PRESERVATIVE TREATMENT OF RED MAPLE

WILLIAM B. SMITH
NAZRI ABDULLAH
DOUGLAS HERDMAN
RODNEY C. DE GROOT

ABSTRACT

The development of additional preservative treatments for underutilized eastern hardwoods, such as red maple, is critical to the development of new market opportunities that require long-term utilization of hardwoods in exterior structures. This project investigated the treatability of red maple sapwood and heartwood with water, toluene, CCA (chromated copper arsenate), ACQ (ammonium copper didecyldimethylammonium chloride), creosote, and toulene- and waterborne copper naphthenate. The efficacy of CCA, and of water- and oilborne copper naphthenate against a brown-rot fungus *(Postia placenta),* a white-rot fungus *(Tratnetes versicolor),* and a soft-rot fungus *(Chaetomium globosum)* was also determined using sapwood blocks in agar block decay tests. Substantial differences were found between heartwood and sapwood treatability. Full-cell impregnation resulted in sapwood samples being thoroughly penetrated and consistently treated to retentions of 30 to 40 pcf (lb. solution/ft.^{3} wood). Preservatives penetrated heartwood only about 3 mm transversely and 15 mm longitudinally. Retentions ranged from 5 to 15 pcf. On an equivalent copper loading basis, the oilborne copper naphthenate was more effective than the waterborne formulation against white- and soft-rot fungi. CCA protected maple sapwood against brown- and white-rot fungi at low retentions, 0.1 percent copper weightlweight. Similar to past work, however, higher loadings were needed for soft-rot protection.

The opportunity for increasing the utilization of certain eastern hardwoods, such as red maple, in exterior construction is highly dependent on the development of wood preservation technology that will protect these hardwoods in the exterior environment. Currently, creosote is accepted as a preservative for treatment of red maple (1). Other preservatives also should be considered for effective treatment of this species in order to expand the options for using treated hardwoods. The goals of this project were to determine the treatability of red maple heartwood and sapwood and to determine the effectiveness of copper naphthenate as a wood preservative for protecting red maple sapwood.

Preservative pressure treatment effetiveness can vary within timber products because of the chemical makeup of the various wood constituents and the treating solutions, and differences in permeability of various wood tissues. For example, while the sapwood of most wood species is able to be penetrated with preservatives using conventional pressure processes, the heartwood is often quite impermeable and resists treatment. If the heartwood is not naturally durable, it can then become susceptible to biological degradation and insect attack. For difficult-to-treat species, AWPA standards (1) usually call for the material to be incised. Although chromated copper arsenate (CCA) is considered an excellent waterborne wood preservative for softwoods, its efficacy with hardwoods has not been particularly successful. This difficulty in satisfactorily protecting with waterborne preservatives is generally attributed to the chemical makeup of the wood itself and penetrability differences among differing cell tissue types.

Preservative-treated hardwoods, used in contact with the ground, are often attacked by soft-rot fungi. Butcher (5) found that when brown rot and white rot attacked treated posts in horticultural soils, the final failure of the posts was always due to soft rot. Similarly, CCA-treated eucalyptus transmission poles in Australia were attacked by soft-rot fungi (10). Most decay studies of hardwoods reported in the literature were done on beech, birch, eucalyptus, or sweetgum. In this study, red maple was chosen; both as a representative diffuse-porous hardwood and a relatively underutilized species in the northeastern United States. The effectiveness of the waterborne and

The authors are, respectively, Associate Professor and Graduate Students, Wood Products Engineering, SUNY College of Environmental Science and Forestry, One Forestry Dr., Syracuse, NY 13210-2786; and Research Plant Pathologist, USDA Forest Serv., Forest Prod. Lab., One Gifford Pinchot Dr., Madison, WI 53705-2398. Appreciation is expressed to the Northeastern Forest Alliance and to the USDA Forest Serv. for financial support. This paper was received for publication in May 1995. Reprint No. 8352.

