 7.5 to 9.0%.

Group 2 (30% MC blocks). Average MC = 27.5%; standard deviation = 3.2%.

Group 3 (60% MC blocks). Average MC = 57.5%; standard deviation = 7.7%.

Ideally, at 30% MC, all water in the lumens would be in vapor form and the cell walls saturated. At 60% MC, the cell lumens would be partially filled with water. In reality, at both 30% and 60% MC, liquid water was probably isolated in certain areas of the wood with the moisture content in other areas below the fiber saturation point. More careful control over the moisture distribution in the blocks was not possible because of the need for ventilation to prevent the buildup of fumigant vapors in the wood and because the blocks were frequently removed from the humidity chambers for GLC monitoring. This problem was partially overcome by using ten replicate samples which tended to average out deviations from the expected. The experiment may be considered to parallel natural conditions because timbers decaying in service are more likely to have an uneven distribution of moisture within the wood.

The data for the three moisture content groups are plotted in Figures 19, 20 and 21. Each plotted point is the average of ten
Figure 19. Concentration of chloropicrin in 8% M.C. blocks.
Figure 20. Concentration of chloropicrin in 30% M.C. blocks.
Figure 21. Concentration of chloropicrin in 60% M.C. blocks.
readings from blocks of the same injection quantity for a particular monitoring period. The graphs show that rapid diffusion of chloropicrin to the ends of the blocks is inhibited in blocks of higher moisture content. Chloropicrin passed through the 8% moisture content blocks very rapidly in a wave pattern with the wave peak occurring before the first monitoring, eight hours after treatment. After 400 hours, the concentration of free chloropicrin vapors at the monitoring sites had diminished considerably and was close to zero in the blocks treated with smaller quantities of chloropicrin. The pattern of chloropicrin movement in the 30% and 60% moisture content blocks was similar to that in the 8% blocks; however, as the moisture content increased the wave peaks broadened and occurred at a later time after treatment. Chloropicrin vapors were still present in the 30% and 60% blocks after the fourth week of monitoring with the highest concentrations present in the 60% moisture content blocks.

In general, the data for each injection quantity in the three moisture content groups were significantly different from each other at $\alpha = .05$ (Table 4). The difference between the 30% and 60% moisture content groups for the 50 $\mu l$ and 100 $\mu l$ injection quantities were the only pairs of curves which were not significantly different. This lack of significance can be attributed to the increased variability about the mean as the moisture content of the blocks increased.

Integrating the areas under the curves for the three moisture content groups provides CT values for the different injection quantities which can be compared to obtain an estimate of the effectiveness of the treatment. The data for the 125 $\mu l$ blocks with CT values is
TABLE 4. F-VALUES FOR A MEAN COMPARISON OF MOISTURE CONTENT DATA IN A TWO-FACTOR ANALYSIS OF VARIANCE. FACTORS: MOISTURE CONTENT, TIME FROM TREATMENT (TREATMENT QUANTITY HELD CONSTANT). CRITICAL $F_{(a = .05; 2, 216)} = 3.00$.

<table>
<thead>
<tr>
<th>Injection quantity in blocks</th>
<th>10 µl</th>
<th>25 µl</th>
<th>50 µl</th>
<th>75 µl</th>
<th>100 µl</th>
<th>125 µl</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% and 30% MC blocks</td>
<td>4.24</td>
<td>102.69</td>
<td>40.01</td>
<td>33.15</td>
<td>103.09</td>
<td>22.43</td>
</tr>
<tr>
<td>8% and 60% MC blocks</td>
<td>207.06</td>
<td>35.09</td>
<td>27.14</td>
<td>7.47</td>
<td>31.54</td>
<td>76.51</td>
</tr>
<tr>
<td>30% and 60% MC blocks</td>
<td>152.02</td>
<td>17.72</td>
<td>1.25</td>
<td>9.15</td>
<td>0.13</td>
<td>16.09</td>
</tr>
</tbody>
</table>
plotted in Figure 22. Integration of the curve area was done with the Hewlett-Packard 9864A digital integrator.

