EXPERIMENTAL FORMULATION OF AN ANTI FOULING PAINT WITH TRIBUTYL TIN OXIDE AS TOXIC PIGMENT

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Results of the experimental formulation of an antifouling paint incorporating TBTO as toxic pigment are presented in this paper. Of the various resins tested, namely, phenolic, cashew nut shell liquid (CNSL), epoxy, linseed oil with rosin and limed rosin, the paint composition with limed rosin gave the critical leaching rate of TBTO. Acid alkali test showed dissolution of matrix and visible migration of toxin to the surface. Accelerated corrosion tests had not recorded any signs of corrosion in panels painted with or without barier coat. Raft exposure studies indicated that the new formulation could resist fouling accumulation on painted panels for 9 months.

INTRODUCTION

Commercial antifouling paints contain either copper, mercury or arsenic compounds in varying concentrations as toxic pigment. Salts of zinc, iron and lead have also been used commonly in formulating antifouling paints. Although preparations containing copper compounds are effective against marine fouling organisms, these compounds accelerate corrosion of steel and aluminium when directly applied on them. Further, protection of some substrates such as plastics and rubbers has been impossible with paints containing cuprous oxide (Bennet and Zedler 1966).

Of late, the use of organometallic compounds as toxic pigments in paints and other surface coatings has been given importance. Organotin compounds are noted for their high toxicity. These compounds have proven merits as fungistats and bacteriostats and also known to have great toxicity to marine fouling animals (Bennet and Zedler *op. cit.*) and wood boring organisms (Bennet and Zedler 1964). Practically no work has so far been done in India on the use of organotin compounds in conjunction with marine antifouling paints.

Vander Kerk and Luijten (1954) were among the first to note the biocidal properties of trialkyltins. In 1946 the British Patent of Tisdale 578 and 312 disclosed the effectiveness of triethyltin and triphenyl tin derivatives for antifouling purposes. Bennet and Zedler (1966) conducted extensive studies using various organotins at Biscayne Bay, Miami Beach, Florida.

As toxic constituent in antifouling paints Tributyl tin oxide offers several advantages. It is a clear, colourless, liquid, readily soluble in common solvents. It is non-setting in nature, highly toxic to marine fouling and wood boring organisms and is noncorrosive in nature.

Recently an attempt has been made at the Central Institute of Fisheries Technology, Cochin in formulating an experimental batch of antifouling paint with tributyl tin oxide (TBTO) a sample of which was imported. As has been suggested by Balasubramanyan (1969) evaluation tests on experimental formulation were undertaken in a sequence of laboratory studies for leaching rate calculations, raft exposure for estimation of actual fouling resistance and service trials for a final performance assessment.

MATERIAL AND METHODS

The characteristics of TBTO tested are presented in Table I.

TABLE I: PROPERTIES OF THE TBTO TESTED*

Structural formula	Molecular weight	Tin (Sn) content %	Water %	General appearance.	Boiling point °C	Freezing point °C	Viscosity 25°C	Solubility in water.
H_9C_4 C_4H_9 H_9C_4-Sn-O-Sn-C_4H_9 H_9C_4 C_4H_9	596.0	38.5 min.	0.25 max.	Clear pale straw liquid	180 (at 2 mm Hg)	Below -5.0	5.3	200 Approx.

* Supplied by Industrial Chemical Division of Albright & Wilson (MFG) Ltd., 1 Knight bridge Green, London-SWI, Kensington 3422.

Various resins namely, phenolic, cashewnut shell liquid, (CNSL) epoxy, linseed oil with rosin and limed rosin were tested to find out the right type of matrix to be incorporated in the paint. The resins were screened mainly based on their solubility in water. Bentonite and calcium carbonate were used as fillers and dibutylphthalate (DBP) as plasticiser with driers. In the dry state limed rosin at 35.9% by weight was loaded with 17.95% by weight of TBTO. By adding thinners, the viscosity of the paint was adjusted to the desired level.

