Control of Incipient Decay With Gases in Douglas-fir Poles

Foreword

In 1962, Messrs. O. F. Hand and A. F. Wetsch, of the Bonneville Power Administration, began a study of gas diffusion systems for controlling decay fungi and insects in Douglas-fir and Western Red Cedar utility poles. Many fumigants were tested in that year, among them Chlorodane, Chloropicrin, Ethylene Dibromide, Vapam, Telone, Cresan M, Cyanogas and Methyl Bromide. Fungi and insects were killed by several of the materials tested as confirmed by bio-assay techniques. Reported as among the most effective tested were Vapam, Cyanogas, Chloropicrin, and Methyl Bromide. Following the work by Bonneville Power Administration, a cooperative research contract was established with the Forest Research Laboratory, Oregon State University, to evaluate chemical treatments for arresting decay in poles.

The description in this report of experiments made by personnel of the Forest Research Laboratory should not be interpreted as a suggested treatment for routine operations. Compounds tested are highly toxic to humans and should be applied by qualified operators who will follow directions of the manufacturer. The maximum allowable exposure over long periods is commonly set at 5 parts per million (ppm) parts of air for sulfuryl fluoride and 20 ppm for methyl bromide. These concentrations can be compared with allowable concentrations of the common chemicals hydrogen peroxide at 1 ppm, hydrogen sulfide at 20 ppm, hydrochloric acid at 5 ppm, and carbon tetrachloride at 10 ppm.

M. W. Belsher
Head, Research and Development Unit
Transmission Design Section
Bonneville Power Administration
Portland, Oregon

Figure 1. — Evaluation of Warburg apparatus for study of methyl bromide absorption by wood at 1.4°C. The break in the curve for methyl bromide and wood is attributable to resetting the manometer.

SERVICE LIFE of Douglas-fir poles could be extended if they could be penetrated readily by fungicides with long-lasting effects. Incipient decay is readily detected in poles (16), and the common decay fungus, Poria carbonica Overholt, is sensitive to fungicides (15). Douglas-fir heartwood resists penetration by liquids, so we investigated an agricultural fumigant, methyl bromide, for penetration and retention; later on, ammonia and sulfuryl fluoride were included for improved retention.

Methyl bromide has a well-established reputation in the food and agricultural pest control industries for its high penetration, relative safety, and convenience of handling. Partridge (12) tested it for control of oak wilt, Ceratocystis fagacearum (Bretz) Hunt, in 4-inch stems of black oak and white oak, with encouraging results. Jones (7) confirmed the effectiveness of methyl bromide for that purpose under field conditions.

1Acknowledgment is due Bonneville Power Administration for financial support provided under a cooperative research contract. R. D. Graham, J. S. Mothershead and M. M. Wilson of Oregon State University cooperated.

This paper was received for publication in May 1967.
The direct fungicidal action of ammonia has been known for some time (10). Roistacher, Eaks, and Klatz (17) developed a procedure for the control of various Penicillia on citrus fruits. Penetration of ammonia in wood has been studied by several workers and applied to the plasticization of wood (18). Sulfuryl fluoride was developed for termite control (8) and its use is widespread in the southern states.

Laboratory Experiments

Pure cultures of P. carbonica were obtained from the U.S. Forest Products Laboratory in Madison. These cultures were maintained on 2.5 percent malt extract agar medium, after testing of nutrient at various concentrations (15). Room temperature was usually suitable for incubation (70°F ± 5°F.). Temperatures exceeding that range have a definite retarding effect on growth rate, and peak summer temperatures inhibited growth.

Cultures exposed to methyl bromide in the usual concentration for 24 hours would no longer grow when placed in incubation under normal conditions.

The methyl bromide treatment was repeated on wood cores freshly removed from an infected pole, and similar results were obtained; no fungal growth resulted with the samples exposed to methyl bromide, although the untreated samples showed profuse growth. For accurate dosage, the absorption of methyl bromide and ammonia in wood was measured with a standard Warburg constant-volume respirometer. The change in pressure within the closed portion of the system was recorded as a function of time in the presence and absence of wood particles of known volume. The Warburg respirometer consists essentially of a manometer with one arm attached to a vessel where the reactions under study are taking place.

