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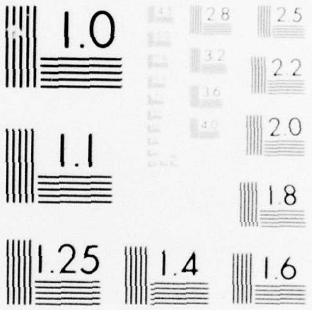

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AN EVALUATION OF LEACHING MECHANISMS FOR ORGANOTIN CONTAINING ANTIFOULING COATINGS.

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Charles P. Monaghan, James F. Hoffman, Elmer J. O'Brien,
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Department of Chemistry
University of New Orleans
Lakefront, New Orleans, La. 70122

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AN EVALUATION OF LEACHING MECHANISMS FOR ORGANOTIN CONTAINING ANTIFOULING COATINGS

Charles P. Monaghan, James F. Hoffman, Elmer J. O'Brien,
Lydia M. Frenzel, and Mary L. Good

Department of Chemistry
University of New Orleans
Lakefront, New Orleans, La. 70122

Abstract

The utility of organotin compounds as antifouling toxicants in marine coatings is now well established. However, the leaching and "killing" mechanisms are poorly understood. Several studies have been carried out to determine the fouling processes and their prevention, and some attempts have been made to design a chemical model for the toxicant leaching process. However, little or no experimental verification of such chemical models exist. For example, the effects of salt content, pH and temperature variations of sea water and the physical and chemical properties of the toxicant are not well defined. We have developed a basic leaching model for a series of organotin toxicants and have designed an experimental approach for the verification, refutation or modification of this model. The results of such a study will be of primary importance in the evaluation of the environmental impact of the large-scale use of these antifouling materials. This manuscript outlines our initial studies and indicates the present status of our proposed model.

has been developed

Fouling on ship hulls and other marine installations is combated primarily by the application of coatings containing leachable antifouling toxicants.[1,2] The evaluation of currently used coatings and the development of new coatings require the formulation of a model system that describes all facets of the toxicant release mechanism. The utility of such a model system is that it allows one to identify those factors that govern fouling control. The understanding of these features should allow the development of more effective products and the improvement of matrices for known toxicants.

Marson's diffusion model[3] provides considerable insight into the mechanism of the leaching of an antifouling compound out of an insoluble matrix. He assumes that the toxicant exists as spherical particles, of equal size and even distribution throughout the coating. He further states that the matrix must be inert with respect to both the toxicant and the leachate and that a thin film of the matrix must completely envelop each toxicant particle. The surface is considered to be identical to any section throughout the coating. It is thought that as the seawater interacts with the surface, a saturated solution of toxicant at the toxicant-leachate interface is formed. As the toxicant is dissolved, cavities are left in the coating which are filled with seawater (see the figure for a diagrammatic representation of the leaching process). Water then diffuses through the thin films surrounding underlying undissolved toxicant particles and dissolves part of the material. Stress builds on the film due to osmotic pressure until it finally ruptures. Thus, the assumption is made that a porous matrix is developed, the size of the pores influencing the diffusion properties of the toxicant molecules through the exhausted coating to the surface.

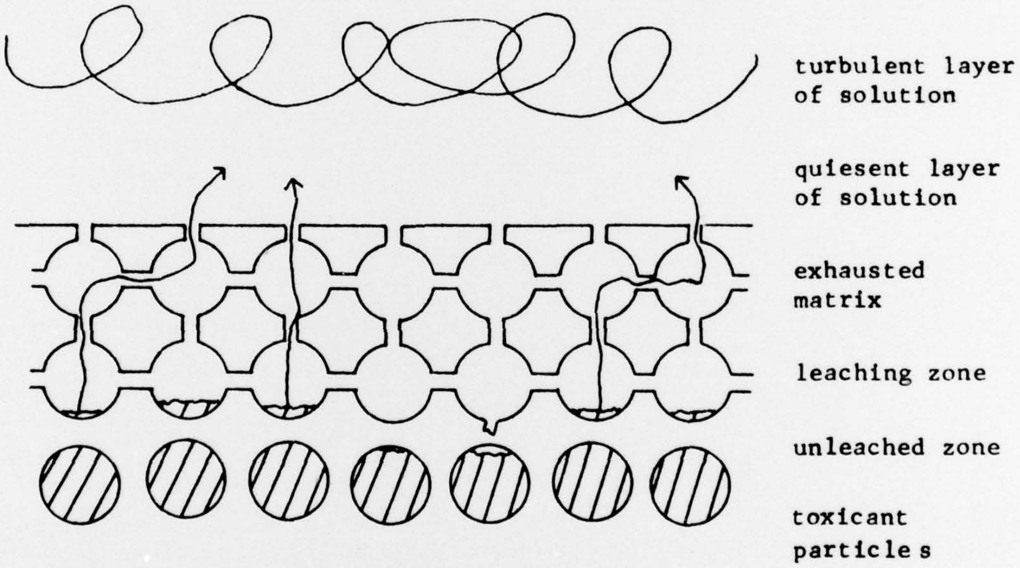


Figure . Diagrammatic representation of leaching from an idealized coating (after Marson[3]).

