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Evaluating Chemicals for Controlling Biodeterioration of Stored Wood Chips

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Abstract

Thirty chemicals or chemical mixtures were evaluated for their effectiveness in controlling fungal degrade in wood chips during outside storage. The chemicals were chosen mainly for their biocidal potential and their promise of contributing little if any to environmental pollution. The effective concentration of each chemical was determined by laboratory-controlled incubation of red pine (*Pinus resinosa* Ait.) inoculated with five mesophilic and three thermophilic wood-degrading fungi. Twenty-three of the chemicals proved effective at various concentrations. They ranged from a low of 0.05 percent (0.3 lbs./ton O.D. chips) for 2-heptadecyl-1,5,5,6-tetrahydro-4,4,6-trimethylpyrimidine to a high of 6.0 percent (61 lb./ton O.D. chips) for thiourea. The remaining seven chemicals proved ineffective at the highest concentration at which any of them were tested.

USE OF CHIP AND MANUFACTURING RESIDUES for pulp and paper has increased in the Northwest alone from about 8 percent in 1947 to 70 percent in 1968 (6); there have been similar increases throughout the other parts of the United States. Therefore, storage of pulpwood in the form of chips has also increased in importance to the pulp and paper industry. Although handling wood in chip form rather than in roundwood has definite advantages, such as space economy and ease and economy of handling, the amount of wood that is deteriorated is generally the same (7) or may be higher than in the roundwood form (4). A common means of commercially controlling degrade in other raw wood products is by applying chemicals toxic to stain and decay fungi. This type of control is applicable to minimize degrade in stored wood chips, although limitations are greater on the kinds and amounts of chemical that may be acceptable.

Objective

The objective here was to Screen 30 chemicals for effectiveness in controlling fungal degradation of stored chips. To be included here, chemicals had to meet most or all of the following criteria: 1) show promise of being an effective biocide, 2) be essentially noncontributory to air or stream pollution, 3) be tolerated in the pulping process, 4) be reasonably priced, and 5) be considered of low toxicity to humans in the concentrations needed to effect control of chip-degrading micro-organisms.

Background

The application of toxic chemicals to chip piles for possible control of biodeterioration has been receiving attention in recent years. Pentachlorophenolate and a mercury preparation were found to inhibit staining of spruce chips during 4-month storage (10). Chlorophenates and borax, alone or in combination, were found effective in reducing biodeterioration in chip piles (8, 11). Nickel ions have also been shown useful to avoid wood loss and heat buildup in chip piles (2) due apparently to selective killing of only the more harmful mesophilic and thermophilic wood decay fungi (1). This, in turn, reportedly permits growth of other noncellulosic fungi capable of further inhibiting the more destructive wood-decay fungi. When tested in simulated chip piles, however, nickel sulfate was found ineffective in controlling wood deterioration (13). The chlorophenates, mercurials, and nickel compounds that have been used to prevent chip degrade were considered either contributory to water pollution or incompatible with the pulping process, hence a screening program was commenced in 1968 at the USDA Forest Products Laboratory to investigate additional biocides that would not have these shortcomings. A result of the work has been that "green liquor" (sodium sulfide plus sodium carbonate), an intermediate in the kraft pulp cooking liquor recovery cycle, showed much promise as a nonpolluting, effective chip biocide (12). Testing additional chemicals involved in the kraft pulping process, sodium sulfide plus sodium hydroxide and the sodium hydroxide alone, showed they were capable of reducing wood substance losses in pine chip piles (4).

