INTERACTIONS BETWEEN PENTACHLOROPHENOL SOLUTIONS AND WOOD.

I. EFFECTS OF TIME AND TEMPERATURE ON DEPOSITION WITHIN CELL WALLS[1]

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ABSTRACT

The amount of cell-wall pentachlorophenol (PCP) did not vary significantly up to 6 months after treatment when Douglas-fir sapwood and heartwood stakes were stored at 6 or 12% moisture content and at temperatures ranging up to 150 F. Total PCP was greater for earlywood than for latewood, but the per cent PCP deposited in the cell wall was similar for both wood zones.

Additional keywords: Pseudotsuga menziesii, wood preservation, PCP, cell-wall interaction, sapwood, heartwood, earlywood, latewood.

INTRODUCTION

The gross distribution of toxic or active components of preservative solutions in treated wood has been routinely measured and experimentally investigated for many years. This interest stems from the obvious relationship between the amount and gross distribution of preservative loaded into a treated member and the ultimate service life of that member.

The distribution of preservative chemicals on a microscopic scale, such as on a cell-wall level, has received far less attention. This is partly because of the assumption that many treating solutions do not penetrate into the cell wall itself and thus do not deposit chemicals there.

Using this reasoning, one could classify the different treating solutions used into two different types: those having a carrier capable of penetrating and swelling wood cell walls, and those utilizing a nonpenetrating and nonswelling carrier. It has been logically assumed that treatments with nonpolar solvents or solutions do not permit toxic chemicals to be deposited inside the cell wall even though capable of partially or completely filling the gross void structure in wood and coating the exterior surfaces of cell walls.

In addition to classifying treatments by the preservative distribution within the cellular structure, one must also consider the chemical interaction between the preservative and the constituents of wood. Preservative treatments can thus be further classified into distinct types according to their chemical interaction with wood substance in addition to their microscopic location. Four different types are proposed:

Type 1 Negligible chemical interaction with wood and negligible penetration into the cell wall (external cell-wall coating treatment)

Type 2 Chemical interaction with the outer surface of fibers and negligible cell-wall penetration (external cell-wall bonding treatment)

Type 3 Penetration into the cell wall but negligible chemical interaction (internal cell-wall coating treatment)

Type 4 Penetration into the cell wall together with chemical interaction (internal cell-wall bonding treatment)

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It seems obvious that preservative treatments using water as the carrier lead to penetration of the cell wall and thus would correspond to treatment types 3 or 4. Several studies have shown the presence of toxic components in the cell walls of wood treated with aqueous solutions of metal compounds (Fengel and Wolfsgruber 1971; Petty and Preston 1968; and Rudman 1966). Exact quantitative data on the amount and distribution of cell-wall preservative in relation to the total preservative loading are still not available. The degree to which the various different constituents of water-borne preservatives are chemically bound to the inner and outer cell-wall surfaces is also not completely known. However, several studies have shown that some bonding to wood occurs and thus some water-borne treatments are of type 4 (Dahlgren and Hartford 1972; Eadie and Wallace 1962; Belford et al. 1957).

The negligible swelling ability of creosote, creosote-petroleum oil, petroleum oil-pentachlorophenol (PCP), and liquefied petroleum gas (LPG)—PCP treatments suggest, on the other hand, that these treatments should not penetrate into the cell walls and thus are type 1 treatments. Cell-wall penetration of preservatives via nonswelling carrier treatments has not received much attention. Walters and Côté (1960) used the electron microscope to investigate distribution of PCP in wood treated with both swelling and nonswelling carriers. PCP crystals were observed in cell walls of samples impregnated with the swelling solvent, but they were not observed in cell walls of material treated with the nonswelling solvent.

A number of recent investigations have shown, however, that some nonswelling carrier treatments do indeed lead to cell-wall penetration. Leutritz (1965) pointed out in a footnote that all of the PCP deposited in wood treated with an LPG process could not be removed by prolonged extraction with chloroform. Extraction with a swelling azeotrope did, however, remove all the PCP. This implies that a certain portion of the PCP present was located in the cell walls and could not be removed by extraction with a nonswelling solvent such as chloroform. The azeotrope, which swelled the wood, penetrated into the cell wall and thus extracted PCP present there. Further indirect evidence of cell-wall PCP in LPG-treated wood was presented by Arsenault (1969) in a study on mechanical properties of treated wood. In this study, the equilibrium moisture content of Douglas-fir and ponderosa pine samples was lowered by LPG treatment. The presence of PCP in the cell wall is analogous to the bulking treatments used to reduce shrinkage (Stamm 1964). Rough calculations show that the reductions in EMC correspond to PCP concentrations in the cell wall of 0.10 and 0.16 lbs/ft^3 for Douglas-fir and ponderosa pine, respectively.

