Pressure treatment of wood with emulsifiable preservative systems

H.M. Barnes

Abstract

Southern pine (*Pinus* spp.) veneer peeler cores were treated with two new water-dispersible preservative formulations based on pentachlorophenol (PWD) and zinc naphthenate (ZWD). The Lowry empty-cell process was chosen for comparison with the Bethell full-cell process. Results indicated that either system could be used with conventional treating-plant equipment and procedures. Heating the ZWD preservative during treatment did not significantly improve treatment.

Currently, most treated wood used in the United States is treated with one of three broad-spectrum preservatives: creosote, pentachlorophenol, or inorganic arsenicals. Compounds under active consideration as wood preservative biocides include alkylammonium compounds, sulfonamides, tetrachloroisophalonitrile, salicylanilide derivatives, benzothiozoles, isothiazolinones, salts of the naphthenic acids, and 3-iodo-2-propynyl butyl carbamate. Detailed reviews of these compounds and their potential as wood preservatives can be found in the literature (4,7,13-15).

Environmental concerns, concurrent with the high cost and short supply of petroleum, have led to increased research and development of new preservative systems using water as the carrier system. Improvements in dispersion and solution technology have led to aqueous systems. In the early 1980s, the Mississippi Forest Products Laboratory initiated a series of studies to examine the use of emulsified systems to treat various commodities. Emulsion systems can reduce the usage of petroleum by up to 85 percent (9,10,12). Treatability trials with emulsifiable penta and zinc naphthenate systems have proven successful for pole stock (3), hardwood peeler cores (5), and log-home logs (6). While not approved for ground-contact usage, these two systems are examples of the use of emulsion technology to disperse organic/organometallic biocides in aqueous carrier systems rather than in oil. The recent success in Australia with pigmented emulsifiable creosote systems is indicative of the flexibility emulsion systems offer in terms of preservative system formulation (8).

This paper describes the treatability of pine peeler cores with emulsified formulations. These cores are generally of low quality and contain a high percentage of heartwood and juvenile wood. Some cores are used as fence posts, but AWPA (1) standards require a higher retention for peeler cores used as posts. Southern pine peeler cores from veneer operations are generally cut into low-grade dimension stock or slabbed for treatment and used as landscape timbers.

Experimental procedure

Materials

Southern yellow pine (*Pinus echinata* Mill. or *P. taeda* L.) plywood peeler cores were selected for treatment. All material was supplied in the green state in 2.6 m lengths. Some peeler cores were slabbed to 90 mm in thickness to simulate landscape timbers. The slabs were retained for treatment as quarter-round fencing boards. Cores ranged from 115 to 150 mm in diameter and were cut into matched halves (122 cm). A central disk was retained for determination of sapwood depth (2). Average sapwood depth was 35 mm as determined using benzidene dihydrochloride indicator. Peeler cores were assigned to individual charges in such a fashion as to minimize the effect of heartwood content on individual charges.

Preservative formulations

Water-dispersible zinc naphthenate (ZWD) treating emulsions were made from a commercial concentrate (M-Gard 550, Mooney Chemicals, Inc., Cleveland, Ohio)[1] containing 63 percent zinc naphthenate (8% Zn as metal) and 37 percent inert ingredients by diluting with water while agitating. The nominal treating emulsion concentration was 0.2 percent zinc (as metal), unless otherwise noted. Pentachlorophenol emulsions (PWD) were prepared from a commercial concentrate (Penta-sperse, Chapman Chemicals, Memphis, Tenn.)[1] containing 25 percent total chlorinated phenols. The nominal emulsion strength was 5 percent chlorinated phenols.

Conditioning schedules

Samples were conditioned prior to treatment using one of the following three schedules:

Kiln-drying (KD). — Samples were kiln-dried using a schedule described by Kelso (11), which used a constant wet-bulb temperature of 52°C. Dry-bulb temperature was varied as follows: 54°C for 24 hours; 60°C for 24 hours; 66°C for 48 hours; 71.1°C for 48 hours; and 77°C for 24 hours. The average wood moisture content (MC) after drying was 17.5 percent.

Presteaming (S). — Some kiln-dried samples were presteamed using a cycle consisting of raising the temperature to 116°C over a 30-minute period and direct steaming the samples for 1 hour at 116°C. This process was followed by a final vacuum of −88 kPa for 30 minutes and immediate treatment with preservative.

Steam-conditioning (SC). — The cycle consisted of raising the temperature to 116° to 118°C over a 30-minute period, steaming for 4.5 hours, and applying a minimum final vacuum of −88 kPa for 1 hour. MCs before and after steaming were 65.7 and 54.9 percent, respectively. Steam-conditioning removed an average of 24 kg of water per m^3 of wood. After weighing the wood to determine moisture loss, the wood was immediately treated.

