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Review

Organotin antifouling paints and their alternatives

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Tributyltin and triphenyltin compounds have excellent biocidal properties and almost all vessels in the world have used these paints since early in the 1960s. Contrary to expectation, as shown by experimental data at the beginning of organotin chemistry, triorganotins are exceptionally stable in the sediment or in dark places in the deep sea. Since triorganotins do not decompose rapidly in seawater, many incidences of deformities in some shellfish have been linked to their presence, even when present at extremely low concentrations.

Alternative tin-free antifoulants containing other biocides, such as copper compounds and organic compounds, have been developed and used since the late 1980s. Some nations have already banned the use of organotin antifouling compounds for small vessels, and in 2001 the International Maritime Organization decided to ban completely the use of the organotin compounds from the year 2003. Therefore, it is necessary to find economically and environmentally better biocidal substances as soon as possible. Moreover, the development of antifoulants containing environmentally safe natural products, fouling release coatings, electroconductive coatings, etc. have long been anticipated from the new point of conservation of the world marine environment. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: organotin compounds; antifouling paints; natural products; triorganotin; self-polishing copolymers; tin-free antifouling paints; biocides; environment; bioaccumlation

INTRODUCTION

Marine fouling is the settlement and growth of a variety of marine organisms on structures immersed in seawater, such as ships' hulls, navigation buoys, sonar equipment and seawater cooling pipes.[1] Primary fouling, which begins at the time of exposure to the seawater, consists mainly of a complex community of bacteria, diatoms, protozoa and algae spores. This is generally followed by other organisms, such as barnacles, algae, hydroids, tubeworms, mollusks or sponges.[2–9]

Marine fouling can be a serious problem in the shipping industry, since it increases the surface roughness of the hull and hence its frictional resistance to its movement through water. It has been estimated that, after 6 months of fouling, a vessel needs to expend 40% more fuel to maintain a normal speed. There are additional costs incurred in cleaning and repainting, plus loss of revenue when dry-docked.[4,8]

Many kinds of compounds have been used as toxicants in antifouling paints. The history of antifouling systems is shown in Table 1.[7,8,10,11] Older systems used copper or lead sheathing

Table 1. History of antifouling systems[a]

Oldest	Copper sheathing on wooden ships
2000 BC	Ships were fastened with copper bolts and the entire bottom was sheathed with lead
300 BC	Arsenic compounds, sulfur, etc. were formulated in wax, tar-type coatings
19th century	The first industrial use of antifouling paints: a soap based on copper sulfide in rosin
Pre-1960s	Conventional antifouling paints were largely based on copper(I) oxide as the toxicant. Other antifoulants: organomercury, organolead, organoarsenic, organohalogen (e.g. DDT), organosulfur compounds
1960–	Organotin antifoulants
1974–	Ablative self-polishing organotin polymers: tributyltin methacrylate/methylmethacrylate copolymer
1980–	Polysiloxane polymers
1990–	Tin-free antifoulants

[a] Ref. 7. Also, see Ref. 12.

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Table 2. Comparative antifouling activity of various toxicants

Compound[a]	LD_{50}		
	Algae (ppm)	Barnacles (ppm)	Rats (oral) (mg kg^{-1})
Cu_2O	1–50	1–10	470[c]
R_3SnX	0.01–5	0.1–1	130–600
R_3PbX[b]	0.1–1	0.1–1	30–200
$RHgX$[b]	0.1–1	0.1–1	8–36

[a] R = alkyl group.

[b] Because of the long-term environmental hazard of lead and mercury compounds, these biocides are not permitted for use in antifouling coatings in many countries.

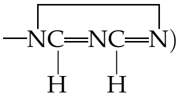
[c] US Nat. Int. Occup. Saf. 1987 (see Ref. 10).

on wooden ships. In the 19th century, many antifoulants, such as copper compounds and arsenic compounds, were used by formulating with wax, tar and rosin matrices. Prior to the 1960s, conventional antifoulants contained cuprous oxide. Organotin compounds began to be used commercially from the 1960s, and today they are used extensively all over the world.[7,8]

The biocidal activities of some common antifoulants are shown in Table 2.[5,6,8,10,13] All of them have high biocidal activity, but lead and mercury compounds are not permitted for use in antifouling coatings in many countries because of the long-term environmental hazard.[2,7,8] Thus, cuprous oxide and organotin compounds are primarily used as antifoulants. In particular, organotin compounds have been used for boat bottom antifouling paints because of their high performances.

It was believed that organotin compounds were very convenient and ideal compounds because they are easily decomposed by UV light and microorganisms after their use. In the early 1980s, an environmental problem caused by them was first found in France as described below. From the late 1980s, antifoulants that do not contain organotin compounds

