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The fate of triorganotin biocides on incorporation into Hypalon paint-based marine antifouling systems: ^{119m}Sn Mössbauer and ^{119}Sn NMR studies

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Incorporation of bis(tributyltin) oxide into a Hypalon paint system results in the formation of tributyltin chloride and a second organotin species, the identity of which remains uncertain. Both compounds are appreciably retained by the dried paint matrix, thereby resulting in marked reduction in the release rate of the tributyltin moiety into aqueous systems. In contrast, tributyltin acetate, tributyltin carbonate and bis(triphenyltin) oxide appear to be incorporated into the paint film in a largely unchanged state. In the case of triphenyltin chloride and triphenyltin acetate, evidence of dephenylation to form diphenyl- and monophenyl-tin compounds has been obtained.

Keywords: Triorganotin, antifouling, Hypalon paint systems, ^{119}Sm Mössbauer, ^{119}Sn NMR

INTRODUCTION

In recent papers[1–4] we, and others, have reported studies of the fate of various tributyl- and triphenyl-tin biocides on incorporation into cured neoprene rubber marine antifouling elastomers. By the use of ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopic techniques, we showed that the tributyltin biocides undergo significant chemical change during the curing process, being converted into tributyltin chloride together with, in some cases, tributyltin stearate and a small amount of dibutyltin distearate. In contrast, it was shown that the related triphenyltin biocides undergo drastic degradation on incorporation into neoprene, suffering cleavage of phenyltin bonds to give a mixture of products in which all stages of dephenylation are present, including stannic chloride. We now report a similar study of the fate of a range of triorganotin biocides on incorporation into a Hypalon® paint system.†

The Hypalon polymer was first produced in the 1930s by the introduction of chloro and chlorosulphonyl functionalities into polyethylene, which has an average molecular weight of 20 000, and which contains one chlorine atom for every seven carbons, and one chlorosulphonyl group for every 90 carbons. The incorporation of triorganotin biocides into a Hypalon-based paint system would provide an antifouling coating of the contact variety, relying on a leaching diffusion action to bring the toxicant to the surface.[5] Also included is a study of the rate of release of tributyltin biocides from the dried paint films into water under simulated environmental conditions.

EXPERIMENTAL

Various triorganotin biocides were incorporated into commercial Hypalon paint systems over a range of concentrations from 0.2% by wt of organotin in the liquid paint up to 10% by wt, depending on the nature of the study being undertaken. The liquid paint was applied to polythene sheeting, and allowed to dry over a period of at least 8 h. The dried coating was then examined *in situ* on the polythene support, or after flaking off the coating to provide a dry powder. The dry coating was then investigated by the following techniques.

(1) ^{119m}Sn Mössbauer spectroscopy, enabling investigation of the environment of the tin atom to be studied *in situ* without further chemical treatment. The Mössbauer spectra were recorded as described in our earlier papers.[1,3,4]

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† Hypalon is a registered trade mark of the DuPont Company.

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(2) Solvent extraction, using refluxing dichloromethane, allowing the final residue from the evaporated extract to be studied by ^{119}Sn NMR spectroscopy using a Bruker WP80 spectrometer. ^{119}Sn NMR chemical shifts are given on the δ scale using tetramethyltin as the internal reference. Shifts to high field are negative in sign.

(3) In the case of the coatings derived from the triphenyltin biocides, the possibility of dephenylation was investigated as follows. The dried coating was heated under reflux in ether with butyl-lithium solution (1.6 mol dm^{-3}, in hexane) for 4 h. The resulting solution was then hydrolysed by the addition of water, the organic layer separated, dried with $MgSO_4$, and evaporated to low bulk before investigation by gas chromatography as previously described.[3] Authentic samples of butyltriphenyltin and dibutyldiphenyltin were prepared by the reaction of butyl-lithium with the appropriate phenyltin halides under the same conditions. It was also established that these stannanes do not undergo further dephenylation under the conditions of the alkylation procedure.

Reactions of triorganotin toxicants with methanesulphonyl chloride

The triorganotin compound (1 mol equiv.) and the sulphonyl chloride (2 mol equiv.) were heated together under reflux in chloroform for 1 h. Evaporation of the solvent gave a viscous liquid which, when frozen at low temperatures, was examined by ^{119m}Sn Mössbauer spectroscopy.

