

# DECOMPOSITION OF BASAMID IN DOUGLAS-FIR HEARTWOOD: LABORATORY STUDIES OF A POTENTIAL WOOD FUMIGANT<sup>1</sup>

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## ABSTRACT

Basamid (3,5-dimethyl-1,3,5,2H-tetrahydrothiadiazine-2-thione), a crystalline powder first used as a soil sterilant, has shown promise as a wood fumigant. This chemical decomposes to methylisothiocyanate (MITC), the primary active ingredient, as well as other products; but the rate of decomposition in wood is too slow to be effective unless certain catalysts are used. This study explored conditions and additives that accelerated Basamid decomposition in Douglas-fir heartwood. MITC production increased with increasing temperature and moisture content. Decomposition was also enhanced by a buffer powder formulated to reach pH 12 when mixed with 100 ml of water and, more efficiently, by copper sulfate. Carbon disulfide, a less fungitoxic compound, was the only other decomposition product detected in this study. Additional tests using a purge-and-trap system indicated that MITC was produced at a steady, moderate rate over a 28-day period. Addition of copper as a catalyst in these tests increased MITC production only during the first 7 days. Chemical analyses of residues at the conclusion of the tests indicated that most of the Basamid remained unchanged, providing a reservoir of chemical that should provide long-term MITC release.

*Keywords:* Basamid, fumigants, internal decay, utility poles, catalysis, Douglas-fir.

## INTRODUCTION

Wood utility poles are routinely pressure-treated with preservatives to protect them against biological deterioration. However, many pole species, such as Douglas-fir (*Pseudotsuga menziesii*), in western North America contain a high proportion of heartwood, which is largely impermeable to liquid penetration. Although the heartwood of Douglas-fir is im-

pervious to liquids, it is permeable to gases (Hand et al. 1970; Graham 1973). Several volatile agricultural chemicals have been added as liquids to the interior of poles via downward-sloping holes, where they vaporize and move through the wood as gases to kill established decay fungi. Poles remedially treated in this manner have been found to be free of decay fungi up to 14 years after treatment (Helsing et al. 1984).

Sodium N-methyldithiocarbamate (Na-MDC), Vorlex (20% methylisothiocyanate, 80% chlorinated C-3 hydrocarbons), chloropicrin (96% trichloronitromethane), and MITC-Fume® (97% solid methylisothiocyan-

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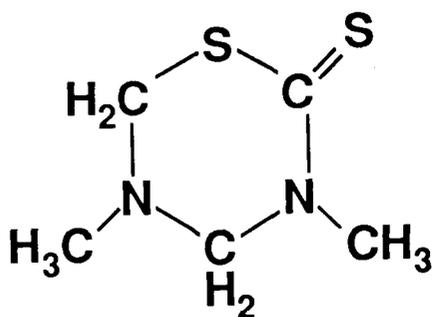


FIG. 1. The chemical structure of Basamid.

ate [MITC]) are the only fumigants registered with the U.S. Environmental Protection Agency for wood application. However, three of these chemicals are applied as liquids, creating potential hazards in safety and handling. MITC-Fume<sup>®</sup>, a solid at room temperature, has proven highly effective as a wood fumigant; however, it is also very volatile, expensive, and not yet widely used.

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

Chemically, Basamid is a heterocyclic ring containing carbon, nitrogen, sulfur, and hydrogen (Fig. 1). It was first prepared in 1897 by Delepine, who reacted carbon disulfide with trimethyltrimethylene triimine (Herschler 1953). Ainley et al. (1944) later elucidated the actual structure of the compound as 3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione (CAS Registry No. 533-74-4). More recently, it has been prepared commercially by reacting carbon disulfide with methylamine and caustic soda (Merck and Co., Inc. 1989).

The chemical has been used under various commercial names including Mylone (Union Carbide Corp.), Crag Fungicide 974 (Union Carbide Corp.), Salvo (Stauffer Chemical Co.), N-521 (Stauffer Chemical Co.), Basamid (BASF

AG), tiazon (USSR), Dazomet, and Fongosan. It has been used in agriculture as a fungicide, herbicide, nematocide, and insecticide (Keays and Zedler 1957; Hartley and Kidd 1987), as well as a slimicide in pulp and paper manufacturing (Herschler 1953) and as a preservative in adhesives and glues (Hartley and Kidd 1987).