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oilborne formulations of copper naphthenate (CuNap) against a white-rot fungus, a brown-rot fungus, and a soft-rot fungus using mini-test blocks in an agar block decay experiment was determined. The results are compared to the effectiveness of CCA-C in protecting treated red maple.

CuNap preservative is made up of naphthenic acid and copper salt. Naphthenic acid consists of a group of alicyclic carboxylic acids derived from petroleum distillation. The major components of naphthenic acid mixtures are monocarboxyclic acids having one or more cycloalkane rings. Other acids in the mixture can include aliphatic, dicarboxcyclic acid, and cyclohexane ring (3,17). Copper naphthenate was first used as a wood preservative as early as 1889 and was commercially available in Denmark in 1911 (11). During World War II, when there was a shortage of creosote, copper naphthenate was widely used. Both copper and naphthenic acid are believed to be toxic to fungi, but the effects of naphthenic acid on decay fungi have not been studied as extensively as the effects of copper.

The effectiveness of CuNap-treated pine against *Coniophora puteana* and *Trametes lilacino-gilva* was reported to be less than that of CCA (4). But Sugai et al. (18) found that several species of wood treated with CuNap by brushing performed very well against fungi and termites in field tests. Tsunoda and Sakurai (19) found that CuNap applied by brushing protected *Fagus crenata, Cryptomeria japonica,* and *Pinus densiflora* against decay fungi, and vacuum/soak-treated C. *japonica* performed very well against *Tyromyces palustris* and *Coriolus versicolor.*

CCA is a broad-spectrum wood preservative that was first patented in 1933. The effectiveness of CCA in protecting softwoods both in laboratory tests and in field exposures is well documented. However, the performance of CCA-treated hardwoods varies from excellent to very poor. In most cases, the failure of CCA-treated hardwoods is attributed to attack by soft-rot fungi. Several theories have been put forward to explain the reasons for the poor performance of CCA-treated hardwoods, including insufficient preservative loading, differing wood cell wall chemical constituents that affect fixation procedures and products, and shallow penetration (6-8, 12,13,16).

In laboratory studies, small-size test specimens of CCA-treated hardwoods were severely attacked by soft-rot fungi as compared to CCA-treated softwoods (7). In the same study, it was found that it was possible to control soft-rot attack by increasing the CCA retention. Ryan and Drysdale (16) found that it required six times more copper retention in the fibers of *Betula alba* than in the tracheids of *Pinus radiata* to prevent soft-rot attack. Higher CCA retention (-35 kg/m^3) significantly extended the service life of hardwood power poles in New South Wales (20). However, Leightley and Norton (14) found that CCA retention of up to 40 kg/m^3 did not protect eucalyptus poles from soft rot.

There are conflicting results regarding the pattern of soft-rot attack on CCA-treated hardwoods and how it differs from that of softwoods. Studies have shown that in both types of wood, soft-rot fungi colonize the wood surface and then attack the vessel, fiber, and tracheid cell walls (12). Even though the depth of fungal altack was reduced by CCA treatment, the severity of attack remains the same for both types of wood. In a study of birch, soft rot attacked primarily those areas high in syringyl-guaiacyl lignin, which were also the areas with the lowest copper retention (9). In that study, soft rot did not attack birch vessels, believed to have higher levels of guaiacyl lignin. When natural susceptibility to decay was compared, it was found that hardwoods in general are more susceptible to soft rot than softwoods (6), likely because the syringyl-guaiacyl lignin found in hardwoods is more susceptible to soft rot than the guaiacyl lignin found in softwoods. Because lignin is one of the reaction sites of CCA, and the micro distribution of copper and arsenic in CCA-treated wood corresponds to the amount and distribution of lignin in the wood (8,9), poor performance of CCA-treated hardwoods may thus be due to uneven distribution of CCA caused by uneven distribution of lignin in the wood cell wall. Further evidence suggests that CCA may react preferentially with guaiacyl lignin (9).

