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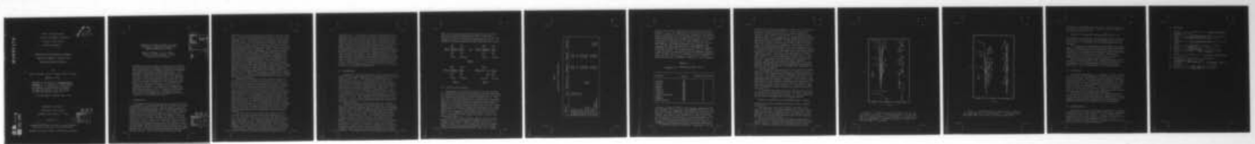

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INFRARED AND NUCLEAR MAGNETIC RESONANCE ANALYSIS OF ORGANOTIN TOXICANTS FOR MARINE ANTIFOULING COATINGS

by

James E. Hoffman, Keith C. Kappel, Lydia M. Frenzel
and Mary L. Good

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INFRARED AND NUCLEAR MAGNETIC RESONANCE ANALYSIS OF ORGANOTIN TOXICANTS FOR MARINE ANTIFOULING COATINGS

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University of New Orleans

Infrared and nuclear magnetic resonance spectroscopies have been employed to elucidate the chemical and structural properties of triorganotin compounds incorporated into marine antifoulant coating formulations. It is necessary to determine the molecular species of the toxicant in order to be able to predict the mechanism of toxicant release and to design new, more effective coatings. In two conventional vinyl antifoulant coatings, the toxicant was found to react with one component in the coating formulation to yield different triorganotin compounds. A change in the $\nu_{asym(SnC)}$ vibration was found to correlate with a change in the coordination geometry of tin. These results indicate that infrared spectroscopy is a powerful technique that can provide insights into the chemical processes occurring in the antifouling coatings.

I. INTRODUCTION

The problem of marine "fouling" of ship hulls and marine installations is well known and has been attacked by many research and development groups. Even the popular press and general technology periodicals have recently highlighted the problem in their publications (1,2,3). The present national difficulties associated with energy shortages make this fouling problem even more crucial. For example, "the drag caused by only a six-month accumulation of marine foulants can force a vessel to burn 40 percent more fuel just to maintain normal cruising speed" (1). Thus any attempt at fuel economy in the shipping industry and in the Navy must place the development of effective antifoulant procedures as a high priority item. The only practical solution through the years has been the utilization of paints and coatings having antifoulant activity. Most of the coatings which have been developed are paint formulations containing a toxicant component. The most widely used toxicant has been cuprous oxide although various compounds of arsenic, mercury, lead and tin have been used. The cuprous oxide coatings are good fouling inhibitors but they have rather short effective life-times. The arsenic, mercury and lead coatings have severe toxicological problems and have been either restricted in use or completely removed from the commercial market. The tin containing coatings have been investigated by a number of groups, particularly by researchers at the Naval Ship Research and Development Center at Annapolis, Maryland. Studies have shown that tin antifoulants possess several advantages over conventional copper antifoulants (4,5). For example, they provide superior antifouling over a longer period of time. When applied on conductive substrates, they do not promote corrosion as do copper based coatings. They exhibit control over several types of algae and barnacles when properly formulated. It has been proposed that the organotin compounds degrade to non-toxic, non-cummulative inorganic forms of tin, but there is no experimental evidence to support this proposition (6,7,8). Thus, the most promising antifoulant coatings which have been designed and characterized are those containing organotin toxicants.

Although the formulation of new coatings containing organotin moieties has been an area of active research, the determination of the chemical form of the toxicant in the bulk and on the surface of the coatings, and the elucidation of the surface release mechanism have received less attention. Thus, this initial report on our studies of these coating systems will review our efforts to devise procedures and background data which will allow the nature of the organotin toxicants to be determined by infrared and proton NMR spectroscopies. It is anticipated that these studies and other related work will eventually provide the tools for the identification of the chemical composition of the tin toxicants as a function of the coating matrix, the curing process, actual aging in normal use, and coating efficiency. Information of this type is essential for the design of new, more effective coatings and for the evaluation of the long term environmental impact of the widespread use of these toxic material.

