Elastomeric Antifouling-Antiboring Coating - A New Approach

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Under favourable conditions, certain objects on immersion in seawater are subject to both boring and fouling. In this communication, the development of coating which would ward off both foulers and borers simultaneously is presented. Tough coatings based on melamine treated cashewnut shell liquid, polymerised rubber with carbon additives, polyester gel coat without fillers were developed for the purpose. Based on studies regarding packing characteristics and particle size, silicon carbide in a finely divided state was introduced into the matrix with a view to create a condition that is hostile to marine borers. The antifouling properties were provided to the matrix by introducing tributyl-tin-oxide. Details of the design of the coating and means of continuous maintenance of the leaching rate are presented. Data relating to field studies are also given.

The menace of marine fouling and boring organisms to the marine structures particularly in the tropics is well recognised. Fouling reduces the speed of ships and fishing boats, increases fuel consumption and adversely affects its handling characteristics and impedes fleet operation. Tighe-Ford (1971) estimated that fouling prevention and antifouling maintenance cost [illegible] maritime industry over 500 million dollars in 1971. The main organisms involved are barnacles, tube-[illegible]s, bryozoans, ascidians, hydroids, sponges and [illegible] as well as micro-fouling species such as diatoms. Marine boring on the other hand reduces significantly the life span of wooden boats and offshore wooden structures as a result of the destructive action by shipworms, *Martesia* and *Sphaeroma*.

Marine fouling and boring adversely affects many of the marine systems by impairing their efficiency. It erodes off the profit of marine operation as it necessitates large maintenance allocation. With the appropriate choice of materials and technologies now available the service life of timbers can be extended even in the most severe marine environment, the search for some effective and cheaper methodologies continues especially in tropical countries.

The early attempts to prevent fouling of wooden hulls of fishing boats made use of copper sheathing. This has been effective as a corrosion rate of 2–4 mil yr^{-1} of copper provided sufficient toxicity for the prevention of settlement of marine foulers. Advances in antifouling paints have produced long-lived (1–2 years) low-leaching antifouling paints. The premature failure was often caused by poor adhesion and abrasion resistance. The development of organometallic structural plastics exhibiting antifouling properties for the fabrication of non-fouling buoys, GRP sonar domes, hull coatings by the US Navy (Dyekman *et al.* 1973) is a significant contribution in this sphere of activity. The organometallic plastics such as polymethylmethacrylates, polystyrene and polyesters were prepared by chemically incorporating biocidal organometallic compounds on polymeric backbone (Montemarano & Dyekman, 1943). Investigations of marine biocidal properties of a series of formulations based on elastomers containing tri-n-butyltin compounds using moulded coatings and solution coatings for marine applications have been reported by the Australian Defence Scientific Service (Woodford, 1972; Dun & Oldfield, 1974). Some studies on the effectiveness of antifouling coats in fishing nets and laminated FRP using tributyltin, triphenyl tin and bromine substituted organometallic compounds were conducted by Sawada *et al.* (1975, 1975a) who observed appreciable antifouling action for about three months.

A scrutiny of literature concerning prevention of marine fouling and boring shows that it has been approached in isolation and the development of a satisfactory coating which wards off simultaneously both marine fouling and boring has not been investigated in detail. The difficulties in this sphere of work is primarily due to conflicting requirements for prevention of fouling and boring. While a toxic barrier at the matrix/seawater interface keeps away the foulers, the marine borers are known for their drilling activity even through lead sheathing of telephone cables in the sea. The requisites for antifouling action are achieved through formulation of a soluble type matrix or continuous contact of poison in the matrix are contrary to the requisites of antiboring surface which should be tough and non-abradable. Therefore, a technical compromise satisfying the two conflicting needs are to be simultaneously met for the formulation of a successful coating.

In this paper, the development and biocidal characteristics of a hard elastomeric coating which maintains a toxic barrier has been described.

Materials and Methods

The toxins used in this study were:

Bis (tri-n-butyltin) oxide – (TBTO)
Tributyl tin acetate – (TBTA)
Triphenl tin hydroxide – (TPTH)
Triphenyl tin acetate – (TPTA)

The elastomer was a synthetic rubber, reinforced with carbon black marketed under the trade name 'Kotoprene' for the protection of metallic structures against corrosion in chemical industries. The FRP composites were prepared by using a layer of surfacing mat and general purpose polyester resin with cobalt naphthanate and methyl ethyl ketone peroxide.

