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FUNGICIDAL EFFICACY OF AMMONIACAL COPPER AND ZINC ARSENIC PRESERVATIVES TESTED BY SOIL-BLOCK CULTURES

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ABSTRACT

Three new preservative formulations—copper-zinc-arsenic-additive (CZAA), copper-arsenic-additive (CAA), and zinc-arsenic-additive (ZAA)—were tested in comparison with four other preservatives by soil-block culture on unleached red pine samples using test fungi *Coniophora puteana*, *Poria monticola*, and *Lenzites trabea*.

Threshold values (based on retentions of all oxides) of 0.1 pound per cubic foot (1.6 kg/m^3) for CAA and 0.2 pound per cubic foot (3.2 kg/m^3) for CZAA were comparable with threshold values of the commercial preservatives ammoniacal copper arsenate (ACA) at 0.1 pound per cubic foot (1.6 kg/m^3) and chromated copper arsenate type C (CCA-C) at 0.3 pound per cubic foot (4.8 kg/m^3). The ZAA formulation had a relatively high threshold value [0.6 pound per cubic foot (9.6 kg/m^3)]. Thresholds based on As_2O_5 retentions only indicated the fungicidal efficacy in decreasing order: ACA or CAA > CZAA > CCA-C > ZAA.

Coniophora puteana (A328, EFPL) was more resistant to all tested preservatives (except ZAA) than the standard strains of *Poria monticola* and *Lenzites trabea*.

Keywords: *Pinus resinosa*, fungicidal efficacy, ammoniacal preservatives, *Coniophora puteana*, *Poria monticola*, *Lenzites trabea*, Cu, Zn, As, soil-block tests, biodegradation, preservatives, water-borne preservatives.

INTRODUCTION

Recent studies of water-borne preservatives resulted in the development of a new system (CFS 1972; Clarke and Rak 1974; Rak and Clarke 1975) comprising ammoniacal solutions of Cu-Zn-As salts in a formulation capable of deeply penetrating difficult-to-treat spruce timber (Rak 1975a). The toxic components of the preservative solution when impregnated into wood strongly resist leaching by water (Rak 1976; Rak and Clarke 1974) and make the wood water-repellent (Rak 1975b) and toxic to fungi. These properties were studied as part of a comprehensive evaluation of the system in comparison with other water-borne preservatives with established performance. Also field tests with stakes treated with the new preservatives were arranged for a complex testing of this new preservative system.

Fungicidal efficacy of the new system was expected to be high from the known toxicity of metal-arsenic salts to wood-decaying fungi. However, formulation variations (Rak 1976)—in particular the ratio of metal oxide to arsenic oxide, higher than that in commonly used ammoniacal copper arsenate preservative—made it advisable to examine the fungicidal efficacy and to determine thresholds of the new formulations to wood-decaying fungi. These were compared with commonly used water-borne preservatives, not exposed to leaching after treatment. Data on fungicidal efficacy of ammoniacal preservatives exposed to leaching after treatment will be published in a separate publication.

MATERIALS AND METHODS

Compositions of the preservative formulations tested are described in Table 1. The new preservative system is represented by formulations of CAA (copper-arsenic-additive), CZAA (copper-zinc-arsenic-additive), and ZAA (zinc-arsenic-additive)

TABLE 1. *Compositions of preservative formulations*[a]

	CAA	CZAA (1:1)	ZAA	Basic Copper Carbonate	ACA	CCA-C	ACC
As_2O_5 (g)	1.42	1.42	1.42	—	1.96	0.57	—
CuO[b] (g)	2.43	1.21	—	3.57	1.97	0.31[c]	0.31[c]
ZnO (CrO_3) (g)	—	2.40	4.79	—	—	(0.80)	(0.80)
NH_4HCO_3 (g)	1.80	2.96	2.55	4.60	—	—	—
NH_4OH (28% NH_3; ml)	25	22.5	25	25	25	—	—
H_2O to volume (ml)	100	100	100	100	100	100	100
As_2O_5 (% of oxide content)	36.9	28.2	22.9	—	49.9	33.9	—
CuO (% of oxide content)	63.1	24.1	—	100	50.1	18.5	27.9
ZnO (CrO_3) (% of oxide content)	—	47.7	77.1	—	—	(47.6)	(72.1)

[a] Preservative code:
CAA — Copper-Arsenic-Additive formulation
CZAA (1:1) — CAA and ZAA mixed in volumetric ratio 1:1
ZAA — Zinc-Arsenic-Additive formulation
ACA — Ammoniacal Copper Arsenate
CCA-C — Chromated Copper Arsenate Type C
ACC — Acid Copper Chromate
[b] applied as $CuCO_3 \cdot Cu(OH)_2$
[c] applied as $CuSO_4$

where the additive component as defined in the new system is a fatty acid (such as decanoic acid), or carbonates of copper or zinc. The additive is soluble in the common solvent ammonium hydroxide, improves fixation of the main preservative chemicals (Rak 1976; Rak and Clarke 1974), and increases the water-repellency of treated wood. In this study the additive is a basic copper carbonate which is in excess of the quantity needed to form metal arsenate from arsenic acid in the solution.