Deposition of PCP in cell walls following LPG treatment has been largely established by two recent studies. Resch and Arganbright (1971) examined Cellon-treated Douglas-fir heartwood utilizing a variety of different methods including selective extraction and electron-probe microanalysis. PCP concentrations in the cell wall as high as 0.19 lbs/ft^3 were measured.

Similar results were found by Leutritz (1971) using the selective extraction technique on both material treated with LPG and penta-petroleum oil (P9) solutions.

An interesting series of studies on arsenical creosote, in which a portion of the arsenic becomes permanently fixed within treated wood, was made by Johanson (1971). Whether this is a type 2, 3, or 4 treatment is not now clear.

With regard to fungal and bacterial attack, the presence or absence of preservative chemicals in wood cell walls, and the degree to which they chemically react with wood substances, has the following implications:

(a) their effect on degradation, as expressed by both threshold levels and the patterns of degradation within the cell wall;

(b) their effect on permanence of the toxic chemical constituents, with reference to leaching into the surrounding environment and redistribution in a treated member.

PURPOSE

The present investigation was carried out to answer a number of important questions raised by our previous research on cell-wall PCP (Resch and Arganbright 1971). The sample material used in that study consisted of Douglas-fir heartwood and sapwood 2-inch by 4-inch lumber commercially treated by the Cellon process. The heartwood samples had been treated approximately 3 years prior to the study analyses, while the sapwood was analyzed 1 week after treatment. Initial tests showed that the amount of cell-wall PCP in the heartwood samples after selective extraction with benzene was independent of the length of the extraction for periods over 12 hr. The amount of sapwood cell-wall PCP, in addition to being much lower than that in the heartwood, decreased greatly with increasing extraction periods.

This raised several important questions. Is the deposition of PCP in the cell wall time-dependent? If so, this would explain, at least in part, the differences observed between sapwood and heartwood. A time effect has been suggested as occurring (Arsenault 1970a), but a second possibility is that sapwood and heartwood simply respond differently to treatment.

With these problems in mind the specific objectives of this study became:

1. To determine whether the deposition of PCP in the cell wall is a time-dependent phenomenon or if it occurs during treatment itself.
2. To determine whether heartwood and sapwood differ in respect to the deposition of PCP in their cell walls.
3. Assuming that deposition is time-dependent, to determine to what extent it is affected by temperature and moisture content after treatment.

MATERIAL

Specimen material was obtained from a single 12-foot-long, thoroughly air-dried, Douglas-fir pole section approximately 12 inches in diameter. Stakes 1 inch square by 36 inches along the grain were cut from sapwood and heartwood portions of the pole. The twenty-five stakes most free of seasoning checks, knots, etc. were selected from both sapwood and heartwood for treatment. After end-sealing, the stakes were carefully bundled using stickers to insure uniform treatment and were treated with a commercial charge of lumber by the Cellon process. Moisture content of the stakes at time of treatment was 12%.

EXPERIMENTAL PROCEDURES

The major portion of the experimentation involved determining the amount of cell-wall and total PCP, at different times after treatment, in stakes which had been stored at different temperatures and moisture contents. Table 1 summarizes the different experimental variables and the level of each that was tested. Desired moisture contents and temperatures were obtained by storing the stakes over appropriate salt solutions in constant temperature cabinets.

The total amount of pentachlorophenol and the amount present in the cell wall were determined by the X-ray spectrographic method (AWPA 1970). A three-inch long section was first removed and discarded from each end of the stakes to eliminate any possible end effects. Analyses at desired times were then made on three wafers $1.0 \times 1.0 \times \frac{1}{8}$ inch cut sequentially along the grain from the remaining portion of each stake. The outer two ⅛-inch wafers were used for the measurement of total PCP and were ground into sawdust together. The center wafer was used to determine the amount of cell-wall PCP as shown by selective extraction.

