FIELD PERFORMANCE OF AMMONICAL COPPER LIGNIN COMPLEX A (CLC-A) TREATED WOOD AFTER POST-TREATMENT PROCESSING

S Tripathi

Forest Products Division, Forest Research Institute, Dehra Dun, India. E-mail: tripathiak04@yahoo.co.in

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TRIPATHI S. 2009. Field performance of ammonical copper lignin complex A (CLC-A) treated wood after post-treatment processing. This study reported the effects of post-treatment processing of ammonical copper lignin complex A treated wood on subsequent retention level of preservative and copper content. Wrapping for 96 hours gave the best protection to wood in ground contact for 36 months, followed by steaming at 50 °C.

Keywords: Alkali, lignin, brown rot, *Mangifera indica*, *Pinus roxburghii*, stake test, leachability, permeability

TRIPATHI S. 2009. Prestasi di lapangan bagi kayu yang dirawat dengan kompleks A lignin kuprum beramonia setelah menjalani pemprosesan lanjutan. Kajian ini melaporkan tentang kesan pemprosesan lanjutan terhadap tahap penahanan pengawet dan kandungan kuprum dalam kayu yang dirawat dengan kompleks A lignin kuprum beramonia. Kayu yang didedah di lapangan selama 36 bulan mendapat perlindungan terbaik apabila melalui rawatan pembalutan selama 96 jam, diikuti oleh rawatan pengewapan pada 50 °C.

INTRODUCTION

Non-durable and plantation grown woods are prone to deterioration and need chemical protection when exposed to exterior conditions. Many preservatives are employed; water-borne preservatives are a major component of the wood treating industry because they produce clean coloured surface wood and are inexpensive. Copper chrome arsenate (CCA) takes at least 21 days for fixation of preservative (Henshaw 1979, McNamara 1989, Christensen 1990). A number of studies have been carried out to investigate fixation of acidic formulation of CCA (Ruddick 1979, Cooper *et al.* 1993). Conversely, ammonia based copper preservatives have been less studied. Best and Coleman (1981) reported that the few preservatives which utilize ammonia to solubilize copper elute ammonia after treatment which results in precipitation of copper and other metal salts in wood. Lebow (1992) suggested that post-treatment handling of ammonical copper zinc arsenate affects the rate of precipitation of the different chemical components.

Ohlsson and Simonson (1992) reported a double step impregnation with an aqueous solution containing modified soluble kraft lignin followed by a second step involving impregnation with a copper salt solution to enable fixation of the lignin into water insoluble form. Fernandez *et al.* (1999) reported organosolv lignin-copper as a natural preservative. Concalves and Schuchardt (1999) reported that oxidized lignin can be used as chelating agent in the treatment of effluents containing heavy metals. Lin and Ziobro (1994) mixed lignin with copper salt to obtain a wood preservative consisting of ammonium salt of lignin with copper and zinc cations, namely, $Cu(NH_3)_4$ and $Zn(NH_3)_4^{++}$ in aqueous medium. The preservative exhibited promising results in southern pine. Tripathi *et al.* (2003) reported efficacy of copper lignin complex against fungi in *Pinus roxburghii* and *Mangifera indica* in the laboratory and field. *Pinus roxburghii* wood in treated form was protected efficiently in the laboratory and field but the performance of mango wood was not satisfactory. It was assumed that the poor performance of mango wood might be due to the lower retention level of preservative or uneven distribution or partial fixation or partial treatability of wood. Therefore, the present study was carried out to investigate the retention level of copper lignin complex A in hard and softwoods due to different post-treatment processes. Performance of treated wood in the graveyard was also done. Copper complex A was prepared utilizing the black liquor of wheat straw, which is often isolated in the pulp and paper industry.

MATERIALS AND METHODS

Isolation of alkali lignin

Black liquor was prepared by pulping wheat straw using the soda process, i.e. NaOH alone with 12.5% chemical charge during cooking. The lignin was isolated by acidification of black liquor using 1 N hydrochloric acid (Browning 1967).

