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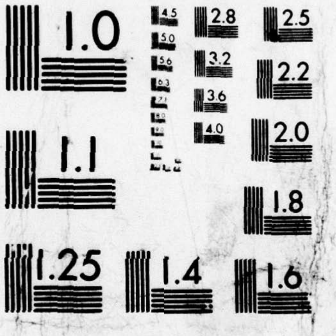

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CURRENT STATUS OF THE CHEMICAL SPECIATION OF ORGANOTIN TOXICANTS IN ANTIFOULANTS.

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by

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CURRENT STATUS OF THE CHEMICAL SPECIATION OF ORGANOTIN TOXICANTS IN ANTIFOULANTS

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Abstract

Although antifouling coatings are complex systems which contain four or five coordinate organotin compounds that are monomeric or polymeric, a simple diffusion model adequately explains the time release of organotin toxicant from the coatings. This result suggests that the mechanism of release is dependent primarily on matrix properties rather than the chemistry of individual compounds. Whereas, our understanding of the leaching of organotin compounds of the type R_3SnY (where R is phenyl or butyl) in aqueous solutions is still incomplete, we believe the Y group to be labile and R_3SnOH or R_3SnCl to be the species formed in seawater.

Introduction

Marine fouling of man-made structures is of significant scientific and economic interest. The increased drag caused by the marine growth on a ship bottom severely reduces maneuverability, and a ship that has a six month accumulation of fouling can use up to 40% more fuel just to maintain a normal cruising speed (Starbird and Sisson, 1973). Putting a ship into dry dock for cleaning and painting is costly in lost service time and revenues. On other structures such as buoys or oil rigs, marine growth causes surface damage and corrosion which results in high maintenance costs. Usually the surface is protected with a coating containing a substance toxic to marine organisms. After the coating is exposed to water, the toxic substance leaches out, repulsing or killing organisms at the surface. Thus, the organisms are prevented from settling on the surface.

In recent years organotin compounds of the type R_3SnY (where R is phenyl or butyl) have been used as the toxic substance in the antifouling coatings. As these compounds are toxic to marine organisms, their use can be tolerated only if they have a minor or temporary impact on the environment. Sheldon (1975) has suggested that the organotin compounds degrade to innocous SnO_2 in seawater, but there is no experimental verification of this suggestion. In order to develop efficient antifouling coatings which result in minimal environmental insult, one must have a complete understanding of the aqueous chemistry of these compounds both in the coating (as the coating interacts with the seawater) and in the bulk seawater.

Results and Discussion

Marine coatings are complex systems. A polymeric matrix and organic solvent are used to disperse pigments and organotin toxicant. Liquid organotins such as tri(n-butyl)tin chloride and bis[tri(n-butyl)tin] oxide are soluble in the paint solvent and disperse homogeneously throughout the coating. Mössbauer

(O'Brien et al., 1978) and infrared spectroscopic studies (Hoffman et al., 1978) have shown that these two organotin compounds are four coordinate in the pure state and that bis[tri(n-butyl)tin] oxide reacts with the organic solvent in one vinyl-type coating mixture to form a tri(n-butyl)tin carboxylate. Solid organotin compounds can either be insoluble such as tri(n-butyl)tin fluoride or partially soluble (depending upon the amount of solvent used) such as tri(n-butyl)tin acetate. The Mössbauer spectroscopic studies indicate that tri(n-butyl)tin acetate and tri(n-butyl)tin fluoride are five coordinate linear polymers in the pure solid state and do not change upon incorporation into a vinyl type coating. Since a wide variety of polymer matrices can be used in the coating as well as several different organotin compounds, an accurate model of the toxicant release mechanism is very difficult to achieve.

A two-parameter diffusion model has been developed which describes the leaching of coatings that may contain either organotin compounds (Monaghan et al., 1978), cuprous oxide, or triphenyllead acetate (Monaghan et al., 1978a). In laboratory tests the toxicant release from coated panels is monitored by analyzing the toxicant in bulk seawater. The concentration, c, of organotin in the bulk solution is given by

$$c = c_s - c_s \exp(-\alpha \frac{A_o}{v} t)$$

where c_s is the organotin concentration at the coating surface, A_o is the surface area of the panel, v is the volume of bulk seawater, t is time, and α is a parameter characteristic of the coating for a given temperature and solution flow condition at the coating surface. The parameter, c_s, does not correlate with the solubility of the organotin compounds, but in other studies on cuprous oxide systems and triphenyllead acetate systems, c_s increases as the toxicant loading in the coating is increased. It is thought that only a fraction of the surface is active in the diffusion process and that α provides a relative measure for comparing the fraction of active surface between various coatings. Results obtained in a study on various organotin compounds in the vinyl-type coating Alum-A-Tox are presented in the table (Monaghan et al., 1978).

The reaction scheme presented in the figure has been suggested (Monaghan et al., 1977) as depicting the organotin reactions occurring in the coating when it is exposed to seawater. The polymeric notation for the starting material in the figure is used to emphasize that organotin compounds can be monomeric or polymeric in a coating. The release of toxicant should be governed not only by the thermochemistry of breaking a Sn-Y bond but also on the ability of water molecules to reach a reactive site. An examination of the c_s values obtained for organotin compounds in the vinyl-type coating Alum-A-Tox in the table, reveals that the c_s values for the acetates (linear polymers) are larger than the c_s values for the chlorides (monomeric units). One would expect the R_3SnCl molecules to be more easily solvated than the R_3SnOAc molecules since a polymeric backbone must be destroyed in the acetates. Thus coatings containing R_3SnCl should have a greater number of solvated R_3Sn-residues for diffusion to the coating surface compared to a similiar coating with R_3SnOAc. This increased availability of solvated R_3Sn-residues should be reflected in higher values of c_s for coatings containing R_3SnCl than for coatings containing R_3SnOAc. Since this is clearly not the case, the R_3Sn-moieties in the coatings containing R_3SnCl must be solvated with difficulty, or the coating porosity is considerably different for a homogeneous coating than for a heterogeneous coating. Inasmuch as the acetates are expected to dissolve partially in the paint solvent and the chlorides are expected to disperse completely, the coatings may differ very much in internal porosity. Since the R_3SnCl molecules are dispersed throughout the coating, water would have to completely diffuse through the matrix to dissolve each R_3SnCl molecule. On the other hand, the acetates are thought to retain their polymeric structure, even if dissolved in the coating (O'Brien et al., 1978). As a polymeric strand of R_3SnOAc is solvated, a channel

