

SEM X-RAY MICROANALYSIS OF TRACHEID CELL WALLS IN SOUTHERN YELLOW PINE SAPWOOD TREATED WITH WATER-DISPERSIBLE PENTACHLOROPHENOL¹

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(Received July 1984)

ABSTRACT

Water-based formulations of pentachlorophenol are an appealing alternative to oil-borne formulations. Their effectiveness is still being evaluated. This study was conducted to determine whether levels of water-dispersible pentachlorophenol in tracheid cell walls increase in proportion to increases in gross retention. Proportionate increases occurred in the S₃ layer between gross retentions of 0.18 and 0.84 pcf (2.9 and 13.4 kg/m³). Increases of pentachlorophenol in the compound middle lamella at cell corners or in the S₂ were not proportional to increases in gross retention above 0.43 pcf (6.9 kg/m³). More pentachlorophenol was detected in the earlywood than in the latewood at all retentions. The P/B ratios for pentachlorophenol in earlywood, but not in latewood, are proportional to gross retention.

Keywords: Pentachlorophenol, preservatives, southern yellow pine, cell walls, scanning electron microscopy (SEM).

INTRODUCTION

In the United States, water-based formulations of pentachlorophenol are being developed for use as a wood preservative (Hatcher 1980, 1981). If effective in protecting the treated wood products from attack by decay fungi and insects, these formulations should prove less costly than those employing more expensive petroleum carriers. In evaluating new formulations, we must consider the distribution of preservative within tracheid cell walls. Relative amounts of preservative within cell walls versus within cell lumens may be as important to wood durability as are differences in chemical toxicity.

The objectives of this study were: (1) to determine whether levels of pentachlorophenol in tracheid cell walls were correlated with gross retentions, and (2) to determine whether treatment characteristics of water-dispersible pentachlorophenol would resemble those of waterborne CCA or those of pentachlorophenol in liquefied petroleum gas.

¹ This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate state and/or federal agencies before they can be recommended. Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife—if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers. This article was written and prepared by U.S. Government employees on official time, and is therefore in the public domain (i.e., it cannot be copyrighted).

² The Laboratory is maintained at Madison, WI, in cooperation with the University of Wisconsin.

LITERATURE REVIEW

The extent to which pentachlorophenol penetrates cell walls during pressure treatments is markedly influenced by the carrier employed. The past assumption that oil-based pentachlorophenol solutions generally coat, but do not enter, the cell walls of treated wood (Wallace 1964) seems applicable to treatments employing heavy oils, but not to treatments using light oils. Zicherman (1975) observed pentachlorophenol in cell walls of Douglas-fir pressure-treated with pentachlorophenol in light petroleum oils. When pentachlorophenol is dissolved in liquefied petroleum gas and a co-solvent, penetration of S_1 and S_2 layers of cell walls occurs (Resch and Arganbright 1971; Wilcox and Parameswaran 1974).

In Douglas-fir commercially treated by the Cellon process (Arganbright 1973), the cell-wall pentachlorophenol increased in reasonably direct relationship to increasing total pentachlorophenol content, regardless of wood type. The total pentachlorophenol retention was greater for earlywood than for latewood, but the percent deposited in the cell wall was similar for both wood zones.

The importance of the swelling characteristics of solvents in contributing to penetration of cell walls by oil-based preservatives has been demonstrated with tri-*n*-butyl tin oxide (TBTO). In beechwood treated with TBTO in a nonswelling solvent (pure, dry diethylene dioxide), the preservative was always deposited on lumen surfaces of cell walls. The deposition tended to increase slightly in thickness at the higher retentions. In beechwood treated with TBTO in swelling solvent (diethylene dioxide + 5% water), a halo-like, dark diffuse band was present within the S_3/S_2 region of the wall close to the lumen. This band appeared to increase in intensity but not in thickness at higher retentions (Bravery et al. 1975).