Treatment cycles

Treatment was done in a 46-cm diameter by 275 cm retort. Air pressure was applied through a filled scale tank mounted on a weighing platform. Gross absorption was measured by weighing the scale tank at various time intervals. Net retentions were calculated based on weight gain and sample volume. Fresh emulsion was added to the working tank after every 3 to 5 charges, as needed. The working tank emulsion was agitated slowly with a mechanical mixer. The wood volume, sample weight increase, and working tank preservative concentration before and after treatment were measured for each charge. Data from like charges were combined. In some ZWD charges, the preservative was preheated to 82°C using steam coils in the working tank. Tem-

---

[1] The use of trade or company names in this paper is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the Mississippi Forest Products Laboratory or Mississippi State University of any product or service to the exclusion of others which may be suitable.

TABLE 1. — *Summary of charge data for the investigation of the effect of initial air pressure and rate of pressure increase on the gross injection of a ZWD preservative into kiln-dried southern pine peeler cores.*

Initial air pressure	Rate of pressure increase	Injection		Refusal time
		Refusal	Net	
(kPa)	(kPa/min.)	------ (kg/m^3) ------		(min.)
0.0	206.8	257.6	256.0	170
0.0	34.5	334.4	256.0	155
69.0	34.5	264.0	208.0	170
207.0	34.5	201.6	147.2	170
345.0	34.5	124.8	96.0	130

perature was maintained using steam coils in the treating retort.

Bethell (full-cell). — Charges were first evacuated (−88 kPa) for 60 minutes and the retort was filled with preservative under vacuum. Next, the pressure was increased to 1,034 kPa over a 30-minute period and maintained until gauge refusal was obtained. Finally, the retort was vented to atmospheric pressure and the treating solution was returned to the working tank.

Lowry (empty-cell). — A transfer pump was used to flood the charge with preservative at atmospheric pressure. The pressure was then increased to 1034 kPa and maintained until refusal. Following removal of the preservative, the cylinder was vented to atmospheric pressure and the kickback was drained from the bottom of the cylinder. A 30-minute vacuum (−88 kPa) completed the cycle.

Rüping (empty-cell). — The Rüping cycle was identical to the Lowry cycle except that a specified initial air pressure was placed on the charge and held for 10 minutes prior to the introduction of the preservative.

Analyses

Two increment borings, nominally 5 mm in diameter, were taken through the widest faces at the midpoint of each sample and were segmented into 13-mm zones for assay gradient determination. Borings from similar charges were combined for assay.

ZWD emulsions were assayed using atomic absorption spectroscopy (Perkin Elmer Model 503 atomic absorption spectrometer, zinc cathode ray tube, acetylene/air mixture). A 0.1 to 0.25 g aliquot of emulsion was placed in a Vycor crucible and ashed in a muffle furnace for 1 hour at 600°C. The ashed residue was resuspended in hot concentrated nitric acid, diluted with water, and analyzed. To determine preservative gradients, a similar technique was performed on ashed wood borings. The assay of pentachlorophenol was done using high performance liquid chromatography as previously described (3).

Results and discussion

Preliminary investigation

A preliminary investigation was designed to determine the effect of initial air pressure and rate of pressure increase on the empty-cell treatment of peeler cores. This preliminary study indicated that a Lowry empty-cell process (no initial air pressure) (Table 1) yielded better injection curves than a Rüping process, with the injection rate decreasing significantly as the initial air pressure increased. Therefore, the Lowry

process was chosen for the remaining test.

Using a fast rate of pressure increase (345 kPa/min.) yielded faster initial uptake rate with the Lowry process, but the rate of injection fell off rapidly after the first 15 minutes of the cycle (Table 1).

Detailed study

Gross injection curves. — The data for all charges with the same preservative, conditioning method, and process were combined. A summary of the data is shown in Table 2.

Effect of conditioning method: For kiln-dried stock, the Bethell full-cell and Lowry empty-cell injection curves with the ZWD system were essentially identical. Presteaming did not improve the empty-cell treatment of kiln-dried stock. The two processes also yielded similar curves for steam-conditioned stock with the Lowry curves being slightly above those for the Bethell treatment. In comparing conditioning methods, the gross refusal loadings were much lower with the steam-conditioned stock, presumably due to the higher wood MC at the time of treatment.

