Studies on Tri-*n*-Butyltin Methacrylate (TBTM). IV. Antifouling Compositions Based on Copolymers of Tri-*n*-Butyltin Methacrylate and Methyl Methacrylate

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Synopsis

Based on reactivity ratios reported earlier, a number of copolymers of methyl methacrylate and tri-*n*-butyltin methacrylate has been prepared. Release of tri-*n*-butyltin oxide into seawater from the copolymer films has been determined at 30°C as a function of time. The copolymers behave in a typical manner—an initial increase in leaching rate followed by a steady state which is reached after about 60 days. Pigmented copolymer films behave in a similar manner, even though the overall leaching rate is slightly lower. Release rate data are also presented for a typical antifouling paint formulation.

INTRODUCTION

An unprotected structure immersed in sea is prone to settlement or fouling by microorganisms. With time this settlement results in the formation of a thick, uneven and hard crust and thus prevention of fouling is of direct concern. A fouled underwater surface results in increased drag resistance, adverse effect on anticorrosive measures, increased dry-docking frequency, and decreased operational availability.

Substantial progress has been achieved in the last two decades on anticorrosive measures, and paints available today offer 5–6 years protection to ship's hulls when they are used in conjunction with other electrochemical protection systems. However, conventional antifouling paints have a consistent life of only about 10–14 months in tropical waters.

A conventional antifouling paint represents a homogeneous mixture of resin and toxic pigment which offers antifouling protection by releasing the toxin to the surroundings. The most widely used toxin is cuprous oxide, which has been in use for over 100 years. It is effective on a variety of bioorganisms. The critical leaching rate for cuprous oxide is about 10 $\mu g/cm^2$/day. To increase the life of an antifouling paint, highly efficient toxins, e.g., arsenates of mercury and lead, DDT, tri-*n*-butyltin oxide, or halides as well as the triaryltins, have been tried. In each case an initial high rate of toxin release resulted in unnecessary depletion. Within a short period of time, the paint film thus becomes too low in toxin content to offer any resistance to fouling.

The problems can be tackled by using toxins in a chemically bound form in a film-forming resin so that chemical release starts before actual leaching in

seawater. The problem is akin to the formulation of controlled release drugs.[1-4] Another concept would be an on-demand release of toxin, i.e., release of toxin only when a fouling organism attempts to sit nearby. However, the present work is restricted only to studies involving chemically bound toxins to prevent fouling for an extended period.

In this communication, the release pattern of tri-*n*-butyltin oxide from methyl methacrylate–tri-*n*-butyltin methacrylate (MMA–TBTM) copolymer films of various compositions is reported for a few formulations containing nontoxic pigments.

EXPERIMENTAL

Synthesis of Copolymer of Tri-*n*-Butyltin Methacrylate and Methyl Methacrylate

Tri-*n*-butyltin methacrylate monomer was synthesized by the method of Montermoso et al.[5] Repeated recrystalization of the monomer (mp 20°C) was necessary before it could be homopolymerized or copolymerized successfully.[6] Methyl methacrylate monomer was freed of inhibitor by washings with aq. NaOH solution (5%), washed free of alkali with water, and dried over anhydrous $CaCl_2$. The monomer was distilled at reduced pressure under nitrogen and stored at -20°C in the dark. Azobisisobutyronitrile (AIBN) was recrystallized from alcohol and dried in vacuum.

Copolymers of MMA and TBTM of various compositions were made utilizing the reactivity ratio of this pair of monomers. The monomers were mixed in appropriate ratio and AIBN was dissolved in the mixture at a concentration of about 10^{-3} mol/L. The ampules containing the mixtures were then degassed by repeated freeze–thawing and sealed under vacuum. They were thermostatted at 60°C and the contents were allowed to polymerize to about 30% conversion. The ampules were cooled, and the contents diluted with appreciable amounts of benzene. Polymers were precipitated in aqueous methanol. They were further purified by dissolution–precipitation technique. The copolymer compositions were determined from the tin content.

