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Effect of chromated copper arsenate (CCA) on corrosion of metallic fasteners: Implications in boat building

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Wooden boat building involves the use of metal fasteners made of iron, copper etc. The scarcity of durable wood necessitates wood preservation. When preservative treated wood is nailed, the possibility of corrosion of the nail cannot be ignored. This demands further studies on the performance of the nail with respect to its resistance to corrosion. The main aim of this study is to find out the rate of corrosion of copper, iron, painted iron nails and galvanized iron screws drawn into rubber wood treated to three different retentions of chromated copper arsenate (CCA) *viz.* 16, 29, 42 kgm^{-3} and wood without any treatment. The experiments were conducted both in the laboratory and under estuarine conditions. The rate of corrosion is estimated by weight loss method. The results show that CCA does not affect corrosion in 16 and 29 kgm^{-3} retentions to a significant level, but in 42 kgm^{-3} retention, the corrosion rate is found to be accelerated significantly when analysed statistically. It can be concluded that in lower retentions, CCA does not influence corrosion of fasteners. The rate of corrosion is least in galvanized iron and painting of iron nail is found to effectively reduce corrosion.

Keywords: Corrosion, Fasteners, CCA, Rubber wood, Salt spray chamber

Corrosion of fasteners is a universal issue that causes great economical losses in any industry. Nails or screws when used in wood, form a sandwich condition which may provide a corrosive atmosphere depending on various factors. Wood is slightly acidic when it is damp and it causes metals to corrode. This is because when a metal fastener is embedded in wet wood or when wood embedded with a fastener undergoes wetting, conditions are created that can accelerate the corrosion of the metal[1]. The corrosion products often result in deterioration of the wood surrounding the metal gradually. When the wood is treated with an inorganic preservative like chromated copper arsenate (CCA), the situation may be more conducive for corrosion or it may retard corrosion. Sometimes the presence of preservative may not influence corrosion of nails at all. All these depend on the type and quality of metal or alloy used as fastener, the wood species used, the preservative constituents and the conditions of the medium in which the nailed wood is exposed. This is especially important when it is exposed to aquatic conditions for the construction of boats, decks etc. The corrosion of iron nails used for boat building is a perennial problem faced by wooden boat builders. In the context of treatment of wood with preservatives, there is a need to study the role of wood preservative on corrosion of fasteners used in wooden boat building.

Not many studies have been conducted regarding the role of wood preservative in corrosion of fasteners. A study by Whitney[2] concluded that diameter loss of galvanized steel bolts may not be serious, but bolts in joints exposed to severe wetting conditions could be weakened due to rusting. For long service life under wet conditions, fasteners in contact with copper containing preservatives should be cathodic with respect to copper[1]. Since CCA-A has higher chromium content, it is less corrosive than CCA-C. Also poles treated with CCA-A have been in service for 35 years without corrosion problems[3]. Aluminised iron fastenings are found more compatible with several boat building timbers and without sacrificing efficiency it can be used instead of expensive copper base alloys[4].

The aim of the present study is to find out whether the presence of CCA in wood influences the corrosion of nails and whether the use of galvanized or painted iron nail reduces corrosion. The study also aims at assessing the effect of preservative retention in wood on corrosion. The impact of corrosion products on the degradation of wood around the fasteners is also studied.

Experimental Procedure

Rubber wood (*Hevea brasiliensis*) panels of size 150×100×25 mm were cut from a freshly felled tree.

The edges and faces of the panels were smoothened using planer. The moisture content of the panels was monitored using a portable moisture meter (Extech Moisture Meter Model 407777). After proper air seasoning the panels having moisture content of less than 25% were selected for CCA treatment. All panels were pressure treated with CCA solution of 7.5% (*w/v*) concentration in a pressure impregnation chamber and the conditions of treatment was arrived at through trial and error method to obtain retentions of 16, 29 and 42 kgm^{-3} (Table 1). The preservative retention was calculated as per ASTM D 2481-81 (ASTM, 1982). The pressure treated panels were then kept for air-drying for six weeks to fix the preservative present in the wood. Eight numbers each of untreated control, CCA treated with the retentions 16, 29 and 42 kgm^{-3} were selected for the experiments.

Nails of copper, iron, painted and galvanized iron, each of length 5 cm were used. These nails are selected because iron and copper nails are used in the construction of wooden fishing canoes in India.

