THE EFFECT OF pH ON DECOMPOSITION OF MYLONE® (DAZOMET) AND TRIDIPAM TO FUNGITOXIC METHYLISOTHIOCYANATE IN WOOD[1]

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ABSTRACT

Mylone® and tridipam are two solid chemicals that decompose to produce methylisothiocyanate (MIT), a highly effective wood fumigant. In this study, two techniques—a rapid, test-tube method and a small-scale, wood-block assay—were used to determine the effect of the pH of various chemical buffers on the decomposition of Mylone® and tridipam in Douglas-fir heartwood samples colonized by *Poria carbonica.* Both chemicals were sensitive to pH, and higher levels of MIT were produced as the pH of the buffers increased. In general, fungal survival was not affected 1 week after chemical treatment. Complete control of *P. carbonica,* however, resulted after 4 weeks of exposure to 50 mg Mylone®/block or 150 mg tridipam/block, when each chemical was combined with a pH-12 buffer.

These results suggest that regulating fumigant treatments according to the degree of fungal attack can substantially improve the precision of decay control in wood maintenance programs.

Keywords: Douglas-fir, wood decay, *Poria carbonica, Poria placenta,* utility poles, fumigants, Mylone®, tridipam, methylisothiocyanate, pH, buffers.

INTRODUCTION

Since the introduction of fumigants in the late 1960s as agents to control wood decay (Ricard et al. 1967; Graham 1973; Hand et al. 1970), these chemicals have become widely used by many electric utility companies in their wood maintenance programs (Goodell and Graham 1983; Morrell and Corden 1986a). All three of the currently registered wood fumigants–Vapam® (sodium N-methyldithiocarbamate), Vorlex® (20% methylisothiocyanate, 80% chlorinated C_3 hydrocarbons), and chloropicrin (trichloronitromethane)—are highly effective. But their high volatility and liquid nature have limited their application and pose potential hazards to applicators. These liabilities have stimulated a search for more easily handled fumigants that can provide comparable control of wood decay.

Methylisothiocyanate (MIT) is a solid that sublimes at room temperature and has performed well as a fumigant in field tests (Helsing et al. 1984). It can be encapsulated in gelatin for improved handling safety (Zahora and Corden 1985); however, the added expense of encapsulation and the hesitancy of chemical producers to have a chemical registered for a relatively small market appear to have limited commercial use of MIT. In an attempt to bypass these problems, we have studied two easily handled formulations that chemical producers may consider

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worth registering. These potential fumigants, Mylone® (tetrahydro-3,5-dimethyl-2*H*-1,3,5,thiadiazine-6-thione, also known as dazomet) and tridipam (N,N′ dimethylthiuramdisulfide), are stable crystalline solids at room temperature that slowly decompose in wood to release MIT and other potentially fungitoxic compounds. In soil, Mylone® decomposes to produce formaldehyde, hydrogen sulfide, methylamine, and carbon disulfide (Ruch and Johnson 1957). It has effectively controlled some species of Basidiomycetes in wood during long-term laboratory and field tests (Eslyn and Highley 1985; M.E. Corden unpublished). Tridipam, which was touted in the 1960s as a soil nematocide, has not been tested for its ability to control decay fungi, but has reduced the populations of several plant pathogens under laboratory conditions (Klopping and van der Kirk 1951; Clarke and Shepherd 1966). Unfortunately, Mylone® and tridipam normally decompose much too slowly in wood to stop decay rapidly. In addition, low wood pH (3–4) lengthens decomposition time (Thorn and Ludwig 1962). To overcome this problem, we varied the pH of chemical buffers in two types of experiments to determine if raising the pH would increase the decomposition rate of Mylone® and tridipam in wood, and thus effectively reduce fungal growth in infested wood samples.

MATERIALS AND METHODS

Two different methods were used to evaluate the effect of pH on the decomposition rate of Mylone® and tridipam. The preliminary experiments were conducted in 2.5- × 100-cm glass test tubes to determine the conditions necessary for chemical breakdown. Once these conditions were identified, a small-scale wood-block assay was used to determine amounts of MIT produced and their fungitoxicity. Mylone® was obtained from Stauffer Chemical Co. (Westport, Conn.); tridipam was synthesized from Vapam® (Thorn and Ludwig 1962).