As expected, net injections were much lower for the peeler cores treated by the Lowry process regardless of the conditioning method used. The difference between gross and net retention with the empty-cell process represents the excess preservative kicked back during the air expansion at the end of the treating cycle. This kickback seems abnormally high with steam-conditioned stock and might be due to the reduced solution viscosity following contact with the heated wood. These data would indicate a preference for using dried stock, unless adequate gradients can be obtained with steam-conditioned stock. Lowry treatment also seems feasible if a proper gradient can be obtained.

Steam conditioning of green stock was not included as a pretreatment for the PWD system because previous work (3) has shown that adequate treatment can be obtained using this method. However, the effect of presteaming of dry stock was unknown. Presteaming did not improve the gross injection of peeler cores treated by either process with the PWD system.

Surprisingly, gross absorption was greater with the Lowry treatment than with the Bethell treatment, but net retention was less. As with the ZWD system, these data indicate the preference for using dry stock. Lowry treatment seems feasible only if proper gradients are obtained.

Effect of heating: For kiln-dried stock, Bethell injection time was shortened considerably and gross injection improved slightly when heated preservative was used. Lowry injection time was about the same as with unheated preservative. While a higher gross injection was obtained with heated preservative, the net injection was considerably lower than that obtained with unheated preservative (Table 2).

With steam-conditioned stock, heating resulted in a lower gross injection for Bethell treatment and a higher gross injection for Lowry treatment. Net injections for Lowry treatment were about the same for heated and unheated preservative.

For all conditioning methods and processes tested, although heating had no deleterious effects on the ZWD emulsion, it also offered no obvious advantage.

Preservative gradients. — The gradients for ZWD preservative are presented in Figures 1 and 2. Figure 3 shows the gradients for the PWD preservatives.

ZWD gradients: Gradients for zinc (as metal) are shown in Figure 1 for each combination of process and conditioning method. The shape of all gradients was the same with a sharp reduction in the retention across the first assay zone followed by an almost linear gradient over the next 5 cm.

Gradients for steam-conditioned cores were slightly lower than those obtained with kiln-dried stock. The difference was substantial, suggesting that reasonable gradients can be obtained with steam-conditioned stock

TABLE 2. — *Summary of charge data for treatment of southern pine peeler cores using water-dispersible preservative formulations.*

Conditioning method/process[a]	No. of charges	Volume treated	Retention Refusal	Retention Net	Injection ratio	Time to refusal
		(m³)	(kg/m³)		(%)	(min.)
ZWD (0.2% zinc as metal)						
Kiln-dried						
Bethell	3	0.434	417.6	--	--	168
Bethell (82°C)	1		428.8	--	--	110
Lowry	4	0.560	361.6	292.8	81.0	180
Lowry (82°C)	1		393.6	260.8	66.3	190
Steam-conditioned						
Bethell	3	0.465	222.4	--	--	68
Bethell (82°C)	1		166.4	--	--	70
Lowry	3	0.466	265.6	96.0	36.1	75
Lowry (82°C)	1		281.6	104.0	36.9	75
Kiln-dried and presteamed						
Lowry	1	0.129	352.0	275.2	78.2	160
PWD (5.0% chlorinated phenols)						
Kiln-dried						
Bethell	1	0.136	363.2	--	--	90
Lowry	1	0.137	420.8	240.0	57.0	90
Kiln-dried and presteamed						
Bethell	1	0.136	361.6	--	--	90
Lowry	1	0.137	430.4	259.2	60.2	80

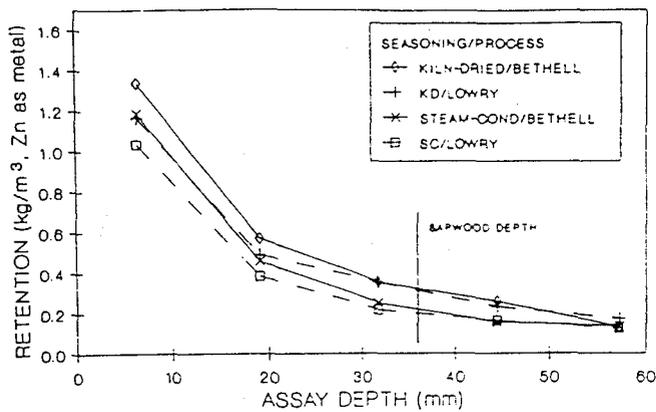[a] All results at ambient temperature unless otherwise noted.