Methods and Materials

A laboratory method was devised to screen biocides by testing them on wood chips. Red pine (*Pinus resinosa* Ait) chips frozen for storage shortly after chipping in

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the green condition, were used. The chips were thawed, then screened to remove fines and small wood splinters; resinous and knot- and pith-containing pieces were rejected. The remaining chips were air-dried at room temperature for 3 days and conditioned at about 27°C (80°F) and 70 percent relative humidity for a minimum of 1 week. Samples of these chips—each sample weighed between 20.00 and 20.05 grams—were then removed. The samples were rewetted, by subjecting to a vacuum of about 29 inches of mercury for 20 minutes followed by flooding with distilled water. The chips were then placed in glass cylinders, 37 mm inside diameter, about 30.5 cm long, plugged at one end (top) with cotton and at the other (bottom) with a rubber stopper that had a hole for drainage (Fig. 1). Then the cylinders of chips were steamed for 30 minutes at 100°C (212°F). After being cooled, the samples were treated with various concentrations of the biocides. For treatment the chips in each cylinder were soaked with 150 ml of test solution for one minute, then the solution was poured off and the chips permitted to drain overnight. This provided for drainage of excess chemical solution from the cylinders and allowed the solution to further diffuse within the chips and the test chemical to possibly react with wood constituents. After being drained, the chips were washed (leached) for 5 seconds by agitating with 100 ml of sterile distilled water. Then they were inoculated with mesophilic (thriving at moderate temperatures) and thermophilic (thriving at temperatures of 40°C and higher) fungi that had been isolated from deteriorated pine, Douglas-fir, and birch wood chips. Laboratory tests indicated all of the test fungi were capable of degrading wood (5). Mesophilic and thermotolerant fungi included a mixture of *Peniophora* G (ME-461) and *Chrysosporium* sp. (ME-PC-8), a *Polyporus* sp. (ME-485) isolated from mixed pine and Douglas-fir chips in storage and a mixture of two stain fungi, *Papulospora* sp. (ME-PC-19) and an unknown (ME-Fb-2). Thermophilic fungi included were *Allescheria* sp. (ME-T-Fb-2-17-69), *Dactylomyces crustaceous* Apinis and Chesters (ME-T-BIC-6), and an unknown hyphomycete (ME-T-Fb-3-1-69X). (In preliminary screening to determine the possible effective concentrations of each of the chemicals included here, only a few mesophilic test fungi were used in a 7-week incubation.)

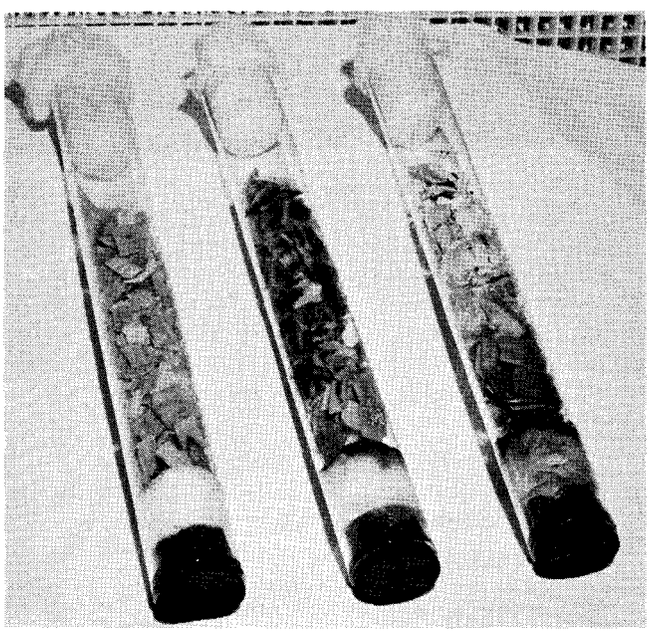

Figure 1.- Cylinders with chip sample used in biocide testing: Control chips at left; center and right are mesophilic stain and decay fungi, respectively.

For inoculation, mycelium was antiseptically scraped from the surface of a test tube culture; the mycelium and 100 ml of sterile distilled water were mixed in a Waring blender for 15 seconds. If the mixture was of two fungi, half of the mycelium from each of two test tubes was used, then blended together. The blend was then antiseptically poured over the chips, agitated back and forth once to insure contact of the bulk of the chips with the inoculum, and subsequently drained.