A series of studies by Yata et al. (1979, 1981a, b, 1982) has demonstrated that cut ends of tracheid cell walls of *Chamaecyparis obtusa* Endl. and *Larix leptolepis*

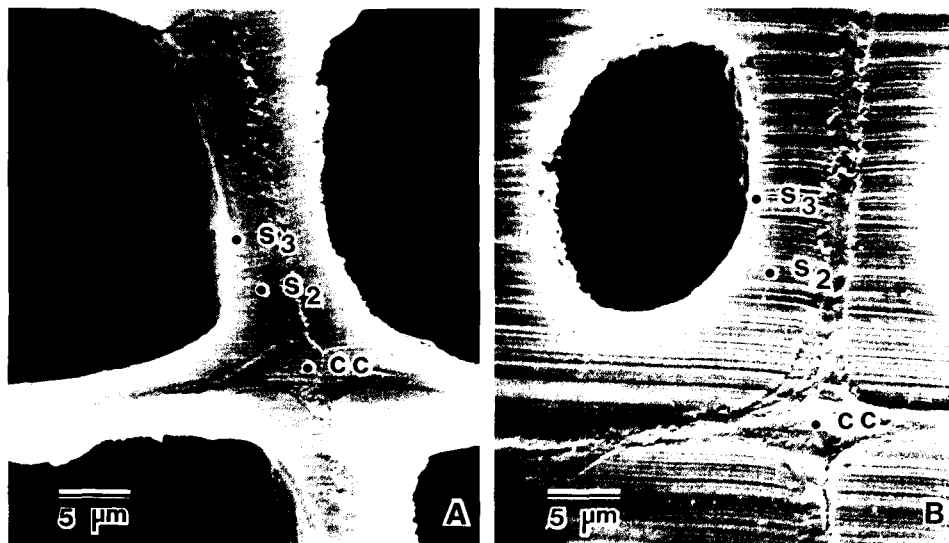


FIG. 1. SEM micrographs of transverse surfaces by earlywood (A) and latewood (B) tracheids showing sites of X-ray spot analyses. Middle lamella at corner cell (CC), S_2 , and S_3 .

TABLE 1. *P/B ratios for chlorine in tracheid cell-wall layers in southern pine sapwood pressure-treated to three retentions with a water-dispersible formulation of pentachlorophenol.*

Cell wall	Gross retention of wood (pcf) ¹	Earlywood		Latewood	
		\bar{x} P/B ratio ²	Standard deviation	\bar{x} P/B ratio ²	Standard deviation
CC	0.18	0.68	0.36	0.40	0.20
	0.43	1.26	0.31	0.94	0.35
	0.84	1.64	0.50	1.19	0.39
S ₂	0.18	0.55	0.31	0.39	0.22
	0.43	0.90	0.24	0.72	0.14
	0.84	1.45	0.38	0.84	0.15
S ₃	0.18	0.56	0.27	0.41	0.23
	0.43	1.10	0.31	1.03	0.31
	0.84	1.91	0.39	1.51	0.30

¹ 1 pcf = 16 kg/m³.

² Each value is mean of 27 observations.

