Wood and Fiber, 9(4), 1978, pp. 262–269

EFFECTS OF WOOD PRESERVATIVES ON PHYSICAL PROPERTIES OF WOOD II. EFFECTS OF DIFFERENT SALT LOADINGS OF COPPER-CHROME-ARSENIC COMPOSITION

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(Received 15 May 1977)

ABSTRACT

Effect of different salt loadings of copper-chrome-arsenic (CCA) preservative on shrinkage, swelling, and equilibrium moisture content at various relative humidities has been reported for *Pinus roxburghii* and *Mangifera indica*. At very low salt retentions, treated wood shows excessive shrinkage and swelling, which reaches a maximum and then falls off with increasing salt loadings. The two woods differ as to the position of these maxima. At higher retention levels, shrinkage and swelling are reduced, but the wood becomes more hygroscopic. The increased hygroscopicity is probably due to CCA salt and the additional water is held by the salt molecules deposited in the cell lumens. At low salt retentions, equilibrium moisture content is lowered at all relative humidities. The general sigmoid character of the adsorption curves is maintained at all levels of retentions.

Keywords: *Pinus roxburghii, Mangifera indica*, salt retention, hygroscopicity, equilibrium moisture content, dimensional stability, shrinkage, swelling, preservation, copper-chrome-arsenic preservatives.

INTRODUCTION

Water-soluble fixed type preservatives have numerous advantages over other types of preservatives. Copper-chrome-arsenic (CCA) preservative composition, first developed in 1933 by Dr. Kamesam (Indian Patent No. 19859), established a broad spectrum of use over the years. Many variations of this original composition are in use all over the world. Despite its excellent performance against biological deterioration, consumers have found that CCA treated wood tends to check more in service compared to untreated wood, and because of this behavior CCA treatments may impair the shape retention property of wood members. Mackay (1973) confirmed this point and found that CCA treatment increased the incidence of check formation and the degree of this degrade increased with increased kiln drying temperatures.

Water-soluble salts reduce the shrinkage and swelling of wood because of their bulking action in the cell wall (Stamm 1934, 1964, 1974). Since components of CCA have also been found to be distributed in the cell wall (Petty and Preston 1968; Greaves 1974), theoretically such a treatment should induce partial dimensional stabilisation and the tendency to check or distort should, therefore, reduce with treatment. Treatment with boron fluoride (BF) demonstrated decreased tendency for wood to check during drying (Bavendamm et al. 1963). Chromium-fluoride (CF) was found to have a bulking effect in pine wood causing a reduction of about 13% in tangential shrinkage at a retention level of 9 kg per cu m (Burmester 1970). However, Gilfedder et al. (1965) reported that eucalyptus poles treated with CCA to salt retentions of 1.3 pcf (21 kg per cu m) checked more than their untreated counterparts. In an earlier study, it was

TABLE 1. *Influence of salt retention on shrinkage-swelling behavior of CCA treated chir and mango*

Wood species	Percent solution used for treatment	Salt retention Oven-dry (kg/m³)	Salt retention (Percent wt. of wood)	Shrinkage (Swollen to oven-dry) (%)	Swelling (oven-dry to reswollen) (%)
	—	Control	—	6.68	7.16
	0.30	1.70	0.0032	6.97	7.95
	0.65	3.76	0.0071	7.12	8.13
Chir	1.00	5.88	0.0111	6.88	7.91
(*Pinus*	1.30	7.71	0.0145	6.77	7.63
roxburghii)	2.00	11.70	0.0221	6.60	7.42
	2.65	15.77	0.0298	6.57	7.37
	4.00	24.29	0.0458	6.30	7.25
	5.00	29.20	0.0551	6.12	6.98
	—	Control	—	5.68	6.03
Mango	0.85	4.90	0.0098	5.80	6.37
(*Mangifera*	1.10	5.81	0.0116	5.80	6.41
indica)	1.35	7.45	0.0149	5.86	6.47
	2.05	12.27	0.0245	5.77	6.35
	2.70	15.60	0.0312	5.51	6.14

found that treatment of various wood species with the two most commonly used water-soluble compositions, CCA (copper-chrome-arsenic) and ACC (acid-copper-chrome), to heavy retentions resulted in appreciable reductions in shrinkage and swelling between fully swollen and oven-dry conditions (Kumar and Jain 1976).