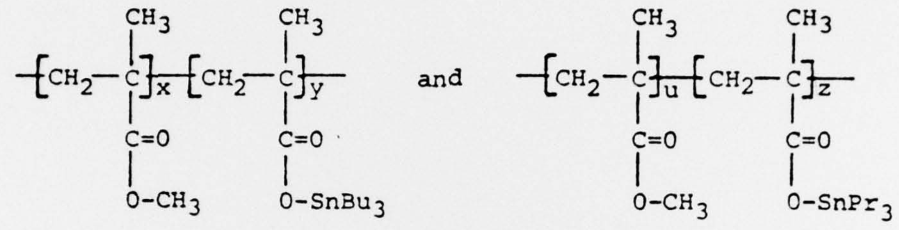
The most effective and widely used organotin coating additives are the triorganotin compounds (R_3SnX where R = alkyl or phenyl and X = F, Cl, Br, I, OH, OCOR, $OSnR_3$, SnR_3 or acrylate). The tributyltin compounds have been used most extensively to date. These materials exhibit a much higher level of toxicity to marine foulants than they do to mammals. The shorter chained alkyls exhibit a high toxicity to mammals and a low toxicity to marine life (9). Thus this initial study is devoted to the evaluation of coatings containing trialkyltin species with special emphasis on the tributyl series. Two general classes of coatings are being investigated: (1) conventional formulations consisting of an organotin compound, usually either bis(tri-n-butyltin) oxide (TBTO) or tri-n-butyltin fluoride (TBTF), thoroughly mixed with the rest of the coating components; and (2) newly developed coating systems consisting of R_3SnX moieties (where X is vinyl, acrylate, or maleate) polymerized or copolymerized through the unsaturated X groups. The conventional coatings presumably have free toxicant not bound to the coating matrix while in the polymer materials the toxicant species is covalently bonded to the matrix. Neat organotin materials have been examined to provide baseline spectra and spectral assignments of functional groups. Correlation techniques have been used to assign the SnC_3, Sn-X, Sn-O and COO vibrational modes in the infrared spectra. These assignments have then been used for the identification of functional groups and chemical entities in the coating formulations.

II. EXPERIMENTAL

Transmission infrared spectra for liquid samples were obtained as thin films between KBr and polyethylene disks in the region 4000-200 cm^{-1}. The spectra of solid samples were obtained as KBr pellets. The spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 283 equipped with a printer accessory, which provides a digital readout of peak positions and relative intensities of the peaks. Peak positions are accurate to ± 3 cm^{-1} in the region 4000-2000 cm^{-1}, and to ± 1.5 cm^{-1} in the region 2000-200 cm^{-1}. Proton nuclear magnetic resonance (^1H nmr) spectra were recorded on a Hitachi Perkin-Elmer R-20B spectrometer operating at a frequency of 60.0 MHz. The organotin and polymer samples were dissolved in $CHCl_3$, $CDCl_3$, and CCl_4 to give a 10% (w/v) solution with a few drops of tetramethylsilane (TMS) added as an internal reference.

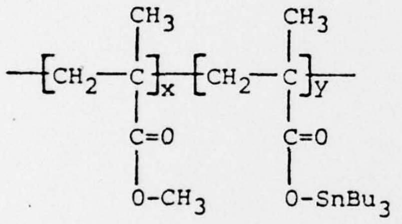
Organotin compounds were obtained from M&T Chemicals, Inc. and were used without further purification. Purity was checked by chemical analysis and by ^1H nmr. The conventional coatings, which contained $(Bu_3Sn)_2O$ and Bu_3SnF were donated by Glidden-Durkee, Standard Paint and Varnish Company of New Orleans, and by the U. S. Navy. All coatings investigated were vinyl based formulations. The Glidden-Durkee coating contains $(Bu_3Sn)_2O$ as the toxicant. The coating from the Standard Paint and Varnish Company (Alum-A-Tox) contains Bu_3SnF. The Navy formulation, 1020A, contains both $(Bu_3Sn)_2O$ and Bu_3SnF as toxicants. Formulations were also obtained which did not contain the toxicants. Experimental organotin containing polymers (OMP's) were donated by Dr. E. Fischer of the David Taylor Naval Ship Research and Development Center (DTNSRDC). The compositions of these polymers are as follows:

OMP-1 is poly(tri-n-butyltin methacrylate/tri-n-propyltin methacrylate/methyl methacrylate); OMP-2 is poly(tri-n-butyltin methacrylate/methyl methacrylate); OMP-4 is the tri-n-butyltin ester of poly(methylvinylether/maleic acid). The formulas for these materials are shown diagramatically below.