Preparation of copper lignin complex A (CLC-A)

A known amount of saturated solution of $CuSO_4.5H_2O$ (AR grade) was added slowly to a slightly alkaline solution (25%) of the purified and dried soda lignin (10 g) until complete precipitation. The green coloured complex was filtered, washed and vacuum dried (Tripathi & Dev 2003). Preservative solutions of 0.25, 0.50 and 1.00% were prepared by dissolving 0.25, 0.50 and 1.00 g of copper lignin complex A in minimum quantity of ammonical solutions (25%) which were further diluted with distilled water to make up 100 ml solutions. The copper content in the complex was determined by IS 2753 (ISI 1991).

Species studied

Pinus roxburghii or chir pine is found in the Himalayan region at 450–2200 m elevation, from Kashmir to Bhutan. Logs from Uttaranchal New Forest Campus, Dehra Dun, India (altitude 640 m, latitude 30° 20' N, longitude 78° 0' E) of 20–25 years old were harvested and processed for sample preparation. The wood has a density of 0.48 g m^{-3}. The heartwood of chir pine is non-durable but easily treatable (ISI 2008). It is used for pattern making, frames for doors and windows and for paving material.

Mangifera indica or mango tree is a large evergreen tree, 10–15 m in height. Its wood is hard and dense. Density of wood taken for the study was 0.58 g m^{-3}. It is excellent for making furniture, provided it is properly seasoned. It is moderately strong and most often used for making cheap furniture, toys, packing boxes, cabinet work, and panels for doors and windows. It is not a durable timber in exposed condition, moderately durable under cover and durable under water in the Indian climatic condition. The heartwood is vulnerable to attack by decay fungi as well as termites. Both heartwood and sapwood are treatable with preservative (ISI 2008).

Permanency test of complex A

Permanency against leachability is one of the important characteristics of an ideal wood preservative. Therefore, leachability of CLC-A was tested at 1% concentration of CLC-A in treated chir and mango wood. Sapwood blocks of dimension 1.9 × 1.9 × 1.9 cm, free from physical defects, in six replicates of each species were taken for leachability evaluation (ASTM 1970, ISI 2008)

Treatment

Stakes (30 × 3.8 × 3.8 cm) were made from defect-free sapwood of mango and chir wood. The stakes were conditioned to a moisture content of 15% in a humidity chamber and then treated with 1.00, 0.50 and 0.25% concentration of CLC-A. It was classified in 6 groups of treatment having 12 samples in each group for each concentration.

All treatments were performed by submerging the stakes in tanks containing the preservative and placing the tanks in treatment cylinder. A vacuum of 74.6 kPa was drawn over the specimens for 30 min, following 392 kPa air pressure for 1 hour. The pressure was released and the specimens were wiped clean of residual solution and weighed. The difference in weight before and after treatmeant was used to calculate gross preservative retention (kg m^{-3}). Each group of 12 stakes was subjected to post-treatment processing as given below:

(1) stickering (10 mm thick spacing) and air drying at 20 to 25 °C
(2) wrapping in plastic bag at 23–25 °C for 48 hours, then stickering and air drying
(3) wrapping in plastic bag for 96 hours at 23–25 °C, then stickering and air drying
(4) steaming for 1 hour at 50 °C (13.78 kPa steam pressure), then stickering and air drying

(5) steaming for 1 hour at 100 °C (103.42 kPa steam pressure)
(6) control stakes

All steam operations were performed in the the autoclave to avoid any excessive ammonia loss to the surrounding. All stakes were conditioned up to 15% moisture content. Six samples from each set were kept for field trials. Three samples from the same group were kept for copper content analysis and three were cut (cross-section and longitudinal) to study the impregnation of salt by various post-treatment processes.

Estimation of copper content

A total of 5 cm thick sections were cut at mid-length of the treated and dried specimens. The sections were ground and subjected to chemical analysis as per standard procedure (ISI 1991).

Retention of preservative

Retention of preservative was measured by two methods.
(1) The amount of preservative absorbed by specimens was calculated as per IS 4873 (ISI 2008) based on weight gain.
(2) Retention of copper was calculated for each set of specimen by the analytical procedure described in IS 2753 (ISI 1991).

Performance of stakes in the field

Six replicates per species after post-treatment processing at all concentrations together with six control stakes were installed in rows at the Forest Research Institute, Dehra Dun.