Five numbers of copper nails were nailed on the radial faces of the panel with a distance of 2 cm between each nail on all the four types of wood panels. Ten numbers each of iron and painted iron nails were nailed on the radial faces of all the four types of wood panels respectively with a distance of 1.2 cm between each nail. After drilling the sides of the panels to sufficient depth, the ten galvanized iron screws were screwed on both sides of all the four types of panels. Two sets of such experimental panels were prepared for laboratory as well as field exposure study in the estuary.

The salt spray experiment was patterned as per ASTM B-117-03. This method is selected because it is considered to be most useful in estimating the relative behaviour of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature or both. The nailed panels were then arranged on the fibre racks as specified in the standard. A 3.5% salt solution was prepared using sodium chloride and the *p*H of the collected solution after atomization at 35°C was measured to be 7.1. A compressed air supply of 100 kN m^{-2} was given for atomizing the salt solution. The exposure zone of the salt spray chamber was maintained at a temperature of 35°C and 95% relative humidity. The test was conducted for a period of 480 h. The experimental panels were collected from the chamber and the nails were carefully removed by cutting open the panel immediately after the experiment was completed. The X-ray photographs of the nailed panels were taken before exposing the panels in the salt spray chamber and after retrieving them, for analyzing whether there is degradation of wood around the fasteners due to the corrosion products.

The other sets of panels were exposed in the Cochin estuary for a period of 100 days (from 21st June to 29th September 2005). The nailed panels were tied on a rope and were immersed in the estuary at one meter below the tidal level at the North Oil Tanker Berth of the Cochin Port Trust. Salinity of the water sample was analyzed based on the Knudsen method. Dissolved oxygen was analyzed by titrimetry using Winkler's method.

In Winkler's method, water is sampled in a 300 mL Biological Oxygen Demand (BOD) amber coloured bottle without air bubble. 2 mL of manganese sulphate solution (Winkler A) is then added immediately. Then 1 mL of Winker B (potassium iodide in potassium hydroxide) is added. The bottle is shaken well after fixing the cap. Next, 1 mL of concentrated sulphuric acid is added and the bottle is well shaken. 200 mL of this sample is titrated with sodium thiosulphte with starch solution as indicator. The concentration of dissolved oxygen in the sample is equivalent to the number of milliliters of titrant used in mg/L.

The hydrographic data of the exposure period is given in Table 2. On completion of the exposure period the panels were retrieved and the nails were removed for analysis as in the previous case. The cleaning of the nails and the calculation of the corrosion rate were done according to the ASTM

Table 1—Conditions of preservative treatment of rubber wood panels

CCA Retentions (kgm^{-3})	Initial vacuum		Pressure applied		Final vacuum	
	Vacuum (cm of Hg)	Time (min)	Pressure kPa	Time (min)	Vacuum (cm of Hg)	Time (min)
16	56	30	172	15	38	15
29	56	30	448	30	38	15
42	56	30	517	90	38	15

standard G1-72 i.e., standard recommended for preparing, cleaning and evaluating corrosion test specimens. Copper nails were cleaned in the solution recommended for cleaning copper and copper alloys. Iron and painted iron nails were cleaned in the Clarke's solution and galvanized iron screws were cleaned using alternative solution for stainless steel. The possible error due to loss of metal during cleaning was reduced by the method of recleaning and reweighing as suggested in the standard. The weight loss of each nail due to corrosion was measured and the corrosion rate was calculated as follows:

Corrosion rate (g m^{-2}.h) = $(K \times W)/(A \times T \times D)$

where $K = 1\times10^4 \times D$ for the unit grams per square meter per hour (g m^{-2}.h); T = time of exposure to the nearest 0.01 h; A = area in cm^2 to the nearest 0.01 cm^2; W = mass loss in grams, to the nearest 1 mg and D = density in g cm^{-3}.

Statistical analysis was carried out using univariate Analysis of Variance (ANOVA).

Results and Discussion

Galvanized iron nails were found more effective in resisting corrosion followed by copper nails. The trend does not vary notably in laboratory conditions as well as in the estuarine conditions.