METHODOLOGY

TREATABILITY

Treatability of red maple sapwood and heartwood, as determined by retention and penetration, was determined with several different wood-preservative compounds. The active ingredients of respective treating solutions were intended to be of a typical strength that would produce a retention comparable in performance to a retention of about 0.6 pcf (9.6 kg/m^3) CCA. The preservative treatment chemicals used represent commercially used categories. Creosote (95”C) and copper naphthenate (1 % Cu metal in toluene) represent oil-type organic chemical treatment. Waterborne chemicals included both acidic CCA-C (1% oxide), alkaline ACQ Type-B (1 % ammonium copper didecyldimethylammonium chloride), and copper naphthenate (1“k) Cu metal). Water and toluene were used as control solutions.

Samples for treating came from freshly harvested red maple *(Acer rubrum* L.) sawlogs. Log diameter ranged from 10 to 16 inches (25 to 40 cm), with the heartwood portion being 4.5 to 7 inches (11.5 to 18 cm) wide. The logs were sawn into 5/4-inch (32-mm) boards in the Wood Products Engineering sawmill. Specific efforts were made during sawing to secure all heartwood and all sapwood boards. Experience with the logs obtained for this study and surveys of local sawmills showed that heartwood was often about 50 percent of log diameter. While this is only about 25 percent of log volume, there will still be substantial amounts of heartwood in lumber potentially cut from logs for structural purposes. Some of the heartwood also had portions with heartrot deterioration. After kiln-drying to below 10 percent moisture content (MC), the boards were planed and ripped into 1- by 1-inch (25- by 25-mm) square strips. From each strip, at least eight 6-inch- (150-mm-) long end-matched specimens were prepared for subsequent pressure treating with preservatives. To enable the study of longitudinal penetration into heartwood and sapwood, the specimen ends were not sealed. Pressure treatment took place via the full-cell process: 15 minutes of vacuum (28 in. Hg, -0.94 bar) followed by 30 minutes of pressure (100 psi, 6.8 bar). There were 15 specimen replicates for each treating group.

PRESERVATIVE EFFICACY

Efficacy of waterborne and oilborne formulations of copper naphthenate was compared to efficacy of CCA-C in protecting red maple sapwood against *Trametes versicolor* (a white-rot fungus),