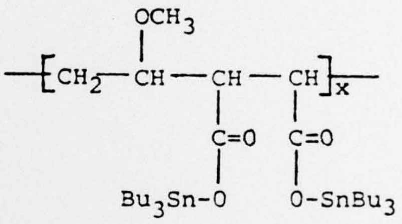
$$-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-CH_3}}}{\mathrm{C}}}\right]_x-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-SnBu_3}}}{\mathrm{C}}}\right]_y- \quad \text{and} \quad -\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-CH_3}}}{\mathrm{C}}}\right]_u-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-SnPr_3}}}{\mathrm{C}}}\right]_z-$$

OMP 1



$$-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-CH_3}}}{\mathrm{C}}}\right]_x-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\substack{\mathrm{C=O}\\ \mathrm{O-SnBu_3}}}{\mathrm{C}}}\right]_y-$$

OMP 2



$$-\left[\mathrm{CH_2}-\overset{\mathrm{OCH_3}}{\mathrm{CH}}-\underset{\substack{\mathrm{C=O}\\ \mathrm{Bu_3Sn-O}}}{\mathrm{CH}}-\underset{\substack{\mathrm{C=O}\\ \mathrm{O-SnBu_3}}}{\mathrm{CH}}\right]_x-$$

OMP 4

III. RESULTS AND DISCUSSION

Assignments of the infrared vibrations of the triorganotin compounds were made by the correlation method, since these are complex molecules and few spectral assignments of comparable compounds are available in the literature (10,11). The Sn-X, Sn-O, and $\mathrm{SnC_3}$ vibrations are of particular interest because these functional groups are the most likely ones to be affected by the leaching of the toxicant from the coating matrix. All of these vibrations occur below 1100 $\mathrm{cm^{-1}}$. Other vibrations of importance to this study are ν_{OH}, which occurs around 3600 $\mathrm{cm^{-1}}$, and the asymmetric and symmetric stretching frequencies, $\nu_{asym(COO)}$ and $\nu_{sym(COO)}$, of the carboxylate group. These vibrations are located between 1650 and 1300 $\mathrm{cm^{-1}}$. Assignments of the vibrational modes of interest are presented in Table I.

Triorganotin compounds ($\mathrm{R_3SnX}$) exhibit either a tetrahedral or a trigonal bipyramidal geometry depending on the nature of the X group. When X is capable of acting as a bridging ligand (e.g. F, OH, $\mathrm{OCOCH_3}$), the organotin compound exhibits a trigonal bipyramidal geometry with the X group bridged between planar $\mathrm{SnR_3}$ moieties. With other X groups,

TABLE I

Assignments of Infrared Bands

Compound	ν_{Sn-X}	$\nu_{asym(Sn-O-Sn)}$	$\nu_{asym(SnC)}$	$\nu_{sym(SnC)}$	$\nu_{asym(COO)}$
Pr_3SnCl	330		593	507	
Bu_3SnCl	323		597	509	
Ph_3SnCl	330				
Bu_3SnF	328		612	510	
Ph_3SnF	368				
Bu_3SnBr	230		596	505	
Bu_3SnI	-		593	503	
$(Pr_3Sn)_2O$		773	586	506	
$(Bu_3Sn)_2O$		770	591	505	
$(Ph_3Sn)_2O$		772			
$(Bu_3Sn)_2$			584	495	
Bu_3SnOAc			609	489	1572
Bu_3Sn acrylate			607	508	1536
Bu_3Sn methacrylate			595	509	1618