Using the selective-extraction method, wafers were extracted in a Soxhlet extractor with hot benzene for 24 hr.[2] Benzene,

[2] Preliminary experiments showed that 24 hours was sufficient to yield constant values for cell-wall PCP in both sapwood and heartwood specimens.

TABLE 1. *Listing and level of experimental factors tested*

Species	Douglas-fir
Type of material	sapwood and heartwood
Replications	3 stakes for each test
Wood Moisture content after treatment (per cent)	6 (following tests at 70 F only) 12
Wood temperature after treatment (F)	70 100 150
Length of time after treatment (days)	2, 4, 7, 14 20, 30, 60 90 and 180

used as a nonswelling solvent (Stamm 1964), should have removed only PCP located on the blocks' exterior surfaces or on lumen surfaces inside the block; any PCP inside the cell walls should have remained. The short longitudinal dimension of the wafers permitted the benzene to contact each cell lumen during extraction. After extraction, the wafers were ground into sawdust and analyzed for PCP as was done for total PCP. The amount of PCP present in the cell wall was then calculated as a percentage of the total PCP on a weight per unit volume basis as follows:

$$\text{Per cent cell-wall PCP} = \frac{\text{Amount of PCP in center } \frac{1}{8}\text{-inch wafer}}{\text{Average amount of PCP in outer two } \frac{1}{8}\text{-inch wafers}} \times 100$$

Six months after treatment an additional two adjacent ⅛-inch wafers were cut from each of five different heartwood and sapwood stakes for determination of earlywood and latewood PCP content. One of each of the two wafers was dissected into earlywood and latewood and each portion analyzed for total PCP. The remaining series of wafers were selectively extracted, then dissected into earlywood and latewood, and finally analyzed for PCP.

RESULTS

Appreciable quantities of PCP (as high as 0.30 lbs/ft^3) were found to be deposited in the cell walls of sapwood and heartwood stakes treated with an LPG carrier system. Sapwood and heartwood were found to contain reasonably equal amounts of cell-wall PCP when expressed as a percentage of total PCP content. This is shown in Table 2, where values for total, cell-wall PCP, and per cent cell-wall PCP are given for the series of stakes stored after treatment at 12% moisture content.

None of the three primary test variables (time, temperature, or moisture content during storage) was found to have a significant effect on the amount of PCP deposited in the cell wall. The amount of cell-wall PCP was not, therefore, found to increase with time as was originally expected. This was true for both sapwood and heartwood stakes stored after treatment at temperatures of 70, 100 and 150 F (Table 2). The results for stakes stored at 70 F and 6% moisture content were similar to those at 12% moisture, and these results are therefore not presented.

Temperature did, however, appear to have a slight effect on the total amount of cell-wall PCP in the sapwood stakes. The average per cent of cell-wall PCP, when taken over all time periods, increased from 69.1 to 72.6 to 74.9% for storage temperatures of 70, 100 and 150 F, respectively, but the amount of cell-wall PCP in heartwood stakes did not appear to be influenced by temperature.

One salient feature of the experimental data was the wide variation in both total and cell-wall PCP concentrations (Table 3). Total PCP content remained fairly constant within a given stake but varied greatly between stakes. However, the amount of cell-wall PCP varied greatly both within and between stakes. Sapwood stakes were found to have approximately 50% more total and cell-wall PCP (0.31 lbs/ft^3) than

TABLE 2. *Total and cell-wall PCP concentrations for Douglas-fir stakes stored at 12% moisture content conditions*