The usual procedures were followed (20), with some allowance for the particular gases used.

All tests were made in three or more replicates at 1.4°C. to allow introduction of methyl bromide in the Warburg flask as a liquid. Vaporization took place rapidly. Diffusion was measured readily, as shown in Figure 1, and approached equilibrium in and out of the wood particles in about 30 minutes. All controls (thermobarometer, wood alone, and methyl bromide alone in addition to air in every instance) followed the same pattern of fluctuating within a range of 60 manometer units, but the methyl bromide and wood systems showed a continuous pressure drop of more than 200 manometer units. These data suggested that the Warburg apparatus was suitable for the measurement of rate and extent of gas absorption by Douglas-fir heartwood, provided system constants were calculated.

The constants were calculated for both methyl bromide and ammonia separately. In those experiments where both methyl bromide and ammonia were used, no effort was made to ascertain the actual amounts of gases absorbed in the Warburg apparatus. In this instance, rather than actual volume of gases absorbed by the wood particles, the chief concern was how the pressure changes compared with that of the single gases. If simple absorption occurred with the gas mixture as well as with the single gas, the same uptake pattern would be seen because the relative pressure of the two gases would be independent of the other, as is usual in nonreacting gas mixtures (4). On the other hand, if solid synthesis were to occur in the wood in the same fashion as it does in wood-free systems, then a different pressure-change pattern would be observed, since some of the gas molecules experience a change of state.

Only one applicable α-value, 0.009, was found for methyl bromide (19). Its low magnitude compensated for the lack of data available on its change with temperature. For ammonia, α-values at several temperatures were available from standard reference manuals (9) and interpolation was made for the particular temperature used of 1144 milliliters gas per milliliter of water at 1.4°C. The k-values obtained for the various flasks used ranged from 1.2 to 1.7 for methyl bromide and from 1.64 to 2.99 for ammonia. The volume of the wood particles was measured by water displacement.

Figure 2 presents the data obtained with the Warburg respirometer. For the gases applied singly, the calculated k-values together with the volume determination of wood particles allowed expression of the pressure changes in terms of microliters or milliliters of the respective gases absorbed per cubic centimeter of wood. Nearly 0.2 milliliter of methyl bromide and 1 milliliter of ammonia were absorbed by each cubic centimeter of Douglas-fir heartwood. Ammonia absorption appeared to be complete within 30 minutes, but with methyl bromide it continued for about 1 hour, although 75 percent of the absorption was completed within 30 minutes.

The absorption pattern, when both methyl bromide and ammonia were present simultaneously, was appreciably different. A slower but protracted

<table>
<thead>
<tr>
<th>Volume Weight</th>
<th>Ammonium Bromide</th>
<th>CH-Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams</td>
<td>cc</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.174</td>
<td>1.2977</td>
</tr>
<tr>
<td>200</td>
<td>.002</td>
<td>.1645</td>
</tr>
<tr>
<td>600</td>
<td>1.060</td>
<td>1.1853</td>
</tr>
<tr>
<td>400</td>
<td>.001</td>
<td>.1645</td>
</tr>
<tr>
<td>200</td>
<td>.992</td>
<td>.3552</td>
</tr>
<tr>
<td>100</td>
<td>.496</td>
<td>.3552</td>
</tr>
</tbody>
</table>

Table 1. — YIELD OF AMMONIUM BROMIDE SALT BY MIXTURE OF METHYL BROMIDE, AMMONIA AND AIR IN SIMPLE SYSTEM.
uptake of the gases took place, actually for a longer time than is shown on the graph. After 2 1/2 hours, slow absorption was still occurring.

