INTERACTIONS BETWEEN SODIUM N-METHYLDITHIOCARBAMATE AND DOUGLAS-FIR HEARTWOOD[1]

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ABSTRACT

Vapam® (NaMDC) is the fumigant most commonly used to arrest and control decay of utility poles. While volatile fungitoxins are detectable only 1 to 2 years after treatment, poles treated with Vapam® remain free of decay fungi for 6 to 17 years. Vapam® decomposes to produce volatile fungicides as well as a number of nonvolatile products that may provide long-term protection. The degree and rate of decomposition of NaMDC were evaluated by using a gas chromatograph and a high-performance liquid chromatograph to analyze extracts from Vapam® mixtures with wood, cellulose, vanillin, starch and glass.

Compounds similar to those produced from Vapam®-soil mixtures were found in the mixtures tested. Of the materials identified, sulfur was the most abundant nonvolatile product in wood mixtures and may play a role in long-term wood protection. Sulfur was present only at low levels in cellulose mixtures. These results, coupled with the low levels of volatile MIT produced in the cellulose mixtures, suggest that lignin is an important site for Vapam® decomposition reactions. Further studies are suggested to determine the role of nonvolatile decomposition products in arresting decay away from the point of application.

Keywords: Fumigants, Douglas-fir, Vapam®, decomposition, preservation.

INTRODUCTION

Agricultural fumigants are widely used to control internal decay of large-dimension wood products and thus to prolong the useful life of utility poles, marine piling, and structural timbers (Goodell and Graham 1983). Three fumigants, Vapam®[2] (33% sodium N-methyldithiocarbamate, or NaMDC), Vorlex (20% methylisothiocyanate in chlorinated C_3 hydrocarbons), and chloropicrin (trichloronitromethane) are registered with the U.S. Environmental Protection Agency for use in wood (Morrell and Corden 1986). NaMDC appears to be the most commonly used of these chemicals.

Field tests have shown that NaMDC eliminates decay fungi from wood in as little as 1 year. Bioassays for the presence of volatile fungitoxic products indicate that the treated poles exhibit little fungitoxicity after 2 to 3 years (Helsing et al. 1984). However, treated poles have been shown to resist reinvasion for 7 to 10 years. The reason for this long-term protection is poorly understood. Of the three

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[2] Mention of trade names or commercial products does not constitute endorsement by the authors or by Oregon State University.

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TABLE 1. *Identification of NaMDC and its decomposition products.*

CAS name[a]	CAS no.	Formula	Abbreviation
Sodium methylcarbamodithioate	137-42-8	$C_2H_4NS_2Na$	NaMDC
Sodium thiosulfate	10102-17-7	$Na_2S_2O_3 \cdot 5H_2O$	
Sodium sulfate	7757-82-6	Na_2SO_4	
N,N'-dimethylthiourea	534-13-4	$C_3H_8N_2S$	DMTU
O-methyl-N-methylcarbamothioate	14128-35-9	C_3H_7NOS	MMC
Isothiocyanato-methane	556-61-6	C_2H_3NS	MIT
2,4-dimethyl-1,2,4-thiadiazolodone-3,5-dithione	6317-20-0	$C_4H_6N_2S_3$	DTD
4-methyl-5-(methylimino)-1,2,4-dithiazolidine-3-thione	20042-85-7	$C_4H_6N_2S_3$	MMDT
Sulfur	7704-34-9	S_8	Sulfur

[a] Underlined letter determines position in CAS alphabetical list.

registered fumigants, NaMDC is the only one that must decompose to kill fungi. The length of time between the loss of fungitoxic vapors and reinvasion by decay fungi suggests either that the fungi present in the soil recolonize the wood at very slow rates, or that decomposition of NaMDC results in the deposition of nonvolatile fungitoxic products that inhibit the germination and growth of fungal spores and hyphae. However, while the fungi that reinvade fumigated wood are different from the original population, recent studies suggest that the reinvasion takes place in a relatively short time—5 years—and is accomplished by a variety of fungi (M. Y. Giron unpublished). Thus, it would appear that nonvolatile products of NaMDC's decomposition may play an important role in long-term protection of wood against fungal decay.