Preparation of authentic triorganotin methanesulphonates

These were prepared as described in the literature[6] by the reaction of the bis(triorganotin) oxide with methanesulphonic acid (2 mol equiv.) in benzene, the liberated water being removed azeotropically.

RESULTS AND DISCUSSION

Comparison of the ^{119}Sn Mössbauer data recorded at 80 K for the dried paint film incorporating tributyltin biocides with that for the pure organotin compounds (Table 1) enables the following conclusions to be drawn. The best fit to the Mössbauer data for the dried paint film originally incorporating TBTO indicated the presence of two tin-containing components (Fig. 1). (It should be noted that the relative areas of absorption lines in Mössbauer spectra are not necessarily directly proportional to the relative proportions of the component tin species, since the area due to any given component depends on the recoil-free fraction of the tin nucleus, which may vary from compound to compound.) The major doublet, Q2, has an isomer shift similar to that of

Table 1 Mössbauer data[a] for Hypalon paints containing tri-n-butyltin

Sample[d]	Component	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Rel. area[b] (%)	ρ[c]
Pure TBTO	Q1	1.21	1.52	1.18	1.18	100.0	1.3
Pure TBTOAc	Q1	1.40	3.54	1.02	0.92	100.0	2.5
Pure TBTCl	Q1	1.51	3.43	1.04	1.04	100.0	2.2
Pure $(TBTO)_2CO$	Q1	1.39	2.68	1.04	1.04	60.0	1.9
	Q2	1.42	3.64	0.80	0.80	40.0	2.6
Dry paint/TBTO	Q1	1.30	1.70	1.36	1.36	11.0	1.3
	Q2	1.49	3.48	1.04	1.04	89.0	2.3
Dry paint/TBTOAc	Q1	1.39	3.44	1.06	1.06	100.0	2.5
Dry paint/TBTCl	Q1	1.53	3.17	1.10	1.12	100.0	2.0
Dry paint/$(TBTO)_2CO$	Q1	1.39	2.70	1.00	1.00	50.3	1.9
	Q2	1.42	3.64	0.80	0.80	49.7	2.6

[a] All spectra were recorded at 80 K with an error of ±0.02 mm s^{-1} for pure compounds and ±0.05 mm s^{-1} for paint samples. Isomer shifts are relative to $CaSnO_3$. [b] Relative area of each phase, i.e. quadrupole doublet. [c] $\rho = \Delta E_Q/\delta$. [d] TBTO, bis(tri-n-butyltin) oxide; TBTOAc, tri-n-butyltin acetate; TBTCl, tri-n-butyltin chloride; $(TBTO)_2CO$ is bis(tri-n-butyltin) carbonate.

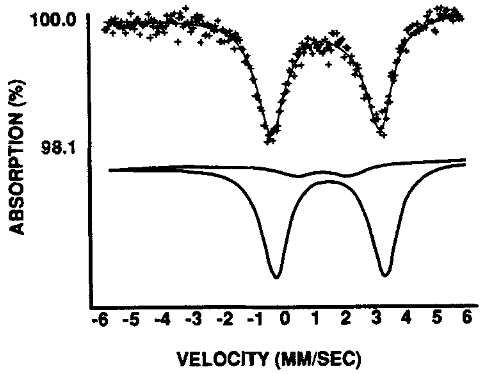


Figure 1 Mössbauer spectrum of dry hypalon paint originally containing bis(tri-n-butyltin) oxide, fitted as two doublets.

tributyltin chloride. However, the quadrupole splitting parameter, although similar to that of tributyltin chloride in the pure state, is much higher than that of tributyltin chloride dispersed in a dried paint film.