In addition, copper carbonate alone and three preservatives with compositions according to the AWPA Standard P5-74 (Standards for Water-Borne Preservatives) —Ammoniacal Copper Arsenate (ACA), Chromated Copper Arsenate, Type C (CCA-C) and Acid Copper Chromate (ACC)—were compared. The pH of the stock CCA-C solution was 1.34 and that of the stock ACC solution 1.76. However, after dilution to concentrations used for treatment of blocks to various retentions, the pH increased and conformed with the requirements of CSA Standard 080 (Wood Preservation) and AWPA Preservation Standards. Three repeated series of tests were carried out on freshly impregnated nonleached wood blocks according to the "Standard Methods of Testing Wood Preservatives by Laboratory Soil-Block Cultures" (ASTM Standard D 1413-76, slightly modified as described below).

The test fungi were *Coniophora puteana* (Schum ex Fr.) Karst. (A 328*), *Lenzites trabea* (Pers.) Fr. (S 644*) (Madison strain 539), and *Poria monticola* Murr. (A 189*) (Madison strain 698) recently specified in the ASTM Standard D 1413-76 as *Poria placenta* (Fr.) Cook. (*Denotes number in the culture collection of the Eastern Forest Products Laboratory, Ottawa.) The 474 ml culture bottles were furnished with 300 g soil (moisture content 2%, water-holding capacity 26%, pH 5.3) and 100 g tapwater. Test blocks of standard size 19 by 19 by 19 mm,—except for the first series where they were 8 (longitudinal) by 19 by 19 mm,—and feeder strips, 4 by

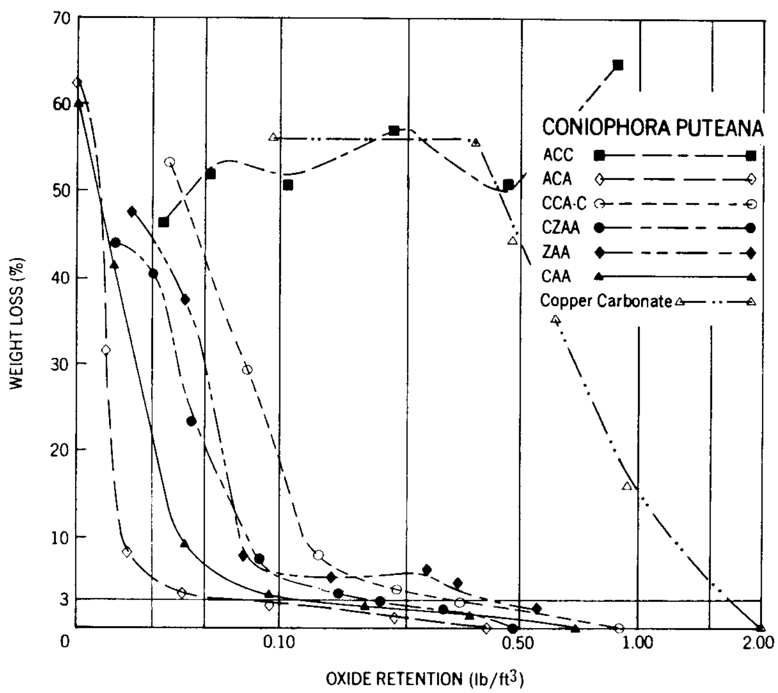

FIG. 1. Weight loss of treated red pine caused by *Coniophora puteana.*

20 by 50 mm, were cut from red pine (*Pinus resinosa* Ait.) sapwood.

Preservative solutions were prepared in a sequence of sixty-eight concentrations increasing in a geometric progression with a ratio of about 2.

A treatment group consisted of six wood blocks incubated in pairs in culture bottles. The preservative content of the blocks was calculated from the pick-up and concentration of the treating solution. Blocks were not leached before testing. Incubation was 8 weeks for the first series and 12 weeks for the others.

Weight losses for the test blocks were calculated from the oven-dry weights before impregnation and after incubation. Thresholds were obtained from graphs on which weight losses of the blocks were plotted against retention. The point at which weight loss reached 3% was considered the approximate threshold. Losses smaller than 3% were considered operational. When thresholds were obtained in more than one series, they were averaged for the same fungus. However, the preservative threshold was represented by the highest average value, without regard to the testing fungus employed.