The specimens were inspected after installation, quarterly in the first year, half yearly in the second and yearly in subsequent years. The inspections were carried out visually by assessing the condition of specimens with regard to termite and fungal attack. The wood was pierced with a knife to determine the extent of decay. From the visual observations, 5 to 10% of attack was taken as slight (1–1.5 score), 11 to 25% as moderate (2–3 score), 26 to 50% as bad (3–4.5 score) and above 50% as destroyed (5 score) (Purushotham *et al.* 1968).

RESULTS AND DISCUSSION

The yield of CLC-A was 41.8 g while the amount of lignin used for reaction was 10 g (Table 1), indicating a four-fold increase. The high yield might be due to the reaction of purified lignin with copper sulphate, where no impurity was present and more binding sites were available. Chir wood had higher retention (4.2 kg m^{-3}) compared with mango wood (2.3 kg m^{-3}).

The efficient service life of the treated wood depends on the extent of fixation of preservative in wood and the end-use of the wood. Therefore, it becomes necessary to estimate the residual active biocidal component after permanency test. Fixation studies revealed that 1.66 kg m^{-3} copper (II) could be fixed in chir, whereas only 0.64 kg m^{-3} could be fixed in mango (Table 1). The higher fixation in chir may be due to the reaction of resin acids and other extractives. Shukla *et al.* (1972) reported that copper and zinc react with chir pine resin, *in vitro*, to produce metal resinates. Retention of preservative also depends on wood density. The higher the density the lower the retention which is evident in Table 1, where mango wood (density 0.58 g m^{-3}) exhibited less retention of preservative. Besides this, permeability and anatomical features may also be responsible for difference in retention of both the species. Therefore, it is assumed that treatment of both the woods with the same concentration of preservative will yield different results in the field.

Of the post-treatment processes evaluated, 96 hours wrapping resulted in the highest retention of CLC-A in chir as well as mango at 1% concentration (Table 2). A concentration

Table 1 Amount of copper complexed, retention and fixation of CLC-A in chir and mango wood

Complex	Yield of CLC-A (g)	Average retention of CLC-A (kg m^{-3})		Average retention of Cu (II) after leaching (kg m^{-3})	
		Chir	Mango	Chir	Mango
CLC-A	41.8	4.2	2.3	1.656	0.638

dependent increase in retention levels was observed in all sets. A slight difference in retention levels of CLC-A at 0.5% was observed in both the species subjected to different post-treatment processes. However, at 0.25% concentration, no remarkable difference in retention levels of CLC-A was observed in both the species in all sets. As explained earlier, mango wood showed lower retention of preservative and similar results were observed for post-treatment processes (Table 2).

As copper is the main biocide complexed with lignin, copper content was also estimated in chir and mango wood (Table 3). It is interesting to note that at 1% concentration, the retention of copper (II) was highest in samples subjected to wrapping for 96 hours in chir wood. However, this was not observed in mango wood, whereby copper (II) retention was almost similar, ranging from 1.25 to 1.50 kg m^{-3}.

Figure 1 shows that steaming has forced the removal of a large quantity of copper on the surface. Removal of copper on the surface was more prominent in chir compared with mango wood. For heating, temperature of the autoclave where the samples were placed was raised to an elevated temperature. On completion of heating when pressure was reduced, some of the penetrating solution contained in the wood was forced out of the wood by expansion of the air within the wood as external pressure was reduced. This was very prominent in chir wood. Large amounts of copper were found on the wrapping material and on the wood specimens after treatment. Heating thus reduced the amount of copper content in chir.

Although many studies on ammonical copper zinc arsenates have been reported (e.g. Kumar *et al.* 1996), fixation in ammonical wood preservative is not as well understood as that of CCA because it is less widely used. It is assumed that in ammonical preservatives, the metals are solubilized by ammonia and become insoluble as the ammonia evaporates. Some of the metals appear to simply precipitate within the wood, while others react with the wood structure.