Table 3. Industrial applications of organotin compounds

Application	Compound
	R_3SnX
Agriculture	
fungicides	Ph_3SnX (X = OH, OAc)
antifeedants	Ph_3SnX (X = OH, OAc)
acaricides	$(c\text{—}C_6H_{11})_3SnX$ (X = OH,  $-N\underset{H}{C}{=}N\underset{H}{C}{=}N$) $[(PhMe_2CCH_2)_3Sn]_2O$
Antifouling paint biocides	Ph_3SnX (X = OH, OAc, F, C1, SCS, $N(CH_3)_2$, $OCOCH_2Cl$, $OCOC_5H_4N-3$), $Ph_3SnOCOCH_2CBr_2COOSnPh_3$, Ph_3SnX (X = F, C1, OAc), $(Bu_3Sn)_2O$, $Bu_3SnOCOCH_2CBr_2COOSnBu_3$, $(\text{—}CH_2C(CH_3)\ (COOSnBu_3))\text{—})_n$
Wood preservative fungicides	$(Bu_3Sn)_2O$, Bu_3Sn(naphthalenate), $(Bu_3Sn)_3PO_4$
Stone preservation	$(Bu_3Sn)_2O$
Disinfectants	$Bu_3SnOCOPh$, $(Bu_3Sn)_2O$
Molluscicides (field trials)	Bu_3SnF, $(Bu_3Sn)_2O$
	R_2SnX_2
Heat and light stabilizers for rigid PVC	$R_2Sn(SCH_2COO-1-Oct)_2$ (R = Me, Bu, Oct, $BuOCOCH_2CH_2$), $(R_2SnOCOCH{=}CHCOO)_n$ (R = Bu, Oct), $Bu_2Sn(OCOCH=CHCOOOct)_2$, $Bu_2Sn(OCOC_{11}H_{23})_2$, $Bu_2Sn(SC_{12}H_{25})_2$
Homogeneous catalysts for RTV silicon, polyurethane foams and transesterification reactions	$Bu_2Sn(OCOCH_3)_2$, $Bu_2Sn(OCO-1-Oct)_2$, $Bu_2Sn(OCOC_{12}H_{25})_2$, $Bu_2Sn(OCOC_{11}H_{23})_2$, $(Bu_2SnO)_n$
Precursor for forming SnO_2 films on glass	Me_2SnCl_2
Anthelmintics for poultry	$Bu_2Sn(OCOC_{11}H_{23})_2$
	$RSnX_3$
Heat stabilizers for rigid PVC	$RSn(SCH_2COO-1-Oct)_3$ (R = Me, Bu, Oct, $BuOCOCH_2CH_2$), $(BuSnS_{1.5})_4$
Homogeneous catalysts for transesterification reactions	$(BuSn(O)OH)_n$, $BuSn(OH)_2Cl$
Precursor for SnO_2 films on glass	$BuSnCl_3$, $MeSnCl_3$[a]

[a] These compounds are used in combination with the corresponding R_2SnX_2 derivatives.

have been developed. In the future, the use of all organotin compounds will probably be completely banned in the world.

ORGANOTIN COMPOUNDS

The first organotin compound was prepared in 1852 by Löwig, but credit for the first comprehensive study of organotins belongs to Edward Frankland. In 1853 he prepared diethyltin diiodide.[7] The first commercially significant property of organotins to become recognized was the ability of diorganotins to inhibit the degradation of poly(vinyl chloride) (PVC) under the influence of heat and UV light. This was first utilized in the USA in the 1940s, and was followed by Europe and Japan in the 1950s. Other uses of the diorganotins are as catalysts for room temperature vulcanization (RTV) silicone, polyurethane foam and transesterification, and as precursors for forming SnO_2 film on glass and as anthemintics for poultry.[2,3,7,8]

In 1950, the research team under the leadership of Professor G. J. M. van der Kerk made important contributions to the study of organotin chemistry. In particular, the powerful biocidal properties of trialkyltin and triaryltin derivatives were established.[5,6] The introduction of biocidal uses of the triorganotin compounds began in the late 1950s, when they were used as agricultural fungicides; their uses in wood-preserving compounds began in 1960 and as antifouling paints in the early 1960s.[4] Other biocidal uses include their use as antifeedants, as acaricides, in stone preservation, as disinfectants and as molluskicides. The industrial applications of organotin compounds are shown in Table 3.[2,7,8,14–16]

In 1950, the annual production of organotin compounds was only around 50 tons. This rose to 2000 tons in 1960 and 16 000 tons in 1970, and production in the mid-1980s was estimated at over 40 000 tons.[4]

As discussed by Blunden *et al.*,[8] the most important use of the organotins is as PVC stabilizers (*ca* 70%); biocidal uses, such as in antifoulants, agrochemicals and wood preservatives, are *ca* 20%. Around 3500 tons per year are used as organotin antifoulants.

PROPERTIES OF TRIORGANOTIN COMPOUNDS

In the organotin series expressed by the formula R_nSnX_{4-n} (R = carbon-bonded organic group, X = inorganic substituent, n = 1–4), it is now well established that the maximum toxicity to all types of living species occurs with the triorganotin compounds R_3SnX. As the length of the carbon chain is progressively increased within a particular series of tri-*n*-alkyltin salt (R_3SnX) the mammalian toxicity reaches a maximum value when R is an ethyl group, and then falls off rapidly with further lengthening of the alkyl chain. The tri-*n*-octyltin derivatives are essentially non-toxic, as shown in Table 4[5,6,8] and in Figure 1.[5,6] With regard to the toxicity of tributyltin (TBT) salts (n-Bu_3SnX) in mammals, the acute oral LD_{50} values are in the range 112–346 mg kg^{-1} (rats), as shown in Table 4. Their biological activity is almost entirely due to the Bu_3Sn moiety, since, in common with other trialkyltin compounds, the variation of the inorganic substituent X does not usually have a significant effect on the toxicity. The 'X' group tends to affect properties such as volatility and solubility.