A special grade silicon carbide, 400 mesh, reagent grade zinc oxide, melamine treated cashewnut shell liquid (CNSL) were also used. Five series of coatings were made, the last two series being improved designs taking stock of the antifouling antiborer performance of series I to III. The coatings were applied on seasoned blocks of *Mangifera indica* measuring 30 x 10 x 3.7 cm and their physical characteristics were determined. For field tests the test blocks were mounted on mild steel frames and exposed at about a metre depth to the free attack of marine borers and foulers as also to the action of tidal currents of seawater of Cochin harbour premises. The first three series of coatings were exposed to the pre (February to May) and post-monsoon (October to January) periods for an initial screening of the antifouling and antiboring performance of the matrices. Data concerning the antifouling effect were gathered by observing the period elapsed for the first settlement of foulers.

Results and Discussion

Series I to III contained the organic biocide only in the polymeric compounds as shown in Table 1. As can be seen from the Table 1, that their physical characteristics such as surface dry, hard dry, scratch hardness and flexibility and adhesions were satisfactory for any marine application. As the coatings were of the high-build type applied on wood, the flexibility and adhesion were determined on a third point flexural leading on a span of 30 cm. All coatings passed a minimum deflection of 30 mm and the yield point was much higher than this value. As in practical applications on boat hulls, a deflection over tens of millimetre is usually not encountered, the flexure tests have not been carried out to ultimate values. The adhesion was good in all cases. The data on fouling and boring characteristics and nature of adhesion of matrices PM–01 to PM–12 are given in Table 2. The number of months elapsed prior to fouling is a reasonably good indication of the toxic availability at the matrix/seawater interface. The coverage of foulers was highest (50–60%) in polyester matrices and least (20–25%) in polymerised CNSL. This indicates that the same biocide behaved differently in different matrix, the reason being that in polyester coating the toxic got locked up in the matrix, whereas in CNSL resin system the toxicant availability was better. Sawada *et al.* (1975, 1975a) who conducted field tests at Ito harbour in Japan reported that tributyltin and triphenyltin compounds in gel coat of FRP boards were effective against foulers for 3 months. The results obtained in the present studies show that biocide incorporation in FRP was not effective in preventing fouling settlement. Coating PM–O to PM-08 failed in adhesion and boring was also observed. The most promising results were obtained when TBTO was incorporated in Kotoprene elastomer, in the field exposure tests.

An observation which merits mention is the fouling by barnacles within a month on polyester and CNSL matrices, but in Kotoprene the period elapsed was two months. The corresponding periods for slime formation were 1, 2 and 3 months. This shows that the

Table 1. *Physical characteristics of polymeric matrices containing organic biocide*

Matrix No.	Polymeric matrix and biocide		Surface dry h	Hard dry h	Scratch hardnesss Kg	Flexibility and adhesion on 3rd point loading mm
PM–01	GP – Polyester	+TBTO	5	24	3	35
PM–02	"	+TBTA	5	24	3	30
PM–03	"	+TPTA	5	5	24	30
PM–04	"	+TPTH	5	24	3	30
PM–05	CNSL	+TBTO	12	72	0.9	50
PM–06	"	+TBTA	12	72	0.9	45
PM–07	"	+TPTA	12	72	0.9	50
PM–08	"	+TPTH	12	72	0.9	40
PM–09	Kotoprene	+TBTO	1	3	0.9	30
PM–10	"	+TBTA	1	3	0.9	70
PM–11	"	+TPTA	1	3	0.9	70
PM–12	"	+TPTH	1	3	0.9	70

Table. 2. *Anifouling and antiboring properties of polymeric matrices containing organic biocide* (Months elapsed for the first appearance of foulers and borers)