TABLE

Leaching Parameters for Alum-A-Tox Coatings

Compound	Name	c_s(ppm)	α(cm day^{-1})
$(C_6H_5)_3$ SnOAc	triphenyltin acetate	7.2	0.16
$(C_6H_5)_3$ SnCl	triphenyltin chloride	2.2	0.18
$(n\text{-}C_4H_9)_3$ SnOAc	tri(n-butyl)tin acetate	12.8	0.19
$(n\text{-}C_4H_9)_3$ SnCl	tri(n-butyl)tin chloride	3.3	0.45
$[(n\text{-}C_4H_9)_3\ Sn]_2O$	bis[tri(n-butyl)tin] oxide	9.9	0.17

would develop through the matrix allowing the water to have access to more R_3SnOAc units without interacting with the matrix. A steady state concentration of organotin at the surface is limited by the availability of solvated R_3Sn-units from the coating interior. The increased availability of solvated R_3Sn-units in a coating which contains R_3SnOAc would result in the observed higher c_s value compared to a coating containing R_3SnCl.

In a highly dilute and slightly alkaline (pH = 8.1) solution such as seawater, the only organotin species expected are R_3SnOH and R_3SnCl regardless of the R_3SnY initially incorporated into the coating (see the figure). That such a result is feasible can be inferred from solution studies in the literature.

Bock and Burkhardt (1961) and Bock, et al. (1962) have demonstrated that triphenyltin hydroxide dissolved in benzene can be used to extract various anions from slightly acidic aqueous solutions. The more acidic the solution, the more effective the extraction. For example, at a pH equal to 0.1, 98.0% of the chloride is extracted by triphenyltin hydroxide into benzene; whereas, at a pH equal to 7.0, only 1.4% of the chloride is extracted. This experimental study provides a basis for the proposed aqueous reaction scheme. In an acidic solution, the equilibrium in equation (2) would be stressed to favor the formation of $R_3Sn^+(aq)$. The increased concentration of $R_3Sn^+(aq)$ would place a stress on the equilibrium in equation (3). To relieve the stress on the equilibrium, the system would adjust to favor the formation of R_3SnCl.

Although we cannot describe the complete tin species that leaches out of the antifouling coating at this time, we have been able to establish that an organotin and not an inorganic tin species is leached (Monaghan et al., 1978). By employing a colorimetric procedure similiar to that described by Aldridge and Cremer (1957) for the analysis of triethyltin and diethyltin compounds using dithizone, we have established that a triphenyltin species leaches out of the vinyl-type coating Alum-A-Tox when triphenyltin acetate or triphenyltin chloride is incorporated into the coating as toxicant. Using the same procedure for the analysis of tributyltin has presented some problems, however. The color of the analyte does not stabilize for some time, and we believe that the visible spectrum of the resulting stable analyte to be that of dibutyltin dithizonate. Aldridge and Cremer (1956) have described the slow degradation of triethyltin dithizonate to diethyltin dithizonate which they determined to be the result of a photochemical reaction. We are of the opinion that a tributyltin species leaches out of the Alum-A-Tox coating containing a tributyltin compound and that the leached species degrades to a dibutyltin species during the colorimetric analysis. Details of the colorimetric analysis are now being organized in manuscript form for subsequent publication.

We are currently evaluating the first part of the organotin aqueous reaction scheme as shown in the figure. By dissolving the various organotin compounds in distilled water, artificial seawater, or artificial river water and then extracting the resulting solutions with chloroform, we expect to be able to determine if the Y group is indeed lost as is predicted. The extracts will be analyzed by infrared spectroscopy and thin layer chromatography.

Acknowledgments

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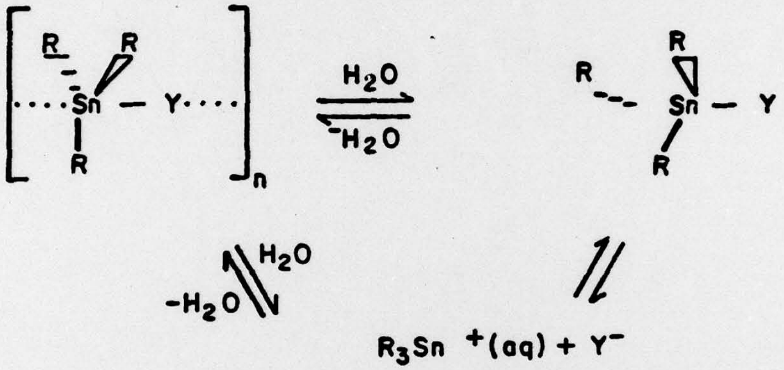
FIG. Proposed reaction scheme of organotin compounds dispersed in antifouling coatings exposed to seawater.



(1)

$$R_3Sn^+(aq) + 2H_2O \rightleftharpoons R_3SnOH + H_3O^+ \quad (2)$$

$$R_3Sn^+(aq) + Cl^- \rightleftharpoons R_3SnCl \quad (3)$$

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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