Figure 22 shows that the highest CT value (1238 µg hrs/ml) for the 125 µl blocks over a 700 hour period was calculated for the 60% moisture content blocks. The value for the 30% blocks is also relatively high (1147 µg hrs/ml) while the value for the 8% blocks is about half of the other two (519 µg hrs/ml). With moisture contents higher than 60% the CT value would be expected to decrease because the increase in moisture would inhibit movement of the chemical, decreasing the size of the initial peak and tail of the curve. The optimum moisture content for treatment to control decay in this size specimen then would be between 30 and 60%, with enough moisture to slow the diffusion out of the block but not enough to completely inhibit diffusion within the block. Previous research (15) with chloropicrin in infected blocks has shown that this statement is true. Treatment was more effective against decay fungi in infected blocks at approximately 36% moisture content than in blocks at 14% or 116% moisture content. In larger specimens with high moisture contents this may mean that treatment holes will have to be spaced closer together to offset the decreased rate of diffusion but that the chemical may stay in the wood longer at higher concentrations.

In a small percentage of the control blocks, volatile compounds were present that could have interfered with chloropicrin resolution. It was not possible to determine if these interferences were present in the treated blocks, however, and any errors caused by them were included in the data.
Figure 22. Concentration of chloropicrin monitored in wood blocks at 8, 30, and 60% M.C.
Injection quantity= 125 μl. C.T. factor (700 hrs.): 8% M.C.= 519. 30% M.C.= 1147. 60% M.C.= 1238.
Radial Movement

No radial movement of chloropicrin was detected at the monitoring sites through the fourth week after treatment. This was unexpected because longitudinal/radial diffusion ratios previously reported range from 16.5 to 53.2 for methyl bromide in pine sapwood and average about 100 for air in other softwoods. Applying these ratios to the longitudinal (p. 52) and radial wood block data, the concentrations of chloropicrin detected at the monitoring sites in the radial blocks would be expected to be within the lower detection limits of the gas chromatograph, especially in the blocks treated with 125 μl chloropicrin.

If heartwood were present in the blocks, the concentration of chloropicrin at the monitoring sites would have decreased since the diffusion rate through heartwood is much less than in sapwood. A benzidine reagent (1), used to test for heartwood in a random sampling of the blocks after treatment, indicated that no heartwood was present.

The presence of an unknown proportion of juvenile wood in these blocks might explain the decreased radial permeability.

Longitudinal Movement and Fungitoxicity in Decayed Blocks

The data for the movement of chloropicrin through the three groups of infected blocks are plotted with CT values, calculated by integrating the area under the curves, in Figures 23, 24 and 25. An evaluation of the fungitoxicity of chloropicrin in the blocks could not be made. G. saepiariu was cultured from all blocks and
Figure 23. Concentration of chloropicrin in wood blocks infected with Gloeophyllum saepiarium. Data in parentheses are CT values for the 24 hour period in μg hrs./ml.
Figure 24. Concentration of chloropicrin in wood blocks infected with Poria sp. Data in parentheses are CT values for the 24 hour period in µg hrs./ml.
Figure 25. Concentration of chloropicrin in wood blocks infected with *Schizophyllum commune*. Data in parentheses are CT values for the 24 hour period in μg hrs./ml.
was not killed even at the highest treatment levels (100 μl) with a chloropicrin CT value of 94.20 μg hrs/ml for the 24 hour treatment. In contrast, the lethal CT value for the fungus over a 24 hour period in the infected wafer experiments was 1.73 μg hrs/ml (Table 3), or more than 60 times difference. The reason for this difference in fungitoxicity is not known; however, the fungus had more time to grow in the wood blocks than the wafers which may have allowed it to produce resistant structures to withstand greater environmental extremes, including higher chloropicrin concentrations. In addition, in larger block specimens, chloropicrin may not have penetrated all areas of the wood, leaving small isolated pockets where fungi may have survived.