Methylisothiocyanate (MIT) is believed to be the major fungitoxic chemical produced by NaMDC's decomposition. However, several other chemicals, volatile and nonvolatile, are produced; these also may inhibit fungal colonization (Table 1). Previous studies have dealt with the decomposition of NaMDC in soil (Elson 1966; Smelt and Leistra 1974; Thorn and Ludwig 1962; Turner and Corden 1963), but there is little research on its decomposition in organic matter. Wood has few minerals but is rich in carbohydrates and phenolics. These may affect both the rate of NaMDC's decomposition and the chemicals produced by it.

In this study, we evaluate the decomposition of NaMDC in wood in order to determine the kinds and amounts of decomposition products generated and to discuss their potential for protecting wood against fungal invasion. This information will aid in efforts to improve the performance of remedial fumigant treatments, and will also enhance our general understanding of how these chemicals function in wood.

Detection of volatile products

The volatile decomposition products of NaMDC were determined, and their proportions measured, by testing the reactions of NaMDC with four organic substrates: starch, cellulose, vanillin, and Douglas-fir heartwood. A fifth material, glass, was also tested as a control. A 0.1-g sample of each test material was prepared and placed into a 67-ml glass bottle. The Douglas-fir heartwood was ground to pass a 3-mm screen; the cellulose consisted of Whatman No. 1 filter paper. NaMDC was added in a 0.3 M solution, 50 μl to each bottle. The bottle was capped with a Teflon®-lined screw cap to retard loss of volatiles.

TABLE 2. *Relative yield of methylisothiocyanate (MIT) and carbon disulfide (CS_2) at selected times after treatment of 0.1 g of various substrates with 50 µl of a 0.3 M NaMDC solution.*

Incubation time (hours)	Reaction product	Relative yield by substrate[a]				
		Glass	Starch	Cellulose	Vanillin	Wood
5	MIT	0.29	0.44	0.44	0.40	0.40
	CS_2	0	0	0	0	0
24	MIT	0.63	0.49	0.54	1.90	1.00
	CS_2	0	0	0	0	0.23
72	MIT	0.07	0	0.06	1.40	0.80
	CS_2	0	0	0	0	0.22

[a] Relative yield of MIT is based on the level of MIT produced in wood 24 hours after NaMDC treatment. CS_2 levels are based on the mole ratio (CS_2/MIT).

At 5, 24, and 72 hours after the NaMDC was added, 7-µl gas samples were removed from the glass jars and injected into a Varian 3700 gas chromatograph equipped with a glass column (3 m by 4 mm inner diameter) packed with 10% Carbowax on 80/100 Supelcoport®. The detector and injector temperatures of the GC were 200 C. The oven temperature was 160 C. A flame photometric detector specific to sulfur compounds was employed. The nitrogen flow rate was 75 ml/min. The concentration of MIT from the treated wood at 24 hours was designated as 1.0. Concentrations of MIT and CS_2 from the other test materials were determined relative to this designation (Table 2).

The volatility of the chemicals being studied raised problems of storage and precise measurement. Both MIT and CS_2 readily diffuse through rubber and similar materials; consequently, standard gas mixtures were difficult to prepare and store. Since these volatiles were formed gradually from NaMDC over several hours or even days, there was some loss from the experimental samples. Furthermore, quantitative GC analysis of small gas samples was complicated by uncertainty of the sample size because the gas sample was injected into an environment of high temperature and pressure. To solve these problems, we developed a trapping procedure that converts MIT to a nonvolatile derivative, an ethoxythiourethane, which is easily determined by HPLC.

A trapping mixture, 2 ml of ethoxyethoxyethanol (EEE), containing 40 mg KOH, was placed in a small open vial in each test bottle. Fifty µl of 0.3 M NaMDC was then added to 0.2 g of Douglas-fir sawdust, 0.2 g of cellulose, and to the glass control. We also evaluated the effect of moisture level on MIT production by adding 50, 100, and 300 µl of water to selected containers. After incubating for 5, 24, and 72 hours, the trapping mixture was diluted to 100 and 1,000 ml with water. Each dilution was analyzed by HPLC for the ethoxythiourethane. A Shimadzu HPLC fitted with a Rheodyne 7125 injector (20 µl) and an E. S. Industries pH stable RP-1 column (5-µm particles, 200 × 4.6 mm) was used. The mobile phase used in these experiments was 33% MeCN (acetonitrile), 67% water.

Detection of nonvolatile products

To determine the role of nonvolatile compounds in fumigant performance, we added NaMDC to Douglas-fir sawdust, cellulose, and glass beads at a ratio of 1:3 for the wood and cellulose and 1:30 for the glass beads. Volume of the NaMDC

varied from 10 μl to 10 ml. The mixtures were incubated in open glass bottles at room temperature for 2 months to allow all volatiles to escape.

