Development of Chemical Preservatives and Coatings to Offset Biodeterioration in Traditional Fishing Craft

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The present communication presents a summary of the findings of the authors in the development of chemical preservatives and surface coatings to offset biodeterioration in fishingcraft. Fortification of creosote had distinct advantage over straight creosote with reference to loading, toxicity and price. Fortified creosote application is 50% cheaper than traditional methods with better prophylactic properties. Possibilities of combining antifouling and antiborer properties in one polymeric matrix with suitable additives and biotoxin are also highlighted.

The traditional craft are kept on open beaches after fishing and undergo partial drying and absorb water when pressed into fishing operation. This alternate drying and wetting provide ideal conditions for fungal growth. The traditional sector alone suffers an annual loss of nearly 100 million rupees per annum for preservative treatment and replacement of damaged timber due to biodeterioration. The authors have developed a fortified creosote and an elastomeric composition combining antifouling and antiboring properties to check biodeterioration in traditional and small mechanised craft.

Materials and Methods

The arsenical creosote was prepared by dissolving a known quantity of arsenic trioxide in creosote and heating upto 90°C to yield a concentration of 0.22% (W/W). Low temperature creosote (LTC) and straight creosote were employed for fortification. Panels of Mango and Haldu were treated by hot dip and brush application after prior seasoning. In hot dip, seasoned-panels were dipped into the preservative kept at 90°C for about 2 h. The panels were then allowed to cool in the preservative for 6 h and dried to constant weight and preservative loading worked out.

Copper creosote was prepared by heating low temperature creosote (LTC) with 5% (W/W) reagent grade cuprous oxide in flasks with air condensers at a temperature of 99+0.5°Cfor 24 h. The product was cooled to ambient temperature and left aside for 1 month for the settlement of solid particles and then filtered. Seasoned mango panels were pressure treated in copper creosote warmed to 40°C at 4-4.2 $kgcm^{-2}$ for 30 min.Arsenical creosote at 40°C and 0.5% bis-n-tributyl tin oxide in fuel oil were also employed for comparison of biocidal properties. The panels were exposed to marine borer attack.

For the preparation of elastomeric antifouling-antiborer coating four toxins were used, namely, Bis (tri-n-butyl tin) oxide (TBTO), tri-butyl tin acetate (TBTA), triphenyl tin hydroxide (TPTH) and triphenyl tin acetate (TPTA) in three different matrices, elastomer, fibre glass reinforced plastic (FRP), and cashew nut shell liquid (CNSL). The elastomer employed was a synthetic rubber, reinforced with carbon black and marketed under the trade name 'Kotoprene'. FRP composites were prepared by using a layer of surfacing mat and general purpose polyester resin with cobalt naphthenate and methyl ethyl ketone peroxide. The third matrix consisted of melamine treated cashewnut shell liquid. Total five series of coatings were made, the fourth and fifth being improved designs based and antifouling-antiborer performance of series 1 to 3. In addition to the organo metallic compound, this improved design contained a special grade silicon carbide (400 mesh) and reagent grade zine oxide in the matrix. Coatings were applied over seasoned *Mangifera indica* blocks measuring 30x10x3.7 cm and their physical characteristics determined. The panels were suspended under water in the Cochin Harbour for assessing the antiborer and antifouling properties. Rate of attack estimated by counting borer holes and also by the determination of modulus of rupture as percent of residual strength. The arsenic creosote was also field tested by applying it on built-in canoes.

Results and Discussion

The higher absorption of arsenic in LTC (Table 1) is due to the higher phenolic content (22 v/w%) than that of normal creosote (5 v/w%). Johanson (1966) noticed the influence of phenolic content of creosote for its affinity to arsenic. The LTC with higher phenolic content is thus more suitable for fortification.

Results of raft trials to determine the antiborer properties of the preservative after 5 months immersion showed (Table 2)that there was no damage of panels treated by hot dip application. Laboratory leaching rate studies showed (Table 3), that the leaching was considerably less in mango panels.