Table 4. Mammalian toxicity of tri-*n*-alkyltin compounds and triphenyl compounds

Compound	Acute oral LD_{50} (rats, mg kg^{-1})
$Me_3SnOCOMe$	9.1
$Et_3SnOCOMe$	4.0
$Bu_3SnOCOMe$	125–136
$Bu_3SnOCO(CH_2)_9Me$	205
$Bu_3SnOCO(CH_2)_7CH{=}CH(CH_2)_7Me$	195
$Bu_3SnOCOPh$	132
$Bu_3SnOSnBu_3$	112–234
Bu_3SnCl	122–349
Bu_3SnF	200
$Oct_3SnOCOMe$	>1000
$Ph_3SnOCOMe$	125–491
Ph_3SnOH	500–600
Ph_3SnF	1170
Ph_3SnCl	125
$Ph_3SnSnSnPh_3$	680–1470[a]

[a] Mice.

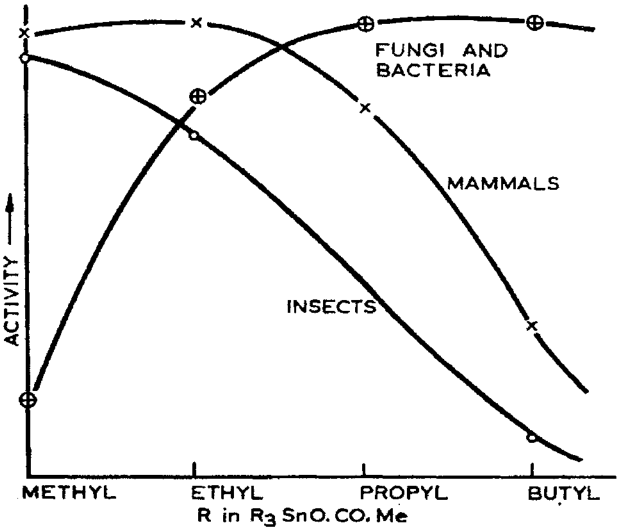


Figure 1. Dependence of the biological activity of tri-*n*-alkyltin acetate on the nature of the alkyl group for different species. Reproduced from Reference 5 by kind permission of the Oil & Colour Chemists' Association.

The acute mammalian toxicities of the common triphenyltin biocides are generally very similar to, and often lower than, those of their tributyltin analogues. It is also interesting to note that the anionic group appears to have an effect on the toxicity in these compounds, as shown in Table 4.[5,6,8]

Although TBT and triphenyltin (TPT) compounds are not unduly hazardous to humans, as discussed above, they are nevertheless very effective biocides against a wide range of marine fouling organisms. Information on the activities of various TBT and TPT derivatives against marine algae, barnacles, shrimps and tubeworms has been published.[5,6]

In Table 2, the activities of the R_3SnX compounds against marine algae and barnacles are compared with those of other antifouling agents, and it can be seen, for example, that the amount of organotin compound required to prevent fouling is usually five to ten times less than that of cuprous oxide. Although the TBT and TPT appear to be less effective against algae than against other marine fouling species, the activity spectrum may be widened by adding other toxicants, such as cuprous oxide, and chemically binding two R_3Sn groups of different biological activities into a polymeric network.[5,6,13]

The exact mechanism by which the triorganotins exert their lethal effects on marine organisms is still not completely clear, although extensive studies in mammals have established that the trialkyltin, at least up to TBT, inhibits the vital process of oxidative phosphorylation and thereby depresses general metabolism; the TPT compounds produce a similar depression of metabolic activity.[5,6]

Histological studies on Ram's Horn snails *Planorbis* spp. have indicated that tributyltin oxide (TBTO) combines with amino acids in proteinaceous tissue.[17] In the case of two animal proteins (rat hemoglobin and a protein from guinea-pig liver supernatant), it has been suggested that a trialkyltin histidine complex is formed, in which the tin atom is a five-coordinate structure with a trigonal bipyramidal geometry and bonds with two nitrogen atoms of two histidine moieties in the protein and the three carbon atoms of the tributyl groups.[18] The original anionic group of the R_3SnX molecule is not directly involved in the bonding in this complex, which explains the anion independence of the biological activity.[5,6]

The activity maxima for different types of livings species are found to be dependent on the length of the alkyl chain in the tri-*n*-alkyltin compounds: for insects, the trimethyltins are usually most toxic; for mammals it is the triethyltins; for Gram-negative bacteria it is the tripropyltins; and for Gram-positive bacteria and fungi, the TBTs are found to show the highest activity, as shown in Figure 1.[5,6]

ORGANOTIN ANTIFOULING PAINTS

Free-association paints

Triorganotin compounds are an important constituent of antifouling paints, which, when applied to a hull, prevent fouling build-up. They have the advantage of being active against a wide range of fouling species, and cause no galvanic corrosion problems on aluminum hulls (unlike paints containing some other metal elements); they are also colorless, and hence allow a wide range of paint colors to be formulated.[4] The organotin compounds used as antifoulants are TBTO, TBT fluoride, TPT fluoride, TBT chloride, TBT methacrylate copolymer, etc., as in shown Table 3.[2,7,8,14–16]

Table 5. Growth inhibition by organotins of marine fouling organisms

Organism	Growth-inhibiting concentrations (ppm)	
	TBTO	TBT fluoride
Barnacles	0.1	0.1
Enteromorpha sp.	0.02	0.01
Chlamydomas sp. (algae)	0.005	0.001
Lobsters	0.02	0.005