Category	Wood Temperature After Treatment (°F)	Length of Time after Treatment (days)* 2	4	7	14	20	30	60	90	180	X
		Sapwood concentrations (lbs/ft^3)									
Total PCP	70	0.32	0.32	0.32	0.34	0.30	0.36	0.34	0.35	0.34	0.33
Cell Wall PCP		0.28	0.18	0.23	0.28	0.18	0.22	0.22	0.21	0.21	0.23
% Cell Wall PCP		87.5	56.3	71.9	81.4	60.0	61.1	64.7	59.0	62.7	69.1
Total PCP	100	0.30	0.31	0.29	0.30	0.28	0.30	0.32	0.33	0.33	0.31
Cell Wall PCP		0.25	0.19	0.17	0.21	0.19	0.24	0.21	0.25	0.22	0.21
% Cell Wall PCP		82.2	61.3	58.6	70.0	67.9	80.0	65.6	75.8	66.7	72.6
Total PCP	150	0.29	0.27	0.26	0.27	0.22	0.25	0.23	0.23	0.23	0.26
Cell Wall PCP		0.26	0.16	0.15	0.22	0.14	0.18	0.16	0.18	0.17	0.19
% Cell Wall PCP		88.5	58.0	56.4	79.6	62.1	70.7	69.6	76.8	73.9	74.9
		Heartwood concentrations (lbs/ft^3)									
Total PCP	70	0.17	0.17	0.18	0.18	0.19	0.21	0.21	0.21	0.20	0.19
Cell Wall PCP		0.15	0.12	0.14	0.15	0.14	0.12	0.14	0.18	0.15	0.14
% Cell Wall PCP		90.2	70.6	75.9	85.2	73.7	58.7	66.7	84.1	73.3	74.9
Total PCP	100	0.30	0.26	0.19	0.24	0.20	0.23	0.24	0.22	0.23	0.23
Cell Wall PCP		0.24	0.15	0.13	0.18	0.15	0.14	0.16	0.16	0.16	0.17
% Cell Wall PCP		80.0	60.0	66.7	75.0	75.0	59.4	68.1	71.2	67.4	74.2
Total PCP	150	0.18	0.18	0.19	0.19	0.21	0.18	0.18	0.18	0.19	0.19
Cell Wall PCP		0.16	0.12	0.13	0.16	0.16	0.09	0.09	0.16	0.15	0.13
% Cell Wall PCP		88.9	68.5	66.7	86.0	76.2	50.0	88.9	81.5	70.2	75.6

* Each value in a given row is the average for the same three stakes sampled at different time periods.

did heartwood stakes (0.20 lbs/ft^3). This is particularly interesting because both types of stakes were treated together and their small size permitted complete treatment. If, however, cell-wall PCP content is expressed as a per cent of total PCP content this difference between heartwood and sapwood stakes largely disappears; sapwood stakes had an average of 72.2% cell-wall PCP as compared to 74.9% for the heartwood stakes. Thus while sapwood and heartwood stakes contain appreciably different amounts of total PCP, an approximately equal portion of the total PCP in each wood type is contained in the cell walls. Over the fairly narrow range of PCP contents measured in this experiment, cell-wall PCP was found to increase in a reasonably direct relationship with increasing total PCP content, regardless of wood type (Fig. 1).

The amount of PCP present in the cell wall was appreciably higher than that measured in the previous study by Resch and Arganbright (1971). In that study, the average per cent cell-wall PCP was 24.6% for Douglas-fir heartwood 2-inch by 4-inch stakes treated to an average retention of 0.22 lbs/ft^3. The present results are similar to the recent results of Leutritz (1971), who applied the same technique to borings removed from LPG-treated southern pine poles. In Leutritz's work on the effect of different extraction solvents, 77.9% of the total PCP was left after extraction with either toluene, chloroform, or ether. Leutritz also extracted borings from southern pine poles treated with PCP in petroleum oil (P9) and found that some PCP also remained. The amount of PCP left as a per cent of the total PCP for nine different treating charges was 26.2%, which is much lower than that of the LPG treated poles.

Dissected latewood zones from sapwood and heartwood stakes were found to contain almost exactly the same amounts of both total and cell-wall PCP after 6 months' storage (Table 4), although the latewood zones had much less total PCP

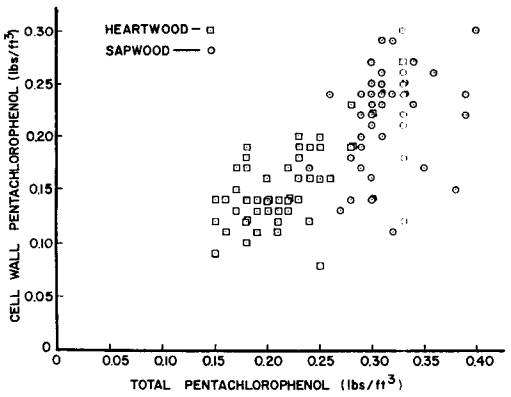

FIG. 1. Cell-wall versus total PCP concentrations (lbs/ft³) for all samples taken from sapwood and heartwood stakes.

than did their corresponding earlywood zones. The maximum concentration in earlywood was 0.33 lbs/ft³ in contrast to a maximum of 0.17 lbs/ft³ in the latewood. Sapwood earlywood had slightly greater amounts of total and cell-wall PCP than did the heartwood earlywood. This difference was much less than the difference in concentrations between earlywood and latewood.