Determination of Leaching Rate

Experimental panels for leaching were of glass (12.5 × 5 × 0.2 cm). They were abraded thoroughly, cleaned with water and methanol and dried in air. Copolymers of different compositions were dissolved (33% by wt) in toluene along with dioctylphthalate to obtain tough and flexible films. The solutions were applied on the panels by a film applicator and allowed to dry. The procedure was repeated until a thickness of about 100 μm (± 10 μm) dry film was achieved. Similar panels were used for determining the leaching rates of a copolymer composition pigmented with iron oxide and zinc oxide. The pigments were mixed with a 33% solution of the copolymer in toluene, plasticizer, and a suspending agent, and ball-milled for 12 h to obtain a homogeneous mix. The panels were coated to a thickness about 100 μm (± 10 μm) of dry film.

The leaching rate apparatus consisted of an assembly of twelve vertically rotating shafts (60 rpm) each provided with a clamp. The experimental panels in triplicate were fixed to the shafts and were immersed in 500 mL of seawater

contained in wide-mouth glass jars. For each set of experimental panels, blanks were also provided consisting of unpainted glass panels in seawater. Every 10 days, the water was replaced by fresh water.

Estimation of Tri-*n*-Butyltin Oxide (TBTO) in Leachate

Leachate (100 mL) was extracted with five 5-mL portions of carbon tetrachloride (spectroscopic grade), to ensure total transfer of TBTO from aqueous to organic phase. The extractions were combined and the TBTO determined by the dithizone method.[7] Dithizone (LR) was purified[8] by dissolving in 5% aq. NaOH solution and then acidifying with $1N$ H_2SO_4 to congo red. The precipitate was filtered and freed of sulfate by repeated washing with distilled water. The material was finally vacuum-dried at 40°C.

RESULTS AND DISCUSSION

The MMA–TBTM pair forms an ideal copolymerization system[9, 10] having the following reactivity ratios at 60°C:

$$r_1 = k_{11}/k_{12} = 1.04 \quad \text{and} \quad r_2 = k_{22}/k_{21} = 0.93$$

Not only the product $r_1 r_2$ is approximately unity, but also the individual r_1 and r_2 values are near unity, signifying that homo- and cross-propagation occur equally rapidly. The system offers copolymer compositions roughly corresponding to monomer feed compositions even at high conversion. Table I shows the copolymer compositions (based on tin content) at three monomer feeds at a conversion of about 30%. These copolymers were used to formulate the various compositions for study of leaching rates.

Solubility of TBTO in Seawater

The solubility of TBTO has been reported by Chromy and Uhacz[11] based on colorimetric determination and by Maguire et al.[12] by gas chromatography. Chromy and Uhacz[11] reported a value of about 1–2 mg/L in "synthetic" seawater (0.5–3% sodium chloride in distilled water). The effect of pH has, however, not been considered by the authors. Solubility measurements of TBTO in sodium chloride solution as well as in seawater were therefore carried out. It may be mentioned that Maguire et al.[12] measured the solubilities in water at various pHs by adding hydrochlorides and glycinates. The seawater system differs markedly from such media and hence need not be considered here further.

TABLE I
Copolymer Compositions Obtained from Methyl Methacrylate
and Tri-*n*-Butyltin Methacrylate Using AIBN As Initiator at 60°C

