

Copper Creosote - A New Preservative for Marine Wooden Structures

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The affinity of certain components in creosote towards inorganic salts was explored. Copper oxide on heating with creosote produces stable compounds which are found to be biologically active. Data regarding preparation of copper creosote, preservation treatment and field test are reported. Comparative data on the performance of creosote, arsenical creosote, copper creosote and TBTO-fuel oil mixture are presented. Data relating to the evaluation of the effectiveness of preservatives by bending modulus test are also presented.

The application of creosote has a long history and, despite the emergence in recent years of other wood preservatives that have economic or technical attractions, creosote continues to be widely used especially for protection of marine wooden structures. Though the accent today is on more durable newer structural materials, preserved wood still continues to be an important structural material. Analytical studies of coal-tar creosote have identified about 200 compounds and more are being added with the application of newer analytical techniques. Becker and colleagues over the years have studied (Cited by working Group 3) the effect of components toxic to wood destroying fungi. Outstanding work by Sweeney *et al.* (1952) of the US Office of Naval Research on the protection of marine structures merit special attention. Working research group (1972) on wood preservatives have reported various aspects such as analytical composition, toxicity towards fungi, insects and marine borers; retention, performance and penetration; creosoted timber in service and allied aspects. It is now well recognised that to ensure adequate protection to timber in tropical seawater, the toxicity of creosote is to be enhanced. A pioneering work in this regard has been accomplished by Johanson who through a series of investigations (Johanson, 1965, 1966, 1967, 1969 and 1970) fortified creosote with arsenious oxide and established its merit as a new preservative for termite control. The arsenical creosote, as it is called, contains a variety of stable arsenical co-

mpounds and has treating properties similar to straight creosote. Studies on the fortification of creosote of Indian origin and its effectiveness against borer attack on *Mangifera indica* and *Adina cordifolia* were conducted by Nair *et al.* (1972). In this paper the author's attempts to fortify creosote with copper and its evaluations are reported.

Materials and Methods

Preparation of copper creosote: Low temperature creosote produced by the Regional Research Laboratory (CSIR), Hyderabad was used in this study. The physical properties and distillation data reproduced from Jain *et al.* (1968) are given in Table 1. The preparation of copper creosote involved only a simple procedure of heating low temperature creosote with 5% (w/w) reagent grade cuprous oxide in large flasks fitted with air condensers at a temperature of $99 \pm 0.5^\circ\text{C}$ for a period of 24 h. The product was then allowed to cool to ambient, temperature left aside for about a month for settlement of solid particles and then filtered through filter paper.

Analytical method: The estimation of copper in copper creosote was done as follows. A weighed amount of the product was digested in a Kjeldahl flask with concentrated analytical reagent grade sulphuric

Table 1. Distillation data on low-temperature creosote*

Temp.	Distillation fraction (%) ISI Method	Tar acids V/W %	Bensol insoluble %	Coke residue (%)wt	Residue above 355°C %	Moisture by volume at 30°C	Specific gravity $^\circ\text{C}$	Flash point at 30°C
Up to 210°C	2.87	22	0.0328	2.15	15.61	0.5	0.9693	140
" 235°C	13.14							
" 315°C	46.66							
" 355°C	19.78							

*Produce of Regional Research Laboratory, Hyderabad

acid. The solution was cleared by the repeated addition of small quantities of 100 volume hydrogen peroxide. The temperature was then raised just enough to produce white fumes of sulphuric acid. The solution was cooled to room temperature and diluted to 100 ml in a volumetric flask. The copper content was then determined by using an atomic absorption spectrophotometer, set at the following parameters.

Wave length 324.7 nm, Spectral band pass : 0.5mm
Lamp current 3 mA, Flame: Air-acetylene

Treatment of wood samples: *Mangifera indica* blocks cut to 15 × 10 × 3.8 cm and kept in the laboratory for over 6 months to equilibrate the moisture content to about 12% were used. The copper creosote was warmed to 40°C and the wooden blocks were pressure treated at 4–4.2 kg cm⁻² for about 30 min. Some of the blocks were treated similarly with arsenical creosote obtained by heating 2% (w/w) As₂O₃ with creosote at 90°C for 5 min and holding at a temperature of 40°C as described by Johanson (1966) and some others with 0.5% bis-*n*-tributyl tin oxide (TBTO) in fuel oil for comparison of biocidal properties.