Evaluations with test tubes

To investigate how chemical decomposition would affect fungal survival in the test tubes, we first exposed heartwood blocks (2.5 × 2.5 × 1.25 cm long) of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) to actively growing cultures of either *Poria carbonica* Overh. or *Poria placenta* (Fr.) Cke. When the wood blocks were thoroughly colonized by the decay fungi, they were cut into cubes 0.5 cm on a side. Either 20 or 50 mg of powdered Mylone® or tridipam was placed in the bottom of each test tube and the wood cubes were fastened on the inside near the lip with a small dab of sterile petroleum jelly. Three cubes that had been colonized by each fungal species were placed in each test tube. To evaluate the fungitoxicity of the decomposition products further, we cut agar plugs 0.3 cm in diameter from the edge of actively growing cultures of the same test fungi and placed three of each species in each test tube near the infested wood samples. We also duplicated these experiments with 50 mg of Vapam® in place of the Mylone® or tridipam. The results of the tests with Mylone® or tridipam were then compared with those from the tests with Vapam®.

Each test tube was sealed with a tightly fitting rubber serum cap. Measured amounts of one of the following phosphate buffers were then injected through the cap: potassium acid phthalate at pH 4.0, sodium and potassium phosphate at pH 7.0, sodium carbonate and sodium borate at pH 10.0, or tri- and disodium phosphate at pH 12.0. A chemical buffer was not added to some of the test tubes.

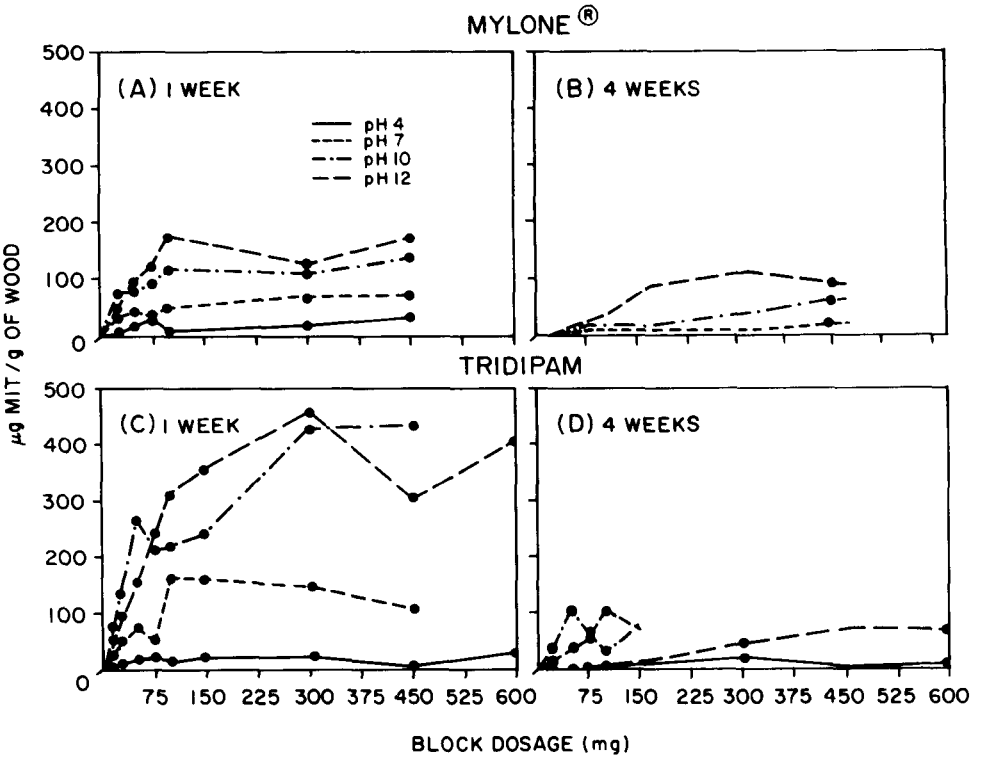

FIG. 1. Effect of the pH of four chemical buffers on the MIT levels in Douglas-fir heartwood blocks colonized with *Poria carbonica* and treated with varying dosages of Mylone® (A, B) or tridipam (C, D). The blocks were incubated for 1 (A, C) or 4 (B, D) weeks, and the amount of MIT extracted from the oven-dried samples was measured with gas chromatographic techniques.