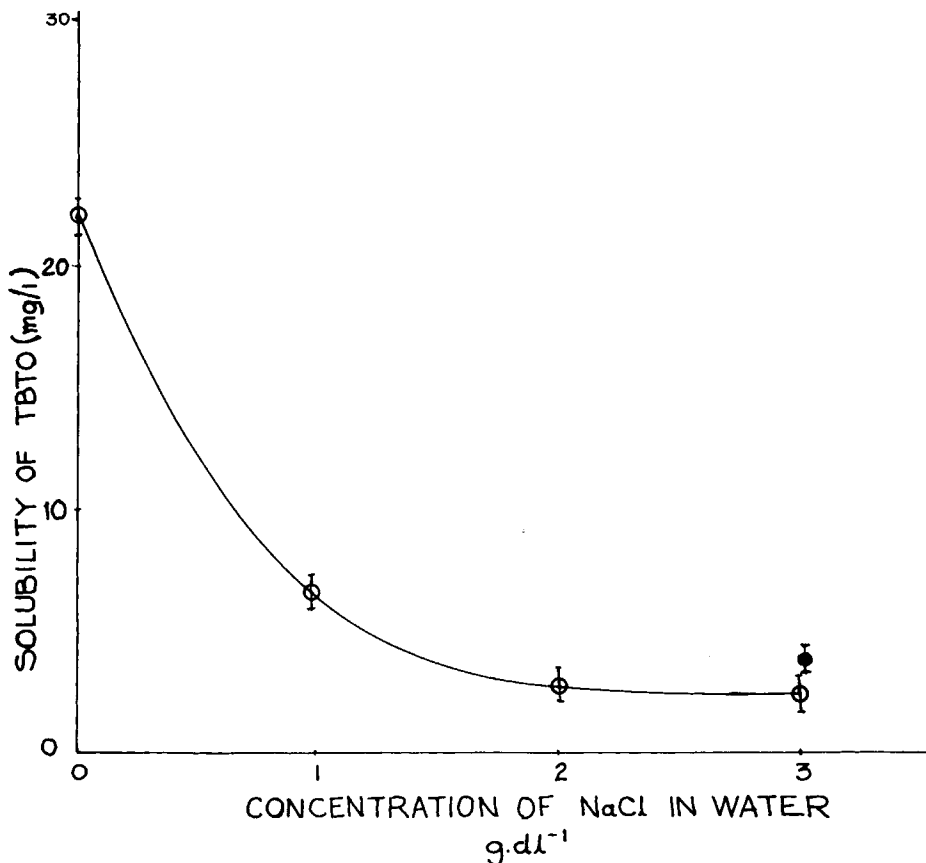| Sample no.	Mole ratio of TBTM in monomer	Percent conversion	Mole ratio of TBTM in copolymer
1	0.25	30	0.26
2	0.43	30	0.40
3	1.00	30	1.00

Fig. 1. Solubility of tri-*n*-butyltin oxide in aqueous sodium chloride solutions at 30°C: (Φ), solubility in seawater at 30°C, (◆).

Figure 1 shows the variation in solubility of TBTO with NaCl concentrations at 30°C. The solubility in seawater is about 3.5–4.0 mg/L compared to about 2.8 mg/L at 3% NaCl solution in distilled water. The reason for the higher solubility in seawater is not clear at present.

