

DISTRIBUTION OF TOXIC ELEMENTS IN DOUGLAS-FIR PLYWOOD TREATED WITH CZAA PRESERVATIVE

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ABSTRACT

Fifteen Douglas-fir plywood panels were treated with a copper-zinc-arsenic additive preservative (CZAA) in an ammoniacal solution in a full-cell process. Individual plies from the centers of the treated panels were assayed for CuO, ZnO, and As₂O₅ on the basis of Cu, Zn, and As content by atomic adsorption spectrophotometry. Retentions of preservative oxides and their distribution in the plies as judged from copper-containing compounds indicated that treated panels could be well protected against biodegradation.

Microscopic identification of species revealed that inner plies were made from fir, spruce, and hemlock. The preservative in them, monitored by copper-containing compounds, was evenly spread in the core plies.

Keywords: *Pseudotsuga menziesii*, *Abies* sp., *Picea* sp., *Tsuga* sp., *Larix* sp., preservative treatments, copper-zinc-arsenic-additive preservative (CZAA), plywood, atomic adsorption spectrophotometry, microscopic examination.

INTRODUCTION

Plywood treated with preservatives is becoming an important commodity in many applications, particularly in houses with wood foundations. In these constructions Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] plywood is used because of its satisfactory strength properties. The plywood must be treated with preservatives prior to its use. Inner plies of plywood panels are often made from softwood species such as spruce, fir, or hemlock: these belong mostly to the category of difficult-to-penetrate species. The plywood must retain high levels of preservatives [at least 9.6 kg/m³ (0.6 lb/ft³) of inorganic preservatives in oxide form], which penetrate with difficulty into refractory species in the inner plies. Treatment of such plywood is therefore a difficult task.

In our tests we were interested in the retention and distribution of ammoniacal CZAA preservative (copper-zinc-arsenic-additives) under industrial conditions. From an industrial charge of 1.6-cm (5/8-inch) Douglas-fir plywood, fifteen panels were randomly chosen and investigated. The aim of this work was twofold: first, to define retention levels of toxic elements and oxides and their penetration in individual plies of each panel, and second, to determine whether the preservative was evenly spread throughout the wood in the plies at the microscopic level.

MATERIALS AND METHODS

Fifteen panels of Douglas-fir plywood, five-ply, 1.6 cm (5/8 inch) thick, treated with CZAA (containing 0.6% w/w CuO, 0.9% w/w ZnO, and 0.7% w/w As₂OS) to a liquid preservative retention from 592.7 to 825.0 kg/m³ with the average 682.5 kg/m³ (37.0 to 51.5 lb/ft³, with the average 42.6 lb/ft³), under conditions described earlier (Krzyzewski et al. 1977) were fully air-dried and then analyzed for retention and distribution of toxic elements in individual plies. Microscopic exami-

nations were also carried out on individual plies to identify the wood species and to detect preservative penetration at the microscopic level.

All analyses were carried out on specimens 19 mm in diameter taken approximately 10 cm (4 inches) from the geometrical center of each full-sized panel. Individual plies from these specimens were separated by a scalpel and examined microscopically (from 15 to 20 microsections from each ply of the specimen). The larger, remaining part of each ply from the specimen was then milled in a Wiley mill and analysed by AAS for copper, zinc, and arsenic. Each of five plies was marked as follows: two surface plies as I and V (face and back), two plies below the surface plies as II and IV (cross-band) and the ply in the center as III (core).

Copper, zinc, and arsenic were detected by atomic adsorption spectrophotometry (by Perkin-Elmer Spectrophotometer Model 303) from solutions prepared from 16 N nitric acid extractions of powdered samples (0.5 g/10 ml of acid) from individual plies. The method, reported separately (Rak 1977), allowed complete extraction of each element (particularly arsenic, which is difficult to extract) from the treated wood substance of the isolated plies. Development and use of special, modified standards for arsenic determination was a necessary condition for its correct, quantitative determination (Rak 1977). Copper and zinc were determined with ordinary AAS standard solutions. An electrodeless discharge lamp for arsenic was used at a wavelength of 193.7 nm, with argon-hydrogen flame. A hollow cathode lamp was used for zinc and copper determination, at wavelengths of 213.9 nm and 324.7 nm respectively, with air-acetylene flame.