The parameters of the minor doublet, Q1, observed in the Mössbauer spectrum of the dried paint sample originally containing bis(tri-n-butyltin) oxide, are sufficiently different from those of the pure compound to suggest that a second new species has been formed. Like bis(tri-n-butyltin) oxide, this species would appear to involve four-coordinate tin(IV) ($\rho = 1.3$). It is possible that it is monobutyltin trichloride, and there is reasonably good agreement with literature Mössbauer data for this compound which, in the pure state, exhibits $\delta = 1.31$, $\Delta E_Q = 1.83\,\mathrm{mm\,s^{-1}}$[1,7] and when dispersed in a PVC matrix, $\delta = 1.17$, $\Delta E_Q = 1.94\,\mathrm{mm\,s^{-1}}$.[8] In view of the complexity of the paint matrix, and the high Lewis acidity of monobutyltin trichloride, some variation in Mössbauer parameters is perhaps not all that surprising. It is of interest that the line-widths for Q1 are significantly larger than is usual, suggesting the possibility of more than one tin site due to interactions with donor atoms present in the paint matrix.

A 12 h Soxhlet extraction of approximately 2 g of the dried paint sample in dichloromethane followed by ^{119}Sn NMR on the extract failed to detect any signals in the spectrum. A more exhaustive seven-day Soxhlet extraction was then carried out on a 5 g sample. The ^{119}Sn NMR spectrum of this extract exhibited two very weak signals at 155.6 ppm and −2.8 ppm. The former signal corresponds to tri-(n-butyl)tin chloride, ($\delta^{119}\mathrm{Sn} = 153$ ppm), but the latter signal could not be identified with certainty. A possible candidate, as argued above, is monobutyltin trichloride, for which $\delta^{119}\mathrm{Sn} = 3.0$ ppm, in the pure state; when dissolved in carbon tetrachloride, $\delta^{119}\mathrm{Sn} = 6.0$ ppm.[9] Both spectroscopic techniques therefore indicate the conversion of the original TBTO to tributyltin chloride. However, it is clear that this is retained in the polymer to a considerable extent, possibly as a result of some coordinative interaction involving a sulphonyl-oxygen donor site on the polymer, thus perhaps accounting for the change in quadrupole splitting observed for this component when dispersed in the dried paint film. (In the pure state, tributyltin chloride has a pseudopolymeric structure involving a five-coordinate tin site, thus accounting for the relatively high quadrupole splitting of $3.42\,\mathrm{mm\,s^{-1}}$.[10] However, the discrepancy between the quadrupole splitting data for the suspected tributyltin chloride formed *in situ* from the reaction of TBTO, and that observed on incorporating the authentic substance into the paint, cannot be readily accounted for. It may well be that the major tin-containing species present in the dried paint film is some other five-coordinate tin, perhaps a sulphonate ester, and tributyltin chloride is present only as a minor component. Mössbauer spectroscopy is unable to resolve components of closely related isomer shift and quadrupole splitting.[2]

Solvent extraction of the dried film incorporating authentic tributyltin chloride revealed a similar retention of the organotin compound by the paint film, the ^{119}Sn NMR spectrum displaying a weak signal at $\delta = 155$ ppm. The apparent reluctance of tributyltin chloride to be extracted from the dried paint film is almost certain to reduce the organotin biocide release rate from the paint and therefore its efficiency as an antifouling coating. Support for this view has also been obtained from a series of release rate studies conducted under simulated environmental conditions (see below).

As indicated by the Mössbauer data, both tributyltin acetate and bis(tributyltin) carbonate appear to be unchanged on incorporation into the dried paint, both retaining associated structures involving five-coordinate tin sites, although in the case of the carbonate a four-coordinate tin site may also be present, as is also found in the pure substance.[11]

We have also investigated the fate of a series of triphenyltin compounds on incorporation into Hypalon paint systems. Again, a comparison of the ^{119}Sn Mössbauer data for the dried paint film

Table 2 Mössbauer data[a] for Hypalon paints containing triphenyltin

Sample[d]	Component	δ (mm s^{-1})	ΔE_C (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Rel. area[b] (%)	ρ[c]
Pure TPTO	Q1	1.09	1.33	0.95	0.95	84.9	1.2
Pure TPTOAc	Q1	1.27	3.26	1.00	1.00	100.0	2.6
Pure TPTCl	Q1	1.33	2.56	0.97	0.97	100.0	1.9
Dry paint/TPTO	Q1	1.11	1.37	0.93	0.93	82.6	1.2
Dry paint/TPTOAc	Q1	1.06	1.59	1.18	1.18	32.9	1.5
	Q2	1.26	3.29	0.90	0.90	67.1	2.6
Dry paint/TPTCl	Q1	1.06	1.60	1.22	1.22	25.9	1.5
	Q2	1.24	2.87	1.00	1.00	74.1	2.3