Leaching Behavior of Copolymer Films / Paints

The leaching rate of conventional and chemically bound biocidal polymer based paints has recently been discussed by Gitlitz.[13] Figure 2 shows the normally encountered leaching rate–time behavior for a conventional antifouling paint based on a physical mixture of the toxin in a paint film along with that of an ideal paint system. The performance of a conventional antifouling paint system depends on the migration of the toxicant from interior to the surface of the paint film, and the leaching rate–time curve is logarithmic in nature.[13] The disadvantages of such an antifouling paint, such as unnecessary depletion of toxins at the initial phase, nonutilization of remaining pigment in the paint film, etc., are discussed in detail.[13] The situation is entirely different in the case of paints involving a polymer in which the toxic organotins are chemically bound and the polymer is hydrolyzable at a controlled rate. When
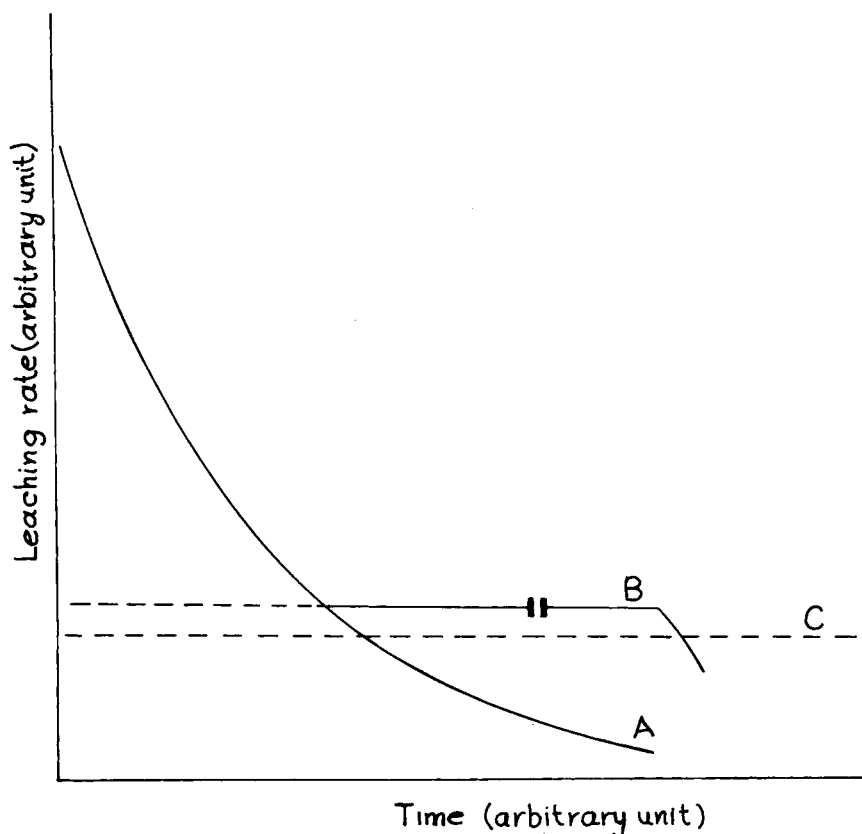
Fig. 2.   Variation of leaching rate of a toxin from a conventional paint formulation (A) and a second generation paint formulation containing chemically bound toxin in resin (B): (---) critical leaching rate (C).