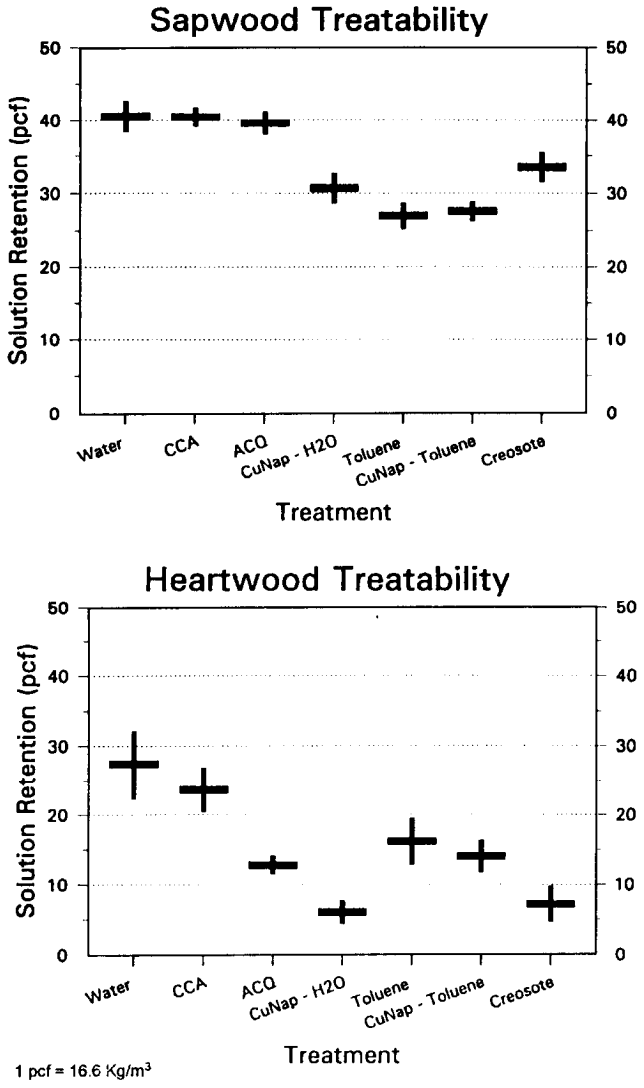

Figure 1.—Treatability of **red maple sapwood and heartwood, weight/volume basis. Horizontal bars represent the average; vertical bars show ± one standard deviation.**

Postia placenta (a brown-rot fungus, currently named *Oligoporaus placentus),* and *Chaetomium globosum* (a soft-rot fungus). This evaluation was made using the agar block test procedures suggested by several researchers (2,21,22).

Decay specimen blocks were obtained by cutting defect-free air-dried red maple sapwood lumber into sticks measuring 10 mm tangential by 20 mm radial by 500 mm longitudinal. These sticks were then crosscut into thin mini-test blocks measuring 5 mm (L) by 10 mm (T) by 20 mm (R). Individual red maple mini-test blocks were labeled with a permanent marker, then put in open glass vials and conditioned in a conditioning chamber maintained at 30°C and 67 percent RH, for a target of 12 percent equilibrium moisture content (EMC). The EMC in the conditioning chamber was verified by determining the MC of control maple mini-test blocks placed in several Ioeations in the conditioning chamber. For each experiment, the initial weight of the test blocks conditioned to 12 percent EMC ($WT_{initial}$) was recorded, then groups of the test blocks were placed together in a container for preservative treatment.

The maple test blocks were treated with several concentrations of waterborne copper naphthenate (Chapman CUNAPSOL-5), oilborne copper naphthenate (Champan CUNAP-8), and with CCA (OSMOSE K-33 type C) preservatives. The treatment schedule utilized 30 minutes of vacuum (28 in. Hg, -0.94 bar) followed by 30 minutes of soaking at atmospheric pressure. Immediately after treatment, the test blocks were wiped lightly to remove free solution with a paper towel and weighed. Copper retention was determined by calculation, from weight gain and solution concentration. Test blocks to be used as controls were treated with either distilled water or with toluene for waterborne and oilborne formulations, respectively.

After weighing, the test blocks were wrapped in aluminum foil and stored in plastic bags to prevent moisture loss. They were then stored at room temperature for 6 days to allow for "wet fixation." Subsequently, each test block was put in individual glass vials and oven-dried for 24 hours at 60°C to complete the "fixation" process. After removal from the oven, the test blocks were again equilibrated to 12 percent EMC (target) in the conditioning chamber. The weight of treated and conditioned test blocks was recorded as $WT_{predecay}$. A 2 percent malt extract agar media was prepared for culturing the white-rot and brown-rot test fungi and controls in petri dishes and also for use in decay chambers. For the soft-rot test, 2 percent Abrams nutrient solution was added to the agar media. Plastic "needle-point" mesh (2.5 perforations/cm) was used as support for the test blocks (20).

Prior to exposure to decay fungi, the experimental test blocks were prepared by putting groups of 12 blocks each in a plastic container filled with distilled water for testing white rot, brown rot, and for control blocks, or with Abrams nutrient solution for testing soft rot. The plastic containers with test **blocks were** placed in a glass jar, and vacuum was applied for 30 minutes, followed by soaking the test blocks for several hours at atmospheric pressure. The test blocks were autoclaved for 25 minutes at 15 psi and 121°C. Four test blocks per petri dish decay chamber were aseptically transferred onto a thin plastic mesh support in each chamber. Four-mm-diameter fungus inoculum sections were cut from 2-week-old decay fungi culture growing in a petri dish and used to inoculate the decay chambers. After 7 to 10 days, and if no contamination was observed, four test blocks were aseptically transferred onto the plastic mesh support in each decay chamber. The decay chambers were incubated in the dark for 12

weeks in a walk-in, controlled-environment room maintained at 28°C.