Cylinders of chips inoculated with mesophiles were placed into incubators maintained at 27°C (80°F), whereas those inoculated with thermophiles were inoculated at 45°C (113°F). After 6 weeks of incubation the cylinders were removed from the incubators for the chips to be reinoculated. This was to simulate re-entry of fungi into piles sterilized by treatment with volatile biocides, and would act as a measure, therefore, of the residual effect of treatment. After an additional 6-week incubation the chips were removed from each cylinder, dried, conditioned, weighed as at test start, and the percent weight losses calculated. To correct for gain in weight by a treating chemical or for loss by possible degradation (e.g., acetyl loss) by a chemical, noninoculated but chemically treated chip samples (controls) were incubated at both 27°C and 45°C with the inoculated samples, and their weight changes determined.

For each group of chip samples treated with a similar concentration of a biocide, weight losses were determined by first calculating the weight loss or gain in the associated control (noninoculated, but treated) chip samples. When a loss in weight was encountered, the loss was added to the final weights of the inoculated samples; the reverse applied if a gain in weight of the controls occurred. Percent weight loss due to attack by each of the test fungi was determined by using this adjusted final weight plus the weight of the chip sample after the original conditioning. The formula used was the following:

$$\textit{Percent weight loss} = \frac{\textit{Dry weight of chip sample-adjusted weight of chip sample exposed to fungal action}}{\textit{Original weight of chip sample}} \times 100$$

Chemical pickup by the chips was determined by taking two of the sterilized 20-gram chip samples, permitting them to drain off excess water, and weighing them. The chips were then repacked in cylinders and treated with a concentration of a biocide. Then each sample was spread on a screen to drain for a few moments, and immediately weighed. Average increase in weight of the two samples and concentration of the treatment solution were used to calculate chemical pickup. It was recognized, however, that the values obtained would only be approximate when, due to differential pickup of the chemical by the wood, the

biocide concentration in the chips materially exceeded the computed amount. No attempt was made to determine if chemical concentration on the chips was affected by the 5-second wash in water to which they were subjected 24 hours after chemical treatment and prior to exposure to decay.

Results and Discussion

Weight losses in the control samples of wood chips ranged from a low of 2.0 percent by *Dactylomyces crustaceous,* to a high of 15.7 percent brought by *Polyporus* sp., following a 12-week incubation period. Concentration of biocide was considered effective if it held weight losses caused by each of the test fungi to a level of 0.5 percent or less. The effective concentration of each of the 30 chemicals screened is provided (if attained at the concentrations tested) in Table 1. The approximate amount of chemical pickup by the chip sample at each of the "effective concentrations" is included in the table in pounds of chemical

Table 1. - BIOCIDAL CONCENTRATIONS INHIBITORY TO SELECTED WOOD CHIP STORAGE FUNGI.