Test blocks of wood treated with copper-creosote, arsenical-creosote and TBTO all in duplicate along with three untreated controls were mounted on immersion racks and exposed to the attack of marine borers at Cochin harbour waters. The test blocks always remained submerged during low water and high water and were subjected to tidal currents. The hydrographical parameters recorded at the test site varied within limits as shown below:

Salinity: 25–32‰; dissolved oxygen: 4–7 ml/l and surface water temperature 26–31°C. The emphasis of observation was on the attack by marine borers which was assessed by noting the borer holes, internal volume of loss of matter and bending modulus of rupture.

Results and Discussion

A great amount of work has been done on the iden-

tification of compounds found in coal-tar in the distillation range of 200–400°C. Among the principal compounds are naphthalene, methyl and dimethyl naphthalene, diphenyl fluorene, phenanthrene, anthracene, pyrene, tar acids (phenol, cresol and naphthols) tar bases and other nitrogen compounds (Martin, 1949; Heiks, 1952). Of the various chemical groups present in creosote, tar phenols including possibly hydroxyaromatic acids have been shown the greatest affinity for arsenic trioxide (Johanson, 1969). It appears that the vicinal hydroxyls in the benzene ring extensively reacted with cuprous oxide forming water stable compounds. Through the reaction of Cu₂O with creosote was studied with respect to Cu₂O concentration and temperature, only the value obtained with 5% copper oxide and 99°C is reported here. The amount of copper oxide that can be incorporated in creosote was found to be 0.38% in the analysis. This can be compared with the value of arsenic oxide treated under similar conditions. For vertical retort creosote a concentration of 0.2 to 0.5% arsenic oxide was reported by Johanson (1967). The stability of copper creosote on long storage suggests a chemical reaction rather than simple solubility. The phenols and hydroxyaromatic compounds establish chemical links with copper oxide providing chemical stability to the resultant compound.

The results of evaluation of this new wood preservative is given in Table 2. A number of agencies contribute to the destruction of timbers in the sea, namely, marine borers, fungi, bacteria and mechanical abrasion. Marine borers such as shipworms, *Martesia* and *Sphaeroma* bored the control panel which had 49 borer holes leaving a residual strength of only 12% in a period of 8 months. It can be seen that low temperature creosote, copper-creosote and arsenical-creosote and TBTO had been effective in varying degrees for reducing borer attack. The area of internal destruction of wood treated with copper-creosote was only 0.10% as compared to 0.93 of the low temperature creosote. The fortification achieved by incorporation of copper is quite evident and in fact a higher level of protective value over arsenical-creosote is shown.

Table 2. Assessment of biodeterioration of wood after exposure to seawater for 8 months (species of wood: *Mangifera indica*)

Name of preservative	No. of borer holes on surface	Area of destructions at the longitudinal midsection, cm ²	Area of destruction, %	Modulus of rupture as % residual strength	Average loading of preservative Kg m ⁻³
Low temp. creosote	6	2.8	0.93	76	180
Copper creosote	3	0.3	0.10	85	180
Arsenical creosote	4	1.7	0.57	80	180
0.5% TBTO in fuel oil	3	2.5	0.83	76	50
Untreated control	49	48.0	16.0	12	0

The assessment of the effectiveness of preservative against borer attack by counting the surface borer holes is commonly done but it has serious draw backs as the surface damage is never a reflection of the internal damage. Estimation of the area of gallery holes would provide a better index of damage but this can be seldom done accurately. In the present study the destruction of wood has been assessed by the widely used simple method of counting the surface borer attack, determining the area of damage at the longitudinal mid-section and by determining the modulus of rupture of the borer infested part. It can be seen that surface borer holes is not at all indicative of the attack and the measurement of the area at the cross section provides a better assessment. Even this is not free from draw back as *Teredo* galleries parallel to grain at a single section alone can be measured. A solution to this is to use an expensive X-ray examination and to compute the figure of resistance from the linear rate of growth and density of attack (Fougerousse & Deschamps, 1968). An easy and reliable method of assessing the destruction is by determining the modulus of rupture which takes into account all forms of biodeterioration including fungal attack. The values of modulus of rupture, expressed as percentage residual strength is given in Table 2. This allows a quantitative assessment of the deterioration of materials under test. Tests are also in progress to study two

other test methods namely, compression strength parallel to and perpendicular to grain and to determine the volume of materials lost by displacement methods.

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