After 12 weeks of incubation, the test blocks were harvested and mycelium was cleaned from block surfaces. One test block from each set of preservative concentration/fungus combinations was saved and stored in formalin-acetic-acid (FAA) for later use in microscopic observation. The remaining 11 test blocks (per set of preservative concentration/fungus combination) were equilibrated to 12 percent target EMC in the conditioning chamber, and their weights recorded as W $T_{Postdecay}$. The weight loss of test blocks due to decay was then calculated. A set of 12 red maple mini-test blocks was used for MC determination, The ovendry weights, predecay weight (immediately after autoclaving), and postdecay weight (after 12 weeks of incubation) were recorded. The MC of these 12 control blocks before and after the decay experiment was calculated, and used to evaluate the MC of test blocks during the decay tests.

Evaluation of the extent of decay in test blocks was determined by the weight loss and visual inspection. The percentage weight loss due to decay was calculated from weight loss corrected for change in weight due to treatment (based on change in weight of control test blocks incubated for 12 weeks but not exposed to fungus) and equilibrated moisture values to determine the extent of decay. Visual determination included examining the test blocks for decay activities such as presence and amount of mycelium covering the test blocks, physical changes such as shape, softness and color after the test blocks were conditioned to 12 percent EMC, and presence of bore holes and cavities.

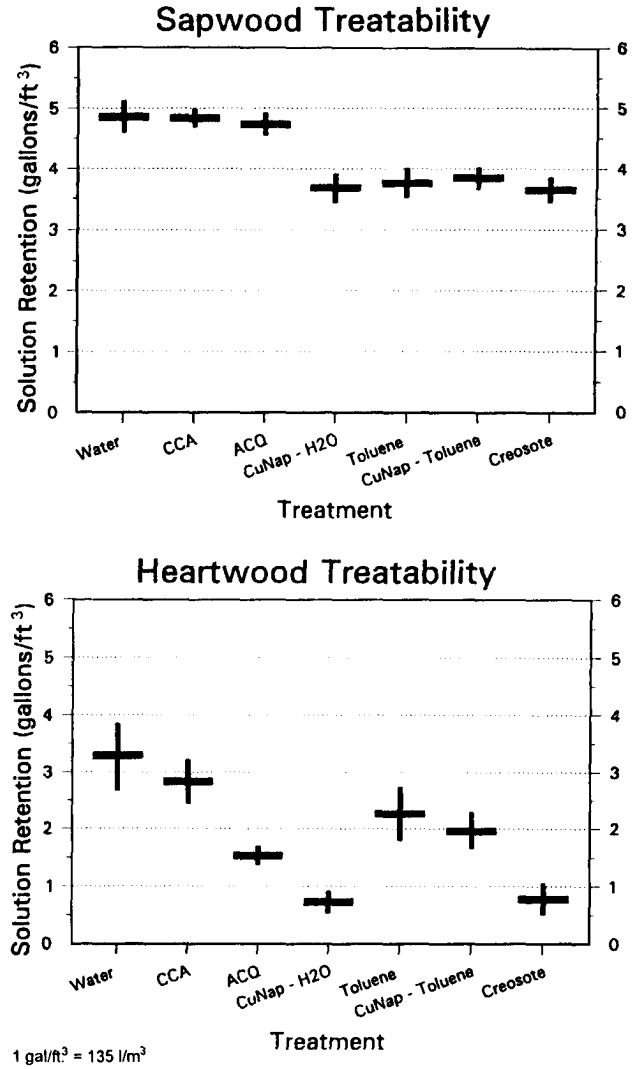

Figure 2. — Treatability of red maple sapwood and heartwood, volumelvolume basis. Horizontal bars represent the average; vertical bars show ± one standard deviation