Figure 1. — Effect of treatment process and conditioning method on ZWD gradients.
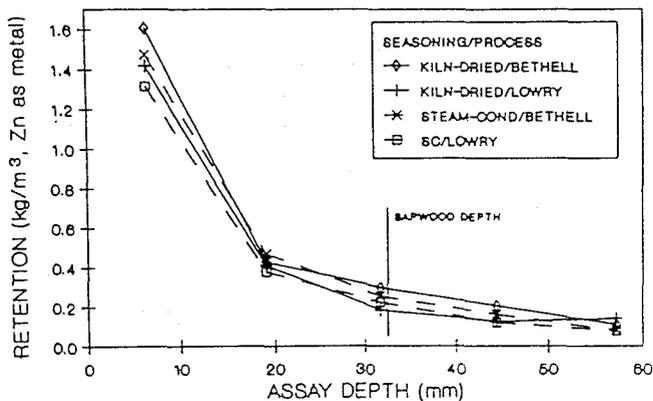

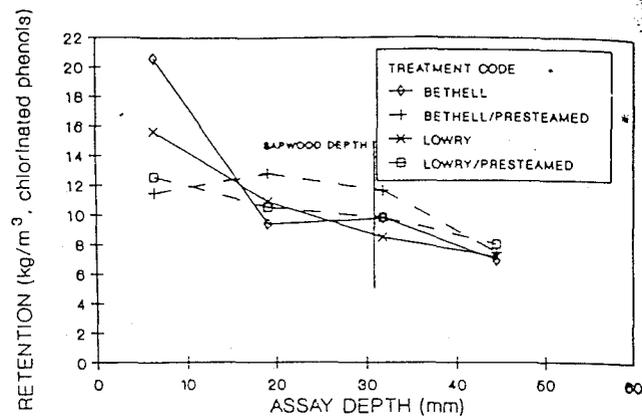Figure 2. — ZWD gradients obtained using heated preservative.

Figure 3. — Effect of treatment process and presteaming on PWD in kiln-dried pine peeler cores.

TABLE 3. — *Summary of charge data for treatment of pine quarter-round fencing boards with two water-dispersible preservative formulations.*[a]

Process	Volume treated	Retention		Time to refusal	Injection ratio
		Refusal	Net		
	(m³)	——— (kg/m³) ———		(min.)	(%)
ZWD (0.2% zinc as metal)					
Bethell	0.16	520.0	–	85	–
Lowry	0.16	424.0	283.2	90	66.8
PWD (5.0% chlorinated phenols)					
Bethell	0.17	422.4	–	90	–
Lowry	0.17	417.6	308.8	95	73.9

[a] All stock was kiln-dried and presteamed for 1 hour prior to treatment.

and Lowry treatment despite the lower net retentions as compared to kiln-dried cores or Bethell treatment. These data also indicate some preservative penetration into the heartwood of pine peeler cores (last two data points on the gradients in Fig. 1), albeit in amounts that are probably insufficient for adequate protection. Retention in this zone is approximately 0.25 kg/m³ or less.

Heating the preservative yielded slightly steeper gradients (Fig. 2) than those found using unheated preservative. Since heating the preservative did not improve the gradients, the use of heated preservative seems an additional expense that cannot be justified by these results.

PWD: With the exception of the Bethell treatment, these gradients were essentially linear (Fig. 3). Presteaming flattened the gradients for both Bethell and Lowry treated stock. For unsteamed wood, the Lowry gradient was flatter than its Bethell counterpart, indicating that adequate treatment can be achieved using an empty-cell process.

*Treatment of quarter-round fencing boards.—*Charge data for the treatment of presteamed quarter-round fencing boards are shown in Table 3. The generally higher refusal injections, as compared to the peeler cores (Table 2), reflect the much higher sapwood content of

this stock. Adequate preservative penetration and retention were noted, regardless of process or preservative system. Bethell injection was equivalent to or greater than the Lowry injection rate. Higher refusal injections were found for the ZWD system than for the PWD system. Treatment times for all processes were equivalent for both preservative systems.

Dispersion stability. — During the treating phase, all effluent streams except the vacuum condensate were recycled into the working tanks. No breaking of either emulsion prior to the addition of new make-up concentrate or during the treating process was noted. The dispersion stability was excellent and neither water-dispersible system offered operating or handling problems when used with standard treating plant equipment. As has been previously noted (3), mechanical agitation of emulsion systems would seem to be consistent with good treating practices.

Summary and conclusions

Similar injection curves were found for both Bethell and Lowry treatment of kiln-dried pine peeler cores with ZWD. This indicates that either process could be used successfully to treat kiln-dried stock. With steam-conditioned stock, the Lowry empty-cell treatment resulted in a low net retention as compared to the Bethell full-cell treatment of similar stock. Overall, the net injection of steam-conditioned stock was considerably lower than that for kiln-dried stock, regardless of process, which indicates that dry stock should be used. No overall improvement in treatability was realized when a heated preservative was used.