Table 2 Various retention levels of CLC-A in chir and mango wood

CLC-A concentration (%)	Stickering	48 hours wrapping	96 hours wrapping	50 °C steaming 1 hour	100 °C steaming 1 hour
		Retention in chir (kg m^{-3})			
1.00	5.1	4.6	5.4	4.5	5.1
0.50	2.4	2.6	2.3	2.5	2.6
0.25	1.2	1.1	1.2	1.2	1.1
		Retention in mango (kg m^{-3})			
1.00	2.1	2.1	2.2	1.6	1.8
0.50	1.1	1.1	0.7	0.9	0.9
0.25	0.5	0.5	0.5	0.5	0.4

Table 3 Retention levels of Cu (II) in chir and mango wood

CLC-A concentration (%)	Stickering	48 hours wrapping	96 hours wrapping	50 °C steaming 1 hour	100 °C steaming 1 hour
		Retention in chir (kg m^{-3})			
1.00	1.80	1.80	2.05	1.85	1.25
0.50	1.05	1.05	1.60	0.95	0.80
0.25	0.65	0.65	0.90	0.60	0.45
		Retention in mango (kg m^{-3})			
1.00	1.50	1.40	1.25	1.25	1.25
0.50	0.60	0.55	0.45	0.60	0.80
0.25	0.25	0.11	0.05	0.09	0.06

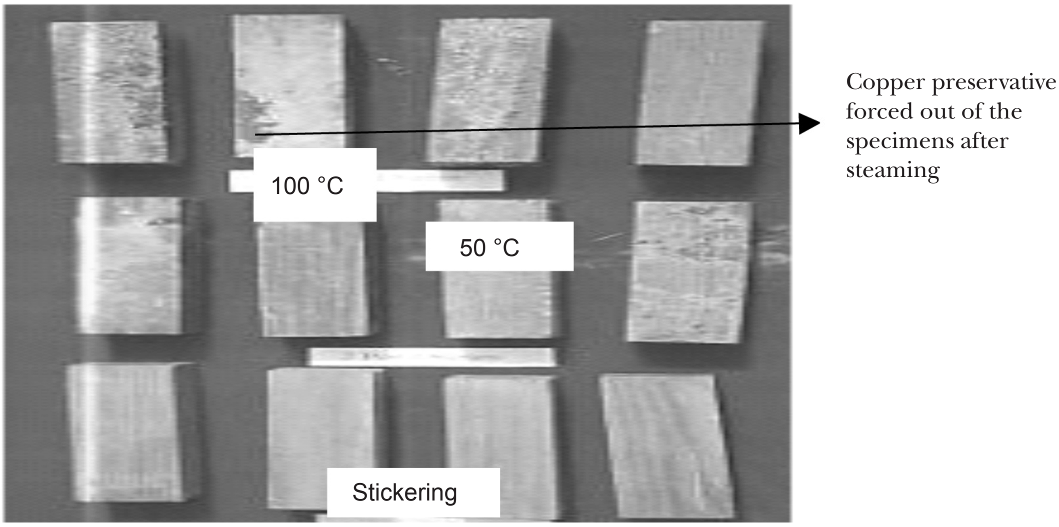

Figure 1 Effect of temperature on treated samples

It seems that delayed evaporation of ammonia appears to be a key factor in fixation of copper. This can be accomplished through wrapping for 96 hours. Wrap treatment for a longer duration caused delayed drying resulting in an increase in copper content of the fibres. The results obtained justify slow removal of ammonia from ammonical-based preservatives in wood (Henningsson *et al.* 1980). This study showed that 1% concentration of preservative performed best among all concentrations.

Figure 2 shows that chir is superior to mango wood. Wrapping for 96 hours was the best. This is in agreement with the findings by Henningsson *et al.* (1980). Improved protection was correlated with the copper content of the wood caused by delayed evaporation of ammonia. The performance of samples treated with different post-treatment processes can be arranged in decreasing order as wrapping for 96 hours > steaming at 50 °C > stickering > steaming at 100 °C > wrapping for 48 hour > control.

Deterioration caused by fungi, termites and other microbes in the soil was recorded after 36 months. A score of 0.5 exhibits negligible amount of attack on sample while 5.0 indicates complete destruction of sample. Figure 2 shows that bio-deterioration in chir wood at all concentrations of preservative is less compared with mango wood. It is interesting to note that untreated chir wood exhibited less decay, i.e. 3.5 score contrary to mango untreated wood, which was completely destroyed. It reveals that the softwood chir performs better than the hardwood mango in the field. In the field, mango wood was mainly affected by soft rot fungi. Figure 2 shows that in chir at 1% concentration, stickering, wrapping for 96 hours, and steaming at 100 and 50 °C cause minimum weight loss, while a decrease in concentration of CLC-A causes an increase in weight loss.