[a–c] The footnotes to Table 1 apply. [d] TPTO, bis(triphenyltin) oxide; TPTOAc, triphenyltin acetate; TPTCl, triphenyltin chloride.

with those for the pure compounds (Table 2) has been made. In the pure state, bis(triphenyltin)oxide (TPTO) exists as a discrete moiety involving only four coordinate tin.[12] The Mössbauer parameters recorded in the present study are consistent with this structure. The Mössbauer spectrum of the dried paint film indicates that bis(triphenyltin) oxide is largely unchanged on incorporation into the paint system. Support for this was obtained on extraction of the dried film with dichloromethane, the ^{119}Sn NMR spectrum of the extract displaying a weak signal at $\delta = -83.9$ ppm, in reasonable agreement with the literature value for TPTO of $\delta = -80.6$ ppm.[9] In contrast, the Mössbauer parameters for the dried paint films incorporating triphenyltin acetate and triphenyltin chloride, respectively, indicate that these compounds have undergone some change on incorporation into the paint. In the case of the paint film originally incorporating triphenyltin chloride, the best fit to the Mössbauer data indicates the presence of two components whose Mössbauer paremeters are comparable with those of diphenyltin dichloride and monophenyltin trichloride, indicating that some dephenylation has taken place in the chlorinated polymer matrix, as is the case when triphenyltin chloride is incorporated into neoprene. (For diphenyltin dichloride $\delta = 1.37$, $\Delta E_Q = 2.86$ mm s^{-1}, and for phenyltin trichloride $\delta = 1.10$, $\Delta E_Q = 1.75$ mm s^{-1}).[3] The Mössbauer parameters of the minor component present in the dried paint film originally incorporating triphenyltin acetate are also comparable with the data for monophenyltin trichloride; however, in this sample, the major component would appear to be unchanged triphenyltin acetate. Further evidence of the formation of dephenylated products in the sample prepared from triphenyltin chloride was obtained by treatment of the dried paint film with butyl-lithium under reflux conditions in hexane/ether, in order to convert mono- and diphenyl-tin species into the related

Table 3 Mössbauer data[a] for the products of the triorganotin/methane sulphonyl chloride model reactions

Sample[d]	Component	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Rel. area[b] (%)	ρ[c]
TBTO/$MeSO_2Cl$	Q1	1.36	1.02	0.99	0.98	19.1	0.8
	Q2	1.49	3.30	1.08	1.04	48.8	2.2
	Q3	1.54	4.24	0.89	0.86	32.1	2.8
TBTCl/$MeSO_2Cl$	Q1	1.51	3.39	1.12	1.12	100.0	2.3
TPTO/$MeSO_2Cl$	S1	1.44		1.20		13.6	
	Q1	1.28	2.60	0.98	1.00	61.1	2.0
	Q2	1.38	4.00	0.88	1.06	25.3	2.9
TPTCl/$MeSO_2Cl$	Q1	1.33	2.52	0.94	0.93	100.0	1.9

[a] All spectra were recorded at 80 K with an error of ± 0.02 mm s^{-1}. Isomer shifts are relative to $CaSnO_3$. [b] Relative area of each phase, i.e. quadrupole doublet or singlet. [c] $\rho = \Delta E_Q/\delta$. [d] Abbreviations as in Tables 1 and 2.