put into seawater, the organotin polymer on the surface gets hydrolyzed, and the toxin is released into the seawater and prevents fouling by micro-organisms. The surface, now depleted of toxin, contains an appreciable amount of carboxylate polymer, which gets dislodged in water by erosion as it has very little mechanical strength. A fresh surface is exposed; the hydrolysis and erosion go hand in hand till the entire paint film is dislodged into water. In addition to affording antifouling utility, the paint film also maintains a fresh surface and is self-polishing. The leaching behavior of an organotin-based antifouling paint is a direct function of the rate of hydrolysis and erosion. Since the rate of hydrolysis is a function only of the availability of hydrolyz-able polymer on the surface (water always being present in excess), the leaching rate should remain practically constant during the entire film life. The life of such an antifouling paint is, therefore, a direct function of the thickness of the paint film. The optimum leaching rate (slightly above the critical) is adjusted by controlling parameters such as the amount of bound toxins, pigment, etc. However, the release of toxin to the surrounding medium is in no way as simple as depicted here. It has been recently described[14,15] that the release of toxin from polymers may be a very complex process involving a
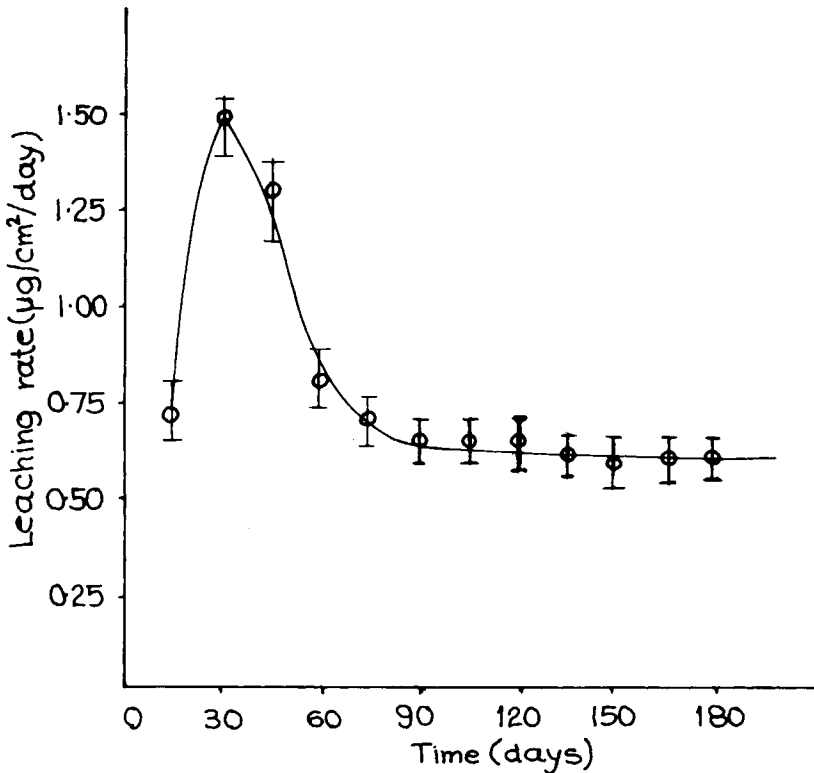
Fig. 3. Leaching rate of tri-*n*-butyltin oxide from a copolymer film containing 30 mol % of tri-*n*-butyltin methacrylate in seawater at 30°C.

number of steps. Diffusion of water slowly into the paint film, the chemical reaction of the polymer with water, and diffusion of the small molecules may be controlled by many unforeseen factors.

Figure 3 shows the leaching rate behavior of TBTO from a copolymer film containing 30 mol% TBTO in the copolymer. The release rate is characterized by a maximum followed by a gradual shift to a steady state value. The leaching rate at the steady state may be designated as L_s and may represent a characteristic factor for an antifouling paint based on the principle of controlled-release polymeric toxins. It is important to note that conclusions, which are based on a few leaching rate determinations before the steady state is achieved, may be erroneous in regard to the usefulness of a specific copolymer in antifouling paint formulations. This type of leaching rate behavior has been observed for all films of different copolymer compositions obtained from MMA and TBTM.

The variation in steady state leaching rate of TBTO in seawater at 30°C as a function of copolymer composition in pure copolymer films is represented in Figure 4. The film thickness and other parameters being constant, the·plot represents the leaching behavior as a function of copolymer composition. The TBTM content in copolymer compositions represents the availability of hydrolyzable groups and hence the amount of TBTO obtainable.
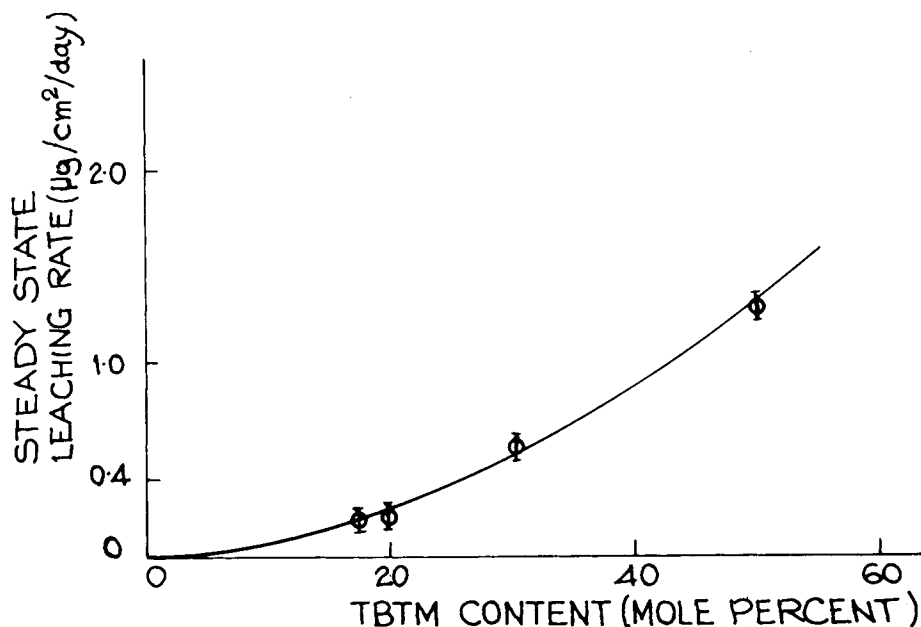
Fig. 4. Variation of steady state leaching rate with tri-*n*-butyltin methacrylate content in copolymers in seawater at 30°C.