This pattern is consistent with the behavior of these two gases, which, when mixed with air in the absence of wood, yielded ammonium bromide salts. These reaction products were obtained in simple systems with 2-liter flasks, where the approximate concentration of the gases was measured by water displacement. Methyl bromide, ammonia, and air were released one by one, in that sequence, into the water-filled flask to take advantage of the higher density of methyl bromide and prevent contact between the highly soluble ammonia and water. The gas-filled flasks were placed at various temperatures and the reaction time required for the occurrence of crystals was recorded. Qualitative tests for ammonium and bromine were performed on dilute water solution of the compound. For bromine, the solution was acidified with dilute nitric acid, then mixed with cold aqueous silver nitrate solution. The bromide ion showed with the formation of a white or pale yellow precipitate. For ammonium detection, the water solution of the unknown compound was made alkaline with cold sodium hydroxide and the mixture heated gently. Ammonia vapors were detected by color change on moist pHydron paper and by odor. The melting point was measured in the usual instrument. The measurement of properties affecting fungi was made by addition of the compound tested in various concentrations to malt extract agar in culture tube slants before inoculation in the usual way. Type and extent of growth were taken into consideration for evaluation of the substance’s effectiveness (11). The salts formed by reaction of both methyl bromide and sulfuryl fluoride showed fungicidal activity, particularly those formed by the latter gas.

Solids formed in the simple laboratory systems always contained both bromine and ammonia, and decomposed between 163° and 225°C., as long as the reaction temperature exceeded 30°C. and air was present. At lower temperatures, the formation of solids was delayed. In addition, with no air present, only compounds with low melting points and lacking bromine were obtained. Table 1 shows the yield of solids synthesized in various relative concentrations of methyl bromide and ammonia. The highest yield, 84.4 percent, was obtained at approximately 4:1 weight ratio.

The effect on wood strength of gas treatment with methyl bromide and ammonia, singly and mixed, was measured in terms of modulus of rupture, through the standard static bending test (1) with wood specimens 1 by 1 by 16 inches at 12 percent moisture content. None of the averages obtained exceeded the 16 percent coefficient of variation indicated in the Wood Handbook (21) for the modulus of rupture, so no significant effect can be attributed to the gas treatment on the basis of these figures.

In preparation for field trials, various plastic sheets and tapes were tested by capping a 2-liter volumetric flask filled with methyl bromide. The gas-filled flask closed off with the material to be tested was then inverted into a beaker and kept in that position for 24 hours. The heavy methyl bromide would accumulate in the beaker should leakage occur. Evidence for that event was secured with the Beilstein test. When no methyl bromide was found in the beaker at the end of the test period, the volumetric flask was opened and the gas content tested to confirm the apparent effectiveness of the capping material. Four-mil Mylar plastic held methyl bromide effectively, but six-mil polyethylene plastic allowed moderate leakage. Mylar tape was also most effective, though standard masking tape was moderately so and may be preferred for cost considerations.

Field Experiments

For experiments with pole sections or poles in service usually those with infected heartwood at the incipient decay stage were chosen. Poles were sampled with an increment borer and the cores cultured on malt extract agar (16).

The Beilstein test was used for the detection of bromine in air as a means of evaluating the occurrence and approximate concentration of methyl bromide. This test is used widely in the convenient form of a “halide leak detector” by refrigeration servicemen and pest-control fieldmen.

The presence of bromine in wood was detected in the same way as in air with the additional steps of drying, grinding, and heating the ground wood to charring in a test tube. The fumes released by the charring wood were tested for bromine with a halide leak detector. This procedure is far from ideal; it did, however, provide useful data when the air intake of the burner was cleaned frequently.
to remove the tars introduced with the charring wood fumes. The odor of ammonia gas in air is unmistakable and was employed for detection. Dissolved ammonia was detected by washing wood particles in distilled water, adding alkali, and heating to release ammonia gas.

Penetration of methyl bromide into pole sections

The first series of field experiments with methyl bromide was performed in a fumigation vault. Pole sections ranging from 8 to 19 inches in diameter and from 28 to 60 inches long were completely coated on their ends with hot liquid paraffin to prevent longitudinal penetration of the gas.

Two holes approximately 1/4 inch in diameter were drilled to the pith in each section in the same vertical alignment at about 1/4 the overall length of the pole from each end to measure penetration and concentration of gases in the wood during treatment (Figure 3). A third hole was drilled at midpoints 24 hours after the gas was released from the vault for further testing of gas penetration. Sections of plastic tubing were introduced into the holes, pushed to the bottom, and sealed with masking tape and liquid paraffin at their point of entry into the poles. The sections of tubing were attached to a gas-measuring device, a fumiscope, distributed by Neil MacLean Company. Methyl bromide was released into the vault to a concentration of 10 pounds per 1,000 cubic feet. Fumiscope readings were taken at various intervals during the 24-hour exposure period. Upon completion of the fumigation, the vault was ventilated and readings were taken on the concentration of methyl bromide at the center of the poles 48 hours later. The temperature ranged from 54° to 78°F. within the vault during the exposure period.