Each mixture was then Soxhlet extracted sequentially for 24 hours each in dichloromethane (DCM), methanol, and water. Because DCM is not compatible with the aqueous mobile phases used in the HPLC, it was removed from the DCM extract, which was then redissolved in methanol. HPLC analysis was performed with the instrument and column described above, and also with columns of C_{18} on 3 μm and 5 μm silica. Because the chromatographic properties of the products vary widely, mobile phases of different strengths were used. Sulfur was eluted using a mobile phase of 100% MeOH. DTD, MMDT, and MIT were eluted using a mobile phase of 16% MeCN, 36% MeOH, 48% water. DMTU, MMC, and MIT were eluted using a mobile phase of 7% MeCN, 13% MeOH, 80% water. Trace (0.01% yield) unidentified components were eluted using mobile phases of 23% MeCN, 54% MeOH, 23% water; and 80% MeOH, 20% water. Retention times were 2 to 10 min. Flow rate was 1 ml/min.

The products, which were identified by comparing them with known samples, are listed and identified in Table 1.

The methanol extracts from cellulose and glass were concentrated to dryness and then mixed with 50% MeOH-50% ethanol. The insoluble salt was identified as $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulfate) by X-ray diffraction. The soluble salt recovered by concentrating the ethanol-methanol mixture was identified as NaMDC $\cdot 2H_2O$ by X-ray diffraction. A Sintag PAD-V X-ray diffractometer with a Cu source was used.

The sulfur contents of the methanol extracts were determined by inductively coupled plasma (ICP) spectrometer (Jerrall Ash ICAP 9000). Further characterization of the sulfur compounds was prevented by wood extractives contained in the methanol and water extracts.

The sulfur in the water extract was assumed to be sulfate, since in a separate experiment, solid Na_2SO_4, identified by X-ray diffraction, was separated as a methanol-insoluble salt. Unextractable sulfur was determined by exhaustively digesting 2 to 3 g of extracted treated wood and cellulose with nitric acid. Initially, 20 ml of acid was added. As heating continued and the nitric acid evaporated, more was added until the evolution of brown NO_2 abated and the digests were clear and pale yellow to colorless (6 to 8 h). The digests were diluted with water and analyzed by ICP. The sulfur found in these digests is assumed to represent sulfur that had been bound to the wood.

RESULTS AND DISCUSSION

Volatile products

After 5 hours, MIT levels were similar in all the test materials except the glass. Both the vanillin and the wood exhibited substantially higher levels of MIT after 24 hours, but these declined somewhat between 24 and 72 hours. MIT levels in the starch and the cellulose declined drastically. The MIT levels in the wood, the cellulose, and the vanillin suggest that the decomposition of NaMDC is strongly influenced by lignin. Cellulose and starch did not appreciably affect the production of MIT, but vanillin, a chemical commonly used in lignin studies, substantially enhanced it. These findings support those of current studies indicating that attack

TABLE 3. *Yield of volatile methylisothiocyanate (MIT) from reaction of NaMDC with wood, cellulose, and glass as measured with an ethoxyethoxyethanol MIT trap.*[a]

Incubation period (days)	Water dosage (μl)	MIT yield by substrate		
		Wood	Cellulose	Glass
1	0	41	—	1
2	0	32	1	3
	50	59	5	2
	200	51	23	9
3	0	34	—	1
7	0	44	—	—
	100	65	—	—
14	0	43	—	—
	50	60	—	—
	700	62	—	—
	300	60	—	—

[a] 0.2 g substrate or glass, 50 μl of 3 M NaMDC.

by brown rot fungi has little influence on MIT adsorption (Zahora 1987). Brown rot fungi cause extensive degradation of the carbohydrate portion of the wood, but only modify the lignin, suggesting that lignin plays an important role in MIT binding.

Estimates of the amounts of MIT produced from treated substrates over a longer period were obtained by the trapping procedure (Table 3). In initial trials, the yield of MIT from treated wood was 30% to 45%, but the yields from treated cellulose and glass were much lower (<5%). Adding water to the treated wood increased MIT yield to between 60% and 65%, somewhat lower than, but comparable to, the 90% yield of MIT reported for soils treated with NaMDC (Smelt and Leistra 1974). Adding water also increased the MIT yield from treated cellulose and glass, but these yields remained much lower than those from treated wood.