Controls contained only agar plugs and wood cubes colonized by decay fungi. After the test tubes had been incubated at room temperature for 1 week, 1-ml air samples were withdrawn from each one with an airtight syringe. The samples were analyzed for volatile chemical content after injection into a Varian 3700 Gas Chromatograph equipped with flame photometric detector for elemental sulfur. A glass column (3-m × 4-mm inner diameter) packed with 10% Carbowax 20M on 80% Supelcoport 80/100 solid support was operated at the following conditions: injector temperature, 200 C; oven temperature, 170 C; detector temperature, 200 C; and flow rate of the nitrogen carrier, 75 ml/min.

After this analysis was completed, the wood and agar samples were removed and placed onto fresh malt agar in petri plates. The samples were observed for evidence of growth, which was used as a measure of fungal survival and chemical effectiveness.

Evaluations with wood-block assay

A more intensive evaluation of the fungitoxicity of decomposing Mylone® and tridipam was conducted with a small wood-block assay. In this test, which was based on the preliminary test-tube experiments, Douglas-fir heartwood blocks (2.5 cm × 2.5 cm × 10.0 cm long) were first autoclaved for 30 minutes at 120

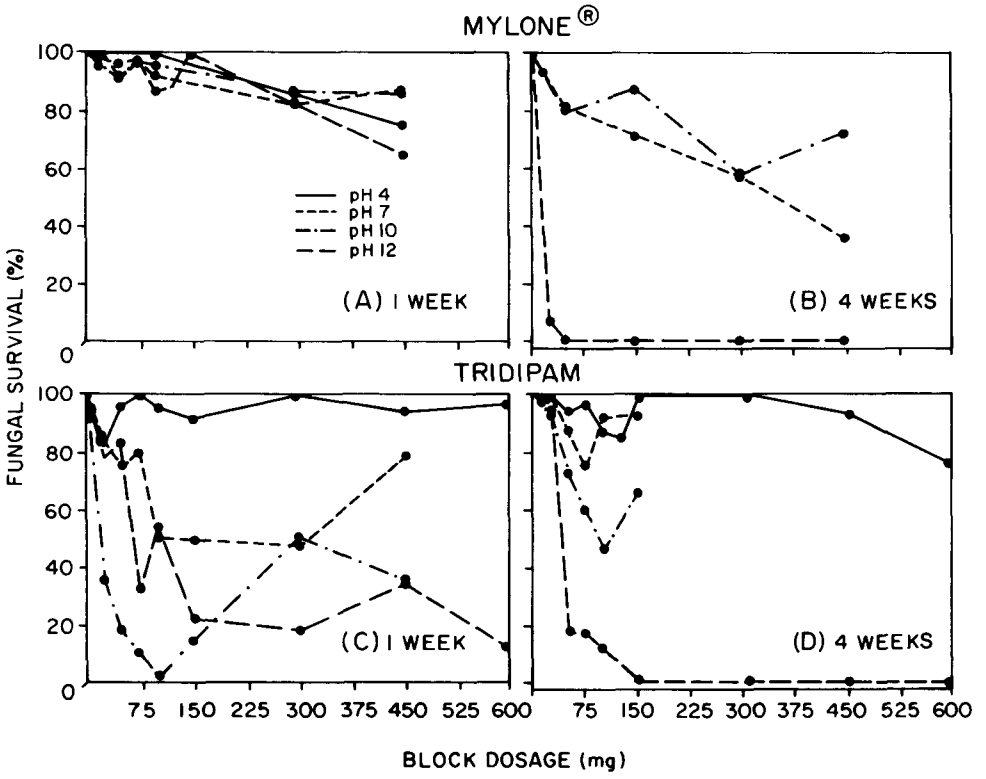

FIG. 2. Effect of the pH of four chemical buffers and varying dosages of Mylone® (A, B) or tridipam (C, D) on the fungal survival in Douglas-fir heartwood blocks colonized by *Poria carbonica*. After the blocks were incubated for 1 (A, C) or 4 (B, D) weeks, wood samples were cut from the colonized blocks and cultured. Complete fungal control resulted after 4 weeks of exposure to 50 mg Mylone® per block with a pH-12 buffer and to 150 mg tridipam per block with a pH-12 buffer.