The variation in leaching rate with TBTM content in copolymer does not follow a linear, but approximately a square relationship. This may be due to the acceleration of the hydrolysis rate by the acid liberated.

The leaching rate as a function of copolymer composition leads to an important conclusion; i.e., a minimum leaching rate of about 0.4 $\mu g/cm^2/day$ of TBTO is necessary in seawater to prevent fouling of underwater marine structure.[11] Since pigment loading is expected to reduce the leaching rate of toxin from copolymer films, a useful TBTM–MMA copolymer composition should not contain less than about 30 mol% of TBTM. This may be termed as a threshold composition for these copolymers.

Having established the useful composition limit, the effect of neutral pigment loading on the leaching rate of TBTO was then examined. Iron and zinc oxide were chosen as representatives of insoluble and sparingly soluble pigments. Two paint compositions were made with 100 parts of iron(III) oxide and zinc oxide and 10 parts dioctyl phthalate with reference to copolymer. The variation of leaching rates with time is represented in Figure 5. After 60 days, the steady states were reached as in the case of unpigmented copolymer film. The leaching rates are also comparable to those for unpigmented copolymer films which show that the release of toxin is not effected by incorporation of pigments and also that the nature of the pigments does not play a very important role.

Figure 6 shows the variation of steady state leaching rate with pigment loading. There is a detectable decrease in leaching rate with pigment loading but the former reaches constant value at about 120 parts per hundred (pph) of pigment. Moreover, at each pigment loading, zinc oxide offers a slightly higher
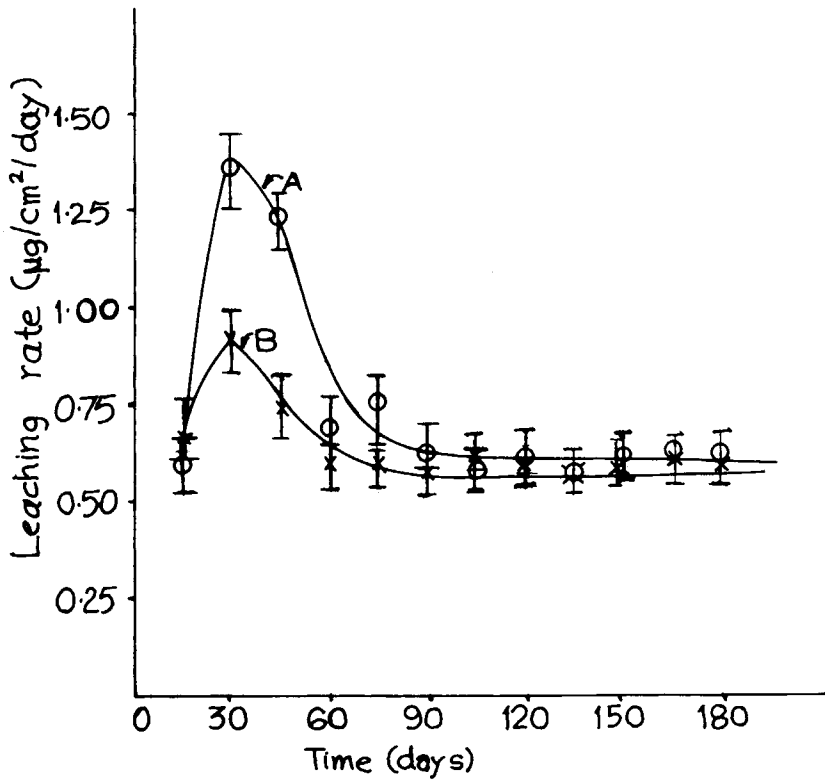