The data of Table 2 indicate that in 30 minutes or less the methyl bromide had penetrated radially to such an extent that equilibrium was reached with the surrounding atmosphere in five pole sections. The other pole sections, which were the four larger ones (18 and 19 inches in diameter), had already absorbed a minimum of 26 ounces per 1,000 cubic feet. After 6 hours, each of the smaller sections still showed more than 100 ounces of methyl bromide to 1,000 cubic feet, although the surrounding concentration had begun to drop indicating leakage in the presumed gas-tight vault; the larger sections had increased their gas absorption to a minimum of 45 ounces and a maximum of 61 ounces per 1,000 cubic feet, which approached the surroundings in gas concentration. After 24 hours of exposure, the gas concentration in all sections had started to decrease consistently with the change in the vault. The range between large and small sections had narrowed to 14 ounces.

This experiment suggested that the well-known penetrating ability of methyl bromide applied to Douglas-fir wood as well as to the other tightly packed commodities to which this gas is frequently applied. These results are consistent with those obtained with oak logs (12).

Treatment of poles in service

The most effective technique selected for field treatment of infected poles in service was as follows. The ground around the pole was excavated to a depth of 18 inches and a width of 1 foot. From four to six boards (the number depends on the diameter of the pole) 2 inches square and 4 feet long, tapered on the last foot of each end, were nailed vertically around the pole at regular intervals so as to form spaces around the ground-line zone of the pole; that is, about 1 foot below the ground level to about 3 feet above. The spacers were then covered with four-mil Mylar sheet sealed at all joints with masking tape, with sealing compound added where cracks or seasoning checks occurred (Figure 4). The lower end of the plastic sheet was sealed against the pole with soil packed mechanically and soaked with water for further compaction. A hole was then punctured in the plastic covering around the pole for the introduction of a rubber tube linking the inside of the tent with a 1-pound can of technical-grade methyl bromide equipped with the usual puncturing device and valve assembly (Figure 4). A total of 2 pounds of methyl bromide was used for a 24-hour period. The temperature ranged from 68°F. (20°C.) at the start to less than 50°F. (10°C.). The moisture content of the poles was measured with a resistance-type moisture meter.

Condition of the fungi in the heartwood of the poles before and after treatment was evaluated by aseptic removal of wood cores and subsequent plating on malt extract agar in the laboratory.

Table 2. — CONCENTRATION OF METHYL BROMIDE IN POLE SECTIONS AFTER THREE PERIODS OF EXPOSURE.

<table>
<thead>
<tr>
<th>Pole Size</th>
<th>Diam. Length (In.)</th>
<th>Exposure (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top Bottom</td>
<td>Top Bottom</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>100+</td>
</tr>
<tr>
<td>10</td>
<td>45</td>
<td>100+</td>
</tr>
<tr>
<td>11</td>
<td>35</td>
<td>100+</td>
</tr>
<tr>
<td>11</td>
<td>49</td>
<td>100+</td>
</tr>
<tr>
<td>13</td>
<td>55</td>
<td>100+</td>
</tr>
<tr>
<td>18</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>18</td>
<td>57</td>
<td>40</td>
</tr>
<tr>
<td>19</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td>19</td>
<td>34</td>
<td>27</td>
</tr>
<tr>
<td>Vault space</td>
<td>100+</td>
<td>69</td>
</tr>
</tbody>
</table>

1Dosage was 10 pounds per 1,000 cubic feet; concentration in logs is in ounces per 1,000 cubic feet. The Fumiscope could not register concentrations of more than 100 ounces per 1,000 cubic feet.
The moisture meter readings of the first pole gassed in service showed more than 25 percent moisture, which confirmed earlier findings where heartwood was decayed. A wood core taken just before gassing was cultured and yielded abundant fungal mycelium. Upon completion of the gas treatment, a second core from the same area as before gassing was free of live fungi. A third core taken 5 days after treatment showed no fungal growth. A core sampled 15 months after treatment showed residual bromine all the way to the center of the pole. A core sampled 11 months after treatment, however, showed some fungal growth but no evidence of wood deterioration.