C. Then they were end-sealed with masking tape and dipped in hot paraffin to retain moisture. After the paraffin had cooled, the tape was peeled off. The blocks were then soaked in sterile distilled water to raise the wood moisture content to about 50%. The moistened blocks were inoculated with agar squares (2.5 cm × 2.5 cm) cut from actively growing cultures of the test fungus, *P. carbonica,* and placed on the exposed cross sections. The inoculum was held in place by two Douglas-fir heartwood blocks (2.5 cm × 2.5 cm × 1.25 cm long) secured with a rubberband. The assembled blocks were incubated until the wood was thoroughly colonized (1 month), then a hole 0.98 cm in diameter × 2.2 cm deep was drilled in the center of each block. Mylone® or tridipam dosages ranging from 10 to 600 mg were added to each hole (see Figs. 1 and 2 for dosages). In addition, a series of blocks received no chemical. Some holes received 1.8 ml of the previously described buffers at pH 4.0, pH 7.0, pH 10.0, or pH 12.0, while others had no buffer added. Each treatment was replicated on four blocks. Following treatment, the holes were sealed with a tightly fitting rubber serum cap, and the blocks were incubated for 1 or 4 weeks at room temperature.

After the incubation period, the outer blocks were removed, and three 0.5-cm-

TABLE 1. *Effect of pH on the decomposition and fungitoxicity of Mylone® after 1 week in sealed test tubes.*

Mylone®	Buffer pH	Fungal survival in[1]		MIT produced	CS_2 produced
		Wood	Agar		
mg		%		*μg/ml air*	
20	4	0	16	482	2.670
	7	0	0	452	0.064
	10	100	22	603	0.093
	12	100	22	324	0.133
	None added	100	100	91	0.133
50	4	0	0	774	3.965
	7	84	84	759	0.073
	10	0	6	673	0.058
	12	0	0	583	0.004
	None added	100	100	27	Trace
Control	—	100	100	—	—

[1] Each test tube contained three Douglas-fir heartwood cubes colonized by *Poria carbonica and three cubes colonized by Poria placenta,* in addition to three agar discs from each fungal species.

thick sections were cut from each end of each block. The outer, or first, section was discarded and the next two sections were each cut into 16 equal-sized pieces. The inner four pieces of the middle, or second, section were used to determine the degree of fungal survival. The inner four pieces of the innermost, or third, section were used to determine the concentration of methylisothiocyanate in the wood.

In the tests to determine fungal survival, the samples were placed onto potato dextrose agar amended with 10 ppm benomyl to retard growth of non-basidiomycetous fungi, and a drop of 10 ppm benomyl solution was applied to the top of each piece. The pieces were observed for evidence of fungal growth over a 30-day period, and this growth was used as a measure of chemical effectiveness.

In the tests to determine MIT concentration, the samples were placed into a test tube containing 5 ml of ethyl acetate. The tube was incubated for a minimum of 24 hours to extract any MIT from the wood before analysis. Then we analyzed that extract (5.0 μl) using the same chromatographic conditions previously described for the test-tube experiments so we could determine the amount of MIT and carbon disulfide present in the wood blocks. The amount of chemical was calculated on the basis of oven-dry weight of the extracted wood.

The results from these chemical tests were compared with fungal survival to determine the relationship between chemical dosage, MIT production, and fungal control.