RESULTS

TREATABILITY

Red maple sapwood was very treatable with all of the preservative treatments investigated (Fig. **1).** Each sample was completely penetrated and was saturated to the maximum theoretical retention level. The heartwood, however, did not treat well. Retentions were substantially lower than those of sapwood. Because of the differences in specific gravity of water, toluene, and creosote, retentions were also calculated on a soh,rtion to wood volume basis **(Fig.** 2). Sapwood retentions of waterborne solutions, except for waterborne copper naphthenate, were higher than retentions of oilborne solutions because of absorption into the cell wall. Transverse penetration into heartwood was only about 3 mm, while into the end grain, longitudinal penetration was only about 15 mm. The 6-inch matched samples used in this study were not end sealed because we wanted to see both transverse and longitudinal penetration results. The retention results reported would have been much lower if the ends had been sealed to more realistically model actual lumber treatment. In a separate investigation, additional heartwood samples of the same size were treated at 200 psi (as opposed to 100 psi) with creosote. The retention increased by about 25 percen~ good but still not particularly high. It appears that for confident use, heartwood faces may need to be incised.

PRESERVATIVE EFFICACY

When retentions of copper in the treated blocks are referenced to the concentration of copper in the treating solution, the copper loading for oilborne copper naphthenate was about half that obtained by the treatment with waterborne copper naphthenate or with CCA **(Table 1).** Therefore, comparisons of treatment efllcacy need to be referenced to both concentration of copper in the treating solution **(Fig. 3)** and to actual concentration of copper in the wood (’llr**ble** 2). That oilborne formulations, in general, result in slightly lower preservative retention is because the preservative

solutions are unable to penetrate into the wood cell wall. Also, carrier solvents with high viscosity can limit both penetration and retention.

Based on the weight loss data **(Table 2** and **Fig. 3),** it was found that treatment of red maple sapwood with 1 percent Cu wt/wt waterborne copper naphthenate (equivalent to retention of 6.8 kg Cu/m^3) did not completely prevent attack by *Trametes versicolor* When red maple was treated with the oilborne formulation **(Fig. 3),** it was found that weight loss due to decay by this white-rot fungus was greatly reduced at 0.25 percent Cu wt/wt (0.8 kg Cu/m^3). On the other hand, CCA-C was found to be very effective in protecting maple against white rot, where low weight loss was achieved when treated with 0.03 percent Cu wt/wt CCA-C solution (0.21 kg Cu/m^3). When tested against *Postia placenta,* a brown rotter, it was found that decay was controlled at a retention of 0.84 kg Cu/m^3 when treated with waterborne copper naphthenate, 0.83 kg Cu/m^3 when treated with oilborne copper naphthenate, and 0.84 kg Cu/m^3 when treated with CCA-C.

TABLE 1. — Average copper retention obtained with preservative treatments in red maple sapwood.

Preservative solution concentration	Copper naphthenate		CCA-C
	Waterborne	Oilborne	
(%Cu as metal)		(kg/m^3)	
0.03	0.21	0.11	0.21
0.06	0.43	0.21	0.41
0.13	0.84	0.45	0.84
0.25	1.67	0.83	1.75
0.50	3.33	1.68	3.45
1.00	6.82	3.18	7.13