Table 1. *Percentage arsenic trioxide taken up (w/w) by the low temperature and normal creosote at various temperature*

	Low temperature creosote		Normal creosote	
Temp.°C	% AS_2O_3 combining	% rate of increase	% As_2O_3 combining	% rate of increase
40	0.01522		0.00300	
50	0.16176	963	0.01230	310.0
60	0.14260	-11.8	0.02623	113.3
70	0.15220	5.6	0.03327	26.8
80	0.19180	26.0	0.03779	13.6
90	0.21800	13.7	0.03840	1.6

Table 2. *Assessment of boring in Haldu and Mango panels treated with fortified creosote*

Preservative	Species	Treatment	Loading kg/m3	% internal damage
Arsenic	Haldu	Brush	22.1	0.8
creosote	Haldu	Hot dip	208.6	Nil
Fortified LTC	Mango	Hot dip	177.5	Nil
Strait creosote	Mango	Brush	23.5	0.9
"	Mango	Hot dip	187.5	Nil
Control	Mango			6.0
	Haldu			5.0

Table 3. *Laboratory leaching studies*

Species of wood	Type of application	Loading (g/cm3)	Period (days)	Leaching after 50 h running time
Haldu	Brush applied	134	36-173	0.05
"	Hot dip	175.4	83-281	0.21
Mango	Brush	118.7	43-194	0.04
"	Hot dip	114.5	81-287	0.04

Table 4. *Biodeterioration of Mangifera indica treated with various preservatives after 8 months of seawater exposure*

Preservative	Borer holes	Area of destruction cm2	% of destruction	Modulus of rupture as %residual strength	Average loading of preservative kg/m^3
LTC	6	2.8	0.93	76	180
Copper Creosote	3	0.3	0.10	85	180
Arsenical creosote	4	1.7	0.51	80	180
0.5% TBTO in fuel oil	3	2.5	0.83	76	50
Untreated control	49	48.0	16.00	12	0

Copper oxide, that can be incorporated when heated with creosote, from Regional Research Laboratory, Hyderabad, at 90°C was 0.38%. This is higher than that of arsenic combining with creosote at the same temperature (Table 1). Johanson (1966) reported a value of 0.2 to 0.5% for vertical retort creosote. As in the case of arsenic creosote, the stability of copper creosote on long storage suggests chemical reaction rather than simple solubility. The phenols and hydroxyaromatic compounds establish chemical links with copper oxide and arsenic trioxide providing chemical stabliity to the resultant fortified creosote. Assessment of biodeterioration of copper creosote is presented in Table 4.

The untreated controls were bored by 49 Martesia. The preservative (Table 4) were effective in varying degrees. The assessment of biodeterioration by the estimation of the modulus of rupture would be a better reliable index as it represents the cumulative action of borers, fungi and bacteria.

Elastomeric coatings

Fouling is prevented by making the surface toxic by antifouling paints (WHOI, 1952) or organo metallic structural plastics with antifouling properites (Dykeman *et al.*, 1975) or using elastomer containing tri-n-butyl tin compounds (Sawada *et al.* 1975, 1975a). Prevention of marine biofouling and marine wood boring are viewed in isolation and several wood preservatives are developed for borer control. A toxic barrier in between the sea water/matrix inferface is required to control fouling and a tough abradable coating is required for controlling boring. A technical compromise satisfying these two properties is attempted by combining biocidal properties in a hard elastomeric coating.

The physical properties of polymeric coatings with organometallic biocides are presented in Table 5. After coating on wood flexibility and adhesion were determined on a third point flexural loading on a span of 30 cm. All coatings had a deflection of 30 mm and an yield point much higher than this and found to satisfy marine applications. The results of marine exposure tests are presented in Table 6. The same biocide behaved differently in different matrix. In polyester coating the toxicant got locked up in matrix while in CNSL resin system the toxicant availability was better. The action of antifouling depends on the toxic availability through diffusion, leaching or contact (WHOI, 1952; Marson, 1969; Van London, 1963; Crank, 1957). TBTO has a

Table 5. *Physical characteristics of polymeric coating with organic biocides*

Matrix No.	Polymeric matrix and biocides	Surface dry (h)	Hard dry (h)	Scratch hardness (Kg)	Flexibility & adhesion on 3rd point loading (mm)
PM-01	GP polyester+ TBTO	5	24	3.0	35
PM-02	GP polyester+ TBTA	5	24	3.0	30
PM-03	GP polyester+ TPTA	5	24	3.0	30
PM-04	GO polyester+ TPTH	5	24	3.0	30
PM-05	CNSL+TBTO	12	72	0.9	50
PM-06	CNSL+TBTA	12	72	0.9	45
PM-07	CNSL+TPTA	12	72	0.9	50
PM-08	CNSL+TPTH	12	72	0.9	40
PM-09	Kotoprene+ TBTO	1	3	0.9	30
PM-10	Kotoprene+ TBTA	1	3	0.9	70
PM-11	Kotoprene+ TPTA	1	3	0.9	70
PM-12	Kotoprene+ TPTA	1	3	0.9	70