The most representative antifouling organotin compound is TBTO ($(n\text{-}Bu_5Sn)_2O$; it is miscible with paint solvents, is a colorless liquid and is widely used in many biocidal applications. It is a powerful fungicide, and will completely inhibit the growth of most fungi at a concentration of 0.5–1.0 ppm. It is also effective against Gram-positive bacteria, but it is not effective against Gram-negative bacteria. It has the advantage of being compatible with many other biologically active compounds, and its activity is maintained even in an alkaline or a dilute mineral acid solution at a room temperature.[4]

TBTO was one of the first organotins used in antifouling paints, and it is used mainly in systems where relatively short-term protection is needed, since its leaching rate from the paint film is high.[7] It is also incorporated into a chloroprene rubber to form an antifouling material for sonar buoys. Other commercial biocidal formulations containing TBTO are used to protect and clean stonework from the effects of algae and lichens, and to protect old books and manuscripts from decay.[4] Antifoulants such as TBTO and TBT fluoride inhibit growth of marine fouling organisms, as shown in Table 5.[7]

For an antifouling coating to be effective, the rate of release of the toxicant must be closely controlled. It must be a great enough to provide a protective barrier, but not too great, or else the life of the coating is shortened and environmental contamination becomes unacceptable.[7]

The critical leaching rate is the minimum value of leaching rate that will prevent the settlement of marine organisms. The critical leaching rates of cuprous oxide and organotin compounds are about 10 $\mu g\,cm^{-2}\,day^{-1}$ and 1 $\mu g\,cm^{-2}\,day^{-1}$ respectively.[7–10,19] It is always necessary for the antifoulants to leach by more than the critical leaching rate in order to

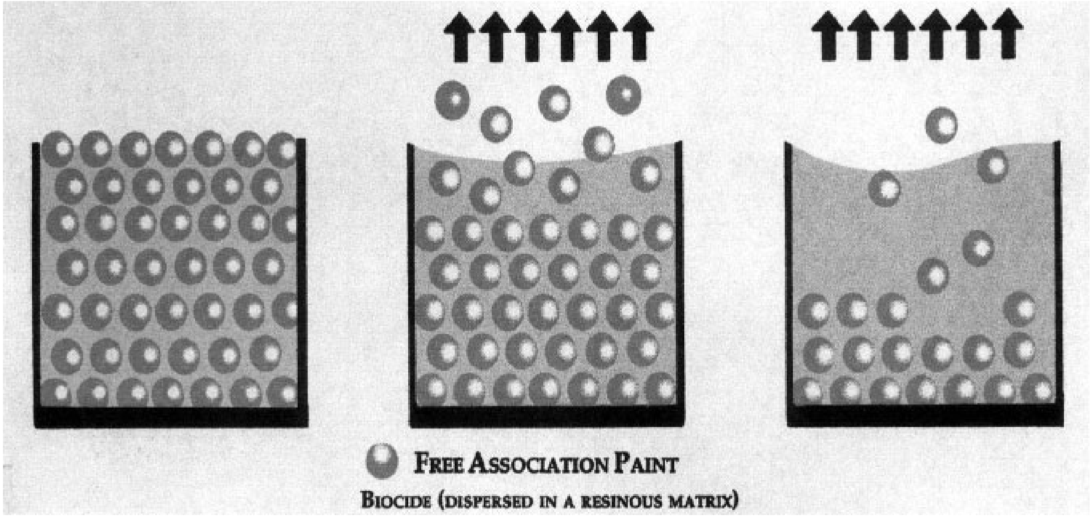


Figure 2. Antifouling paint systems. TBT as a biocide does not bond with resinous molecules. The biocide leaches freely from the resinous matrix. Reproduced from Reference 20 by kind permission of ORTEP-Association.

show an antifouling effect. The solubilities of organotins in seawater are as follows:[7]

8–10 ppm for TBTO
6 ppm for TBT fluoride
1 ppm for TPT fluoride.

Hence, TBTO, having a high solubility in seawater, gives relatively short-term protection. On the other hand, TPT fluoride is used in a long-life antifouling paint. These organotins can provide satisfactory control of shells and algae settlements for 6 to 24 months on a ship.[19]

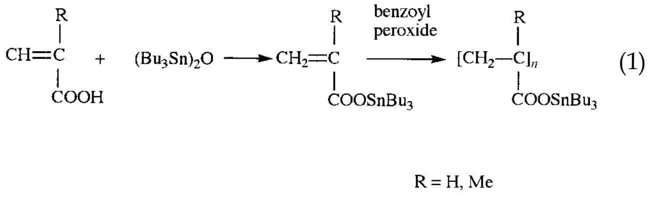
The optimum release rate required for an organotin compound such as TBTO or TBT fluoride is about 1.0–1.2 $\mu g\ cm^{-2}\ day^{-1}$. TBTO behaves like a solvent and migrates from a paint film; hence, after an initial period of effectiveness, its activity falls off with time. Tetrachlorophthlate behaves as a plasticizer to TBTO. Its mixture leads to a lower leaching rate and hence to it being effective over a longer period.[5,6]