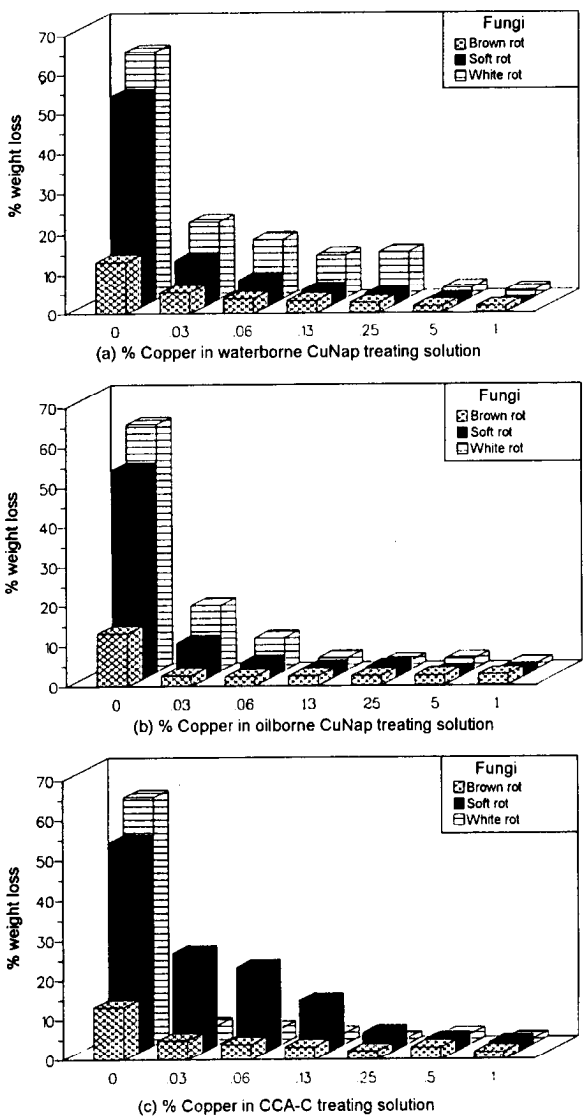

Figure 3. — Percent weight loss of preservative-treated red maple sapwood in 12-week agar-block decay tests: (a) waterborne copper naphthenate; (b) oilborne copper naphthenate; (c) CCA-C.

When preservative-treated red maple was exposed to *Chaetomium globosum,* a soft rotter, control was achieved at a retention of 0.84 kg Cu/m^3 when treated with waterborne copper naphthenate, 0.45 kg Cu/m^3 when treated with oilborne copper naphthenate, and 3.45 kg Cu/m^3 when treated with CCA-C. The poor performance of CCA in protecting red maple against soft-rot fungi confirmed results of other studies on the low efficacy of CCA in treated hardwoods (7,8, 12). In order to control the attack by *Chaetomium globosum,* it requires 0.84 kg Cu/m^3 when treated with the waterborne copper naphthenate, about half that amount of copper retention when treated with oilborne copper naphthenate, and four times more copper loading when treated with CCA-C.

DISCUSSION

Interestingly, the waterborne treatments used in this study showed much different retentions in the heartwood specimens, but retentions for water, CCA, and ACQ were comparable in the sapwood **(Figs. 1 and 2). The** retention of waterborne copper naphthenate was lower than the other waterborne treatments in both sapwood and heartwood. We surmise that this reflects breakdown of the formulation within the capillary pore structure of wood cell walls. Differences in retention of oilborne preservatives in the heartwood probably reflect viscosity differences of the treating solutions.

While specific explanation of reasons for the variable effectiveness of copper

TABLE 2. — Copper retention versus average percent weight loss in red maple sapwood blocks that were treated with different preservatives and exposed to different fungi for 12 weeks.