Retentions of toxic elements were expressed in kilograms per cubic meter of treated wood. Oxide retentions (CuO , ZnO , and As_2O_5) were calculated from these figures. Retentions of individual toxic elements (Cu, Zn, and As) were tabulated along with total oxide retentions. Oxide retentions in individual plies were statistically evaluated and average values (with minimum and maximum) were plotted for face and back plies, both cross-band plies and cores, which were combined from fifteen full-sized panels and plotted as histograms (Fig. 1). The species from which every individual ply had been derived was identified microscopically.

Fifteen to twenty cross sections, approximately $20 \mu\text{m}$ thick, cut from water-swollen pieces of individual plies, were stained with chrome azurol S (0.5% w/w in 5% aqueous solution of sodium acetate) to measure penetration of copper-containing compounds of the preservative into the walls of treated wood cells. To find out whether the microscopic stain can carry the copper compound from its original location inside the cell walls (after treatment) further into the wall during the staining process and therefore make an artefact we carried out the following test:

A small block of white spruce was treated under intermittent vacuum and atmospheric pressure with the CZAA preservative. After air-drying, the block was microtomed and cross sections were stained with chrome azurol S. One section was placed in the microscope and a boundary between treated and untreated cells was found. Continuous observation began immediately as a drop of stain was put on the wood section. A first micrograph was taken within 3 min after staining. The preservative did not spread any further during the next 30 min of continuous microscopic observation. Then a second matched micrograph was

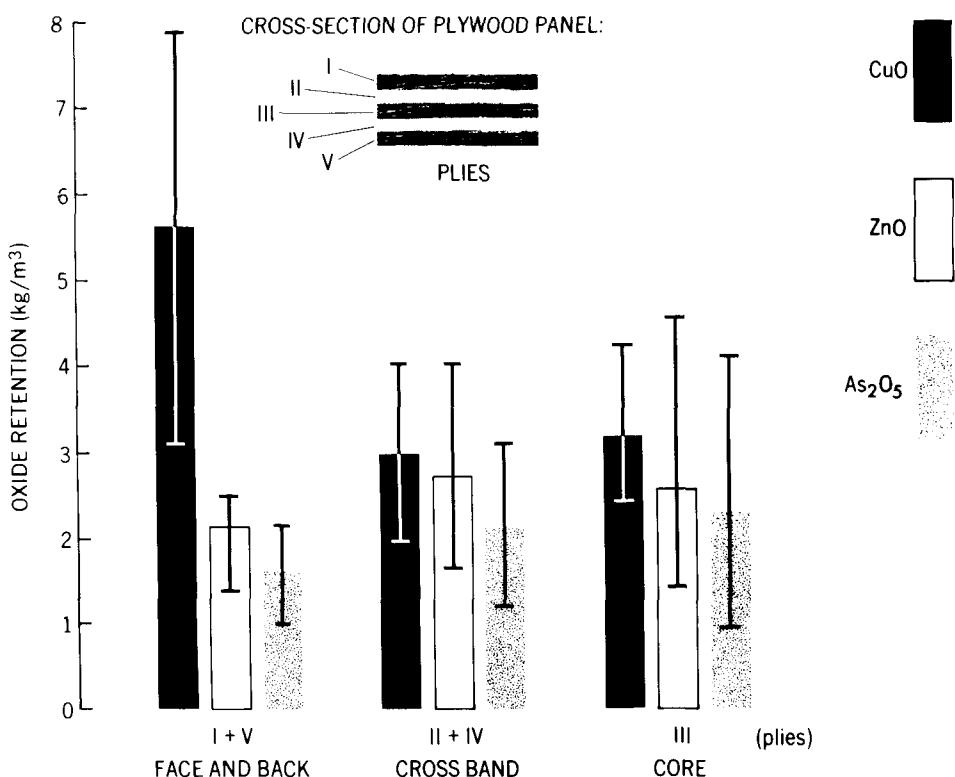


FIG. 1. Oxide distribution in combined plies of CZAA-treated Douglas-fir plywood. (The range is given by the minimum and maximum values.)

taken. Numerous groups of partially treated cell walls similar to those photographed were found on the other microsections.