Matrix No.	Barnacles	Isopods	Hydroids	Molluscs	Tube worm	Algae	Slime	Fouling % area	No. of borer holes	Adhesion
PM-01	1	–	1	1	–	–	1	50	3	Binding poor to fair Flaking
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	1	–	1	–	–	–	2	20	3	Binding poor, blister formed
PM-06	1	–	1	–	–	–	2	25	3	"
PM-07	1	–	1	–	–	–	2	25	3	"
PM-08	1	–	1	–	–	–	2	20	2	"
PM-09	2	–	–	–	–	–	3	25	–	Binding satisfactory
PM-10	2	–	–	–	–	–	3	30	–	"
PM-11	2	–	–	–	–	–	3	30	–	"
PM-12	2.	–	–	–	–	–	3	25	–	"
Control	1	–	1	1	1	1	1	100	1	—

Table. 3. *Physical characteristics of polymeric matrices containing organic biocide, silicon carbide and zinc oxide*

Matrix No.	Matrix system	Surface dry h	Hard dry h	Scratch hardness Kg	Flexibility and adhesion on 3rd point loading mm
PM-13	Kotoprene + TBTO + SiC + Zno	1	3	1.4	45
PM-14	" + TBTA + SiC + "	1	3	1.5	45
PM-15	" + TPTA + SiC + "	1	3	1.5	45
PM-16	" + TPTH + SiC + "	1	3	1.5	45
PM-17	CNSL + TBTO + SiC + "	8	48	1.2	35
PM-18	" + TBTA + SiC + "	8	48	1.3	35
PM-19	" + TPTA + SiC + "	8	48	1.4	35
PM-20	" + TPTH + SiC + "	8	48	1.4	35

Table 4. *Biocidal and binding properties of polymeric matrices containing organometallic compound, silicon carbide and zinc oxide*

Matrix No.	Months elapsed for settlement of major foulers	Area fouled %	No. of Borer holes	Nature of adhesion
PM-13	9	Sparee	Nil	Satisfactory
PM-14	7	"	3 at edge	"
PM-15	7	"	5 at edge	Begins to fail
PM-16	8	"	Nil	Satisfactory
PM-17 @	5	–	Profuse*	Blistering and flaking
PM-18 @	5	–	Profuse*	"
PM-19 @	5	–	Profuse*	"
PM-20 @	5	–	Profuse*	"
Control	1	100	Completely riddled by borers. The modulus of rupture as residual strength was 6%	

* The internal damage of timber was over 50%

@ Coating failed in adhesion in 5 months. Foulers and borers entered through the area of failure. Observations on foulers and borers beyond 5 months are no longer reliable.

presence of slime is not an essential pre-requisite for barnacle fouling but it is significant to note that a delayed formation of slime has also delayed settlement of barnacles showing that slime may have some influence in barnacle settlement. This observation agrees closely with that of Liberatore *et al.* (1972) and Nair & Pillai (1975) who noted that slimed glass surface attracted and retained more barnacles than the clean ones.

The results presented above, show distinct possibilities of combining the antifouling and antiboring properties on a suitably prepared matrix. As is well known (Woods Hole Oceanographic Institution, 1952; Marson, 1962; Van London, 1963; Crank, 1957) the antifouling action depends upon the toxic availability through diffusion, leaching or contact, the present observations point to the fact that though TBTO exhibit a wide spectrum of activity (Hof, 1969; Zedler, 1964) it has not performed satisfactorily as the toxic did not find access to travel through the matrix and reach the seawater/matrix interface. Following on this premise, it was considered on theoretical grounds that incorporation of zinc oxide which has moderate solubility in seawater would improve the toxicant availability of TBTO by way of providing pores/paths in the coating system. The antiboring properties were imparted through the incorporation of highly abrasive material namely, silicon carbide. The modified design formulations designated as series IV and V were then evaluated, for their physical characteristics (Table 3) and for effective long life in seawater (Table 4). In all the cases (PM–13 to PM–20) period elapsed for the settlement of any major forms of foulers showed definite increment. Observations on CNSL base coatings (PM–17 to PM–20) could not be continued beyond 5 months as a result of deterioration of the binding of the coating with wood which caused fouling at areas where fracture occurred. Elastomeric coating PM–13 demonstrated fouling and boring free life span of 9 months. This observation confirms the reasoning that the diffusion of the organometallic compound is enhanced through the vacant path or pores formed as a result of dissolution of sparingly soluable zinc oxide. This observation merits consideration in employing similar techniques in the prevention of biodeterioration of materials for ocean engineering applications.

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