Table 4 Mössbauer data[a] for the products of the triorganotin oxide/sulphonic acid reactions

Sample[d]	Component	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Rel. area (%)	ρ[c]
TBTO/MeSO$_3$H	Q1	1.62	4.44	1.00	0.98	100.0	2.7
TPTO/MeSO$_3$H	S1	0.01	—	1.32	—	5.2	—
	Q1	1.04	1.07	0.88	1.66	11.7	1.0
	Q2	1.45	4.16	0.92	1.20	83.1	2.9

[a–c] The footnotes to Table 3 apply. [d] Abbreviations as in Tables 1 and 2.

butylphenylstannanes, which could be identified by gas chromatography by comparison with the authentic stannanes. The resulting chromatogram revealed the presence of tributylphenylstannane as the major component, together with a trace of dibutyldiphenylstannane. Similarly, a monophenyltin species was shown to be present in the sample originally containing triphenyltin acetate. In the Hypalon system, dephenylation does not occur to the same extent as in the curing of neoprene elastomers containing the above range of triphenyltin biocides, presumably a reflection of the prevailing conditions, i.e. room-temperature drying of the Hypalon system compared with the curing of neoprene at 150 °C.

In order to shed more light on the possible products formed in the reactions of bis(tributyltin) oxide (TBTO) on incorporation into Hypalon paint films, we have carried out a series of experiments between TBTO and a model sulphonyl derivative. Heating together TBTO and methanesulphonyl chloride in chloroform resulted in the formation of a clear liquid, the low-temperature frozen Mössbauer spectrum of which consisted of three unresolved doublets (Table 3; Fig. 2). The second doublet, Q2, had parameters which matched those of tributyltin chloride. The third doublet, Q3, had a large quadrupole splitting, with $\rho = 2.8$, indicative of a high-coordination tin site, and was initially thought to be due to the tributyltin methanesulphonate ester. The Mössbauer data for the authentic methanesulphonate ester (Table 4) (prepared from the reaction of TBTO with methanesulphonic acid[6]) are broadly similar, but nevertheless differ from the above data by more than the commonly accepted experimental error. It is possible that the parameters for Q3 in the products of the sulphonyl chloride reaction are less reliable as a consequence of the fitting for unresolved quadrupole doublets. Nevertheless the line widths and line shapes give clear evidence of an additional large quadrupole component. However, ^{119}Sn NMR studies did not lend support to the above tentative conclusions. The ^{119}Sn NMR spectrum of the products of the sulphonyl chloride reaction exhibited two signals at $\delta = 121.2$ and -8.2 ppm. No signal corresponding to tributyltin chloride was evident. The corresponding spectrum of the authentic methanesulphonate ester exhibited a single peak at $\delta = 68.7$ ppm. Thus, these results do not support the proposed formation of the polymer-bound alkylsulpohonate (and tributyltin chloride) in the reactions of TBTO with the sulphonyl chloride moiety present in Hypalon paint systems. Clearly a reaction occurs between such components but, as yet, we are uncertain of the nature of the products. The reaction of bis(triphenyltin) oxide with methanesulphonyl chloride is similarly complex.

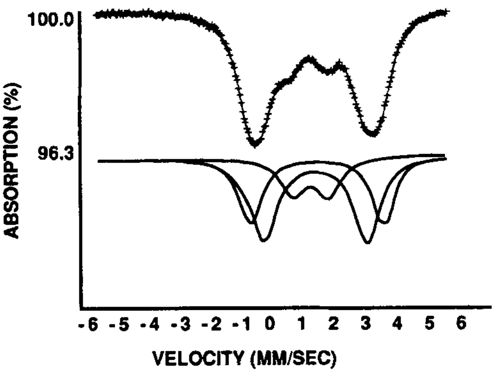
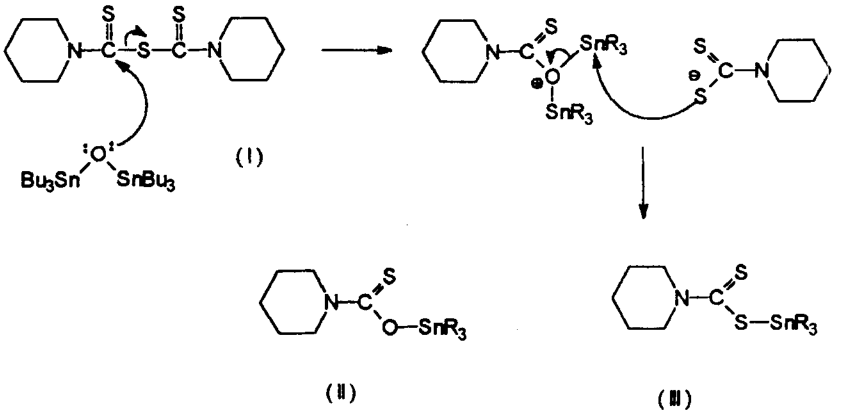


Figure 2 Mössbauer spectrum of the product from the reaction of bis(tri-n-butyltin) oxide with methanesulphonyl chloride.