Table 6. *Antifouling and antiboring properties of polymeric matrices containing organometallic biocide*

Matrix No.	Slime formation (months)	Algae	Hydro ides	Tube worms	Modi- olus	Barna cles	Fouling area %	Borers	Physical property
PM_01	1	-	1	-	1	1	50	3	Binding poor to fair
PM-02	1	-	1	-	1	1	60	3	"
PM-03	1	-	1	-	1	1	60	3	"
PM-04	1	-	1	-	1	1	50	3	"
PM-05	2	-	1	-	-	1	20	3	"
PM-06	2	-	1	-	-	1	25	3	Binding poor with blisters
PM-07	2	-	1	-	-	1	25	3	"
PM-08	2	-	1	-	-	1	20	2	"
PM-09	3	-	-	-	-	2	25	-	"
PM-010	3	-	-	-	-	2	30	-	Binding satisfactory
PM-011	3	-	-	-	-	2	30	-	"
PM-012	3				-	2	25	-	"
Control	1	-	1	1	1	1	100	1	

wide spectrum of activity (Hof, 1969; Zedler, 1964) but owing to the locking up of the toxic in the matrix it failed in its performance in this study when incorporated in polymeric matrix and CNSL. The physical properties of modified formulations containing TBTO, TBTA, silicon carbide, and zinc oxide in Kotoprene and CNSL are

Table 7. *Physical properties of polymeric matrices with organometallic bodies, silicon carbide and zinc oxide*

Matrix	Matrix system	Surface dry (h)	Hard dry (h)	Scratch hardness (kg)	Flexibility adhesion on 3rd point loading (mm)
PM 13	Kotoprene+ TBTO+SiC+ZnO	1	3	1.4	45
PM 14	Kotoprene+ TBTA+SiC+ZnO	1	3	1.3	45
PM 15	Kotoprene+ TPTA+SiC+ZnO	1	3	1.5	45
PM 16	Kotoprene+ TPTH+SiC+ZnO	1	3	1.5	45
PM 17	CNSL+TBTO+ SiC+ZnO	8	48	1.2	35
PM 18	CNSL+TBTA+ SiC+ZnO	8	48	1.4	35
PM 19	CNSL+TPTA+ SiC+ZnO	8	48	1.4	35
PM 20	CNSL+TPTH+ SiC+ZnO	8	48	1.4	35

Table 8. *Biocidal binding properties of polymeric matrices with organometallic compound, SiC and ZnO*

Matrix	Fouling (months)	Area fouled	Marine borers	Nature of coating
PM 13	9	Sparse	Nil	Satisfactory
PM 14	7	"	3	"
PM 15	7	"	5	Begins to fail
PM 16	8	"	Nil	Satisfactory
PM 17	5	"	Profuse	Blistering and flaking
PM 18	5	"	"	"
PM 19	5	"	"	"
PM 20	5	"	"	"
Control	1	100	Completely riddled. Modulus of rupture as % residual strength 6	

Table 9. *Expenditure for preservation of trditional craft (15m OAL) by indigenous method and fortified creosote*

Material	Qty.	Rate Rs.	Amount Rs.	Periodicity of application	Labour	Total Rs.
Sardine oil, l	48	10/l	480	Half yearly	6x50=300	938
Resin, kg	5	28/kg	140			
Black oxide, kg	6	3/kg	18			
Arsenical creosote						
Creosote; l	15	12/l	180	Annual	50x2=100	363
As_2O_3, g	50	60/kg	3			
Brush, bucket			80			
Copper creosote						
Creosote, l	15	12/l	180	Annual	50x2=100	363
Copper oxide, g	50	60/kg	3			
Brush, bucket			8			

presented in Table 7. The moderate solubility of ZnO provide path ways or pores in the coating system by their dissolution thereby allowing the toxic to come to the matrix seawater interface and prevent fouling. The highly abrasive silicon carbide provided antiboring properties to the coating.Formulations with Kotoprene prevented fouling upto 9 months but those with CNSL could perform successfully only upto 5 months (Table 8)as the coating failed.

The cost of preservative treatment by traditional and fortified creosotes is presented in Table 9. The traditional method appears to be 2.5 times costlier than treatment by fortified creosote.

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