the tin atom is four coordinate with a distorted tetrahedral geometry. Due to the complexity of these triorganotin molecules, a composite set of vibrations (asymmetric and symmetric stretching frequencies) will be observed for the SnC_3 part of the molecule rather than a single Sn-C vibration. For trigonal bipyramidal molecules with D_{3h} site symmetry only the $\nu_{asym(SnC_2)}$ is infrared active. For the molecules with C_{3v} site symmetry (distorted tetrahedron) the $\nu_{asym(SnC)}$ and $\nu_{sym(SnC)}$ are both infrared active. Experimentally, two vibrations are observed for all of the trialkyltin compounds in the SnC_3 region. The infrared inactive $\nu_{sym(SnC)}$ mode is a weak band in the infrared for the five coordinate complexes which indicates that the site symmetry of the tin compounds is lower than D_{3h}. The $\nu_{asym(SnC)}$ is sensitive to changes in coordination number as is shown in Table II. Five coordinate triorganotin compounds exhibit the $\nu_{asym(SnC)}$ between 603-612 cm^{-1}; whereas, the $\nu_{asym(SnC)}$ occurs between 584-597 cm^{-1} for the four coordinate complexes. The asymmetric SnC_3 stretching frequency is observed in the organotin containing polymers (OMP's), and occurs between 587-592 cm^{-1}. This implies that the tin moiety is four coordinate in these formulations. For the conventional coatings investigated in this study, the $\nu_{asym(SnC)}$ is unobservable because of vibrations which occur in this region of the spectrum from other paint components.

TABLE II.

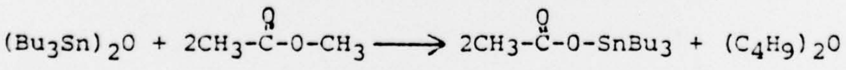
$\nu_{asym(SnC)}$ vs. Coordination Number of Tin

Compound	$\nu_{(cm^{-1})}$	Coordination Number
$(Bu_3Sn)_2$	584	4
Bu_3SnCl	596	4
Bu_3SnBr	596	4
Bu_3SnI	593	4
$(Bu_3Sn)_2O$	591	4
Pr_3SnCl	593	4
$(Pr_3Sn)_2O$	586	4
Bu_3Sn methacrylate	595	4
Bu_3SnF	612	5
Bu_3SnOAc	610	5
Bu_3Sn acrylate	607	5

The Sn-O-Sn asymmetric vibration, $\nu_{asym(SnOSn)}$, has been assigned to an intense band between 770-775 cm^{-1} for molecules of the type $(R_3Sn)_2O$ (see Table I). In the commercially available coating formulations which contain bis(tri-n-butyltin) oxide (TBTO) as the toxicant (i.e. Glidden-Durkee and Navy 1020A), the $\nu_{asym(SnOSn)}$ is not observed, even though the concentration of toxicant is high enough to be easily observed by infrared analysis. In the Navy 1020A formulation, which also contains tri-n-butyltin fluoride (TBTF) as toxicant, the Sn-F vibration is observed. The toxicant is presumably unchanged upon addition to the coating formulation. In the two coatings which employ TBTO as the toxicant, a band is observed at 1634 cm^{-1} in the spectrum of the Glidden-Durkee formulation, and at 1648 cm^{-1} in the spectrum of the Navy 1020A formulation. These bands were not observed in either TBTO, TBTF, or the paint formulations without toxicant. The absence of $\nu_{asym(SnOSn)}$ and the presence of the band around 1640 cm^{-1} implies that the toxicant (TBTO) undergoes a reaction upon mixing with one of the components of the paint. The peak around 1640 cm^{-1} can be assigned with considerable certainty to the formulation of a tributyltin carboxylate in both of these coatings.

Upon addition of TBTO to both the Navy 1020A and Glidden-Durkee formulations without toxicant, an infrared spectrum identical to the spectrum of the formulation with toxicant was observed. (see Figure 1B and 1D, and Figure 2B and 2C). No $\nu_{asym(SnOSn)}$ was observed in these spectra which again indicates that TBTO has undergone a reaction. For the Navy 1020A formulation without toxicant, the addition of tributyltin acetate (TBTA) to this coating yields a material which has an identical spectrum to that in Figure 1B. When TBTF is added to the formulation without toxicant, no reaction is observed (see Figure 1C).

It has been reported that bis(triethyltin) oxide reacts with carboxylic acids and esters (12). The TBTO in Navy 1020A was found to react with butyl acetate, one of the components of the solvent, according to the following reaction:



$$(Bu_3Sn)_2O + 2CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-O-SnBu_3 + (C_4H_9)_2O$$

Tributyltin acetate precipitates from the reaction mixture upon cooling.