In actual practice, several salt retention levels are used depending upon the end-use and location of the treated wood product. This investigation was carried out to evaluate the effect of various salt loadings on the sorption-shrinkage-swelling behavior of wood. One softwood—chir (*Pinus roxburghii* Sargent) and one hardwood—mango (*Mangifera indica* Linn.) were chosen for the study because of their easy-to-treat character and also widespread use for various purposes after preservative treatment.

MATERIALS AND METHODS

Defect-free, flat-sawn boards of chir (*Pinus roxburghii* Sargent) and mango (*Mangifera indica* Linn.) were obtained from trunks of sound trees, felled from the New Forest area in Doon Valley in Northern India. To get true tangential samples, a 7.5-cm-wide panel having its faces tangent to the growth rings was machined to 2.5-cm thickness and 1.25-cm-wide strips were cross-cut from each panel to obtain samples sized 7.5 cm × 2.5 cm × 1.25 cm, the largest dimension being in the tangential direction and the smallest in the axial. Eight positions for measuring the tangential dimensions were marked on both radial faces. For mango, four samples were chosen randomly for each treatment level. In chir, three samples were treated for each retention level to cover a wider range of salt retentions. An equal number of samples were treated with water in each case to serve as controls. The salt loading was controlled by varying the concentration of the impregnating solution, which was approximated from the quantity of water impregnated under similar conditions (Table 1). The treating solutions were made from a 10% stock-solution of CCA having the following composition using laboratory grade reagents:

As_2O_5 $2H_2O$ — 1 part
$CuSO_4$ $5H_2O$ — 3 parts
$Na_2Cr_2O_7$ $2H_2O$ — 4 parts.

Treatment was carried out under a vacuum of about 65 cm Hg in a desiccator and the salt retentions were calculated from the percentage strength and amount of solution absorbed by the individual samples during treatment, calculated on swollen volume basis. Tangential dimensions in swollen condition were measured to 1/1000 cm along the marked positions (on radial faces) with a dial gauge jigged suitably on a sliding mechanism. Treated samples were stacked under weight and allowed to air-dry to about 10% moisture content over a period of about one month, to allow fixation of the preserving chemicals in the wood. These were then dried slowly to 5% moisture content in a humidity chamber and finally oven-dried at 105 C for 24 hours and weighed. Tangential dimensions in oven-dry condition, after cooling the samples to ambient room temperature over dried silica gel, were measured on exactly the same locations used for swollen condition measurements. All samples were once again swollen in water and swollen dimensions were measured. The samples were allowed to come to equilibrium with atmospheric conditions, stacked under load to prevent warping, twisting, etc. These were finally conditioned at various relative humidity conditions in a humidity chamber to study the influence of salt on the equilibrium moisture content (EMC) pattern and swelling behavior. Shrinkage was calculated as percent of the initial dimensions swollen in salt solutions and swelling values were obtained as percent of the oven-dry dimensions as follows:

Shrinkage (%) = [(Swollen dimension) – (Oven-dry dimension)/ (Swollen dimension)] × 100

Swelling (%) = [(Conditioned or swollen dimension) – (Oven-dry dimension)/ (Oven-dry dimension)] × 100

RESULTS AND DISCUSSION

Shrinkage and swelling observed in samples, treated to different salt loadings between oven-dry and swollen conditions, are given in Table 1 for the two wood species studied. Both species present a similar trend, i.e., at very low salt retentions, shrinkage and swelling values exceed the respective values for untreated controls, reach a maximum at retention levels of about 4 kg per cu m for chir and 8 kg per cu m for mango and with further increase in retentions, shrinking and swelling values fall gradually.

The rate of increase and decrease and the position of maxima in shrinkage and swelling with respect to salt retentions are not the same for the two species, the change being steeper for chir than mango. These differences are attributed to species differences, particularly with respect to ease of penetration of chemicals into the cell wall. Internal cell wall layers of some hardwoods are reported to be resistant to penetration by CCA type salts (Dickinson 1974).

Hygroscopicity and resultant swelling of wood are largely attributed to hydroxyl groups located on lignin and polysaccharide chains (Tarkow et al. 1950). Species differences are, therefore, likely to arise because of differences in chemical nature of wood and possibly also from the number of hydroxyl groups that are responsible for such changes and the number which actually get eliminated during the course of reaction with preserving chemicals.