Figure 2 shows an example of a group of cell walls after staining, a few of which (cell walls C, D, E, and F) were only partially penetrated by the preservative and stained dark blue. About half of the thickness of the walls of these cells was not penetrated at all, so the neighboring cells (A and B) were not penetrated. Figure 2 is a typical micrograph of the boundary between penetrated and nonpenetrated cell walls of spruce latewood. The observation confirmed that the staining technique distinguishes between fully and partially penetrated cell walls. It also confirms that the original location of the copper-containing compounds can be determined exactly, by the stain used for microscopic examination, without any further movement of the copper within the cell wall.

RESULTS

Microscopic examination of the plies

The face and back plies (I + V) were Douglas-fir, except that four veneers were larch. The inner (II + IV and III) plies were made from spruce, fir, or hemlock—all difficult-to-penetrate species according to MacLean (1935). Spruce was found in 17 plies (37.8%), fir in 24 plies (53.3%), and hemlock in 4 plies (8.9%). Results are given in Table 1.



FIG. 2. Microscopic cross section of CZAA-treated white spruce from the small block (not from the plywood) with unpenetrated (A and B) and partially penetrated (C, D, E, F) cell walls of latewood tracheids. Chrome Azurol-S staining.

Microscopic examination of the inner plies for distribution of copper-containing compounds from the center of the full-sized treated panels indicated that wood tissues in the plies were thoroughly penetrated.

Distribution of toxic elements in the plies

Retentions of toxic elements (in kg/m³, Table 2) in the face and back plies were from 2.52 to 6.30 for copper, from 1.14 to 2.01 for zinc, and from 0.63 to 1.39 for arsenic. In the cross-band plies, retentions varied from 1.47 to 3.15 for copper, from 1.33 to 3.21 for zinc, and from 0.79 to 2.03 for arsenic. Core retentions of copper varied from 1.94 to 3.36, zinc from 1.15 to 5.37, and arsenic from 0.63 to 2.67. These retentions vary over a wide range. When we calculate oxide retentions from these figures (Table 3), evaluate them statistically using a *t*-test, and plot them as histograms for the individual plies (Fig. 1), we obtain a definite trend: the copper oxide retention, high in the face and back plies, drops significantly (at the 99% probability level) in the cross-band plies and remains at the lower level in the cores. On the other hand, arsenic oxide, the retention of which is less than half that of copper in the face and back plies, significantly increases (at the 95% probability level) in the cross-band plies and stays at this higher level in the cores. The zinc oxide retention, low in the face and back plies, increases in the cross-band plies, but the increase is not significant at the 95% probability level.

TABLE I. Species identification in individual plies of treated Douglas-fir plywood panels.

Panel no.	Ply no.				
	I	II	III	IV	V
1	D	F	S	F	D
2	D	F	F	F	D
3	D	S	S	S	D
4	D	S	S	H	L
5	D	H	F	S	D
6	D	F	F	F	D
7	D	F	F	S	*
8	D	S	F	F	L
9	D	F	F	S	D
10	D	F	F	S	D
11	D	S	S	S	L
12	D	F	F	F	D
13	D	F	S	H	L
14	D	S	S	F	D
15	D	F	H	F	D

CODE:

D	Douglas-fir	[<i>Pseudotsuga menziesii</i> (Mirb.) Franco]
F	Fir	(<i>Abies</i> Sp.)
S	Spruce	(<i>Picea</i> Sp.)
H	Hemlock	(<i>Tsuga</i> Sp.)
L	Larch	(<i>Larix</i> Sp.)

* Missing specimen.

The largest difference between copper oxide on one hand and zinc oxide and arsenic pentoxide on the other is in the face and back plies, and narrows toward the center of the panels (See Fig. 1).