The $\nu_{asym(COO)}$ vibration in TBTA in the solid state occurs at 1572 cm^{-1}, but when dissolved in an inert solvent such as chloroform, the band is shifted to 1640 cm^{-1}. This finding is in complete agreement with our assignment of the 1640 cm^{-1} band of the TBTO reaction product to the formation of TBTA in the coating matrix.

The Glidden-Durkee coating uses methyl isobutyl ketone and xylenes as a solvent system, and TBTO does not react with either component. However, this formulation also contains rosin, a natural product which is primarily abietic acid,

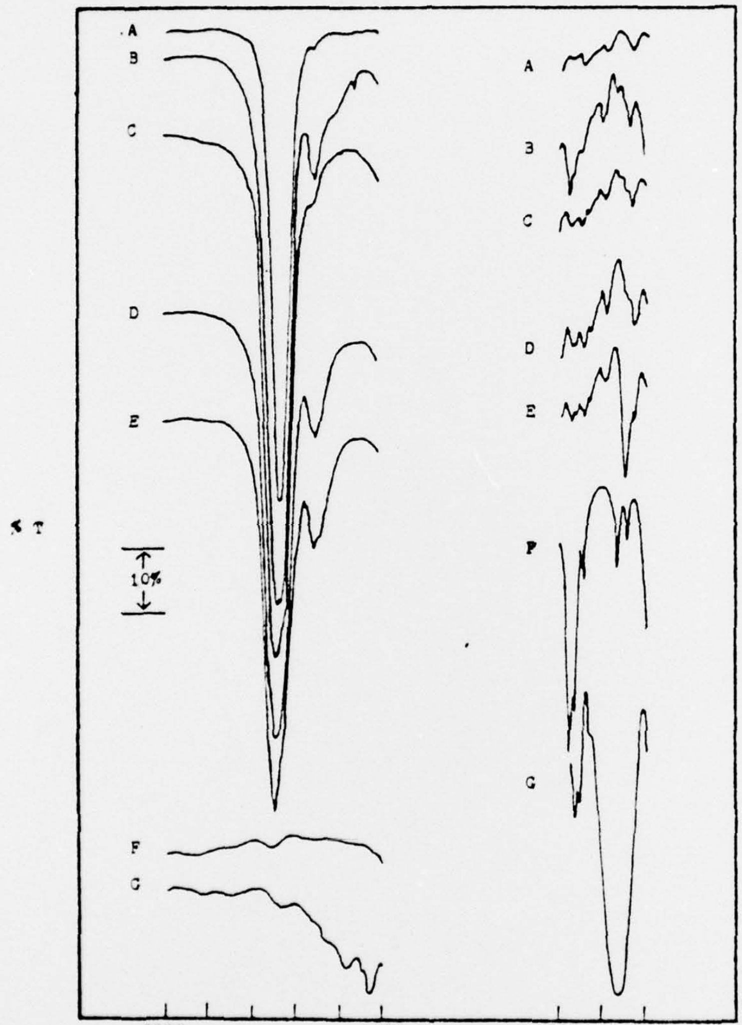


Figure 1. Infrared spectra of Navy 1020A coatings and triorganotin toxicants. (A) without toxicant, (B) with toxicant, (C) without toxicant plus added TBTF, (D) without toxicant plus added TBTO, (E) without toxicant plus added TBTA, (F) neat TBTF, (G) neat TBTO.