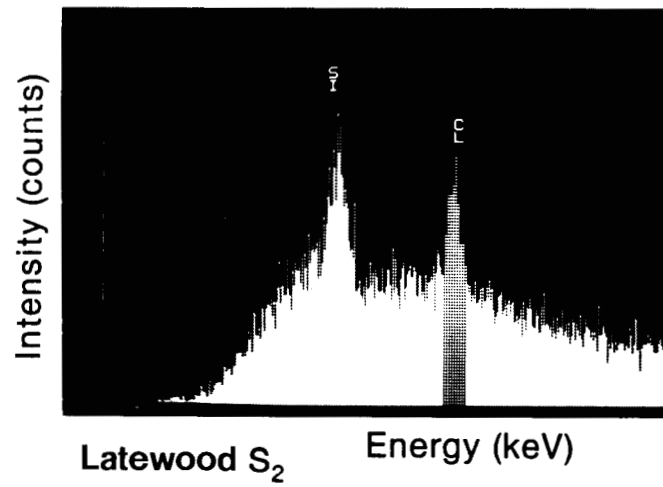
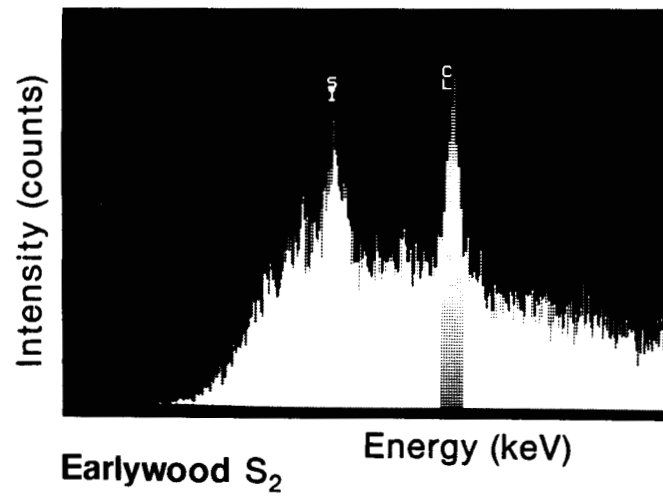
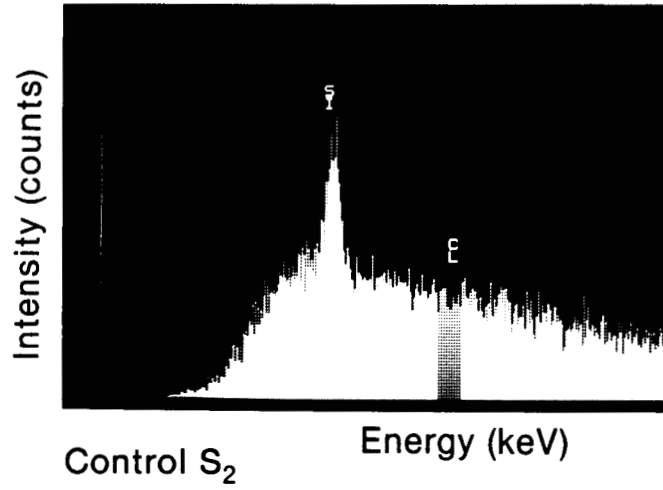
Gord. are more permeable to aqueous solutions of copper, zinc, and chromium compounds than are lumen surfaces. Within cell walls, the I + P layer [compound middle lamella] and the S₁/S₂ boundary were the most permeable layers to cations of copper and zinc. In wood treated with either K₂Cr₂O₇ or K₂CrO₄, the chromium content of the I + P layer was higher than that of the secondary wall. Dichromate and chromate anions entering exposed cut ends of tracheid cell walls always diffused more deeply within cell walls of tracheids in the middle of annual rings than in cell walls of tracheids in the latewood or in the initial earlywood of annual rings.

In softwoods pressure-treated with waterborne, chromated copper arsenate (CCA), the preservative content of ray cells is much greater than that of tracheids (Greaves 1974). Crossfield pit membranes receive the heaviest treatment; tracheid bordered pits are also well treated.

In both hardwoods and softwoods pressure treated with CCA, the middle lamella primary wall region between cell walls tends to be better treated than the adjacent S₂ layers (Drysdale et al. 1980; Greaves 1974). *Pinus sylvestris* L., *Alstonia scholaris* R. Br., *Acer pseudoplatanus* L., *Betula alba* L., and *Fagus sylvatica* L. pressure-treated with CCA, increased gross preservative retentions did not produce proportional increases of preservative in the S₂ layers. Increased gross retentions for CCA in those species did not influence distribution within cell walls, but did increase the amount of preservative deposited in discrete spots. Consequently, Drysdale et al. (1980) concluded that microdistribution patterns of preservative within cell walls of these species were not the sole factor controlling soft-rot development.

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FIG. 2. Representative EDXA spectra showing chlorine intensities from S₂ layers in untreated control and of earlywood and latewood of southern pine sapwood treated to 0.43 pcf with water-dispersible pentachlorophenol.



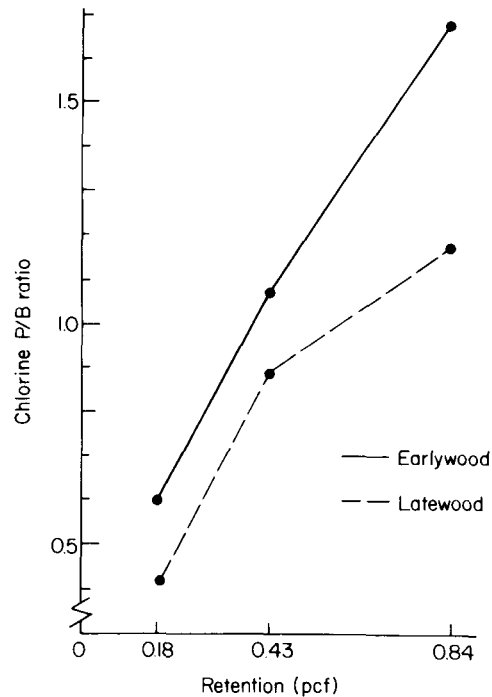


FIG. 3. Mean P/B ratios of chlorine for all observations in earlywood and latewood of southern pine sapwood treated with water-dispersible pentachlorophenol (1 pcf = 16 kg/m³).