The exact pathways of fixation reactions are not known. However, it is postulated that the trivalent chromium complexes formed during fixation are polynuclear, which are stereochemically suited to cross-link cellulose fibers (Nicholas 1972). At low salt retentions, these cross-links are probably missing and so cannot produce any dimensional stability. Since hemicelluloses form a supporting matrix for the cellulose and lignin framework, their partial removal produces simple displacement effects and may change the stress distribution in the cell wall causing greater shrinkage (Runkel and Luthgens 1956). Increased shrinkage at low salt levels may thus result from the following reasons:

(i) Rupture of linkages between cellulose-hemicellulose-lignin system, resulting in an increase in the number of hydroxyl groups for possible reaction with preserving chemicals,

(ii) Partial depletion of hemicellulose with acidic solutions of the preserving salts.

It was observed that reswollen dimensions after fixation of the preserving chemicals were slightly greater than the initial swollen dimensions obtained immediately after treatment with CCA solutions. The increase was only 0.4 and 0.2% of the initial swollen dimensions for chir and mango respectively. In fact, the wood continued to swell for the first three days after treatment with CCA. Since dimensions of controls treated with water stayed constant, the increase cannot be attributed to relaxation of growth stresses, and is most probably caused by the action of chemicals on

TABLE 2. *EMC—Swelling behavior of CCA treated chir and mango at various relative humidity conditions*

Wood species	Salt retention (kg/m³)	Conditioned at 35 C and								M.C. diff. between 70% R.H. and 85% R.H.
		30% R.H.		70% R.H.		85% R.H.		90% R.H.		
		EMC (%)	Swelling (%)	EMC (%)	Swelling (%)	EMC (%)	Swelling (%)	EMC (%)	Swelling (%)	
Chir	Control	5.81	1.71	12.20	3.60	17.69	5.10	20.90	5.93	5.49
	1.70	5.60	1.84	12.13	3.70	17.20	5.50	20.77	6.19	5.07
	3.76	5.79	2.15	12.08	3.83	17.32	5.42	20.61	6.30	5.24
	5.88	5.90	1.88	12.50	3.71	17.83	5.38	20.58	6.14	5.33
	7.71	5.91	1.65	12.51	3.41	17.80	5.10	20.54	5.81	5.29
	11.70	5.95	1.52	12.54	3.38	17.89	5.02	20.70	5.78	5.35
	15.77	6.20	1.52	12.80	3.36	18.15	4.80	20.87	5.72	5.35
	24.29	6.46	1.50	12.87	3.30	18.30	4.76	21.00	5.65	5.43
	29.20	6.66	1.43	13.27	3.20	18.36	4.68	21.11	5.47	5.09
Mango	Control	5.12	1.35	10.40	2.75	15.56	4.06	18.93	4.93	5.16
	4.90	5.03	1.43	10.20	2.89	15.29	4.21	18.55	5.10	5.09
	5.81	5.45	1.27	10.70	2.62	15.77	4.04	18.95	4.93	5.07
	7.45	5.48	1.25	11.23	2.74	16.37	4.05	19.10	4.94	5.14
	12.27	5.51	0.98	11.57	2.62	16.70	3.99	19.13	4.80	5.13
	15.60	5.68	0.90	11.70	2.60	17.35	3.84	19.24	4.69	5.65

wood constituents and change of stress distribution within the cell wall as observed by Runkel and Luthgens (1956) in their studies.

Various workers reported partial dimensional stabilisation of wood with waterborne preservatives and fire retardant compositions (Burmester 1970; Stamm 1974; Kumar and Jain 1976). These studies were carried out at very high salt retentions resulting in bulking of the cell wall. Chudnoff (1955), however, reported that significant reductions in shrinkage were obtained even at salt retentions of 0.006 g/cm³ of zinc chloride. No data on dimensional behavior of wood treated with low salt retentions of CCA are reported. Excessive checking of CCA treated wood has, however, been reported by many workers (Gilfedder et al. 1968; Mackay 1973). Kauman (1960) observed that lower concentrations of various single salts, e.g. sodium chloride, zinc chloride, etc., tended to increase total shrinkage of *Eucalyptus camaldulensis* and such excessive shrinkage resulted from collapse. Mango and chir normally do not collapse during drying and no collapse of cells could be detected in treated samples. Since CCA salts react with wood substance, causing a slight increase in swollen dimensions, the increase in shrinkage can be attributed to this increase as total shrinkage calculations are based on swollen dimensions, measured after treatment with CCA.

TABLE 3. *Analysis of variance for swelling as affected by conditioning and CCA loadings*

Wood species	Source of variation	DF	Sum of squares	F Ratio
Chir	Relative humidity (R)	4	538.74	2541.22***
	Salt retention (S)	8	7.63	17.92***
	Interaction (R × S)	32	1.82	1.08[N.S.]
	Error	90	4.75	
	Total	134		
Mango	Relative humidity (R)	4	371.02	2318.87***
	Salt retention (S)	5	1.59	7.95***
	Interaction (R × S)	20	.80	1.00[N.S.]
	Error	90	3.64	
	Total	119		

N.S. Not significant
*** Significant at 0.1% level.