In the case of nails exposed in the salt spray chamber in wooden panels, copper nails were found to have a corrosion rate value of 0.1581 g m^{-2}.h in 42 kg.m^{-3} panels, 0.1287 gm^{-2}.h in 29 kg.m^{-3} panels, 0.1063 g m^{-2}.h in 16 kg.m^{-3} and 0.0988 g m^{-2}.h in the control panel (Fig. 1). Maximum corrosion rate was found for iron nails. Among the iron nailed panels, corrosion rate was maximum with a value of 0.9922 g m^{-2}.h for panel having retention of 42 kg.m^{-3}. This is significantly higher than the rate of corrosion of nails in control panel, which was 0.7918 gm^{-2}.h. In the case of 16 and 29 kg.m^{-3} the values were 0.8122 and 0.8050 g m^{-2}.h respectively, which is not significantly different from the control panel. This suggests that higher retentions accelerate corrosion. Painted iron nails are found to corrode to a lesser extent than bare iron nails. In this case also higher rate of corrosion was found for 42 kg.m^{-3} with a value of 0.7241 g m^{-2}.h. The corrosion rate of fasteners nailed to panels having 16 and 29 kg.m^{-3} retention were 0.5726 and 0.6725 g m^{-2}.h respectively. Corrosion rates of 29 and 42 kg.m^{-3} panels were found significantly higher than the control panel, which has a value of 0.5785 g m^{-2}.h. In the case of galvanized iron nails corrosion rate was, 0.0521, 0.0471, 0.0426 and 0.0389 g m^{-2}.h for fasteners nailed to panels having retentions 42, 29, 16 kg.m^{-3} and control panel respectively.

In the case of panels exposed in the estuary, the corrosion rate values of copper nails were 0.1058, 0.0879, 0.0846 and 0.0716 g m^{-2}.h in control, 16, 29 and 42 kg.m^{-3} retention panels respectively (Fig. 2). Iron nails were also found to have similar values as that of control panel having a corrosion rates of 0.1959 and 0.1594 g m^{-2}.h for 16 kg.m^{-3}, 0.1921 g m^{-2}.h for 29 kg.m^{-3} and 0.1480 g m^{-2}.h for 42 kg.m^{-3}. In the case of painted iron nails, corrosion was maximum in control panel with a value of 0.2087 g m^{-2}.h. Fasteners nailed to panels having 16 kg.m^{-3} retention also have corrosion rate of 0.2080 g m^{-2}.h. Corrosion rates of 0.1837 and 0.1883 g m^{-2}.h were estimated for panels having retentions 29 and 42 kg.m^{-3} respectively. For galvanized iron nails rate of corrosion was negligible with 0.0219, 0.0026, 0.0019 and 0.0016 g m^{-2}.h for control, 16, 29 and 42 kg.m^{-3} retention panels respectively. Observed data indicate that painting of iron nail did not reduce corrosion. Also the rate of corrosion was found to decrease with increase in retention. This may be due to the biodeterioration of wood treated to low preservative retentions and the susceptibility to biodeterioration of untreated wood. It

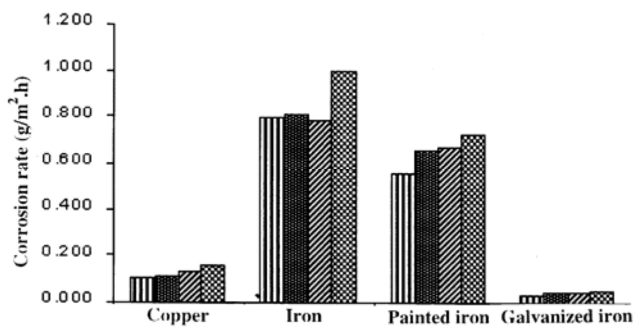

Fig. 1—Corrosion rate of fasteners nailed to CCA treated wood exposed in the salt spray chamber

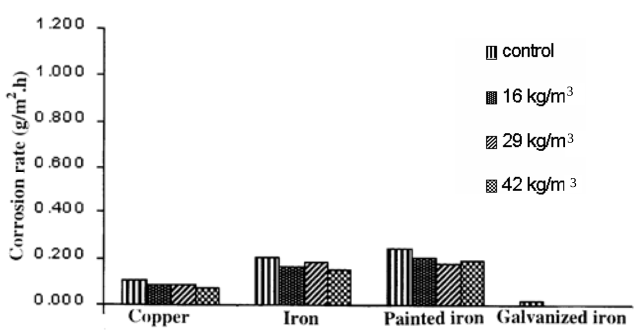

Fig. 2—Corrosion rate of fasteners nailed to CCA treated wood exposed in the Cochin estuary

was also observed that on prolonged exposure, deterioration of rubber wood in lower retentions of CCA *viz*. 16 and 29 $kg.m^{-3}$ was more than in wood treated to 42 $kg.m^{-3}$ due to attack by *Sphaeroma* spp. and *Teredo* spp. (Sreeja & Edwin, unpublished work). The degradation of wood by biological agencies permits increased contact with the outside environment which in turn accelerated corrosion.