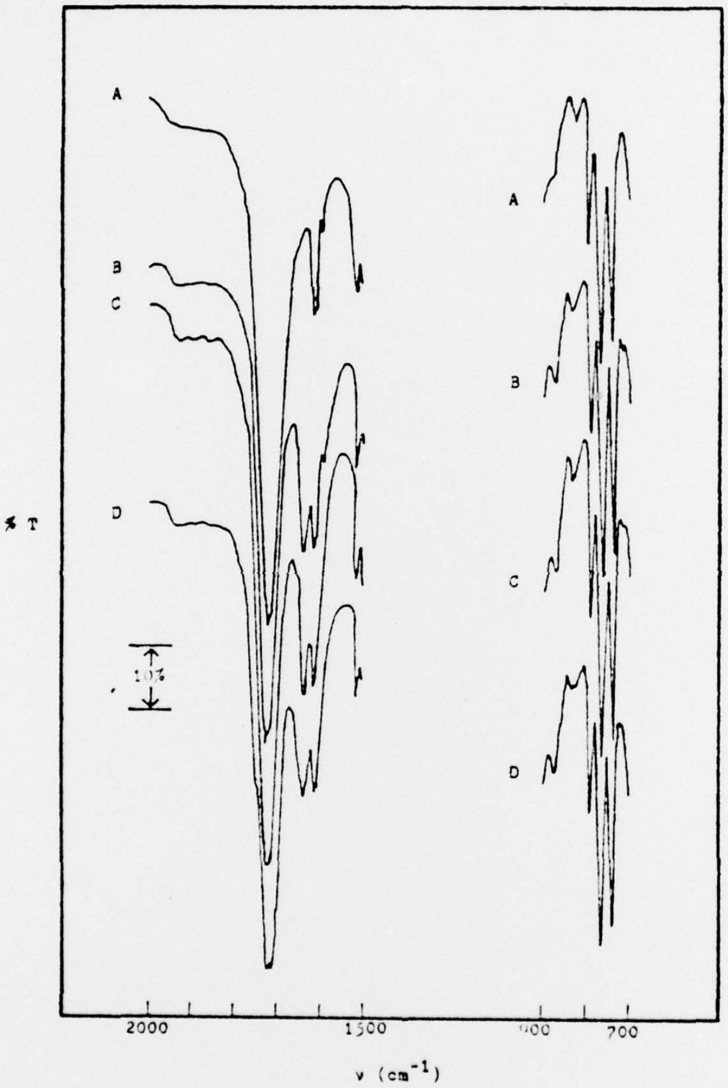
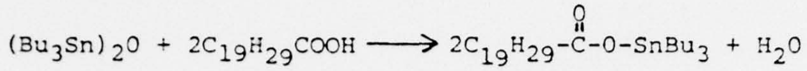


Figure 2. Infrared spectra of Glidden-Durkee coatings. (A) without toxicant, (B) with toxicant, (C) without toxicant plus added TBTA, (D) without toxicant plus added TBTO.

$C_{19}H_{29}COOH$. Bis(tributyltin) oxide does react with the rosin to yield the tributyltin ester of abietic acid, according to the following reaction (13):



$$(Bu_3Sn)_2O + 2C_{19}H_{29}COOH \longrightarrow 2C_{19}H_{29}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}SnBu_3 + H_2O$$

The infrared spectrum of the reaction mixture exhibits a band at 1637 cm^{-1} in the spectrum of the Glidden-Durkee coating with toxicant. The products of the above reaction were not isolated.

The Alum-A-Tox coating system contains TBTF as the toxicant. It appears that no reaction occurs between the toxicant and the paint formulation, but a conclusive investigation by infrared is not possible due to bands of the paint formulation which overlap the vibrations of interest. Tributyltin fluoride did not react with the Navy 1020A so it appears likely that it will not react with the Alum-A-Tox.

The information obtained and conclusions reached on the reactions of the toxicants in the antifoulant formulations is in agreement with the observations obtained by Mossbauer spectroscopy, which are presented in the following paper.

IV. CONCLUSIONS

From this investigation, it is apparent that the toxicant in the coating must be identified in order to accurately predict the lifetime, effectiveness and environmental impact of antifouling coatings. Bis(tributyltin) oxide which was added as the toxicant in two of the conventional formulations, was found to react with one component of the paint formulation to yield a tributyltin carboxylate. Infrared and nuclear magnetic resonance spectroscopies were found to be excellent tools for the identification of the organotin species and for the investigation of molecular rearrangements.

Future work will be directed to the identification of changes in the toxicant during and after exposure of the coating to aqueous and saline environments. Efforts will also be expended to determine the chemical form of the organotin species leached from the coatings into the environment.

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

Infrared and nuclear magnetic resonance spectroscopies have been employed to elucidate the chemical and structural properties of triorganotin compounds incorporated into marine antifoulant coating formulations. It is necessary to determine the molecular species of the toxicant in order to be able to predict the mechanism of toxicant release and to design new, more effective coatings. In two conventional vinyl antifoulant coatings, the toxicant was found to react with one component in the coating formulation to yield →

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different triorganotin compounds. A change in the $\gamma_{asym(SnC)}$ vibration was found to correlate with a change in the coordination geometry of tin. These results indicate that infrared spectroscopy is a powerful technique that can provide insights into the chemical processes occurring in the antifouling coatings.