The inorganic group X of the compounds R_3SnX will affect the solubility and consequently the release rate of organotin toxicant. For the majority of ships, which are dry docked at intervals of about 12 to 18 months, the ordinary paint formulations containing simple triorganotin additives of the above types are quite satisfactory, since they provide adequate protection over the above period.[5,6]

These organotins do not directly bond with the matrix resins. Such paints are called TBT free-association paints. The release from the dispersion state in a resinous matrix is shown in Figure 2.[20] The biocide leaches free from the resinous matrix. The initial release is rapid and uncontrolled. Subsequent release declines steadily from the matrix, such that the antifouling performance of the paint diminishes with time. Thus, it is difficult to control the rate of release of TBT biocides from a free-association paint system so as to provide a constant leaching level.[10,20]

Self-polishing copolymer systems

In the 1970s, there were many studies on the bonding of organotin compounds with a polymeric system in order to increase the performance life of antifouling coatings. For example, acrylic or methacrylic acid reacts with TBTO to give esters, and the polymer (copolymer) of TBT acrylate or methacrylate is obtained by the polymerization of the esters (and methylmethacrylate) with benzoyl peroxide, as shown in Eqn. (1).[21,22]



$$\underset{\text{COOH}}{\overset{\text{R}}{\text{CH}=\text{C}}} + (Bu_3Sn)_2O \longrightarrow CH_2=\underset{COOSnBu_3}{\overset{R}{C}} \xrightarrow{\text{benzoyl peroxide}} [CH_2-\underset{COOSnBu_3}{\overset{R}{C}}]_n \qquad (1)$$

R = H, Me

By using these polymers, the release of the organotin biocide from the surface of the paint film by hydrolysis in seawater provides the antifouling action. In consequence, the depleted outer layer of the paint film, containing a hydrophilic carboxylate group, is easily eroded by moving seawater, with the result that a fresh surface layer of organotin acrylate polymer is exposed. In addition, an important effect of the continuous renewal of the paint film's surface is an overall smoothing or 'polishing' of the coating. These polymers are called ablative polymers.[8,23] At the paint surface, seawater hydrolyzes the TBT copolymer bond and the TBT biocide and copolymer resin are slowly

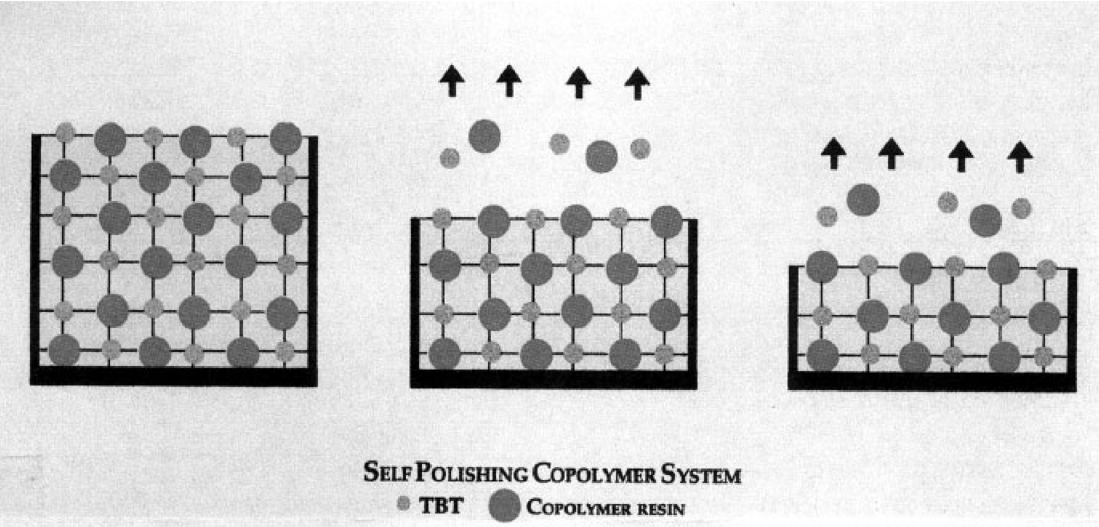


Figure 3. TBT copolymer system. TBT biocide is slowly released at a controlled rate. Reproduced from Reference 20 by kind permission of ORTEP-Association.

released at a constant rate. A uniform antifouling performance is achieved throughout the life of the paint.

The advantages of the self-polishing copolymer systems compared with the free-association paints are as follows:[10,20]

1. The system is able to provide controlled biocide release at a constant and minimal rate, since TBT biocide bonds directly with the matrix polymer and the rate of the hydrolysis is easily able to be regulated by the polymerization conditions.
2. The life of the coating is proportional to its thickness, is accurately predictable and is able to provide a long fouling-free performance.
3. The erosion process results in a smoother, 'polished surface', which reduces hull roughness. This has a significant effect on the reduction of frictional drag, leading to conservation in fuel consumption.
4. Hulls can be repainted directly without the need to remove any remaining old copolymer coating.