The *Poria* species was unable to infect the blocks sufficiently to be cultured from any of the blocks including the controls. A longer incubation period or more favorable conditions appears to be necessary for this fungus to invade the wood.

*S. commune* also did not adequately infect the blocks and no fungus could be cultured from approximately half of the blocks at all treatment levels, including the controls. At the highest levels of treatment, *S. commune* was cultured from four of the blocks. If the single block which did not culture the fungus is attributed to poor infection, then the results indicate that this fungus can survive chloropicrin concentrations greater than 96.65 μg hrs/ml, the CT value for the 100 μl blocks of this group.

Based on the culture results and physical appearance, the blocks were loosely categorized as to the extent of their infection.
Although the interior of all blocks had not decayed beyond incipient stages, advanced decay was present in the outer endgrain surfaces of about half of the *G. saepiarium* blocks, and these blocks were therefore classified as "decaying". Following this classification system, the blocks which were sporadically infected with *S. commune* were classified as "inconsistently infected", and the blocks inoculated with *Poria* sp. as "uninfected". Performing a three-way analysis of variance on the chloropicrin concentration data and contrasting the data from one fungus infected group to another showed that a strong linear effect relating the degree of decay in the blocks to the chloropicrin concentration over time is present (Table 5).

When the CT values for the three groups are plotted against injection quantity (Figures 26, 27, 28) a series of linear data plots result. These plots show that relatively high chloropicrin CT values (slope of the plot) were associated with the "uninfected" *Poria* sp. inoculated blocks, intermediate CT values were associated with the "inconsistently infected" blocks inoculated with *S. commune* infected blocks and relatively low CT values associated with the "decaying" *G. saepiarium* infected blocks. A statistical comparison of the three regression lines (Table 6) showed that the *Poria* sp. CT plot was significantly different from the *G. saepiarium* and the *S. commune* CT plots, however, the CT plots for *G. saepiarium* and *S. commune* were not significantly different. This lack of significance is attributed to the large variance about the *S. commune* CT regression line possibly caused by the sporadic infection of the blocks from this group. Even though the *G. saepiarium* and *S. commune* CT plots were
**TABLE 5.** F-VALUE FOR A MEAN COMPARISON OF BLOCKS INOCULATED WITH *Gloeophyllum saepiarium*, *Poria sp.*, AND *Schizophyllum commune* IN A THREE-FACTOR ANALYSIS OF VARIANCE. FACTORS: TIME FROM TREATMENT, INJECTION QUANTITY IN BLOCKS, FUNGUS INFECTION BLOCKS. CRITICAL F \( (\alpha = .05; 2, 360) = 3.00 \).

<table>
<thead>
<tr>
<th>Stage of Fungal Infection</th>
<th>Relative CT Value</th>
<th>Fungus Infecting Blocks</th>
<th>F-Ratio Contrast Between Pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decaying</td>
<td>Low</td>
<td><em>G. saepiarium</em></td>
<td>-30.03</td>
</tr>
<tr>
<td>Inconsistently Infected</td>
<td>Intermediate</td>
<td><em>S. commune</em></td>
<td>-86.41</td>
</tr>
<tr>
<td>Uninfected</td>
<td>High</td>
<td><em>Poria sp.</em></td>
<td>-14.67</td>
</tr>
</tbody>
</table>
TABLE 6. STATISTICAL COMPARISON OF CT VALUE REGRESSION LINES FROM FIGURES 26, 27, AND 28. CRITICAL $F$ ($\alpha = 0.5; 2, 6$) = 5.14.*

<table>
<thead>
<tr>
<th>CT Plot Comparison</th>
<th>$F$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. saepiarium - S. commune</td>
<td>0.91</td>
</tr>
<tr>
<td>G. saepiarium - Poria sp.</td>
<td>9.72</td>
</tr>
<tr>
<td>S. commune - Poria sp.</td>
<td>67.11</td>
</tr>
</tbody>
</table>