Although this model has been used to describe the leaching properties of Cu_2O in vinyl coatings[2,4], it appears to be amendable for use in characterizing antifouling coatings containing organotin compounds as well. By testing this model its value can be determined, but probably more important is that experiments would be performed which allow characterization of those factors important to antifouling control. To provide parameters for testing, those chemical equations governing the toxicant release mechanism must be outlined so that the products can be predicted. A toxicant release and degradation scheme proposed by Sheldon[5] for the widely used trialkyl organotin species is as follows:

$$R_3SnY + H_2O \rightarrow R_3SnOH + HY \tag{1}$$

$$2R_3SnOH \rightarrow (R_3Sn)_2O + H_2O \tag{2}$$

$$(R_3Sn)_2O + CO_2 \rightarrow R_3SnO(CO)OSnR_3 \tag{3}$$

$$R_3SnO(CO)OSnR_3 \xrightarrow{u.v.} R_2SnO + R' \tag{4}$$

$$R_2SnO \xrightarrow{u.v.} RSnO(OH) + R' \tag{5}$$

$$RSnO(OH) \xrightarrow{u.v.} SnO_2 + R' \tag{6}$$

The most attractive feature of this scheme is that it predicts SnO_2 to be the end product of degradation reactions. As SnO_2 is non-toxic to humans, the use of organotin compounds in antifouling coatings would present no environmental hazard if this chemical model were correct. Unfortunately, rigorous tests of the model have not been carried out, and some of the steps are subject to criticism. For example, the role of the physical state of the starting material is undefined. Spherical toxicant particles are assumed in the diffusion model, but some organotin compounds are liquids and are expected to form a homogenous system with the matrix. Moreover, the scheme requires that $(R_3Sn)_2O$ be formed. If it can be shown that formation of $(R_3Sn)_2O$ is unfavorable, then later steps are in doubt.

For most R groups considered, dehydration of R_3SnOH is not spontaneous and can take place only under special conditions. $(CH_3)_3SnOH$ is dehydrated only with difficulty; sodium in benzene is required. $(C_2H_5)_3SnOH$ and $(C_3H_7)_3SnOH$ can be dehydrated by placing the compound under vacuum with $CaCl_2$ or P_4O_{10}. $(C_6H_5)_3SnOH$ will form $(C_6H_5)_3SnOSn(C_6H_5)_3$ only by azeotropic distillation in benzene or toluene. However, formation of $(C_4H_9)_3SnOSn(C_4H_9)$, does appear to be spontaneous.[5]

As the quantity of water becomes large, the reverse reaction of equation (2) becomes more favorable by Le Chatelier's principle. In aqueous solutions the R_3SnY compounds are very insoluble and concentrations can never become very high; therefore, the collision probability of two R_3SnOH molecules is very small. Even if $(R_3Sn)_2O$ is formed, it is not likely to diffuse out of the coating since it is expected to be very insoluble. The hydrogen bonding possibilities (and subsequent dissolution and/or hydrolysis) which exist for R_3SnOH are much less pronounced for $(R_3Sn)_2O$ where essentially only van der Waal's interactions are anticipated. It seems reasonable to believe that the formation of $(R_3Sn)_2O$ in seawater is a minor reaction at best.