It is generally assumed that ammonia plays a very important role in solubilization of copper, mobility of cations in wood due to swelling of wood and subsequent evaporation of ammonia results in efficient precipitation (Stamm 1955, Jin & Archer 1991). It was observed that almost all samples except the controls developed mould on the surface only after 15 days of treatment. The possible reason may be that the presence of ammonia which acts as nitrogen source in wood, unfortunately, promotes the growth of mould.

On cumulative basis, wrap for 96 hours proved best while wrap for 48 hours was worst between all post treatments (Table 4). Preservative protected all samples of chir and mango wood in ground contact compared with the control where the mean deterioration was 84.3%.

Table 5 shows that the concentration of preservative is significantly and positively correlated with copper content and retention ($p < 0.01$, $r = 0.488$ and 0.543 respectively), while a significant and negative correlation was observed between concentration and weight loss ($p < 0.05$, $r = -0.136$). This proves that

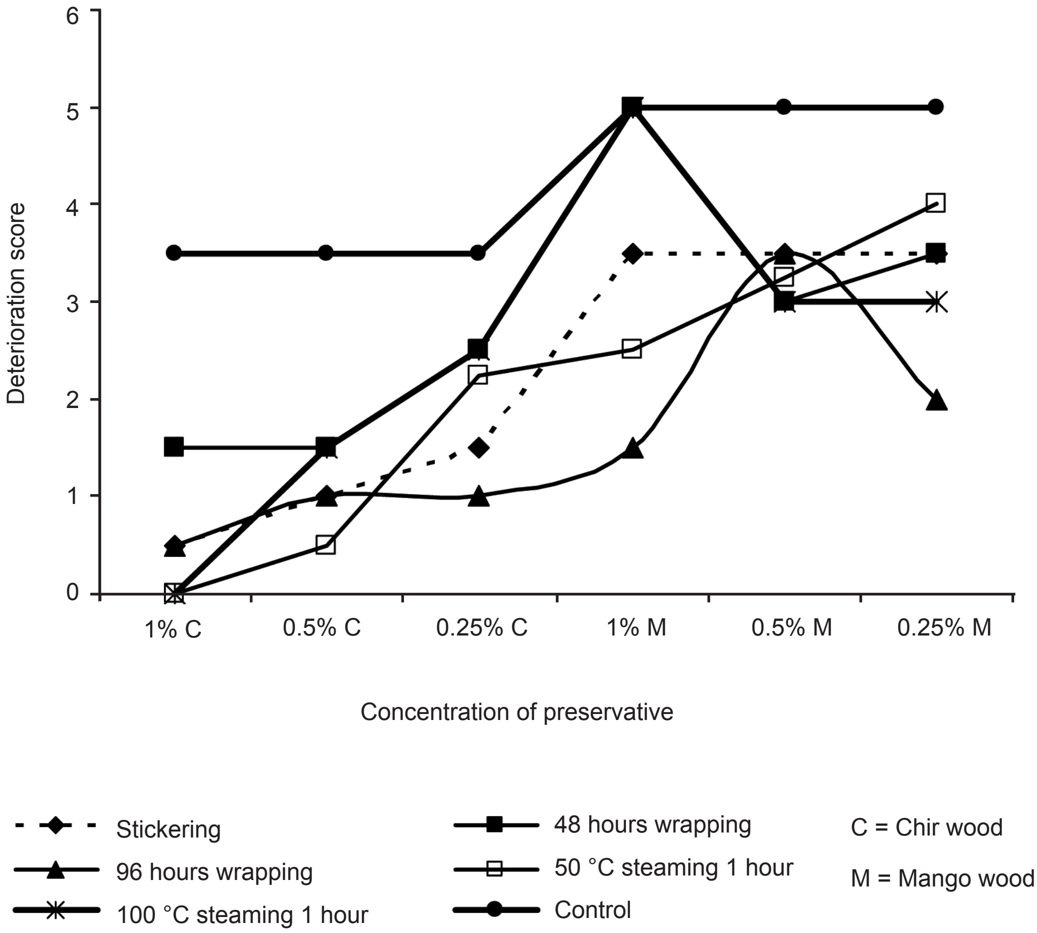

Figure 2 Deterioration of chir and mango wood in the field

increase in concentration of preservative causes increase in copper content and retention of preservative in wood and it also establishes the fact that the higher the retention the lower will be the decay of wood. Similarly a significant and negative correlation between weight loss and retention and copper content was observed ($p < 0.01$, $r = -0.678$ and -0.576 respectively).