The representative ablative self-polishing polymer is TBT methacrylate/methylmethacrylate copolymer.[24] Since their introduction in 1974, ablative self-polishing coatings have been widely accepted and utilized on most major ships throughout the world.[4] The antifouling systems with such self-polishing organotin polymers are shown in Figure 3.[20]

The most common organotin monomers used in such coatings are TBT acrylate or methacrylate, which can be polymerized with a number of other monomers, including alkylacrylates and methacrylate, maleic anhydride, styrene, vinyl chloride, vinyl acetate, etc.[4] In continuing tests by the US Navy, ablative organotin antifouling coatings demonstrated more than 48 months of 100% fouling-free service in 1983. The Navy also estimated that these formulations can reduce fuel costs by about 10 to 15% a year.[8]

Comparison of antifouling performance

As the high performance ablative self-polishing antifoulants are utilized on most major shipping throughout the world, concern about the environmental effects of antifouling paints has occurred in areas where mollusks, such as oysters and marine snails are present. Numerous countries have begun legislative controls.

In 1992, the publication *TBT Copolymer Anti-fouling Paints: The Facts*[20] was compiled by companies belonging to the European Chemical Industry Council (CEFIC) from the Organization Environmental Programme Association (ORTEPA) and the Marine Painting Forum. This brochure reported on comparative data collected from several hundreds of vessels in around 1990 or before, and the performance achieved by each of the systems. The benefits of high-performance antifouling paints can be expressed under four main categories, direct fuel savings, extended drydocking intervals, reduced maintenance and indirect savings, as follows:[20]

Fuel savings	$500 million
Extended drydocking	$400 million
Reduced maintenance	$800 million
Indirect savings	$1000 million
Total	$2700 million

This total figure of around $3 billion per annum is a sum of economic significance.

The brochure claimed that the use of the organotin polymer antifouling paints provided very large environmental benefits, because a lower fuel consumption by the world's shipping fleet reduces the releases of greenhouse gases and those emissions that are responsible for acid rain, even though the paints cause problems for some species of shellfish. As shown in Table 6,[20] the effectiveness of fouling-

Table 6. Antifouling performance[a] comparison[20]

System	Months out of dock	Ratio of fouling (%)	Satisfactory (%)
Conventional	24	82	36
Organotin copolymer	48	23	92
Organotin copolymer	60	30	90
Tin-free systems	36	40	79

[a] Each vessel can be assigned a fouling rating (FR). Fouling ratings are represented by percentage ratings, where 0FR = 0% fouling and 100FR = 100% fouling. An inspection rating of up to 10FR (10% fouling) is accepted as 'satisfactory'.

free performance for 3 years in the tin-free systems is lower than that of the fouling-free performance for 5 years in the organotin polymer systems.

The brochure also reported that the self-polishing antifouling paints offer economical and environmental benefits:

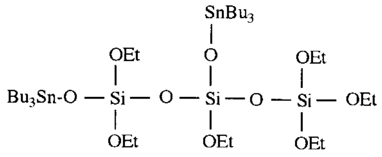
1. Fouling-free performance 5 years is achievable — something unequalled by any other antifouling system.
2. World fleet fuel consumption is reduced by 7 million tons ($0.5 billion) a year, thereby contributing to a saving of natural resources.
3. As a consequence of not burning this fuel, 22 million tons of CO_2 and 0.6 million tons of SO_2 are not emitted to the environment each year, thereby reducing greenhouse gas and acid-rain effects.
4. Fuel savings and the reduction in dry docking and other indirect costs give rise to overall savings of about $3 billion a year.
5. Proposals to monitor and control the worldwide usage of TBT-based paint are supported by the chemical and marine paint manufacturing industries. Adherence to these proposals will greatly contribute to the safety for man and the environment.

Research on organotin antifouling paints has continued since the publication of this 1992 brochure. Recently antifouling coatings are expected to have a 10 year service life. Therefore, high performance and cost-effective organotin antifouling paints are now used for most of the vessels in the world.

Polysiloxanes

Another recent development in antifouling coatings, introduced in the 1980s, is the use of tributyltin bonded to a different polymer. Whereas organotin acrylates are typically linear polymers that are applied as solutions and form films by solvent evaporation, polysiloxanes are moisture-cured to a three-dimensional network when the solvent evaporates and thus provided a denser and more durable film. Organotin polysiloxane coatings are not ablative, and mostly remain on the hull; they are compatible with and are often combined with other organic resins, and the precise formulation can provide a highly controlled release of antifoulant for a long service life.[4]

The organotin polysiloxane coatings consist of triorganotin groups chemically bonded to a siloxane polymeric backbone. The function of this composition is the provision of a chemically controlled release mechanism for the antifoulant via the hydrolysis of the tin–oxygen–silicon bonds. The controlled release of the organotin moiety is the key to assuring a good antifouling performance over a predicted period of service. A typical TBT polysiloxane prepolymer structure (1)[4] is shown here:



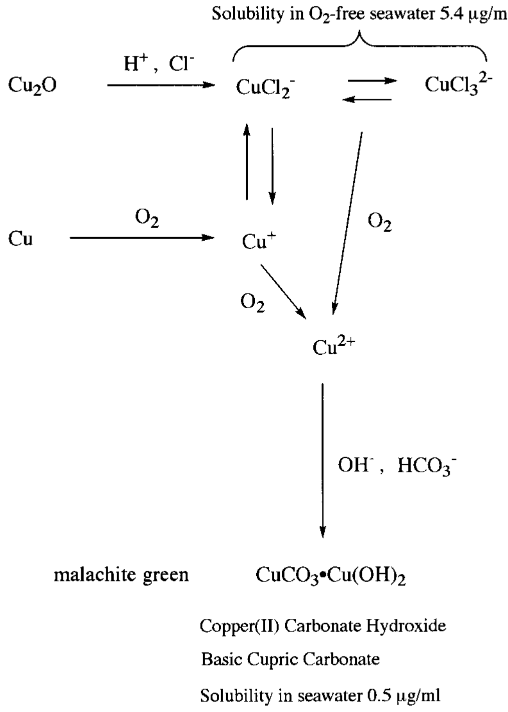
$$Bu_3Sn\text{-}O-Si(OEt)_2-O-Si(OEt)(OSnBu_3)-O-Si(OEt)_3$$