TABLE 4. *Statistical analysis of influence of salt retention level on swelling of wood*

Wood species	CCA retention kg/m^3	Average swelling at all conditions %	Difference with control	Significance
Chir	Control	4.703	—	
	1.70	5.021	+.318	**
	3.76	5.059	+.356	**
	5.88	5.005	+.302	**
	7.71	4.719	+.016	N.S.
	11.70	4.627	−.076	N.S.
	15.77	4.555	−.148	N.S.
	24.29	4.491	−.212	*
	29.20	4.354	−.349	**
Mango	Control	3.822	—	
	4.90	4.000	+.178	**
	5.81	3.848	+.026	N.S.
	7.45	3.893	+.071	N.S.
	12.27	3.744	−.078	N.S.
	15.60	3.632	−.190	**

* Significant at 5% level of probability.
** Significant at 1% level of probability.
N.S. Not significant.

TABLE 5. *Analysis of variance for equilibrium moisture content as affected by conditioning and CCA retentions*

Wood species	Source of variation	DF	Sum of squares	F Ratio
Chir	Relative humidity (R)	3	2617.70	3815.35***
	Salt retention (S)	8	16.08	8.79***
	Interaction (R × S)	24	753.59	137.3***
	Error	72	16.47	
	Total	107		
Mango	Relative humidity (R)	3	2587.22	44454.10***
	Salt retention (S)	5	31.96	329.38***
	Interaction (R × S)	15	12.61	43.30***
	Error	72	1.40	
	Total	95		

*** Significant at 0.1% level of probability.

Increase due to this is, however, marginal and a larger part of the shrinkage is attributed to reasons described earlier.

At higher salt loadings, more chemical becomes available to bulk or cross-link (or both) the cell wall resulting in an overall reduction in shrinkage and swelling of wood. Similar results were obtained with other wood species (Kumar and Jain 1976).

Dimensional changes and the corresponding equilibrium moisture content (EMC) of treated and untreated wood samples when conditioned to various relative humidity conditions are given in Table 2. Trends are similar for both species at all relative humidities; samples having low salt retentions tend to swell more than the controls and swelling falls off with increasing salt retentions. Analysis of variance shows that salt retention has a significant effect on swelling at the 0.1% level of significance for both species (Table 3). The interaction of conditioning to various relative humidities and salt retention level has no significant effect. Dimensional changes at very low salt retentions (4.9 kg/m^3 for mango and up to 5.88 kg/m^3 for chir) are significantly different from those of the control, there being an increase in swelling. Swelling of samples having salt loadings of 7.71 to 15.77 kg/m^3 in chir and 5.81 to 12.27 kg/m^3 in mango is not significantly different from that of the controls. The effect again becomes statistically significant beyond these retentions, when a decrease in swelling occurs (Table 4).

Equilibrium moisture content of treated wood at various relative humidity conditions is also affected by CCA retentions. Conditioning has a combined effect with amount of salt to affect EMC (Table 5). In chir the effect is significant only at very high retention levels, whereas EMC of mango is affected significantly at all retention levels studied (Table 6). In both cases, wood samples treated to low salt retentions tend to have lower EMC than those of controls. This may not be due to bulking effect, which should have been accompanied with a corresponding decrease in shrinkage. It is probable that hemicelluloses, which are more hygroscopic than the other major constituents of wood

TABLE 6. *Statistical analysis for influence of salt retention level on equilibrium moisture content of wood*

Wood species	CCA retention kg/m³	Average of EMC at all conditions	Difference with control	Significance
	Control	14.15	—	
	1.70	13.93	−.22	N.S.
	3.76	13.93	−.22	N.S.
	5.88	14.20	−.05	N.S.
Chir	7.71	14.19	+.04	N.S.
	11.70	14.27	+.12	N.S.
	15.77	14.50	+.35	N.S.
	24.29	14.65	+.50	**
	29.20	14.85	+.68	**
	Control	12.50	—	
	4.90	12.24	−.26	**
Mango	5.81	12.72	+.22	**
	7.45	13.03	+.53	**
	12.27	13.23	+.73	**
	15.60	13.49	+.99	**

** Significant at 1% level of probability.
N.S. Not significant.

(Christensen and Kelsey 1958), are preferentially attacked by acidic solutions of preservatives and lose their hygroscopicity. Heat polymerisation of hemicelluloses in the presence of inorganic salts as reported by Stamm (1959) may also render them less hygroscopic. At higher salt retentions, a major part of CCA remains in the cell lumens and the increase in EMC results from the hygroscopic nature of the CCA composition, which far exceeds the effects due to chemical modification of cell-wall constituents and bulking. The higher EMC of CCA-treated wood is in agreement with earlier results (Keating and Gilfedder 1965; Kumar and Jain 1976).