No discernible differences were noted in the shape of the ZWD gradients between the type of process or the conditioning methods. Gradients for kiln-dried stock were slightly higher than those for steam-conditioned stock, and Bethell gradients were slightly higher than those for the Lowry process. This was surprising given the difference in net retentions between kiln-dried and steam-conditioned stock. These data may also indicate that the ZWD formulation was stable within the wood structure and that no breaking of the emulsion occurred. Had the breaking of the emulsion systems occurred, one would reasonably expect an extremely high loading of preservative in the outer 20-mm zone, with very low retentions in the inner assay zones. Gradients were characterized by an initial drop across the outer assay zone followed by an almost linear gradient across the inner zones. Gradients for heated preservative were steeper than those for wood treated at ambient temperature. Sapwood penetration was complete, with some additional penetration into the heartwood.

Gross injection with the PWD system was greater for Lowry treatment. Net retention was lower with the PWD system than with the ZWD system. Presteaming kiln-dried stock did not improve gross injection but did tend to flatten the resultant gradients. Little difference was noted between PWD gradients treated by different processes. PWD gradients tended to be more variable than those for ZWD. Both ZWD and PWD formulations are compatible with existing treating-plant equipment and procedures.

This research illustrates the validity of pressure treatment with emulsifiable systems. Emulsions seem to offer greater flexibility in designing and formulating preservative systems and are likely to become increasingly important in the marketplace. New micro-emulsion technology, coupled with a better understanding of oil/biocide relationships and the development of new biocides, should produce emulsion systems that are viable in ground-contact. Future research should focus on the relationship between treating parameters and basic properties of emulsion systems, an area not addressed in this paper.

Literature cited

1. American Wood-Preservers' Association. 1985. Standard C-5 fence posts. In: Book of Standards. AWPA, Stevensville, Md.
2. _____. 1985. Standard M-2 for purchase of treated timber products. In: Book of Standards. AWPA, Stevensville, Md.
3. Barnes, H.M. 1983. Influence of processing variables on the treatment of wood with a water-dispersible penta formulation. Proc., Am. Wood-Preservers' Assoc. 79:213-221.
4. _____. 1985. Trends in the wood-treating industry. Forest Prod. J. 35(1):13-22.
5. _____. 1986. Treatment of hardwood peeler cores with water-dispersible preservative formulations. Wood and Fiber Sci. 18(3):397-412.
6. _____. 1986. Zinc naphthenate pressure treatment of pine logs for log homes. Forest Prod. J. 36(11/12):63-68.
7. Butcher, J.A. 1980. Current status of AAC preservatives in New Zealand. Inter. Res. Group on Wood Preservation. IRG/WP/3141.
8. Greaves, H., J.B. Watkins, and C.W. Chin. 1986. PEC-A family of improved oil-based preservatives. Record, 1986 BWPA Annual Convention.
9. Hatcher, D.B. 1980. Dura-Treet 11, a water dispersible pentachlorophenol. Proc., Am. Wood-Preservers' Assoc. 76:308-320.
10. _____. 1981. Dura-Treet 11, a water dispersible pentachlorophenol, update. Proc., Am. Wood-Preservers' Assoc. 77:50-57.
11. Kelso, W.C., Jr. 1974. Effect of filtration of creosote on treatability of southern pine pole sections. Proc., Am. Wood-Preservers' Assoc. 70:123-126.
12. Kirchner, R.P. and J.M. Taylor. 1983. A water dispersible oil-borne preservative for treatment of timber. Record, 1983 BWPA Annual Convention. pp. 26-37.
13. Nicholas, D.D. 1982. Preservative treated wood. In: Encyclopedia of Materials Science and Engineering. M. B. Bever, ed. Pergamon Press, N.Y.
14. _____. 1983. Trends in the use of chemicals for preservative treatment in wood. Advances in Production of Forest Products, AICHE Symposium Series 79(233):75-78.
15. _____ and A.F. Preston. 1984. Interaction of preservatives with wood. In: The Chemistry of Solid Wood, R.M. Rowell, ed., ACS Symposium Series 207, pp. 307-322.

Features

Technical Section

Departments

Cover

Go then, and plant a tree, lovely in sun
and shadow,
Gracious in every kind — maple and
oak and pine.
Peace of the forest glade, wealth of the
fruitful meadow,
Blessings of dew and shade, here-
after shall be thine.

The Planting of a Tree, Stanza 4
Marion Couthouy Smith (1853-1931)