1

Release of the TBT toxicant in seawater can be summarized thus:[25]

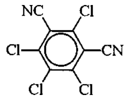
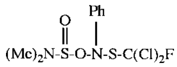
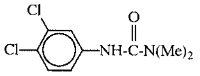
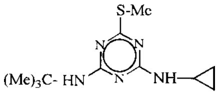
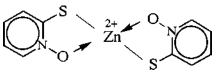
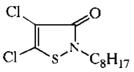
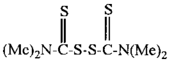
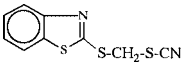
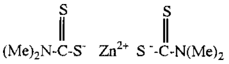
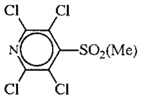
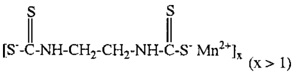
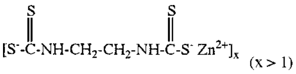
$$\equiv Si\text{–}OSnBu_3 + H_2O + Cl^- \longrightarrow \equiv Si\text{–}OH + Bu_3SnCl + OH^- \quad (2)$$

The variation of the organotin to silicon ratio can be used to specify release rates, resin compatibility, longevity, and other film properties. The polysiloxane coating is largely insoluble, and mostly remains on the hull. Panel tests have



Scheme 1. Sequence of reactions in the dissolution of copper and cuprous oxide.

Table 7. Nomenclature and structures of booster biocides currently used in antifouling paints

 Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile)	 $(Me)_2N\text{-}\overset{O}{\overset{\|}{S}}\text{-}O\text{-}\overset{Ph}{\overset{|}{N}}\text{-}S\text{-}C(Cl)_2F$ Dichlofluanid (*N*-dimethyl-*N*-phenylsulfamide)
 Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea)	 Irgarol 1051 (2-methylthio-4-t-butylamino-6-cyclopropylamino-*s*-triazine)
 Zinc pyrithione (zinc complex of 2-mercaptopyridine-1-oxide)	 Sea-Nine 211 (Kathon 5287) (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one)
 $(Me)_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S\text{-}S\text{-}\overset{S}{\overset{\|}{C}}\text{-}N(Me)_2$ Thiram (bis(dimethylthiocarbamoyl)disulfide)	 TCMTB (2-thiocyanomethylthio)benzothiazole)
 $(Me)_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S^-\ Zn^{2+}\ S^-\text{-}\overset{S}{\overset{\|}{C}}\text{-}N(Me)_2$ Ziram zinc bis(dimethyl thiocarbamate)	 TCMS pyridine (2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine)
 $[S^-\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}S^-\ Mn^{2+}]_x\ (x > 1)$ Maneb (manganese ethylene bisdithiocarbamate)	 $[S^-\text{-}\overset{S}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}S^-\ Zn^{2+}]_x\ (x > 1)$ Zineb (zinc ethylene bisdithiocarbamate)

shown an erosion rate of less than 3 μm $month^{-1}$. The release rates of these organotin polysiloxane are 0.5–1.5 μg cm^{-2} day^{-1} and they have demonstrated over 3 years service without any fouling.[25]

TIN-FREE ANTIFOULINGS

Tin-free antifoulings are mercury compounds, cuprous oxide, organoarsenics, organoleads, organohalogens, orga-

Table 8. Properties of common antifouling paint booster biocides[29]

Biocide	Solubility[a] (mg l^{-1})	Release rate[b] (μg cm^{-2} day^{-1})	Degradation data		Other applications
			Half-life in seawater	Principal degradation mode	
Irgarol 1051	7	5.0	100 days		Herbicide
Diuron	35	3.3		Biotic	Herbicide
Dichlofluanid	1.3	0.6	18 h		Fungicide
Zinc pyrithione	8	3.3			
Sea-Nine 211	14	2.9	<24 h	Biotic	
TCMTB	10.4		740 h	Hydrolysis	Fungicide
TCMS pyridine		0.6			
Chlorothalonil	0.9		1.8 days	Biotic	Fungicide
Zineb	0.07 –10		96 h	Hydrolysis	Fungicide
Cuprous oxide		25–40			
TBT		1.5–4.0		Hydrolysis Photolysis Biotic	

[a] In seawater.
[b] ISO test system.

nosulfurs and zinc compounds. As shown in Table 2, the lead and mercury compounds have high antifouling activities, but they are not permitted for use in antifouling coatings in many countries because of their long-term environmental hazards.[5,6,13]

Tin-free antifouling systems composed of seawater-soluble matrices containing tin-free biologically active ingredients (a copper component and organic biocides) are now available. The copper component is typically cuprous oxide, and the others are copper thiocyanate (CuSCN), metallic copper and a copper alloy, e.g. cupronickel (Cu 90%, Ni 10%).