	Chemical	Solvent	Inhibitory concentration of chemical in treating solution[1] (%)	Pickup of chemical at inhibitory concentration before 5-second wash[2] (lb./ton O.D. chips)
	ORGANIC SULFUR COMPOUNDS			
1.	2-(Thiocyanomethylthio) benzothiazole	Water suspension	1.0	7.0
2.	2-(Thiocyanomethylthio) benzothiazole + 2-hydroxypropyl methanethiolsulfonate	Water suspension	0.20+0.18	4.0
3.	2-(4-Thiozolyl) benzothiazole	Water	1.25	13.0
4.	Sodium 2-mercaptobenzothiazole	Water	1.0	9.5
5.	Sodium 2-mercaptobenzothiazole + sodium dimethyldithiocarbamate	Water	>0.1 + 1.1 [3]	–
6.	Sodium dimethyldithiocarbamate	Water	4.0	39.5
7.	Sodium dimethyldithiocarbamate + formaldehyde	Water	0.5 + 0.5	9.4
8.	Sodium N-methyl dithiocarbamate	Water	4.0	36.2
9.	3,5-Dimethyl-tetrahydro-1,3,5,2H-thiadiazine-2-thione	Water suspension	0.75	7.6
10.	Sodium pyridinethione	Water	0.5	5.7
11.	Sodium pyridinethione + sodium borate	Water	>0.08 + 3.92[3]	–
12.	Methylenebisthiocyanate	Water	1.5	13.6
13.	Thiourea	Water	6.0	61.0
	HETEROCYCLIC NITROGEN COMPOUNDS			
14.	Methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate	Water suspension	4.0	24.9
15.	cis- N-[(1,1,2,2-tetrachloroethyl)-thio]-4-cyclohexene-1,2 dicarboximide	Water suspension	4.0	45.2
16.	2-Heptadecyl-1,5,5,6-tetrahydro-4,4,6-trimethylpyrimidine	Ethyl alcohol	0.05	0.3
17.	8-Hydroxyquinoline sulfate	Water	3.5	39.5
	AROMATIC COMPOUNDS			
18.	Sodium O-phenylphenate	Water	1.0	10.2
19.	Sodium O-phenylphenate + borax	Water	0.5 + 0.5	10.2
20.	Biphenyl	Acetone	4.0	19.2
21.	Alkyl dimethylbenzyl ammonium chloride	Water	2.5	17.0
	NONAROMATIC ORGANIC COMPOUNDS			
22.	Propionic acid	Water	1.75	17.7
23.	Paraformaldehyde	Water suspension	1.0	13.5
24.	n-Dodecylquanidine hydrochloride	Water	3.1	24.0
25.	t-Butyl hydroperoxide	Water	2.5	24.0
26.	Rosin amine-D acetate	Water	>5.0[3]	–
27.	Hexamethylenetetramine	Water	>10.0[3]	–
28.	Hydroxylamine sulfate	Water	>4.0[3]	–
	INORGANIC COMPOUNDS			
29.	Borax + boric acid	Water	>2.0 + 2.5[3]	40.7
30.	Nickel sulfate	Water	>4.0[3]	–

[1]Concentration needed to keep weight losses by eight fungi at a level of 0.5 percent or less.

[2]Assumption is that biocide solution picked up by treated wood was identical in concentration of chemical to that in original treating solution.

[3]No control effected at highest concentration.

per ton of ovendry chips. No attempt was made to provide cost comparisons between the different chemicals, because costs can be altered significantly with major changes in demand and manufacturing technology.

The first group of chemicals in Table 1 are organic sulfur compounds; some have been used as slimicides, whereas others have proved effective in controlling plant pathogens. Eight, 1, 2, 3, 4, 7, 9, 10, and 12, were fungitoxic at low concentrations. The chemical 2-(thiocyanomethylthio)-benzothiazole, 1, alone or in mixture with 2-hydroxypropyl methane thiolsulfonate, 2, was highly effective, particularly in the mixture with 2 that exceeded all other compounds in this group in toxicity. The compounds, 3,5-dimethyl-tetrahydro-1,3,5,2 *H*-thiadiazine-2-thione, 9, and sodium pyridinethione, 10, were similar to the first two compounds in toxic levels. The four remaining effective compounds, 3, 4, 7, and 12, were toxic at somewhat higher levels than were 1, 2, 9, and 10. Two of the organic sulfur compounds, 5, and 11, were non-inhibitory at the highest levels tested, whereas a third, thiourea, 13, was effective only if a concentration of 6.0 percent (61 lb./ton O.D. wood) was reached. Additionally, sodium dimethyldithiocarbamate, 6, and sodium *N*-methyl-dithiocarbamate, 8, were effective only at fairly high concentrations. Number 8 had been shown, in the preliminary 6-week test, however, effective at a low concentration of 0.2 percent. Increasing the test period to 12 weeks and incorporating a second inoculation at the end of 6 weeks necessitated a twentyfold increase in chemical concentration to attain the desired earlier level of control. This particular chemical is a fumigant which, according to the preliminary results, successfully eradicated the fungi inoculated at the start of testing. It volatilized, and apparently lost much of its effectiveness during the first 6 weeks of storage; hence much higher concentrations were needed to overcome the re-introduction of test fungi during final testing. This raises questions such as how long will this chemical and other fumigants used here effectively persist in a chip storage pile and, after the chips in a pile are sterilized, how long before wood-degrading fungi are naturally re-introduced into most of the pile? Sodium *N*-methyl-dithiocarbamate is undergoing field test here, and hopefully will supply some of the answers.