*Reduced model included ten data points from the CT plots being compared. Plots were compared as pairs only.
Figure 26. Concentration/time values vs. injection quantity of chloropicrin in wood blocks infected with *Gloeophyllum saeplarium.*
Figure 27. Concentration/time values vs. injection quantity of chloropicrin in wood blocks infected with *Schizophyllum commune*. 

\[ y = 2.0020 + 1.0371x \]
Figure 28. Concentration/time values vs. injection quantity of chloropicrin in wood blocks infected with *Poria* sp.
not statistically significant, the data trend supports the observation that the diffusion rate of chloropicrin is slower through wood with more advanced stages of incipient decay.

Although I found no reports concerning diffusion rates of gases through decayed wood, the pressure permeability of wood to liquids and gases is known to be greater in decayed wood than sound wood (28). This suggests that the rate of gas diffusion through wood also would increase with increased severity of decay. My data show that the reverse is true.

Two possible explanations for this phenomenon are suggested below:

(i) The breakdown of the cell walls by fungal enzymes increases the total internal surface area of the wood, exposing a greater number of hydroxyl groups on the cellulose structures which are free to hydrogen bond with small polar molecules. Chloropicrin may be bonding in some manner to the wood structure which would reduce the amount of chemical moving through wood as a gas.

(ii) The enzymatic breakdown of the cell walls may create greater void space in the wood which in effect provides more space for chloropicrin vapors to occupy, effectively reducing chloropicrin vapor pressure. The reduced vapor pressure of chloropicrin would account for its slower diffusion through the wood blocks which would result in lower concentrations per unit time being detected at the monitoring sites. Because the void space created by cell wall degradation in incipient stages would be relatively small when compared to the void space already present in sound wood this explanation would be less plausible than the previous one.
If chloropicrin is retained in decayed wood by one or both of the methods mentioned above, it would also be retained to a lesser extent in sound wood, explaining the presence of fungistatic vapors in Douglas-fir transmission poles nine years after treatment (16). Although there is no evidence at present to support either of the above theories, future research is planned which may provide this information. If chloropicrin is retained in significant quantities in wood, it could be considered for long-term timber preservation in addition to its use as a temporary wood fungicide.

Movement Across Gluelines

Very low concentrations of chloropicrin were present at the monitoring sites located across gluelines in the outer untreated laminates only 3 cm from the treatment sites. Chloropicrin movement across the thin gluelines, (Figures 35-40, Appendix 1) was somewhat greater than movement across the normal-thickness gluelines (Figures 29-34, Appendix 1), but was still much less than that observed in the longitudinal direction (p. 52). No difference was noted in chloropicrin concentrations as the treatment quantity was increased.

The highest chloropicrin concentrations monitored in the beams were about 20 times less than the highest concentrations in the 8% moisture content blocks (p. 52), even though the monitoring sites in the beams were much closer to the treatment sites.

A volatile substance which would have interfered with the chromatographic resolution of chloropicrin was present in relatively small amounts in approximately half of the control beam monitoring sites. This substance may have interfered with the analysis initially,
causing the apparent chloropicrin peak at the eight hour monitoring in some blocks, but was not present in appreciable quantities in later monitorings. Considering the short distance between the treatment and monitoring sites and the small quantities of chloropicrin which were detected, it is clear that a relatively small proportion of chloropicrin diffuses across gluelines (as compared to longitudinal movement) and that in-service treatment of laminated timbers will be much more effective if all laminates are treated. Since the amounts of chloropicrin diffusing across the thin gluelines was not much greater than across normal-thickness gluelines, "thin spots" in the gluelines of laminated timbers cannot be depended upon to distribute the chemical to untreated laminates.
CONCLUSIONS

**Chloropicrin Movement**

Treatment of individual laminates within a laminated timber is necessary to effectively stop decay if a vapor barrier is not used to slow fumigant loss from the wood.