These findings, together with the occurrence of a large decay pocket above the treated zone, may explain the growth pattern experienced with the cores cultured at various time intervals. Although destruction of the mycelium present within the treated zone took place during gassing, new hyphae later could have grown into the treated area from the decay pocket above.

Reconditioning used poles

Poles out of service were reconditioned in a gas-tight enclosure where the temperature could be maintained between 80°F. and 160°F. for 24 hours. The lower part of the enclosure was provided by a trough-shaped metal tank used to dip poles and the upper part by a 6-mil polyethylene sheet. Sand pressed the plastic tightly against the metal to form a gas-proof seal. An electric heater with fan was installed under the plastic to maintain suitable temperature and to distribute the gases.

The gases were released gradually and alternately until a total of 1 pound methyl bromide and 0.3 pound ammonia was applied for each pole. All methyl bromide was introduced as gas, not as liquid. Its state as a gas could be verified readily by listening at the point of release when opaque plastic sheet is used. A smooth, steady hissing sound is heard when it has properly vaporized, but when it escapes from the cylinder as a sputtering mixture of liquid and gas, the sound is irregular. Quick, thorough vaporization requires that the gas be warmed, as, for example, by passage through a copper coil immersed in a bucket full of warm water.

The poles remained covered for 24 hours, then the plastic sheet was removed. Ten percent of the poles were sampled within a foot of the ground line for culturing to evaluate the kill of fungi. Powder formed on surfaces of the poles was tested for bromine and ammonia, and its composition tested qualitatively for bromine and ammonia. Decomposition seemed to occur above 225°C. Tetramethyl ammonium bromide decomposes slightly above 230°C. These compounds do not exhibit a true melting point.

The beige powder on the surface of the poles and on all flat surfaces of the electric heater after fumigation showed positive tests for bromine and ammonium. Immediately after treatment, one pole showed atypical Poria carbonica growth; all others were free from fungi. Because of driving rain during the sampling, difficulty was experienced in maintaining the pole surface free from contamination. The pole with atypical fungal growth was sampled twice again with one boring on each side of the original one. No growth was found in these later samples.

The beige compound obtained was readily soluble in water. Its synthesis appeared to have been speeded by heat, as its concentration increased inversely with distance from the heater, with a maximum concentration on the heater itself. The newly formed compound was obvious from the heater at one end of the poles to the midpoint, then decreased in concentration to the opposite end of the poles. Sampling of the poles 6 months later after incubation outdoors failed to yield live P. carbonica. Cores tested for bromine and ammonia after 1 year showed positive results for both substances in more than 90 percent of the samples. These six poles have been put back in service as supporting members of a standard
pole-frame barn. Subsequent experiments yielded similar results and these later poles were returned to normal service. Further sampling is planned on all these poles.

Multi-gas treatment of green pole sections

A section of untreated, green pole stock 2 feet long and 9 inches in diameter was placed in a retort. Steam was then released in the enclosure until a temperature of 250°F (15 pounds per square inch) was reached. After 48 hours of continuous exposure, the pole section was removed from the retort and both ends were packed with insulation material to prevent longitudinal heat loss. The insulated pole section was then placed in a horizontal metal gas chamber made from a 20-gallon drum. Air was partially evacuated down to a pressure of 6 p.s.i. below atmospheric. Methyl bromide was then introduced until the pressure rose to 5 p.s.i. below atmospheric, after which ammonia was used to return the chamber to atmospheric pressure. Exposure was allowed for 24 hours at 70°F. The gas chamber was then opened and the wood tested for bromine.

No ammonium bromide salt was found on the surface of the pole section that had been heated before exposing it to a mixture of methyl-bromide and ammonia gas, except where the pole section had touched the treating chamber so that the metal wall was heated. All wood cores taken from the pole showed presence of bromine by the Beilstein flame test and by the silver nitrate precipitation test.