Hypalon paint is also known to contain other components with which the organotin biocides might interact. These include stearic acid and *N*-pentamethylenethiuram disulphide (**I**). The former is known to react with bis(triorganotin)



Scheme 1 Proposed reaction between $(R_3Sn)_2O$ and dipentamethylene thiuram disulphide.

oxides to give the related triorganotin stearates.[2] The disulphide (**I**) is likely to react with the organotin oxides to give the esters **II** and **III** (Scheme 1). The dithiocarbamate esters (**III**) have been prepared by Shrivastava and Kumar[13] by the reactions of triorganotin oxides with carbon disulphide and piperidine.

Mössbauer parameters for the model stearates and dithiocarbamates are presented in Table 5. Comparison of these values with the Mössbauer parameters of the dried paint films originally containing the bis(triorganotin) oxides reveals little similarity except in the case of the major component found in the bis(tributyl)tin oxide system, for which there is a close resemblance with the data for tributyltin stearate. However, no evidence of the presence of this compound was found in extracts of the dried paint films when studied by ^{119}Sn NMR spectroscopy. No signal at $\delta \simeq 90$ ppm (expected for this compound)[2] was observed, and its formation in the paint film must remain conjectural.

We have also carried out a study of the rate of release of tin species from a range of dried Hypalon paint films prepared from paint systems into which tributyltin compounds (usually TBTO and TBTOAc, at an initial total level of 0.08% by wt of the liquid paint) had been incorporated, together with, in some cases, appropriate urea-based herbicides, e.g. Diuron. A dried, painted film sample of area 5 cm^2 was exposed to a continuous flow of doubly distilled water at the rate of 120 $cm^3\,h^{-1}$, and the total tin content of the effluent monitored over a period of 5–10 days by solvent extraction (using a toluene solution of tropolone), followed by a graphite furnace AA approach involving the addition of picric acid as a matrix modifier.[14] All of the samples studied exhibited a similar release rate of approx. 0.05 $\mu g\,Sn\,cm^{-2}\,day^{-1}$. A level of 5 $\mu g\,Sn\,cm^{-2}\,day^{-1}$ (as TBTO) has been claimed as the minimum needed to prevent marine fouling.[15] The low release rates observed are also consistent with our earlier difficulties experienced in attempting to solvent extract organotin species from the dried paint films.

Table 5 Mössbauer parameters[a] of triorganotin stearates and dithiocarbamates

Sample[d]	Component	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	Rel. area (%)	ρ
TBT stearate	Q1	1.44	3.58	0.99	0.95	100.0	2.5
TPT stearate	Q1	1.25	3.29	0.93	0.97	100.0	2.6
TBT dtc	Q1	1.44	2.16	1.03	1.04	100.0	1.5
TPT dtc	Q1	1.29	1.75	0.95	0.99	100.0	1.4

[a] All spectra recorded at 80 K with an error of ±0.02 mm s^{-1}. Isomer shifts are relative to $CaSnO_3$.
[b] Relative area of each phase, i.e. quadrupole doublet. [c] $\rho = \Delta E_Q/\delta$. [d] TBT, bis(tri-n-butyltin); TPT, bis(triphenyltin); dtc, dithiocarbamate.

CONCLUSION

In summary, it is clear that some chemical change occurs on incorporation of TBTO into Hypalon paint systems. However, apart from the formation of tributyltin chloride, the nature of the products remains unclear. What is evident is that the organotin species appear to be strongly held within the paint film. Tributyltin-doped Hypalon paint systems are unlikely, therefore, to provide significant protection against marine fouling. Bis(triphenyltin) oxide, on the other hand, seems to be largely unchanged on incorporation into Hypalon paint. In contrast, in the case of triphenyltin chloride and triphenyltin acetate, there is evidence of destruction of the biocidal triphenyltin moiety as a result of dephenylation reactions.

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