Accelarated chemical tests were conducted to eliminate unsatisfactory formulations. Paints were applied over ground glass panels of size 15 x 10 cms. and immersed in two litres of artificial sea water of pH 8.2 at a temperature of 30°C. Air was bubbled through a 7 mm glass tube at the rate of 7 bubbles per second. The arrangement of the leaching rate experiment is as shown in the photograph. At regular intervals the leachate was analysed for tin content with dithiol reagent following the method of Snell and Snell (1958). Preparations which did not give satisfactory leaching rate of 1.25 gram sn/ Sq. cm/day (Bennet & Zedler 1966) were eliminated and those which gave satisfactory leaching were aged in sea water for different periods and subjected to further testing, adopting the method of Van London (1963). The leaching rate study was further supplemented by acid-alkali test as designed by Mare Island Naval Ship Yard and reproduced in the Woods Hole Monograph on marine fouling and its prevention (1952). Physical tests were done as per IS/419/1959 and IS/101/ 1965. (Table V). Erosion studies were made by applying the paint on a disc of 25 cm. diameter and rotating at 14 knots per hour, underwater to simulate the motion of ships. Centrifugal forces which have no conterpart under service conditions were applied to the paint film and the condition of the

Photograph showing the arrangement of leaching rate experimeut.

paint film studied. Paints which withstood 200 hrs. without erosion were rated as satisfactory. The stability of the formulated paint was determined by the method of Anderton (1964). Effect of cathodic protection on the paint film was studied by the method of Bansfield (1958). Biological evaluation was done by raft exposure studies.

RESULTS AND DISCUSSION

Matrix solubility or dissolution is an important property of antifouling paints which coutrols the leaching rate of the paint. Various resins, namely phenolic, cashew nut shell liquid (CNSL) linseed oil with rosin and limed rosin were tested to determine the right type matrix for incorporation in the paint. Of these resins, limed rosin gave the critical leaching rate of TBTO, namely 1/μgm sn/sq.cm/day. Table II summarises the results of the leaching rate experiment.

TABLE II: LEACHING RATE OF THE PREPARATION IN NATURAL SEA WATER

Period of seasoning in months	Leaching rate μgm Sn/Sq cm/day
Without seasoning	1.6240
1	1.5820
2	1.5980
3	1.5880
4	1.5926
5	1.5612
6	1.5376
7	1.5256
8	1.4972
9	1.4882
10	1.4530
12	1.5312

As evident from Table II, an average leaching of 1.5423 μgm sn/sq. cm./day was observed for 12 months. For reducing the rapid solubility of the poison, Deeks *et. al.* (1968) tried co-polymers such as butyl acrylate. Since the polymers had little antifouling action Deeks *et. al* (op. cit) also tried high pigment volume concentration, with cuprous oxide, and obtained paints of extra ordinary effectiveness and length of life. However, no such co-polymerisation was found necessary in this study, as the paint maintained the steady leaching rate for one year, (Table II). By employing the equation $y=0.01183x + 1.6143$, where x is the period of immersion in month and y the leaching rate in μgm/Sq. cm. per month, the rate of decrease was found to be 0.01183 μgm/Sn/Sq. cm. per month (Fig. I). At the rate of this decrease, namely 0.01183 μgm Sn/Sq. cm/month it was possible to predict that the paint will maintain the critical leaching rate for 32 months and thus retain its antifouling properties.