The second group of chemicals, heterocyclic nitrogen compounds, includes 2-heptadecyl-1,5,5,6,-tetrahydro-4,4,6-trimethyl-pyrimidine (Table 1, chemical 16) found effective at a much lower concentration than any of the other 29 chemicals. In ethyl alcohol solvent it proved inhibitory at a concentration of only 0.05 percent (0.3 lb./ton O.D. chips). Although soluble in water at this concentration, ethyl alcohol was used as the solvent because higher, nonwater-soluble concentrations were included in the test. Baechler (3) found this pyrimidine effective in aqueous solution against the decay fungus, *Lenzites trabea* Pers. ex Fries, at a concentration of 0.07 to 0.10 percent. The remaining three heterocyclic nitrogen compounds were all inhibitory at fairly high concentrations (Table I, chemicals 14, 15, and 17). A wide discrepancy in amount of chemical pickup was apparent between chips treated with the same concentration (4.0 percent) of chemicals 14 and 15; 24.9 and 45.2 lb./ton O.D. wood were picked up by them, respectively, during treatment. Both chemicals were applied in a water suspension; it is believed that differences between them in solid size and adherence qualities resulted in their differential pickup and retention by the wood chips undergoing treatment.

The aromatic group contains compounds of which all were toxic at fairly low concentrations. Only one, biphenyl, 20, was insoluble in water, and was, consequently, tested in an acetone medium. It proved inhibitory at a fairly high solution concentration (4.0 percent), although chemical pickup at this concentration was only 19.2 lb./ton O.D. chips. Calculation of this small a pickup was probably due, however, to rapid evaporation of the acetone solvent, prior to weighing the treated chips, which led to a lower weight than would have been experienced had a slower evaporating water solvent been used. Sodium *O*-phenylphenate, 18, alone and in mixture with borax, 19, proved effective at concentrations of 1.0 percent and 0.5+ 0.5 percent, respectively, with both resulting in chemical pickups of 10.2 lbs./ton O.D. chips. Sodium *O*-phenylphenate was tested as long ago as 1934 (9), and on pine found effective against stain and mold fungi. However, due to the greater effectiveness of the chlorinated hydrocarbons, such as sodium pentachlorophenate, sodium *O*-phenylphenate has been little used commercially for protection of stored wood. The chlorinated phenolics were not included in this study because of their greater threat to the environment and because of problems encountered with halogenates in the pulp and paper process.

Three of the seven nonaromatic organic compounds were not sufficiently toxic at the highest concentrations to effect the desired level of control. Of these three compounds, rosin amine-D acetate, 26, had been tested on wood boxes, and found to provide protection from fungal attack at a concentration of 5.0 percent (14). A similar concentration of this chemical failed, however, to effectively control the wood chip storage fungi used in this test. Propionic acid, because of its apparent harmlessness environmentally, was extensively tested and separately reported (15). As indicated (Table 1, 22) it was found effective at a concentration of 1.75 percent (17.7 lb./ton O.D. wood). Paraformaldehyde was sufficiently toxic in aqueous suspension at a concentration of 1.0 percent (13.5 lb./ ton O.D. wood). The remaining two compounds within this group were inhibitory at higher concentrations, both becoming effective at 24.0 lb./ ton O.D. wood.

In the last category, inorganic compounds, neither borax plus boric acid, 29, nor nickel sulfate, 30, proved adequate at the highest concentrations (Table 1). Borax and boric acid have proved effective in controlling decay and stain fungi on hardwoods but not on pine (9). Hence, the results were not unexpected. Nickel sulfate, reported to be an effective means to protect stored chips from wood-degrading fungi (1,2), was tested by Springer, et al., (13) in simulated chip piles and found an inadequate means of protection. The results here confirm their findings.

Some of these chemicals are undergoing additional laboratory testing to determine their efficacy in holding down spontaneous heating in stored chips. However, before any of these chemicals can be recommended for use on wood chip piles, it is necessary that they undergo final testing in the

field. This type of testing will eventually be conducted on the most promising of the chemicals.

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