DISCUSSION

It was previously supposed that deposition of PCP into the cell walls of wood occurred by a slow diffusion process following treatment, and that increasing levels of cell-wall PCP would be measured as the length of time after treatment increased. If deposition were diffusion-controlled, the amount of cell-wall PCP would also increase as storage temperature increased because the rate of most diffusion phenomena increase with increasing temperature. The present study shows that there is as much cell-wall PCP 2 days after treatment as at 180 days after treatment. This would indicate that deposition of PCP into the cell wall occurs mostly during the treating process itself, and therefore suggests that the amount of deposition may be controllable.

It has been further suggested that PCP left after extraction with a nonswelling solvent may be the result of precipitation or a chemical reaction with wood substance. The fact that PCP is a weak acid makes this hypothesis a possibility. The prior finding, however, that cell-wall PCP can be completely removed by extraction with a swelling but neutral solvent such as methanol would suggest that no reaction has taken place but, rather, that the PCP has simply entered into the void structure of the cell wall (Resch and Arganbright 1971). The phenomenon might therefore be classified as a Type 3 treatment as proposed earlier.

The mechanism by which PCP deposition from a nonswelling carrier occurs is not known and the extent to which it oc-

TABLE 3. *Minimum and maximum PCP concentrations in individual stakes*

	Minimum	Maximum	Average for all stakes
Sapwood Stakes			
Total PCP (lbs/ft³)	0.22	0.40	0.30
Cell wall PCP (lbs/ft³)	0.09	0.30	0.21
Cell wall PCP (%)	34.3	100.00	72.2
Heartwood Stakes			
Total PCP (lbs/ft³)	0.14	0.33	0.20
Cell wall PCP (lbs/ft³)	0.02	0.27	0.15
Cell wall PCP (%)	45.0	100.00	74.9

TABLE 4. *Total and cell-wall PCP concentrations in earlywood and latewood portions from five treated stakes six months after treatment*

	Earlywood	Latewood
Heartwood		
Total PCP (lbs/ft³)	0.27	0.16
Cell wall PCP (lbs/ft³)	0.21	0.14
Per cent cell-wall PCP	77.8	87.5
Sapwood		
Total PCP (lbs/ft³)	0.32	0.16
Cell wall PCP (lbs/ft³)	0.28	0.13
Per cent cell-wall PCP	87.5	81.3

curs in other similar processes has not been clearly established. The findings of Leutritz (1971) of "fixed" PCP after pentapetroleum oil treatment would indicate that the phenomenon is not unique to LPG treatment, although much lower levels of fixed PCP were measured in the oil carrier system than in the LPG treatment.

Incorporation of a toxic chemical into the cell wall may affect ultimate service life in two different ways: it may affect long-term preservative permanence, and it may affect the pattern of fungal attack (or the threshold limit). Several recent papers on poles treated with an LPG system would indeed indicate that presence of a toxic chemical in the cell wall is advantageous (Arsenault 1970b; Davies 1971).

SUMMARY

1. Four different types of preservative distribution in wood were proposed.
2. A significant portion of the total PCP impregnated into the sapwood and heartwood of Douglas-fir stakes via an LPG carrier system appears to be deposited in the cell wall.
3. The amount of PCP deposited in the cell wall did not change with increasing time after treatment.
4. Neither storage temperature nor wood moisture content after treatment were found to affect the amount of cell-wall PCP
5. Cell-wall PCP levels increased as total PCP content increased.
6. Cell-wall PCP when expressed as a proportion of total PCP was approximately the same in earlywood and latewood, although total PCP content in latewood tissue was much lower than in corresponding earlywood.
7. Wide variations in the amount of cell-wall PCP was observed in serially matched specimens, although their total PCP content was reasonably constant.

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