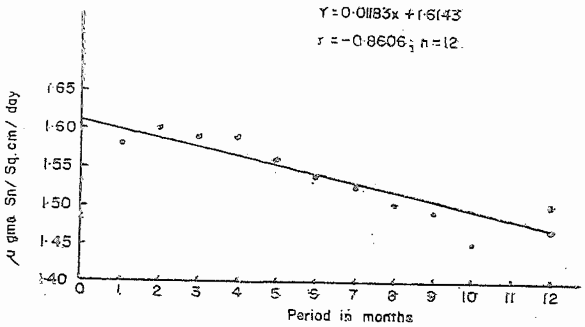

Fig.I. SHOWING THE LEACHING RATE OF T B T O IN SEA WATER

The steady state of leaching of the antifouling paints depends upon the release of toxic from the interior of the paint film by the degeneration of matrix thereby making available deeper stores of toxin in the paint available at the surface so as to prevent to settlement of fouling organisms. This was studied by employing the acid-alkali test developed by investigators of the Mare Island Naval Ship Yard and reproduced in the Woods Hole monograph on marine fouling and its prevention (1952). It consisted of two successive extractions of the paint film applied to a panel, in acid and alkaline medium. Alternate immersion in sea water at pH4 and in normal sea water of pH 8.4 helped to regenerate the toxic pigments after exhausting the surface matrix. The leaching rate of the panels varied from 1.213 to 1.521 μgm Sn/Sq. cm./day. Comparison of leaching rates after the successiv treatments (Table III) in acid and alkaline solutions indicate that the matrix has been dissolved by the alkaline solution. Thus it was apparent that the paint maintained the critical leaching rate by gradual dissolution of the matrix and visible migration of toxins to the surface. Data presented in Table III shows an inverse relationship between the period of immersion and leaching rate, suggesting gradual exhaustion of toxin.

TABLE III: LEACHING RATE OF TIN BY ACID-ALKALI TEST

Period of immersion in sea water pH4	Leaching rate of Sn in μgm Sn/Sq. cm/day
1 day	1.521
2 days	1.346
3 days	1.322
4 days	1.412
5 days	1.328
6 days	1.219
7 days	1.248
8 days	1.321
9 days	1.251
10 days	1.213

The present paint formulation was applied over aluminium magnesium alloy panels with and without anticorrosive paints namely zinc chromate. Accelerated corrosion tests in salt spray chamber for 96 hours have not recorded any signs of corrosion in both the panels (Table IV). This suggested that TBTO based paint under reference did not cause galvanic corrosion as has been the finding of Summerson et. al (1964). Tests were also conducted (Table IV) to study whether paint coating containing TBTO was damaged by cathodic protection when electric currents of 1.2V were applied to such painted panels for a period of 7 days. No damage were noticed to the paint film.

Results of biological evaluation of the paint by raft exposure are presented in Table VI. The paint was tested for its antifouling properties along with one of the best commercial antifouling paints to assess their comparative performance. The panels were exposed subtidally, one foot below low water line from the Institute's quay during post monsoon and pre-monsoon periods when the quantity and quality of fouling were very high. Periodic checking was made and fouling data recorded as shown in Table VI.

TABLE IV: ACCELERATED SALT SPRAY TEST

Sheathing material used.	Plan of Test	Duration of test.	Observation
Aluminium magnesium alloy (M57S)	One coat of wash Primer followed by one coat of Zinc chromate and 2 coats of the present formulation.	96 hrs.	No damage to the paint film noticed. No corrosion near 'x' cut.
Aluminium magnesium alloy (M57S)	As above but without Zine chormate paint.	96 hrs.	No damage to the paint film noticed. No corrosion near 'x' cut.

TABLE V: PHYSICAL PROPERTIES OF TBTO TESTED AS PER IS 1419/1959 & IS 101/1965.

The paint passed the following test:

Time of surface drying	—	Below 1 hr.
Tack free drying	—	8 - 10 hrs.
Resistance to acid	—	Film intact. No damage to paint film.
Resistance to alkali	—	Film intact. No damage to paint film.
Flexibility	—	Film intact.

As evident from the table, the commercial antifouling paint containing cuprous oxide got 50% area fouled from the 6th month onwards, while the persent laboratory formulated TBTO preparation resisted fouling far beyond that period. The tests could not be continued owing to the onset of monsoon. Unpainted controls were fouled 50% of the area from the 3rd month onwards. Service trials conducted on one of the Institute's vessels showed that the paint resisted fouling accumulation for 14 months establishing its superiority over the conventional paint composition both in the laboratory, field and service trials.

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TABLE VI: COMARATIVE ESTIMATION OF FOULING (BIOLOGICAL EVALUATION) OF THE PAINT FORMULATION AND ONE OF THE COMMERCIAL ANTIFOULING PAINTS BY RAFT EXPOSURE.

Months of exposure	Oct. 1	Nov. 2	Dec. 3	Jan. 4	Feb. 5	Mar. 6	April 7	May 8	June 9
Control	VL	VL	M	M	H	VH	VH	VH	VH
Commercial antifouling paint.	Nil	Nil	Nil	L	L	M	M	H	H
Formulation with TBTO.	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Key. VL — Sparce growth (5% to 30% surface area fouled)
L — Light growth (30% surface area fouled)
M — Medium (50% ,,)
H — Heavy (75% ,,)
VH — Very heavy (Super imposed growth))

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