Radial movement of chloropicrin through sapwood and juvenile wood of southern pine is very slow, the quantities diffusing through wood being 100X less than that of longitudinal diffusion.

Phenol-resorcinol gluelines are relatively impermeable to chloropicrin vapors even when the adhesive spread rate is greatly reduced.

Polyethylene sheeting can be used as an effective vapor barrier to limit the escape of chloropicrin vapors from the wood and to provide a reservoir for escaping fumigant vapors which can then diffuse into the wood at sites remote from the treatment zone. When a vapor wrap is employed the need to treat individual laminates is lessened.

With increased decay of wood specimens, the amount of chloropicrin diffusing through the wood decreases. This suggests that chloropicrin is retained in the wood structure with greater amounts retained in decayed wood.

GLC analysis of gas samples was an effective means of quantifying the amounts of chloropicrin moving through the laminated arch in vapor phase. Bioassay methods were also effective in determining relative chloropicrin vapor concentrations in the arch and substantiated the GLC data.
CT factors for chloropicrin in wood reach a maximum at approximately 30 to 60% moisture content. Wood at moisture contents greater or less than this would be expected to be less effectively treated.

**Chloropicrin Fungitoxicity**

The lethal chloropicrin CT factor for *Gloeophyllum saepiarium* was much greater in large infected wood specimens than in thin infected wooden wafers. This suggests that the fungus developed resistant structures in the infected blocks, or that in a large specimen chloropicrin may not adequately penetrate all areas of the wood, leaving small isolated pockets where fungi may remain protected.

Lethal chloropicrin CT factors for *Gloeophyllum saepiarium* in infected wooden wafers ranged from 18.4 µg hrs/ml for four hour exposures to 1.73 µg hrs/ml for 24 hour exposures. For *Poria* sp., lethal chloropicrin CT factors ranged from 15.0 to 13.4 µg hrs/ml for the four and 24 hour exposure periods, respectively.
RECOMMENDATIONS FOR THE TREATMENT OF LAMINATED PINE TIMBERS

(i) Decay may be controlled by treatment with 0.5 cc of chloropicrin per square centimeter of cross sectional area at appropriately spaced intervals along the timber.

(ii) Treatment sites should be spaced at about 2m intervals along the decayed length of the timber for wood at about 8% moisture content. Treatment sites should be spaced closer together for wood of higher moisture contents.

(iii) Treatment holes should contact all laminates.

(iv) A vapor barrier should be employed to retain fumigant vapors in the timber, to limit escape of the chemical into the surrounding environment and improve penetration, especially in severely decayed wood.
BIBLIOGRAPHY


Figure 29. Concentration of chloropicrin in normal thickness glueline beams. Injection quantity 10 μl.
Figure 30. Concentration of chloropicrin in normal thickness glue line beams. Injection quantity 25 μl.
Figure 31. Concentration of chloropicrin in normal thickness glueline beams. Injection quantity 50 µl.
Figure 32. Concentration of chloropicrin in normal thickness glue line beams. Injection quantity 75 μl.
Figure 33. Concentration of chloropicrin in normal thickness glueline beams. Injection quantity 100 µl.
Figure 34. Concentration of chloropicrin in normal thickness glueline beams. Injection quantity 125 µl.
Figure 35. Concentration of chloropicrin in thin glueline beams. Injection quantity = 10 µl.
Figure 36. Concentration of chloropicrin in thin glueline beams. Injection quantity = 25 μl.
Figure 37. Concentration of chloropicrin in thin glueline beams. Injection quantity = 50 μl.
Figure 38. Concentration of chloropicrin in thin glue line beams. Injection quantity = 75 µl.
Figure 39. Concentration of chloropicrin in thin glue line beams. Injection quantity = 100 μl.
Figure 40. Concentration of chloropicrin in thin glue line beams. Injection quantity = 125 μl.