CONCLUSIONS

Post-treatment processing appears to play an important role in the precipitation of ammonical based copper preservative in wood. Chir wood performed better than mango wood both in treated as well as untreated form in ground contact. Field evaluation revealed that CLC-A possessed better protective capacity at higher concentration. Lower retention levels of preservative and copper in mango wood resulted in significantly more attacks by termites and fungi. The study suggests that 96 hour wrap treatment for ammonical CLC-A preservative is the best post-treatment process.

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Table 4 Mean deterioration (%) caused by termites and fungi in chir and mango wood treated with CLC-A by different methods after 36 months of ground contact

Treatment	Chir				Mango				Mean
	CLC - A Concentration			Mean	CLC-A Concentration			Mean	
	1.0%	0.5%	0.25%		1.0%	0.5%	0.25%		
Stickering	8.83 (17.25)	19.83 (26.42)	29.66 (32.99)	19.44 a (25.55)	68.83 (56.04)	69.00 (56.15)	69.33 (56.36)	69.05 a (56.18)	44.25 a (40.86)
Wrapping for 48 hours	29.66 (32.98)	29.50 (32.86)	49.16 (44.50)	36.11 a (36.78)	99.16 (86.39)	59.66 (50.55)	69.66 (56.56)	76.16 ab (64.50)	56.13 a (50.64)
Wrapping for 96 hours	10.00 (18.39)	19.33 (26.05)	18.66 (25.57)	16.00 a (23.34)	29.00 (32.56)	69.83 (56.66)	39.50 (38.92)	46.11 a (42.71)	31.05 a (33.02)
Steaming at 50 °C	2.66 (9.14)	9.50 (17.92)	48.66 (44.21)	20.27 a (23.76)	50.33 (45.17)	64.66 (53.50)	79.83 (63.30)	64.94 a (53.99)	42.61 a (38.87)
Steaming at 100 °C	2.0 (7.80)	29.66 (32.97)	49.50 (44.69)	27.05 a (28.49)	98.83 (85.03)	65.66 (54.11)	65.33 (53.90)	76.61 ab (64.35)	51.83 a (46.42)
Control	70.33 (56.98)	70.50 (57.08)	69.33 (56.35)	70.05 a (56.80)	98.50 (84.50)	98.16 (83.67)	99.00 (85.99)	98.55 a (84.73)	84.30 a (70.77)
Mean	20.58 a (23.76)	29.72 a (32.22)	44.16 a(41.39)		74.11 a (64.96)	71.17 a (59.11)	70.44 a (59.14)		
Species mean		31.49 (32.45) a				71.91 (61.08) a			
Concentration (mean)	1%: 47.34 (44.35) a; 0.5%: 50.44 (45.66) a; 0.25% : 57.30 (50.28) a								

Values in parentheses are arcsin values.
CD $_{(0.05)}$species × condition = 0.98; CD $_{(0.05)}$ condition = 0.69; CD $_{(0.05)}$species × concentrations = 0.69; CD $_{(0.05)}$ concentrations = 0.49
Same alphabets represent significantly different groups (a); ab represents insignificant difference between the groups.

Table 5 Simple correlations between copper content, retention of preservative and weight loss

Correlation	Concentration	Copper content	Retention	Weight loss
Concentration	1.00	0.488**	0.543**	-0.136 *
Copper content	0.488**	1.000	0.523 **	-0.576**
Retention	0.543 **	0.523**	1.000	-0.678**
Weight loss	-0.136*	-0.576**	-0.678**	1.000

** Significant at the 0.01 level (2-tailed), significant at the 0.05 level (2-tailed)

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