RESULTS AND DISCUSSION

Test tube experiments

The results of the preliminary decomposition tests indicated that after 1 week Mylone® and tridipam were both affected by increased pH; however, the MIT levels detected in the test tubes containing Mylone® did not appear to increase with an increased pH level (Tables 1 and 2). There was little difference in fungal survival between *P. placenta* and *P. carbonica,* and these results were combined.

TABLE 2. *Effect of pH on the decomposition and fungitoxicity of tridipam after 1 week in sealed test tubes compared with that of Vapam®.*[1]

Chemical	Dosage	Buffer pH	Fungal survival in[2]		MIT produced[3]
			Wood	Agar	
	mg		%		*μg/ml air*
Tridipam	20	4	78	0	10
		7	100	0	10
		10	0	0	90
		12	0	0	211
		None added	78	90	15
Tridipam	50	4	100	33	7
		7	89	0	15
		10	0	11	150
		12	0	0	589
		None added	100	100	15
Vapam®[1]	50	4	0	0	15
		7	0	0	15
		10	34	11	20
		None added	0	56	15
Control		—	100	100	—

[1] Vapam® contains 32.7% sodium N-methyldithiocarbamate in water.
[2] Each test tube contained three Douglas-fir heartwood cubes colonized by *Poria carbonica* and three cubes colonized by *Poria placenta*, in addition to three agar discs from each fungal species.
[3] Trace amounts of carbon disulfide were detected in all of the tridipam treatments containing pH buffer.

These tests indicate that when the pH was low, fungal survival was higher in the tridipam treatments, but lower in the Mylone® treatments. In addition, considerable amounts of carbon disulfide were detected in the test tubes containing Mylone®, while only trace amounts of this chemical were detected in the test tubes containing tridipam. These results indicate that the rate of Mylone® decomposition to MIT was enhanced in the pH 4 and 7 range and hindered by pH 10 and 12. Conversely, tridipam decomposition to MIT was enhanced by high pH (10, 12) and hindered by low pH (4, 7).

One effect that was not studied was the role of the buffer base in chemical decomposition, because each buffer used a different chemical to achieve the appropriate pH. Studies in which acids such as hydrochloric or bases such as sodium hydroxide would be used in place of the buffers might eliminate these potential interactions; however, wood acidity would probably lower the pH to the degree that it would have little effect on decomposition and might affect fungal survival. Conversely, the buffers have the capacity to mitigate some of this acidity and should be more effective decomposition agents.

Wood-block assays

While the preliminary test-tube trials provided a guide to the effect of pH changes on MIT production, the wood-block assays provided a more realistic measure of chemical effectiveness. Generally, for both Mylone® and tridipam, the rate of MIT production was closely correlated with the pH of the buffer added at the time of treatment; a more basic pH resulted in a higher level of MIT production 1 week after treatment (Figs. 1A, C and 2A, C). These results differed from the test-tube experiments with Mylone® and suggest that the presence of

wood altered the decomposition products. Blocks incubated for 4 weeks exhibited similar effects, although the levels of MIT detected per oven-dried gram of wood declined by 50 to 80%.

After 1 week, fungal survival in the Mylone®-treated blocks differed little from untreated control blocks in spite of MIT levels that ranged from 4 to 170 mg per oven-dried gram of wood (Figs. 1A and 2A). These results suggest that the high levels of MIT were only present for a relatively short time and could not effect control. Test results after 4 weeks indicated that the addition of buffers at pH 4, pH 7, or pH 10 continued to have little effect on fungal control; however, addition of a pH 12 buffer resulted in complete control of *P. carbonica* at dosages greater than 50 mg per block (Figs. 1B and 2B). At this time point, only 20 mg of MIT per oven-dried gram of wood was detected. When 50 mg of Mylone® per block and a pH 7 buffer were used, the MIT level was 50% of that from the pH 12 treatment; with a pH 10 buffer, the level was 75%. Even so, the MIT had little influence on fungal survival. These results suggest that initial high dosages followed by continued exposure to lower levels of MIT may provide effective fungal control. Previous studies of Mylone® have shown that fungi are controlled in blocks receiving the dry chemical only after 3 months (M. E. Corden, unpublished). In our studies, the rate of fungal control was considerably swifter, indicating that chemical effectiveness can be tailored to particular decay situations. When decay is already underway, the application of Mylone® with a high pH buffer can rapidly release MIT to control infestation. When the wood is relatively sound and long-term protection against decay is needed, the addition of these chemicals along with buffers at pH 7 or pH 10 would seem advisable.