By considering the reactions

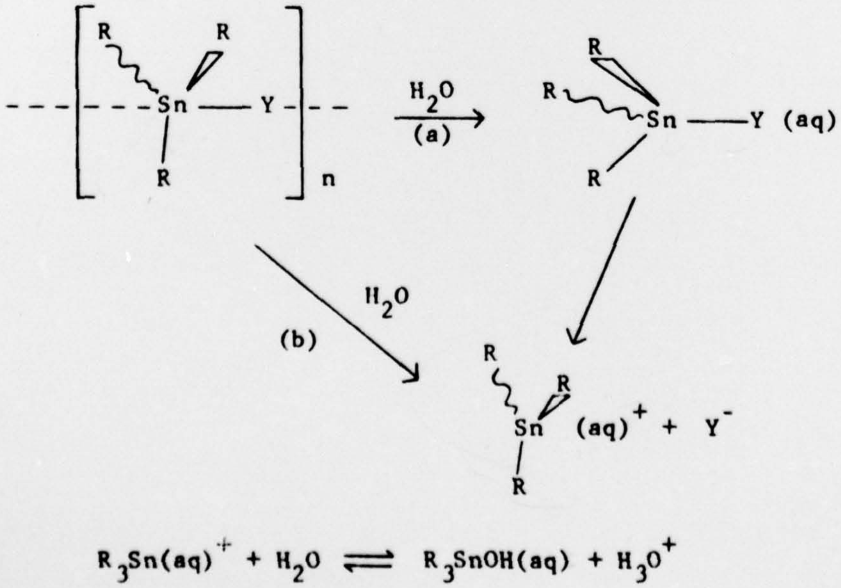
$$(R_3Sn)_2O \underset{-H_2O}{\overset{H_2O}{\rightleftharpoons}} 2R_3SnOH(aq) \qquad (7)$$

$$R_3SnOH(aq) \rightleftharpoons R_3Sn(aq)^+ + OH^-, \qquad (8)$$

one can further argue that R_3SnOH is the most logical species to be leached from the coating. The alkaline environment of seawater (pH = 8.1-8.3) favors the reverse reaction in equation (8), and the presence of excess water favors the products in equation (7). Strong evidence for the formation of R_3SnOH in an alkaline aqueous environment is given in the polarographic work reported by Kochkin, et. al.[7] $(C_2H_5)_3SnOH$, $(C_2H_5)_3SnOSn(C_2H_5)_3$, and $(C_2H_5)_3SnO(CO)C(CH_3) = CH_2$ all had the same $E_{1/2}$ of -1.5v. $(C_4H_9)_3SnOSn(C_4H_9)_3$ and $(C_4H_9)_3SnO(CO)C(CH_3) = CH_2$ had an $E_{1/2}$ of -1.4v. In both cases the hydrolysis of R_3SnY to form R_3SnOH would explain the identical $E_{1/2}$ value for compounds with different Y groups and the same R group. The electrochemical reduction wave for this set of compounds can be explained by

$$R_3SnOH + e^- \longrightarrow R_3Sn\cdot + OH^-.$$

The most striking feature of many of the organotin compounds that are used in the antifouling coatings is their insolubility in water. One can consider that the rate of hydrolysis is determined not only by the thermochemistry of breaking a Sn-Y bond (where Y is Cl, F, $OSnR_3$, OAc, $-O(CO)CH_2-$) but also by the ability of water to get to a reactive position in the organotin compound. One can further consider that the detailed hydrolysis of R_3SnY is



(9)

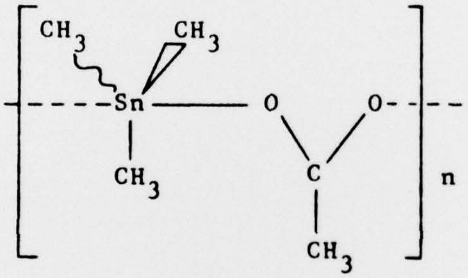
$$R_3Sn(aq)^+ + H_2O \rightleftharpoons R_3SnOH(aq) + H_3O^+ \qquad (10)$$

$$2R_3SnOH(aq) \rightleftharpoons R_3SnOSnR_3 + H_2O \qquad (11)$$

where the starting material is represented by an R_3SnY which may have any degree of association to a neighboring molecule in the solid state, may be a part of an associated structure in the liquid state, or may be an absorbed species in a coating. Reaction path (a) is probably followed only in rare cases such as triphenytin fluoride where the strong Sn-F bond would inhibit ion formation. One would expect path (b) to be the preferred reaction for most organotin systems. The rate of formation of $R_3Sn(aq)^+$ will depend on the size of the R group since the larger the R group, the more the Sn atom is protected from attack by water, and the slower the rate of hydrolysis of the starting material. With a common R group the rates of hydrolysis for R_3SnY for a varying Y should be

$$F < Cl < Br < I.$$

Since $(CH_3)_3SnOAc$ has a rather open structure[8]



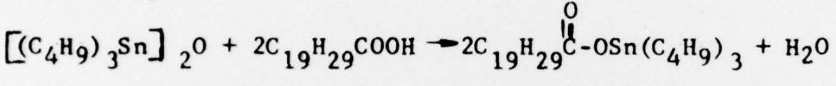
and the other acetates should have similar structures, the R groups would not protect the Sn and the polymeric linkage from attack by water. Thus, the R_3SnOAc compounds should hydrolyze faster than most of the R_3SnY compounds because of the greater accessibility of the tin atoms to attack by water.