Statistical analysis was carried out using ANOVA to find out the significant difference, if any, in rate of corrosion for four different types of fasteners exposed in laboratory and field conditions, nailed in wood at four different retentions of CCA. Rate of corrosion was significantly different for all combinations of nail types and retention. Rate of corrosion in the laboratory condition was significantly higher than that in the field. The significance is valid at 1% level (R^2=0.985). When Tukey's test was conducted keeping nail type as variable, corrosion rate of each type of nail was found to differ significantly from other types of nails. When Tukey's test was conducted keeping retention as variable, significantly high rate of corrosion was found only in case of iron nails used in 42 $kg.m^{-3}$and painted iron nails used in 29 and 42 $kg.m^{-3}$ in the accelerated condition.

According to a study conducted at the National Physical Laboratory[5] of UK the chromium salt constituent may have a small protective effect, while the arsenate radical a slightly corrosive one; in addition, the copper itself is potentially corrosive, because copper-based preservatives can leach soluble copper compounds to some extent and this copper can then plate out as metal on to iron, zinc and aluminium, forming galvanic cells that accelerate the corrosion of the substrate metal. The leaching from freshly treated wood being much greater than that after a period of fixation, it is recommended that preserved wood be allowed to age for seven days before fasteners are inserted in the wood[5]. To improve service life of nail in marine environment, galvanized nails and screws are reported to be more useful[6]. The present study also suggests that galvanized iron nails and screws are more effective in providing better service life to any structure by surviving in vulnerable conditions.

There are several factors that directly influence metal corrosion in the aquatic environment, including the hydrographical parameters of the environment like dissolved oxygen, *p*H, salinity, conductivity and physical factors like temperature and extent of water movement[7]. Higher temperatures generally increase corrosion rates. However, corrosion needs a liquid phase and if drying occurs, higher temperatures may be beneficial[8]. In this study also, high salinity of the salt spray resulted in high corrosion rate. Other factors like high temperature and humidity also accelerated the corrosion process. The average *p*H in the field condition was also higher than that in the salt spray. Since the experiment was conducted during the monsoon season, the salinity was very low during most part of the experiment (Table 2). The monthly average salinity (‰) and dissolved oxygen (mg L^{-1}) data of the experimental site in Cochin estuary during monsoon season for the last five years including the experiment period is collected by this Institute (Table 3). The sudden fluctuations in the salinity value may be because of the tidal effect or heavy rain on the particular day of sample collection. The monthly average values of the data given in the experimental table also have similar values.

Table 2—Hydrographical parameters of Cochin Estuary during the experiment

Date	Water temperature (°C)	*p*H	Dissolved Oxygen (mg L^{-1})	Salinity (‰)	Turbidity NTU
21/06/05	26	6.89	4.8	0.39	32
07/07/05	27	6.89	4.6	0.20	29
19/07/05	25	7.05	6.8	2.56	20.3
04/08/05	25	7.49	5.4	0.42	28
24/08/05	28	7.77	6.6	11.40	10
06/09/05	27	7.52	3.4	0.57	16
20/09/05	30	7.52	6.4	3.73	11

Table 3—Salinity and dissolved oxygen value of Cochin estuary during monsoon for the last five years (2002–2006)

Month	2002		2003		2004		2005		2006	
	D.O. (mg L^{-1})	Salinity (‰)	D.O. (mg L^{-1}).	Salinity (‰)	D.O. (mg L^{-1})	Salinity (‰)	D.O. (mg L^{-1})	Salinity (‰)	D.O. (mg L^{-1})	Salinity (‰)
June	5.4	2.45	5.2	18.58	5.0	5.75	4.9	4.66	5.7	4.62
July	5.5	6.26	5.7	1.76	5.9	1.96	5.9	1.29	5.7	1.41
August	5.7	2.20	5.2	3.36	6.6	3.46	5.9	3.88	6.2	6.68
September	5.5	16.50	5.4	12.45	5.4	11.85	5.1	2.15	6.1	3.30