Basamid decomposes slowly in wood and has successfully controlled decay fungi there after long exposures (Graham and Corden 1980; Eslyn and Highley 1985). Such slow decomposition could be useful if the chemical were applied before decay had to be eradicated. However, in pure form Basamid does not decompose rapidly enough to diffuse and kill actively growing decay fungi in wood (Highley and Eslyn 1986; Morrell et al. 1988). To be effective there, a chemical must be able to eliminate an actively growing fungal colony within 6 to 12 months after application.

Under dry conditions and ambient temperatures, Basamid is stable and not considered biologically active. Effectiveness against target organisms depends on the decomposition products formed and the rate at which they are released. Among the decomposition products reported are MITC, methylamine, hydrogen sulfide, and formaldehyde (Ruch and Johnson 1957; Torgeson et al. 1957). Acid hydrolysis also yields carbon disulfide (Ruch and Johnson 1957; Hartley and Kidd 1987; Worthing 1987). MITC is considered to be the most important volatile toxicant produced (Munnecke et al. 1962; Goksoyr 1964; Spencer 1981) and has received the most attention in Basamid evaluations. MITC production is dependent on several environmental conditions including moisture, temperature, pH, and the presence of trace metals.

The relative ratios of decomposition products formed from Basamid are also pH-dependent. Acidic media hydrolyze Basamid to carbon disulfide, formaldehyde, and methylamine (Ruch and Johnson 1957; Hartley and Kidd 1987). Under neutral or basic conditions, the reaction shifts toward the production of MITC and hydrogen sulfide along with form-

aldehyde and methylamine (Ruch and Johnson 1957). Miller and Morrell (1989) demonstrated that MITC was produced at a greater rate at pH 10 than at pH 4 or 7. In soils, MITC production increased with pH up to 6.5, but then decreased up to pH 7.7 (Munnecke and Martin 1964). In one of the first tests of Basamid in wood, alkaline buffers (pH 10 and 12) greatly enhanced MITC production and fungal control in wood blocks (Morrell et al. 1988).

Decomposition of some dithiocarbamates can be enhanced by the addition of certain metals. For instance, NaMDC decomposition increases in the presence of copper, manganese, iron, and zinc (Ashley and Leigh 1963). Goksoyr (1964) showed that very low levels of cupric sulfate synergistically decreased acetate respiration of yeast while simultaneously increasing the production of MITC from Basamid. Chandra and Bollen (1961) have suggested that soil minerals may actually catalyze the primary step in Basamid decomposition.

While there have been several studies of Basamid decomposition in soil, little information exists on how additives affect Basamid decomposition in wood. This paper describes tests designed to determine the effect of moisture and temperature as well as selected additives on the decomposition of Basamid in Douglas-fir heartwood. After an initial screening, two additives were selected for further study of their effects on both the rate of decomposition and the balance of decomposition products. Additional tests employing a purge-and-trap system were used in order to determine whether volatile products were escaping from the vials or reacting with the wood and to assess residual Basamid in the wood at the end of the test period.

#### MATERIALS AND METHODS

##### *Initial screening of additives*

Several powdered additives were tested for their ability to enhance the decomposition of Basamid to MITC. On the basis of the weight of Basamid used, the following percentages of metals or other substances were added: 0.5, 1,

5, and 10% copper sulfate; 1% copper chloride; 1% manganese sulfate; 1% magnesium sulfate; and 5% of a buffer powder consisting of sodium phosphate (di and tri basic) formulated to reach pH 12 when mixed with 100 ml of water.

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

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

##### *Effect of additives on decomposition*

On the basis of the initial screening, tests were run to determine the effects of wood and of promising additives on the rate and efficiency of Basamid decomposition into MITC and other products including primary amines and carbon disulfide. Glass vials (40 ml) equipped with Teflon-lined silicone septa were