Oxides of all three toxic elements were combined for individual plies in each panel. The data (Table 2) show that total oxide retentions (kg/m^3) in the face and back plies varied from 7.03 to 11.78, in the cross-band plies from 5.37 to 10.26, and in the cores from 5.40 to 12.41. These data, particularly averages of total oxide retentions in combined plies, (9.28 for the face and back plies, 7.48 for the cross-band plies, and 8.01 for the cores), closely approach the total oxide retention ($9.6 \text{ kg}/\text{m}^3$, $0.6 \text{ lb}/\text{ft}^3$) required by CSA Standard 080-15 for treated plywood in ground contact exposures.

DISCUSSION

Microscopic examination of individual plies of the CZAA-treated Douglas-fir plywood was carried out on samples from the center of full-sized panels. This location is considered as the most difficult-to-reach by the penetrating preservative and therefore to be a significant position for evaluation of preservative penetration of the whole panel. The copper-containing compounds of the preservative, detected by microscopic examination, were present in all plies of all panels and were well spread throughout each ply. Although the spread of other elements (zinc and arsenic) was not microscopically tested, we presume that they also were well spread in each ply, even in variable amounts as detected by the AAS analysis. If the retentions of preservative oxides were higher as would be the case in treatments with higher contents of preservative salts, the product would

TABLE 2. Elemental and total oxide retentions in individual plies of CZAA-treated Douglas-fir plywood panels.

Panel no.	Ply no.	Element			Total oxides	
		Cu (kg/m ³)	Zn (kg/m ³)	As (kg/m ³)	(kg/m ³)	(lb/ft ³)
1	I + V	5.09	2.01	0.63	10.17	0.63
	II + IV	3.09	2.66	1.62	9.65	0.60
	III	2.83	1.30	1.10	6.69	0.42
2	I + V	3.47	1.34	0.66	7.03	0.44
	II + IV	2.72	1.74	0.97	7.07	0.44
	III	2.57	1.15	0.98	6.15	0.38
3	I + V	5.14	1.15	0.63	8.84	0.55
	II + IV	1.88	1.56	1.35	6.37	0.40
	III	2.31	5.37	0.98	6.07	0.38
4	I + V	3.15	1.91	1.39	8.44	0.53
	II + IV	1.78	1.61	0.98	5.75	0.36
	III	1.94	1.17	0.98	5.40	0.34
5	I + V	3.88	1.14	1.25	8.19	0.51
	II + IV	2.20	1.84	1.39	7.17	0.45
	III	2.41	1.80	1.39	7.38	0.46
6	I + V	2.52	1.93	1.25	7.46	0.46
	II + IV	3.15	3.15	2.03	8.66	0.54
	III	3.36	3.15	2.03	11.23	0.70
7	I + V	3.36	1.93	1.10	8.29	0.52
	II + IV	2.41	1.49	1.10	6.56	0.41
	III	2.83	1.36	1.27	7.19	0.45
8	I + V	4.94	1.35	0.97	9.35	0.58
	II + IV	2.57	2.31	1.62	8.56	0.53
	III	2.73	2.56	1.88	9.48	0.59
9	I + V	4.82	1.93	1.10	10.27	0.64
	II + IV	1.47	1.57	1.49	7.45	0.46
	III	2.57	2.18	1.62	8.60	0.54
10	I + V	4.88	1.53	1.10	9.68	0.60
	II + IV	2.10	1.93	1.39	7.16	0.45
	III	2.99	3.66	2.67	12.41	0.77
11	I + V	4.72	1.76	0.98	9.60	0.60
	II + IV	1.57	1.33	0.79	5.37	0.33
	III	2.10	2.93	2.42	9.99	0.62
12	I + V	6.30	1.57	0.98	11.35	0.71
	II + IV	2.88	3.21	1.73	10.26	0.64
	III	2.20	1.90	1.39	7.47	0.47
13	I + V	4.46	1.80	1.24	9.71	0.61
	II + IV	2.46	2.07	1.49	7.94	0.49
	III	2.73	1.94	1.39	7.96	0.50
14	I + V	6.03	1.94	1.20	11.78	0.73
	II + IV	2.31	2.07	1.62	7.95	0.50
	III	2.31	2.68	1.45	8.45	0.53
15	I + V	4.04	1.99	0.97	9.02	0.56
	II + IV	1.99	1.89	0.97	6.33	0.39
	III	2.04	1.69	0.63	5.63	0.35

TABLE 3. Oxide retentions in combined plies.