Bendtsen (1966) observed that water in salt-treated wood may be considered to exist in two places—in the cell wall representing the normal equilibrium moisture content of untreated wood, and additional moisture held by the hygroscopic chemical. On this basis and on the assumption that the moisture content-relative humidity behavior of both wood and salt is similar, he proposed that total moisture content of treated wood would be a function of the wood as well as the salt-wood ratio as follows:

$$M = 100\,(A + BX)$$

where M is the moisture content of treated wood in percent, A is the EMC of untreated wood per unit weight of wood, B is the EMC of salt per unit weight, and X is the amount of salt per unit weight of

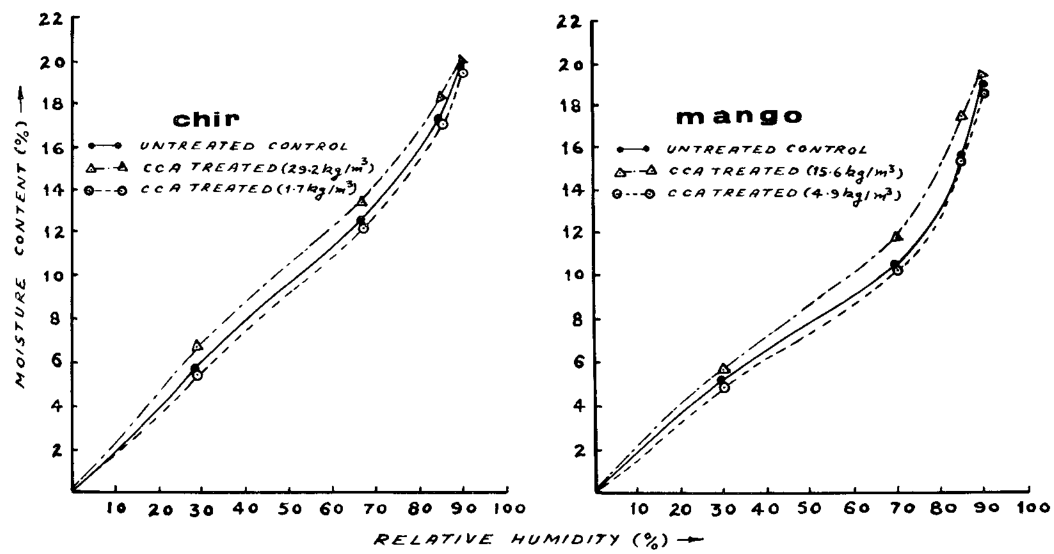

FIG. 1. Sorption curves for treated and untreated chir and mango wood.

dry wood. Up to a salt-wood ratio of 0.1, almost linear curves were obtained for ammonium sulfate, zinc chloride and sodium chloride, proving the validity of the above relation. This also implies that no significant bulking of the cell wall occurs at up to 10% loading of the salt, as bulking should have resulted in decreased EMC of treated wood. The lowering of EMC in case of wood treated with low CCA retentions is thus attributed to reasons other than bulking.

The EMC-relative humidity curves for the two species at very low and high salt retentions are shown in Fig. 1. The general sigmoid character of the curve (as in the case of untreated wood) is retained irrespective of whether there is an increase or decrease in moisture content due to treatment. It appears that the basic surface and capillary characters of wood, responsible for sigmoid adorption curves, are not changed and the effect of CCA is not different from that of many other single salts (Bendtsen 1966), although gross capillary and surface properties such as water vapor diffusion rates and free water uptake are reduced by CCA treatments (Mackay 1973; Kumar and Jain 1976).

CONCLUSIONS

Treatment of wood with CCA type preservatives to salt retentions used for indoor use increases its dimensional changes with changing EMC conditions, although EMC of treated wood is reduced. This may be the cause of the increased incidence of checking of CCA treated wood when exposed to alternate wetting and drying. Treated wood in such places must be suitably protected against water. At higher retention levels, dimensional changes are reduced although hygroscopicity is increased.

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