MATERIALS AND METHODS

Materials

This study was done in conjunction with another investigation on durability of southern pine sapwood treated with alternative formulations of pentachlorophenol (DeGroot 1984). Boards of southern pine sapwood were pressure-treated with water-dispersible pentachlorophenol using the full cell process described in ASTM D 1758 (ASTM 1980). All boards were 2 × 4 inches (5.1 × 10.1 cm) nominal dimension in cross section and 37 inches (94.0 cm) long; most of them were longleaf pine (*Pinus palustris* Mill.).

Boards were pressure-treated to gross retentions of 0.18 pcf (2.9 kg/m³), 0.43 pcf (6.9 kg/m³), and 0.84 pcf (13.4 kg/m³). The water-dispersible pentachlorophenol concentrations, which were provided by IDACON, Inc.,³ were diluted with a 50:50 tap water:distilled water solution to achieve desired strengths.

The cross-sectional distribution of pentachlorophenol in treated boards was determined by the lime ignition method (AWPA Standard A5, AWPA 1982). For these analyses, the cross section of each board was divided into three zones: an outer zone from 0–0.3 inch (0.0–0.8 cm) deep, an intermediate zone 0.3–0.6 inch (0.8–1.5 cm) deep, and an inner zone more than 0.6 inch (1.5 cm) deep. Boards

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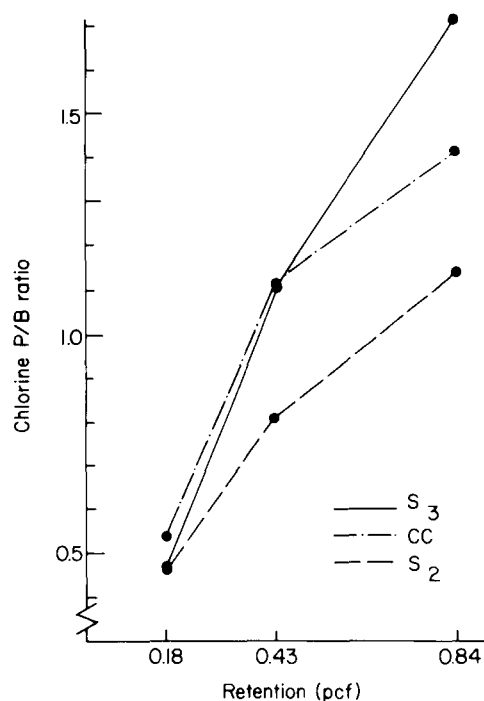


FIG. 4. Mean P/B ratios of chlorine in cell-wall layers CC, S₂, S₃ of tracheids in both earlywood and latewood of southern pine sapwood treated with water-dispersible pentachlorophenol (1 pcf = 16 kg/m³).

were treated in April 1981 and air-dried. Retention levels are reported on a weight-gain basis.

SEM/EDXA analyses

Scanning electron microscopy/energy dispersive X-ray analyses (SEM/EDXA) were made of wood from three boards randomly selected from each retention group and from three boards randomly selected from the control group (no treatment). The middle lamella at cell corners (CC), and the S₂ and S₃ layers of tracheid cell walls were examined in three springwood and three latewood cells in each of the three cross-sectional zones of treated boards, for a total of 18 tracheids per board. Only one latewood and one springwood cell was examined per zone in each of the control boards.

Transverse surfaces of earlywood and latewood in each zone were analyzed for chlorine X-rays (Cl-K_a 2.550–2.730 keV) in the middle lamella at cell corners (CC) and in the S₂ and S₃ layers of cell walls (Fig. 1). We recognize that with the thin cell walls of earlywood tissues and with the relatively thin S₃ of latewood, the width of the three-dimensional volume actually being excited by the electron beam may be greater than the particular cell-wall layer being analyzed (Russ 1974).