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Fig. 5. Variation of leaching rate with time for copolymer (30 mol % TBTM) film containing 100 pph ZnO and 10 pph DOP (A) and a typical paint formulation (B).
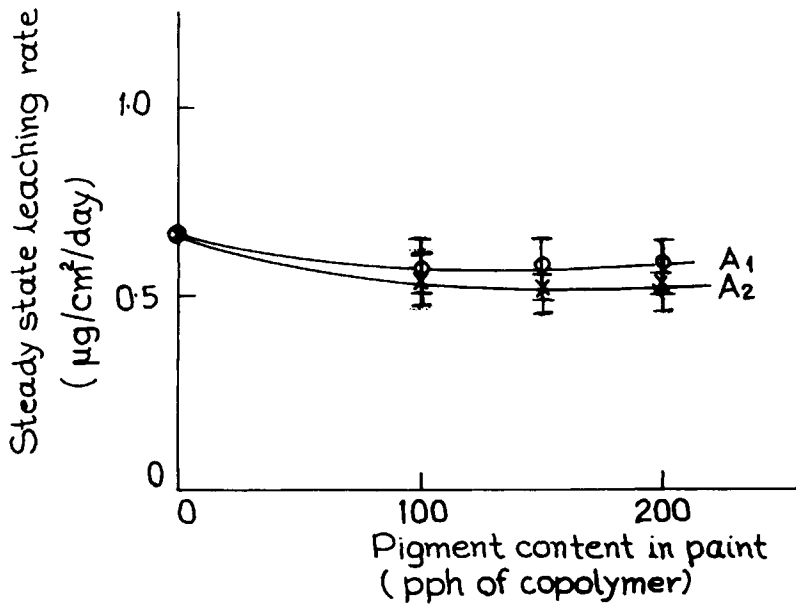

Fig. 6. Variation of leaching rate with pigment concentration for zinc oxide (Al) iron oxide (A2).

release of toxin than does iron oxide; this is probably due to higher solubility of zinc oxide in seawater which results in better erosion of the paint film.

The establishment of a steady state leaching rate within a period of about 60 days marks a welcome departure from the conventional antifouling paints. This phenomenon of steady state behavior allows one to devise a paint composition, the life of which may be computed from the thickness of paint film. In principle, it is thus possible to formulate a paint composition of predictable antifouling life based on thickness and copolymer content, but, in practice, the effect of natural erosion of the film surface must be considered. A few paint compositions based on the present findings have been formulated and have been put to raft trials.

CONCLUSIONS

The solubility of tri-*n*-butyltin oxide is higher in seawater than in an aqueous solution of sodium chloride (3%).

The leaching rate of TBTO from MMA–TBTM copolymer film is a function of composition of copolymer. Copolymers containing 30 mol% and higher TBTM content offer the leaching rate necessary and sufficient for prevention of fouling.

Leaching rate data for ascertaining suitability of a copolymer composition or paint containing toxic copolymer may be unrealistic if steady state is not reached.

Pigment loading does not affect the nature of the leaching behavior of the copolymer. Pigments may lower slightly the steady state leaching rate.

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