If R_3SnOH is indeed the released species, then it is also feasible that this molecule is the biologically active compound as well. Since organotin compounds containing the Sn-O bond undergo a variety of substitution and addition reactions;[9] R_3SnOH should certainly be reactive enough to be considered.

Since the physical features of a coating may be somewhat different from the idealized coating envisioned by Marson, a structural description of each pure organotin compound and of each organotin compound as it exists in various coatings is necessary. One must then examine the assumptions of the diffusion model to note any descrepancies between the model and the real system. Only after all descrepancies are minimized can an adequate understanding of a real coating system be achieved.

Mössbauer studies[10] and infrared studies[11] have shown that R_3SnF, R_3SnOH, and R_3SnOAc (R = propyl, butyl, phenyl) are all associated structures with trigonal bipyramidal coordination about the tin atom. The compounds $[(C_6H_5)_3Sn]_2O$ and $(C_6H_5)_3SnCl$ are molecular solids with the tin atom exhibiting four fold coordination. These toxicants, being mixed into various matrices as suspensions, retain the chemical properties of the pure compounds when dispersed throughout the coating matrix. On the other hand,

R_3SnCl, R_3SnBr, R_3SnI, and $(R_3Sn)_2O$ are all liquids (except for the phenyl compounds described above) and mix with the coating matrix to form a homogenous system. Marson's model could be used for these later compounds only if one considers that micropores develop as the result of some matrix dissolution. The film fracture aspect of Marson's model could probably be abandoned. It has been further determined in our laboratory that $[(C_4H_9)_3Sn]_2O$ reacts with the matrix in a vinyl and in a vinyl-rosin type coating. Mössbauer measurements show a larger quadrupole splitting for the organotin species than is known for $[C_4H_9)_3Sn]_2O$ and an additional infrared peak in the $1640 cm^{-1}$ region supports the proposition that a tributyltin carboxylate has been formed. It is thought that $[(C_4H_9)_3Sn]_2O$ reacts with the rosin in the vinyl-rosin coatings to yield the tributyltin ester of abietic acid by



$$[(C_4H_9)_3Sn]_2O + 2C_{19}H_{29}COOH \rightarrow 2C_{19}H_{29}\overset{O}{\overset{\|}{C}}\text{-}OSn(C_4H_9)_3 + H_2O$$

The vinyl coating studied (Navy 1020A) utilizes n-butyl acetate in its solvent; $[(C_4H_9)_3Sn]_2O$ reacts with n-butyl acetate to form $(C_4H_9)_3SnOAc$. Thus, in all of the coatings we have studied having $[(C_4H_9)_3Sn]_2O$ as the toxicant, evidence exists that the actual tin species in the coating is the corresponding carboxylate or high molecular weight ester. From these studies it is immediately apparent that a detailed investigation of the identity of the organotin compound in the coating as well as a physical description of the matrix is necessary prior to any leaching experiments.

At this point, no mention has been made of the degradation of R_3SnOH. Steps (3) thru (6) in Sheldon's scheme are unlikely because they rely on the formation of $(R_3Sn)_2O$ which is unfavorable. Three possibilities for the removal of R_3SnOH from the seawater environment can be considered. It is possible that the material is not degraded at all, but is adsorbed on suspended silicates. This is a satisfactory fate for R_3SnOH since it is removed from solution. Although it is not very realistic for the open sea, it could occur in harbors. A study on the ability of various clays to remove R_3SnY type compounds has begun. Tobias[12] has mentioned that R_3SnY compounds are stable in aqueous solutions for weeks or months. It is conceivable that R_3SnOH will eventually react with the water to form some hydrated tin species over an extended period of time. To check this aspect of the model, solutions of R_3SnY compounds in artificial seawater will be made up and analyzed periodically for decomposition products. Another possibility is that suggested by Sheldon, namely reaction with ultraviolet light. $(C_6H_5)_3SnOAc$ is known to degrade to SnO_2 upon exposure to air and ultraviolet light.[13] Studies on R_3SnY type compounds in seawater are being initiated in our laboratory to ascertain the role of light in the decomposition of these compounds. Mössbauer backscatter techniques (^{119m}Sn) which are being developed in our laboratory on the R_3SnY compounds in coatings should allow detection not only of the starting material but also of materials trapped in the exhausted matrix. ATR infrared spectroscopy and ESCA may also prove useful in the same studies. All of these techniques will be used to verify or disprove the outlined chemical mechanism of toxicant release.