Examinations and analyses were performed with a Cambridge² Mark 2A stereoscan electron microscope and a Tracor Northern² TN 2000 Si(Li) energy-dispersive spectrometer. Operating parameters were standardized as previously de-

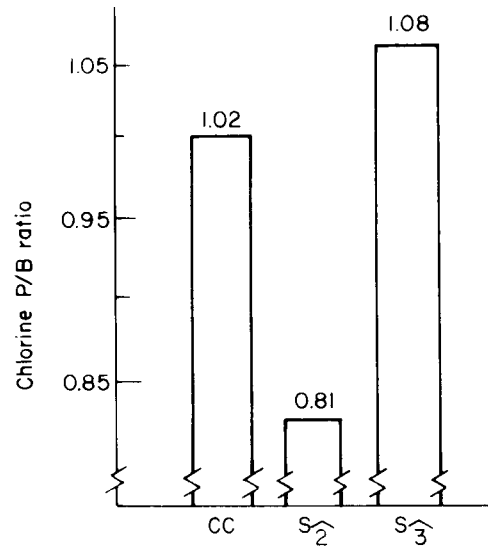


FIG. 5. Mean P/B ratios for chlorine in tracheid cell-wall layers (CC, S₂, S₃) when all observations are combined for analysis. (Includes earlywood and latewood at all three retentions—0.18 pcf, 0.43 pcf, 0.84 pcf.)

scribed (DeGroot and Kuster 1984). A spot size of 0.06 μm was placed for 100 seconds at the site of each analysis. The stored spectral data were processed using the peak/background (P/B) ratio technique developed by Statham and Pawley (1978) and Small et al. (1978). We used analysis of variance tests of P/B ratios in making comparisons between retentions and tissues. Statistically significant differences are reported at the 5% level of probability.

RESULTS AND DISCUSSION

Untreated control boards had P/B ratios of 0.03, 0.03, and 0.02 for pentachlorophenol in CC, S₂, and S₃ layers, respectively. P/B ratios for all cell-wall layers in the treated wood were substantially greater (Table 1).

The distribution pattern of water-dispersible pentachlorophenol was significantly affected by anatomical characteristics of earlywood and latewood and by retention levels to which the boards were treated. Earlywood consistently had more pentachlorophenol than latewood (Figs. 2 and 3). This was the only significant distribution pattern observed at the lowest retention level of 0.18 pcf (2.9 kg/m³). At retentions of 0.43 and 0.84 pcf (6.9 and 13.4 kg/m³), significant differences in pentachlorophenol content occurred among cell-wall layers. Differences among zones were significant only at the highest retention.

The proportional differences between P/B ratios for pentachlorophenol in earlywood and latewood were nearly equal at the lower and upper retentions. At 0.43 pcf (6.9 kg/m³), the earlywood/latewood ratio of P/B ratios was less than at the other two retentions. This retention-dependent, proportional difference between earlywood and latewood is just barely significant. There appears to be a tendency toward proportionate differences between earlywood and latewood, as

there is for Douglas-fir commercially treated by the Cellon process (Arganbright 1973), but more evidence is needed to verify this.

More pentachlorophenol was also detected in cell walls of wood treated to higher gross retentions than in cell walls of wood treated to low retentions (Figs. 3 and 4), but the gains in P/B ratios for the middle lamella area in corners of tracheid cell walls (CC) and in the S_2 layers were not proportional to gains in gross retention. This lack of proportionality between gross retention and retention in the CC and S_2 layer paralleled results previously observed in wood pressure-treated with waterborne CCA (Greaves 1974).

By contrast, increments in P/B ratios for chlorine in S_3 layers approximated relative increments in gross retention of pentachlorophenol (Fig. 4).

Significantly less pentachlorophenol was detected within the S_2 layer of tracheid cell walls than in the CC or the S_3 layer when all samples were combined for analysis (Fig. 5).

The S_2 layer of tracheid cell walls showed the least response to increases in gross retention. The S_2 layer of latewood cells, in particular, showed small relative gains per increment of gross retention above 0.43 pcf (6.9 kg/m³) (Table 1). In the CC, proportionate relationships between gross retention and P/B ratios existed at retentions of 0.18 and 0.43 pcf (2.9 and 6.9 kg/m³), but not with the higher retention. Above 0.43 pcf (6.9 kg/m³) only the S_3 layer of earlywood cells showed an increase in P/B ratios of chlorine approximately proportional to the gain in gross retention.