Discussion

For saturation equilibrium to be reached inside and outside a pole, 50 pounds of methyl bromide and 48 pounds of ammonia should be used for 1,000 cubic feet of wood (Table 3). If, however, the chief aim is to synthesize ammonium bromide salts, a lower proportion of ammonia should be used. For a pole 10 inches in diameter and 50 feet long, an appropriate dosage would be 1.5 pounds methyl bromide and 0.4 pound ammonia. These amounts of gases should yield 1.34 pounds of ammonium bromide salts, or about 0.15 percent, based on weight of the wood.

For in-service treatment, 1 pound of methyl bromide and 0.3 pound of ammonia should yield a salt concentration of 1.24 percent, based on weight of the wood, which should be ample for residual control of Poria carbonica.

To ensure formation of salts in the wood and to lessen losses by deposition of salts on exposed surfaces, the interior wood should be warmer than surrounding air when treated. We found subsequently that heating is unnecessary if the methyl bromide is replaced by sulfuryl fluoride, which is possibly even more effective as a fungicide.

Multi-gas diffusion treatment of poles in service is of particular interest with the use of such gases as methyl bromide and other halogen-containing fumigants with ammonia in the presence of air. This treatment should apply also to other wood structures where penetration and residual action of the fungicidal agent is difficult.

Residual action from methyl bromide can be expected from the ionization of the gas molecule either before or after penetration into the hyphal cytoplasm:

$$\text{CH}_3\text{Br} + \text{HOH} \rightarrow \text{CH}_3\text{OH} + \text{HBr}$$

Besides the acid, the reaction yields another toxic substance, methanol, of well-known disinfectant properties, but the concentrations available are not likely to be sufficiently high for significant effect.

Ammonia can function in several distinct ways in the treatment of wood: direct fungicidal action, temporary and permanent modification of the substrate when used in the presence of oxygen, and synthesis of fungicidal compounds in place when used simultaneously with reactive halides or halogens.
Permanent modification of the substrate has been reported to involve the reaction of the sulfhydryl group of thiamin with an ammonia molecule, which thereby alters the availability of this all-important vitamin to fungi (2, 6).

When oxygen is present during the amination process, drastic changes appear to occur in the lignin component of the wood. Polymerization may result from linkage of phenyl rings through nitrogen and oxygen bridges. The simultaneous oxidation and amination of natural compounds, particularly in ponderosa pine bark, and related pure, model compounds was studied in some detail by Ricard (14). The reaction altered the physical, chemical, and biological characteristics of the substrate. The well-known stability of humus is believed attributable in large part to this type of reaction.

Synthesis of fungicidal compounds in place when used simultaneously with reactive halides or halogens may be extremely useful for residual protection of the treated wood.

When ammonia and methyl bromide molecules are allowed to collide, the following sequence of reactions can be expected (5):

\[
\begin{align*}
CH_3Br + NH_3 & \rightarrow CH_3NH_2Br \\
CH_3NH_2Br + NH_3 & \rightarrow CH_3NH_3 + NH_4Br \\
CH_3NH_2 + CH_3Br & \rightarrow (CH_3)_2NHBr
\end{align*}
\]

Repetition of the successive amination and bromination builds up the alkyl radical of the compound until \([\text{(CH}_3)_4N]^+\text{Br}^-\) is formed. This compound is typical of the well-known quaternary ammonium salts (13). Their germicidal properties are widely recognized and are used commercially for many purposes because their relative stability and versatility make them exceptionally effective; their cost, however, is limiting.

The beige compound actually recovered from the multi-gas diffusion treatment of the pole sections is a water-soluble ammonium salt containing bromine with a decomposition point within 5°C. of that of tetramethyl ammonium bromide. Sulfonyl fluoride hydrolyzes in water to yield sulfuric and hydrofluoric acids. These acids react with the ammonium hydroxide resulting from the solution of ammonia in water and yield ammonium sulfite and fluoride (3). Ammonium fluoride has been used for some time as a wood preservative.

The use of these gases results in several reactions that should impart a variety of residual fungicidal properties to the wood. These would make circumvention of the treatment by a fungal mutant or adapted form of a wood-destroying fungus highly improbable.

**Literature Cited**