RESULTS

Figures 1 and 2 show weight losses and preservative retentions for *Coniophora puteana* and *Lenzites trabea*, respectively. *Poria monticola* was used only in the I. series. The results for this fungus are given only in tabular form. The 3% loss thresholds in all series for all three fungi are shown in Table 2.

Thresholds based on total oxide retentions obtained in individual experimental series (when more than one series was carried out) were averaged for the same test fungus. The threshold of the most resistant test fungus was considered for general evaluation of the fungicidal efficacy of each preservative. The most resistant fungus to the ZAA preservative was *Len-*

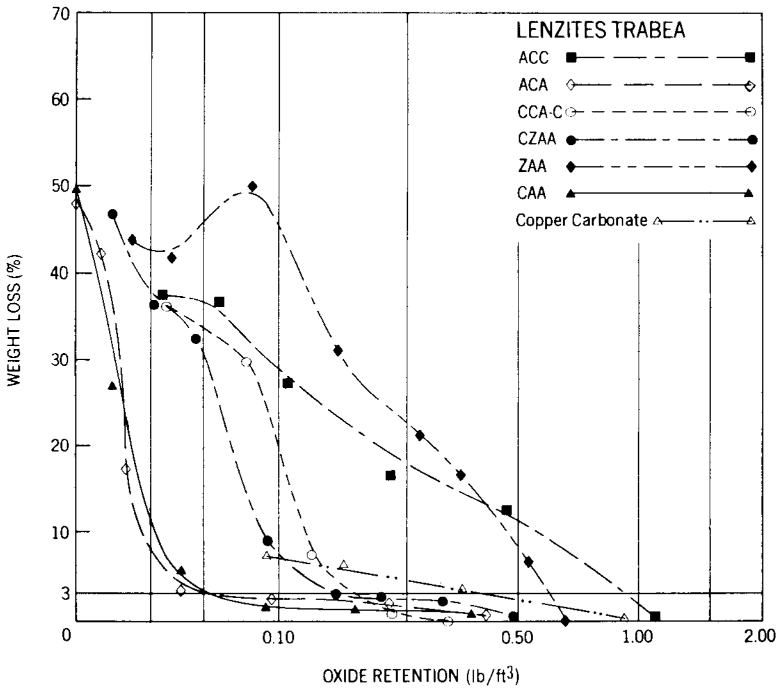

FIG. 2. Weight loss of treated red pine caused by *Lenzites trabea.*

TABLE 2. *Toxicity thresholds for preservatives tested. Total oxides, lb/ft^3 (kg/m^3)*[a]

	I. series[b]		II. series[c]		III. series[c]		Average[d] threshold values	
	Coniophora puteana	*Poria monticola*	*Coniophora puteana*	*Lenzites trabea*	*Coniophora puteana*	*Lenzites trabea*	*Coniophora puteana*	*Lenzites trabea*
CAA	0.085	0.050	0.125	0.050	—	—	0.105	0.050
	(1.4)	(0.8)	(2.0)	(0.8)	—	—	(1.7)	(0.8)
CZAA	—	—	0.15	0.10	0.25	0.20	0.20	0.15
(1:1)	—	—	(2.4)	(1.6)	(4.0)	(3.2)	(3.2)	(2.4)
ZAA	0.50	0.08	0.2	0.5	0.6	0.7	0.43	0.60
	(8.0)	(1.3)	(3.2)	(8.0)	(9.6)	(11.2)	(6.9)	(9.6)
Basic								
Copper	—	—	1.3 $<$ 1.9	0.37	—	—		
Carbonate	—	—	(20.8 $<$ 30.4)	(5.9)	—	—		
ACA	—	—	0.055	0.050	0.090	0.060	0.072	0.055
	—	—	(0.9)	(0.8)	(1.4)	(1.0)	(1.2)	(0.9)
CCA-C	—	—	—	—	0.34	0.18		
	—	—	—	—	(5.4)	(2.9)		
ACC	—	—	—	—	$>$ 1.0	0.9		
	—	—	—	—	($>$ 16.0)	(14.4)		

[a] Preservative code:
CAA — Copper-Arsenic-Additive formulation
ZAA — Zinc-Arsenic-Additive formulation
CZAA (1:1) — CAA and ZAA mixed in volumetric ratio 1:1
ACA — Ammoniacal Copper Arsenate
CCA-C — Chromated Copper Arsenate Type C
ACC — Acid Copper Chromate
[b] 8-week-long incubation time
[c] 12-week-long incubation time
[d] Average calculated for the same test fungus from more than one experimental series.

zites trabea, and to all other preservatives was *Coniophora puteana*.

The lowest thresholds, about 0.1 lb/ft^3 (1.6 kg/m^3), were found with the CAA and ACA preservatives. Both contained arsenic and copper, with the higher content of arsenic in the ACA. Low thresholds of 0.2 and 0.3 lb/ft^3 (3.2 and 4.8 kg/m^3) were also obtained for CZAA and CCA-C, respectively.