Mylone® decomposes to a number of compounds depending on the pH of its environment. When acidic solutions are used, breakdown products are primarily methylamine, formaldehyde, and carbon disulfide. Under neutral conditions, hydrogen sulfide, methylamine, formaldehyde, and methylisothiocyanate (Ruch and Johnson 1957) are produced. Although MIT was detected in pH 4 treatments, the levels were extremely low after 1 week and not detectable after 4 weeks, suggesting that small variations may have created localized environments that were conducive to MIT production in the pH 4 treatments. These conditions apparently disappeared during the longer incubation periods. In addition, interaction between Mylone® and wood may have resulted in MIT emission, but these levels were insufficient for fungal control.

The results of the tridipam tests also indicate that increased pH enhanced MIT production, although the degree of fungal control varied (Figs. 1C, D and 2C, D). Only one of the pH treatments (pH 10, 100 mg of tridipam per block) eliminated *P. carbonica* from the infested wood after 1 week, and there appeared to be little difference between the degree of fungal control at pH 7, pH 12, and the remaining pH 10 treatments (Fig. 2C). Incubating the blocks for an additional 4 weeks produced some degree of fungal control in the treatments at pH 10 and at pH 12 (Fig. 2D). When the infested wood blocks were exposed to tridipam for 4 weeks at dosages above 150 mg per block at pH 12, complete fungal control resulted (Fig. 2D). Treatments at pH 10 reduced fungal survival by 30 to 40%.

Although it has not been thoroughly tested, tridipam appears to decompose similarly to Vapam®, from which it is synthesized. As a result, there are many potential ways by which decomposition may occur and at least 14 potential de-

composition products (Turner 1962; Elson 1966). In addition to the production of volatile fungitoxins such as MIT, deposition of nonvolatile chemicals may also occur in the wood (Morrell and Corden 1986a, b). Although these compounds may not eliminate established fungal infestations, they may prevent other organisms from colonizing the wood. Studies to determine the role of these nonvolatile compounds in wood protection are underway.

The results of the tridipam treatments again indicated that the addition of the pH 12 buffer enhanced fungal control. However, the variation in MIT levels in blocks treated with pH 7 or pH 10 buffers after 4 weeks suggests that these treatments will also result in fungal control after long-term exposure. Unfortunately, moisture conditions in our block test make it difficult to maintain constant conditions for more than 4 weeks. Therefore, larger-scale tests are now underway.

Initially, in both the Mylone® and tridipam treatments at pH 10 or pH 12, the level of fumigant concentration was high, followed by a gradual decline (Figs. 1A–D). These results are consistent with previous findings (Goodell et al. 1980), and suggest that there is some delay between the highest level of fumigant production and fungal control. It is unclear why this high chemical concentration in the Mylone®-treated wood was so effective at pH 12 but not at pH 10; however, previous studies indicate that fungal control with all of the treatments should occur upon longer incubation (Eslyn and Highley 1985). Our results indicate that actively decaying wood should be treated with the combination of Mylone® and pH 12 buffer. Where decay is less active, Mylone® combined with a pH 10 buffer may also provide long-term prophylactic protection.

CONCLUSIONS

The results indicate that the rate of decomposition of both Mylone® and tridipam to MIT can be controlled by varying the pH of simultaneously applied buffers. Generally, pH 12 buffers provided the greatest levels of MIT emission and fungal control in wood blocks, although pH 7 and pH 10 buffers also produced substantial amounts of MIT. Long-term treatments at pH 7 and pH 10 may also provide eventual fungal control, but our procedures could not allow for testing this hypothesis.

Ultimately, Mylone® and tridipam, in combination with selected buffers, could provide a way to regulate the degree of control for particular decay situations. This approach, coupled with the use of solid fumigants, could substantially improve the precision of decay control in wood maintenance programs.

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