Statistically significant differences in uptake of pentachlorophenol among the tracheid cell-wall layers appeared as retentions were increased above 0.18 pcf (2.9 kg/m³) (Fig. 4). At 0.18 pcf, differences in amount of pentachlorophenol among individual layers of tracheid cell walls were not significant. Above that retention, the amount of pentachlorophenol in the S_2 layer was significantly different from that in the S_3 and in the CC. This difference and the loss of proportionality between retention and P/B ratios in the CC, but not in the S_3 , contributed to a significant cell-wall layer times retention effect.

This distribution pattern could reflect a concentration-dependent reaction within the wood tissue. This might be triggered either by increased concentration of dispersed droplets of pentachlorophenol-laden oil or by increased concentrations of a chemical dispersing agent that reacts with cell-wall components to impede movement of pentachlorophenol. At low concentrations, pentachlorophenol would disperse uniformly through all wood tissues. At higher concentrations, the process would reduce the proportionate increase within cell walls, especially within the S_2 layer. That the relationship between P/B ratios and gross retentions is best for the S_3 layer suggests that much of the pentachlorophenol added with each increment in gross retention is deposited there and in the lumens of tracheids. The correspondence between P/B ratios and gross retentions in the CC at the lower two retention levels, with a departure at the highest retention, suggests that preservative also enters the cell wall through the middle lamella plus primary cell-wall region, but as treatment concentrations increase, this pathway becomes relatively less effective. Evidence for a selective barrier or filtration process is also seen in results from chemical analysis of these boards (DeGroot 1984). Significantly more pentachlorophenol was found in the peripheral 0.3 inch (0.8 cm) zone than in the more central portions of the boards used in this study.

TABLE 2. Mean P/B ratios for chlorine, all observations at each retention combined.

Retention pcf ¹	\bar{x} P/B ratio ²
0.18	0.50
0.43	0.99
0.84	1.42

¹ 1 pcf = 16 kg/m³.

² Each value is average of 162 observations.

By contrast, we did not detect significant differences among zones at retentions of 0.18 and 0.43 pcf (2.9 and 6.9 kg/m³) with SEM/EDXA.

Differences among zones were significant only at the highest retention. This was due principally to a relatively large increment of pentachlorophenol within the centrally located earlywood. This distribution pattern does not agree with results from chemical analysis of the same wood material. P/B ratios for pentachlorophenol levels in latewood were comparable in all zones at all retentions.

As a result of the disproportionately low loadings in the S₂ layers and in the CC as gross retentions increased, the mean P/B ratios for all observations, within each retention (Table 2) show a lack of proportionate agreement with gross retentions above 0.43 pcf (6.9 kg/m³).

CONCLUSIONS

With pressure treatments of water-dispersible pentachlorophenol by a full-cell process, partitioning of the preservative between earlywood and latewood increases proportionately with increments in gross retention. The pentachlorophenol content of earlywood is proportional to gross retention, but that of latewood increases at a lower rate than does gross retention. Levels of pentachlorophenol in the S₃ layer of tracheid cell walls approximate a proportional relationship with gross retention, but levels of pentachlorophenol in the S₂ layer and in CC do not increase in proportion to increases in gross retention. In the S₂ layers of tracheid cell walls, especially in the latewood, there is relatively little gain in pentachlorophenol with increments of gross retention above a 0.43 pcf (6.9 kg/m³). Thus, additional protection through increased retentions of these treatments would seemingly come from the envelope of pentachlorophenol on the lumen walls and presumably lining all the pathways through which preservative is forced during the treating process. Furthermore, relatively less protection will be given to latewood versus earlywood per increment of retention above 0.43 pcf (6.9 kg/m³).

The larger amounts of pentachlorophenol in earlywood than in latewood, and the proportional increases of pentachlorophenol in the S₃ with gross retention, paralleled results previously reported for Douglas-fir treated by the Cellon process. The lack of proportionality between gross retention and pentachlorophenol content in the S₂ layer, especially in the latewood, parallels distribution phenomena reported for CCA.

Additional field and laboratory experiments are needed to determine whether the increments in gross retention, or in any of the component retentions most closely predict the gains in protection that can be realized with added preservative.

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