The preservative containing arsenic and zinc (ZAA) had a threshold of 0.6 lb/ft^3 (9.6 kg/m^3). Still higher values were found with the ACC (> 1.0 lb/ft^3; > 16 kg/m^3) and the basic copper carbonate (1.3 to < 1.9 lb/ft^3; 20.8 to < 30.4 kg/m^3).

Two new preservative formulations—CAA and CZAA—showed thresholds similar to those of ACA and CCA-C, which are commercially used formulations. This indicates that the new formulations may perform in ground contact exposures satisfactorily.

The other three preservative formulations (ZAA, ACC, and copper carbonate) provided only limited protection. However, the new ZAA preservative, when compared with the standard ACC preservative, indicated sufficient fungicidal efficacy for above-ground exposures.

We have also calculated other thresholds that were based on the content of As_2O_5 only (not on the basis of all oxides). The resulting figures showed how the thresholds increased when the copper oxide was partially replaced by other metal oxides (ZnO or CrO_3) in the formulation. While both CAA and ACA preservatives had the lowest arsenic threshold (0.04 lb/ft^3; 0.64 kg/m^3), this value was higher for the CZAA (0.06 lb/ft^3; 0.96 kg/m^3) and still higher for the CCA-C (0.12 lb/ft^3; 1.9 kg/m^3) and ZAA (0.14 lb/ft^3; 2.2 kg/m^3). We do not emphasize the numerical values of these thresholds (based on As_2O_5): they only indicate the order of decreasing fungicidal efficiency found in this study: ACA or CAA > CZAA > CCA-C > ZAA.

DISCUSSION

This study showed that *Coniophora puteana*, a fungus frequently isolated from decayed wood in North America (Duncan and Lombard 1965; Rennerfelt 1963), was tolerant to high concentrations of preservatives containing arsenicals. Its tolerance to sodium arsenate had been shown earlier by Unligil (1972), and it was suggested as test fungus for preservatives containing arsenicals. Therefore, it was used in our experiments.

When we compare the data in this work with other references, we must keep in mind that our thresholds were obtained from treated but nonleached samples. Our thresholds obtained for CCA-C and ACC corresponded well with those reported in the literature for varied CCA formulations and for ACC. The variability in the thresholds is evident from the following data in the literature. In testing three different formulations of CCA with *C. puteana* Wallace (1968) obtained, in wood-agar tests, thresholds within the range of 0.03 and 0.32 lb/ft^3 (0.48 and 5.1 kg/m^3) of total salts and, in soil-block tests, < 0.1 lb/ft^3 (< 1.6 kg/m^3). Using *L. trabea* as the test fungus, he found in wood-agar tests thresholds within the range of 0.14 and 0.45 lb/ft^3 (2.3 and 7.2 kg/m^3) of total salts and in the soil-block tests 0.17 and 0.22 lb/ft^3 (2.7 and 3.5 kg/m^3). Rennerfelt (1963) obtained, in soil-block tests with *C. puteana*, threshold values for CCA of about 0.3 to 0.4 lb/ft^3 (5 to 6 kg/m^3) oxides. For six different formulations of CCA accepted in New Zealand, McQuire (1972) found a threshold of about 0.3 lb/ft^3 oxides (4.8 kg/m^3) using *L. trabea* and *P. monticola* in soil-block tests. Becker (1964) stated for CCA a general threshold of 1 kg/m^3 (0.06 lb/ft^3) of total salts against brown rot fungi. Variability of the thresholds can be illustrated by results of soil-block tests carried out with the same preservatives and the same testing fungi in two laboratories (Smith and Gjovik 1972). They tested CCA and found the thresholds for *Lenzites trabea* (617) as different as 0.08 lb/ft^3 (1.28 kg/m^3) in one laboratory and 0.38 lb/ft^3 (6.09 kg/m^3) in the other. We do not consider such variability unusual since the soil-block test operates with biological materials (testing fungus and wood), both with known natural variability. Repetition of soil-block tests is, therefore, in order and can only bring more reliable data.

Variability similar to that of CCA also can be seen with the ACC preservative. For ACC Rennerfelt (1963) found a threshold of > 1.7 lb/ft^3 oxides (> 27 kg/m^3) using *C. puteana* in soil-block tests. Cowling (1957) obtained thresholds of 0.1 and 0.23 lb/ft^3 (1.6 and 3.7 kg/m^3) of total salts with two *L. trabea* strains in modified wood-agar tests. Becker (1964) gave for ACC a threshold of 15 kg/m^3 (0.9 lb/ft^3) salt against brown rot fungi. However, in our study with ACC *C. puteana* provided no threshold values for tests of samples with retentions up to 16.0 kg/m^3 (1.0 lb/ft^3).

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