Related studies have found that solid NaMDC·$2H_2O$ is relatively stable in air, while NaMDC in solution oxidizes readily. We believe that evaporation of water from substrates treated with 33% NaMDC leaves solid NaMDC·$2H_2O$, which does not degrade to MIT. Conversely, adding water maintains the NaMDC in solution, where it oxidizes, generating MIT.

Nonvolatile products

The DCM extracts of the wood, cellulose, and glass samples yielded more covalent products than did the other extracts. The methanol extract contained hydrates of the recovered NaMDC and $Na_2S_2O_3$ and traces of covalent products, while the water extract contained sulfate. Also, the methanol and water extracted from the wood considerable amounts of materials which interfered with subsequent HPLC analysis.

The HPLC analyses yielded several nonvolatile chemicals, including sulfur, DTD, MMDT, and DMTU (Table 4). Since DTD and MMDT also interconvert, they are listed together.

All these products have been found to result from the decomposition of NaMDC in soil and air (Benghiat et al. 1958; Turner and Corden 1963; Elson 1966). Our

TABLE 4. *Identity and relative levels of NaMDC and its decomposition products in wood, cellulose, and glass as determined by solvent extraction and HPLC analysis 75 and 134 days after treatment.*

	Percent yield by substrate and incubation time (days)[b]					
	Wood		Cellulose		Glass	
Decomposition product[a]	75 days	134 days	75 days	134 days	75 days	134 days
NaMDC + $Na_2S_2O_3$[c]	25.0	10.0	44.0	20.0	35.0	4.0
			23			33
Sulfur	20.0	30.0	5.5	1.8	9.7	5.7
Sulfate	11.0	4.9	2.5	Tr.	BD	BD
Unextractable sulfur[d]	4.7	3.5	0.9	0.7		
DMTU	4.0	9.5	6.2	5.8	4.0	3.7
DTD + MMDT	1.1	3.3	1.3	0.03	BD	0.02
MIT + MMC	BD	0.7	BD	0.2	BD	2.5
Total nonvolatiles	65	62	60	51	49	49

[a] For a key to abbreviations see Table 1.
[b] Yields are based on the percent of sulfur in each product. BD = below detectable levels.
[c] Values are totals for NaMDC + $Na_2S_2O_3$, except for 2 runs in which each chemical was individually determined.
[d] Yields are determined by ICP analysis of digests of extracted wood or cellulose.

study revealed that considerable NaMDC remained in the treated cellulose and glass after 134 days of incubation. This residual NaMDC may result when water evaporates from the reaction mixtures, leaving solid NaMDC dihydrate, which is stable and will survive indefinitely if the humidity remains below the deliquescence point (between 50% and 75% RH). This solid NaMDC could provide a reservoir for long-term chemical protection. Of the remaining decomposition products, sulfur appeared to be most prominent in wood, representing 20% to 30% of the total products generated.

Since the majority of the substances formed during NaMDC decomposition are nonvolatile, it is unlikely that they actively protect wood at any distance from the point of application. The exception may be the sulfur. Although sulfur is not a highly toxic fungicide, it is absorbed by fungal spores (Agrios 1969). It may inhibit spore germination, and thus could be an effective barrier to recolonization by decay fungi. Decay tests of Douglas-fir heartwood blocks treated with selected levels of DMTU, DTD, and sulfur indicate that these compounds are capable of protecting wood at concentrations ranging from 0.12% for sulfur to 1.1% for DMTU (Zahora 1987). Furthermore, since the volatiles MIT, COS, and CS_2 can travel considerable distances through the wood to react with moisture and oxygen, it is possible that sulfur is carried by these compounds and deposited away from the original point of application. Further tests, however, are needed to verify this mechanism and to measure its effects on fungal spores. Moreover, our tests were performed on blocks treated with only one compound. They cannot account for synergistic reactions among the potential NaMDC decomposition products.

Finally, analysis of the extracted wood and cellulose revealed that a portion of the sulfur appeared to be covalently bound to each substrate. The nature of this bound sulfur and its significance in decay resistance are not known.

CONCLUSIONS

NaMDC decomposition in wood follows a pattern similar to that in soil. While NaMDC's various decomposition products may provide some protection of wood

near the application point, it is likely that only volatile products and the sulfur produced from their decomposition play a major role in protecting wood away from the point of application. Further studies should be undertaken to determine the extent of deposition of decomposition products in wood at distances away from the treatment zone.

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