Preservative solution concentration	Preservative retention Cu as metal	Brown rot (*Postia placenta*)	Soft rot (*Chaetomium globosum*)	White rot (*Trametes versicolor*)
(% Cu as metal)	(kg/m^3)			
Control (untreated)				
0.00	0.00	13.2 (3.6)[a]	52.6 (7.5)	62.0 (10.2)
Waterborne CuNap				
0.03	0.21 (0.01)	4.4 (2.0)	11.7 (3.4)	19.1 (3.4)
0.06	0.43 (0.02)	3.8 (1.3)	6.7 (2.6)	14.8 (2.7)
0.13	0.84 (0.03)	3.2 (0.6)	4.1 (2.2)	10.9 (2.5)
0.25	1.67 (0.05)	2.6 (0.8)	3.1 (1.8)	11.6 (1.5)
0.50	3.34 (0.10)	1.7 (0.2)	1.6 (0.4)	2.5 (0.6)
1.00	6.82 (0.21)	1.6 (0.6)	0.3 (0.2)	1.9 (0.3)
Oilborne CuNap				
0.03	0.11 (0.01)	6.5 (2.2)	8.7 (3.7)	16.0 (4.4)
0.06	0.21 (0.01)	3.1 (1.1)	3.6 (1.1)	6.6 (2.2)
0.13	0.45 (0.03)	1.7 (0.7)	1.8 (1.0)	2.1 (0.1)
0.25	0.83 (0.07)	0.5 (0.1)	0.4 (0.1)	0.8 (0.1)
0.50	1.68 (0.15)	0.4 (0.1)	0.6 (0.1)	0.7 (0.9)
1.00	3.18 (0.22)	1.6 (0.1)	1.4 (0.3)	1.3 (0.2)
CCA-C				
0.03	0.21 (0.01)	4.9 (1.6)	25.1 (5.3)	4.9 (2.6)
0.06	0.41 (0.01)	3.9 (1.9)	21.5 (6.1)	4.1 (3.0)
0.13	0.84 (0.03)	3.2 (0.2)	13.1 (3.9)	2.8 (1.1)
0.25	1.75 (0.05)	2.1 (0.8)	5.0 (2.4)	1.6 (0.1)
0.50	3.45 (0.09)	3.1 (0.3)	3.4 (1.7)	2.6 (0.5)
1.00	7.13 (0.18)	2.0 (0.6)	2.6 (1.1)	1.5 (0.5)

[a] Values in parentheses are standard deviations.

from the three types of preservative formulations may not be possible, reasonable speculation can be provided. For red maple treated with CCA-C, perhaps the arsenic and chromium in the solution somehow interfere with the fixation and relative efficacy of copper (15). Various complexes that likely formed (such as copper chromate complexes with guaiacyl lignin, and arsenic and chromium complexes) when maple was treated with CCA-C could contribute to the lower efficacy against soft rot. In contrast, copper without the interference of reaction with arsenic or chromium (CuNap), may be present in wood in the form of copper bound to carbohydrates and lignin and as adsorbed copper (14). Also, some absorbed copper from treatment with waterborne copper naphthenate could have been leached out during predecay sample preparation, which could explain the higher weight loss due to decay. Less copper may have been lost from the oilborne copper naphthenate treatment perhaps because the oilborne formulation afforded some degree of water repellency in the short-term leaching of predecay sample preparation.

In a study done by Archer et al. (3), it was found that both agar-block and soil-block tests may be used effectively to screen preservatives. In our current study, however, procedures used did not seem to be particularly favorable for the brown-rot fungus, *Postia placenta. The* actual MC of test blocks play an important role in determining the decay capability of fungi. In generaI, white-rot fungi are capable of attacking wood over a wide range of MC above the fiber saturation point, and soft-rot fungi are capable of withstanding extreme MC levels in wood. Brown-rot fungi, however, usually require somewhat lower MC. hr this study, no specific attempt was made to bring the MC of the test blocks to each optimum for decay by the three types of fungi.

SUMMARY

This study illustrated that red maple sapwood is easily treated. The heartwood, however, is diffucult to penetrate with wood preservatives. As the heartwood is not anticipated to be naturally durable, any industrial treatment application and use must take careful account to satisfactorily provide protection. In agar-block decay tests, oilborne copper naphthenate protected sapwood against fungi at a low retention level. Higher loadings of waterborne copper naphthenate were necessary for protection from white rot, and higher loadings of CCA for protection from soft rot. Since wood in actual use is challenged by many fungi in addition to the three studied in this project, field test verification is strongly recommended.

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