Plies	Statistic	Oxide		
		CuO (kg/m ³)	ZnO (kg/m ³)	As ₂ O ₅ (kg/m ³)
I + V	minimum	3.15	1.42	0.97
	average, \bar{x}	5.58	2.10	1.60
	maximum	7.89	2.50	2.12
	standard deviation, s	1.32	0.39	0.33
	coeff. var., %	23.67	18.48	20.42
II + IV	minimum	1.97	1.65	1.21
	average, \bar{x}	2.98	2.52	2.10
	maximum	3.94	3.99	3.11
	standard deviation, s	0.65	0.72	0.53
	coeff. var., %	22.52	28.45	25.07
III	minimum	2.43	1.43	0.96
	average, \bar{x}	3.18	2.56	2.27
	maximum	4.20	4.56	4.11
	standard deviation, s	0.49	1.41	0.88
	coeff. var., %	15.48	48.81	38.64

probably be sufficiently protected for ground contact exposures against wood-decaying fungi, such as Basidiomycetes.

However, under biodegrading factors we also include so-called soft rot, caused mainly by cellulose-decomposing microorganisms from the Ascomycetes and *Fungi imperfecti*. It was shown years ago (Findlay and Savory 1954) and confirmed more recently (Hulme and Butcher 1977) that preservatives containing large amounts of copper can be used successfully to protect wood against soft rot fungi that decompose material from the surface. Our analyses suggest that CZAA-treated plywood retained high levels of copper oxide in the face and back plies (on the average 5.6 kg/m³, 0.35 lb/ft³) and satisfactory levels of it in the cross-band plies and cores (on the average 3.0 kg/m³, 0.2 lb/ft³). Combining these findings with the established fact that copper is well fixed in CZAA-treated wood (Rak 1976), we presume that the distribution of copper in the CZAA-treated plywood may also offer a good chance of withstanding exposure to conditions favoring soft rot.

CONCLUSIONS

Analyses of 15 Douglas-fir plywood panels (1.6 cm, 5/8 inch) treated with CZAA preservative in an industrial treating plant show:

1. Oxide retentions in individual plies analyzed on specimens taken from the center of the panels were always highest for CuO, lower for ZnO, and lowest for As₂O₅.
2. From the face and back plies to the cross-band plies As₂O₅ and ZnO retentions increased while CuO retentions decreased. This difference between the face and back plies (I + V) and the cross-band plies (II + IV) was statistically significant for CuO and As₂O₅. Variations in oxide retentions from the cross-band plies to the cores (III) were not statistically significant for all oxides.

3. The face and back plies retained substantially more CuO than As₂O₅. However, this difference was smaller in the cross-band plies.
4. The inner plies were made from difficult-to-treat species: spruce, fir, and hemlock. Microscopic examinations of these plies showed that the copper-containing compounds of the preservative were evenly spread even in the cores.
5. Retention of toxic elements in individual plies and the spread of preservative at microscopic levels as monitored by copper-containing compounds would suggest good protection of CZAA-treated plywood against biodegradation. Treatments with higher salt concentrations in the treating solution would probably result in oxide retentions sufficient for protection of the plywood even in ground contact exposures.
6. The chrome azurol-S staining method appeared to be reliable for detection of copper-containing compounds penetrating cell walls to various degrees, and was suitable for microscopic examination of CZAA-treated wood.

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The Wood Technician: A Comment

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1. Improved communication with students and teachers in the public system regarding the profession of wood technology.
2. More direct influence upon the direction of wood technician programs.

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