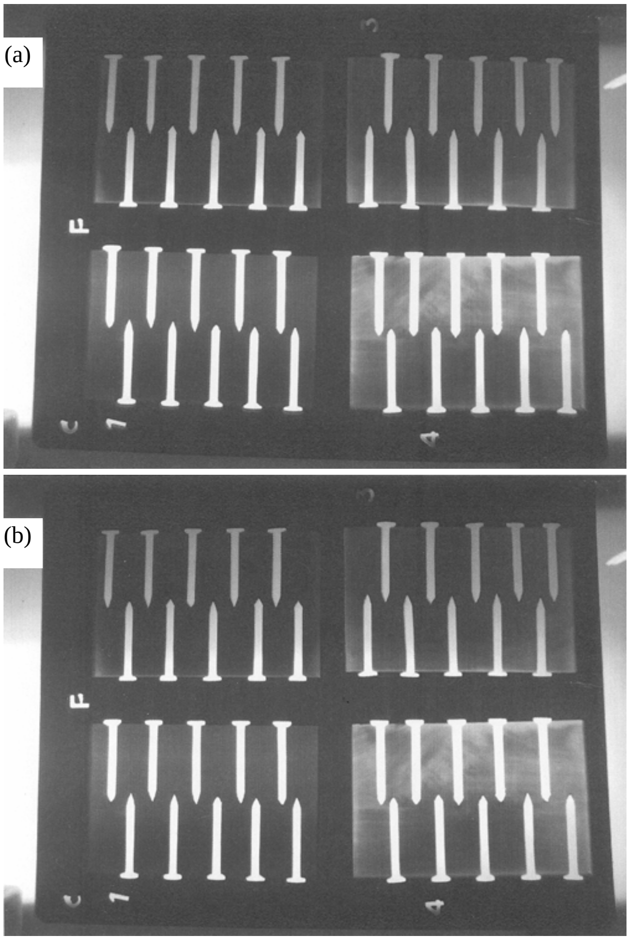

Fig. 3—X-ray photograph of copper nails on the experimental panels (a) before exposure and (b) after exposure, in the estuary.

The possibility of establishment of electrolytic cells exists in the timber structure on exposure to relatively harsh environment of weather combined with CCA chemicals. Corrosion rates are related to electrical conductivity of the moist wood, which is influenced by the moisture level and the presence of soluble preservative by-product salts. If the moisture content of the wood is below 18 percent, the corrosion rate of metals will be very low. Thus, when the treated timber moisture content will climb above that level corrosive conditions may occur. In a long term study conducted by Forest Service Division of USDA[9] on fasteners used in CCA treated wood, stainless steel nails and screws alone did not exhibit any visual signs of corrosion and the weight loss over fourteen year period was negligible. Wood always contains moisture and the acid in it, aided by salt if immersed in seawater, acts as a bulk electrolyte in which various electrochemical cells can be formed. This can be more vigorous than the micro-cells set up in atmospheric corrosion. The wood can be degraded by alkali formed at a cathode as well as by iron salts formed at a rusting iron anode. The shaft of a fastener inserted into wood lacks oxygen and becomes anodic, and the exposed head becomes cathodic. The cathodic alkali gives negligible protection to the head as it is soon washed away, but may cause alkaline degradation of the wood at the area of emergence. Cathodic protection on wood vessels should be done with care so that the products of the cathode reaction do not accumulate and cause wood deterioration[10]. In this study, the detailed examinations of the X-ray radiograph show that the wood in touch with the fastener remains intact (Fig. 3). No gaps could be observed in any of the panels where the fastener penetrates into the wood. The degradation of wood may be less because of the presence of the preservative components. The cell formation may have taken place between the nail and the preservative ions and thus the wood cells would have escaped from degradation. This can be ensured only after prolonged experiment in which the preservative components are completely exploited during the service period.

Conclusion

CCA does not accelerate corrosion of fasteners nailed to it in 16 and 29 kg.m^{-3} retentions to a significant level, but in 42 kg.m^{-3} retention, the rate of corrosion of nails is significantly high. The rate of corrosion was least in galvanized iron and painting of iron nail is found effective in reducing corrosion. Also corrosion products do not found to accelerate the degradation of wood around the fasteners.

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