The cuprous oxide and metallic copper are easily converted to malachite green ($CuCO_3{\cdot}Cu(OH)_2$) — basic cupric carbonate. It is formed via cupric ions by oxidation and carbonation with oxygen and carbon dioxide in air, as shown in Scheme 1.[26] The solubility of malachite green in seawater is very low (0.5 μg ml^{-1}), and hence the rate of the formation of cupric ions as a main active component is slow.

The copper component used in antifouling paints alone is not effective against diatoms and algae. Therefore, secondary biocides must be incorporated into the paints to control these organisms.[27]

The organic biocidal compounds are termed organic booster biocides and they are mainly agrochemicals. The representative organic boosters are Irgarol 1051, Diuron, Sea-

Table 9. Concentration of antifouling paint organic booster biocides in some coastal environments

Biocide	Location	Concentration		Date	Ref.
		Dissolved (ng l^{-1})	Sediment (ng g^{-1})		
Irgarol 1051	Bermuda	590		2001	30
	Côte d'Azur, France (Mediterranean)	640		1996	32
	UK, Hythe Marina	403		2001	33
	Almeria, Spain	772		2001	34
	Baltic Sea (restricted water exchange)	440	220	2000	31
	North Sea (higher water exchange)	170	25	2000	31
Diuron	UK, Hythe Marina	6742		2001	33
	Catalonia, Spain	2190		2001	34
Sea-Nine 211	Catalonia, Spain	3700		2001	34

Nine 211, Dichlofluanid and Zinc pyrithione, etc. as shown in Table 7.[28]

The other organic boosters are pyridine triphenylborane, 2,4,6-trichlorophenylmaleimido, zinc bis(dimethyl thiocarbamate), *N*-(fluorodichloromethylthio)phthalimido, diiodemethyl-*p*-tolylsulphone, etc. The properties of common organic boosters are shown in Table 8.[29]

These organic boosters have been used after the ban of TBT antifoulants. In areas of Europe and the USA, contamination of some organic boosters in the coastal waters has already been reported. These concentrations are shown in Table 9.[30–34]

A recent UK Environment Agency R&D report (Environment Agency, 1998) suggested that Diuron, Igarol 1051, ZPT and Dichlofluanid were in use in the UK. Diuron and Irgarol 1051 occupy >95% of the market share. In the UK, these two biocides were found at concentrations above the limits of detection for the analytical method used (gas chromatography coupled to flame photometric detection (GC–FPD), or high-performance liquid chromatography coupled to mass spectrometry (HPLC–MS), etc.) in areas of high boating activity.[33]

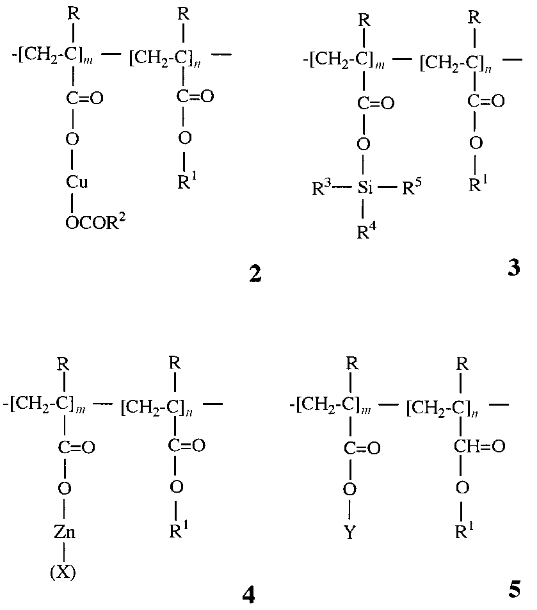
In the Blackwater Estuary, Essex, UK, the concentrations of the organic boosters Irgarol 1051, Diuron, Dichlofluanid and Chlorothalonil in seawater and sediments were found to be enhanced at the end of one boating season. For example, the maximum concentration of Chlorothalonil is high (688.2 μg l^{-1}) although its half-life is only 1.8 days, as shown in Table 8. Its contamination was more widespread, consistent with its use in agriculture, than the other biocides.[35]

In 2001, Thomas *et al.*[33] reported that 'a simple risk assessment indicates that at present Irgarol 1051 (max 403 ng l^{-1}, median 208 ng l^{-1}, average 17.5 ng l^{-1} (average is a value of median data of all sample stations)) and Diuron (max 6742 ng L, median 632 ng l^{-1}, average 71.8 ng l^{-1}) represent a lower threat to the environment than TBT. However, it cannot be assumed that their use will have no environmental harm, and further data are required on the fate and effects of all antifouling paint booster biocides'.

In Table 8, the half-lives of Sea-Nine 211 and ZPT are shown to be very short. There are many recent reports[28,36–39] on Sea-Nine 211. Sea-Nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazoline-3-one, Kathon 5287) has a broad-spectrum activity against bacterial slime, algae, barnacles, tubeworms, hydroids, bryozoans, tunicates and diatoms. It was degraded rapidly in the environment by microorganisms. The biodegradation of the compound is mainly responsible for its short half-life in water (generally <24 h) and aquatic sediment (<1 h), under both aerobic and anaerobic conditions.[36]

However, in practice, a high concentration (2600–3700 ng l^{-1}) of Sea-Nine was reported in the Spanish Mediterranean marine environment in the summer of 1999,[34] though subsequent data suggest that unusually high levels were found only in June or August.[40,41] These data show that reliable information on the environmental experiments will be obtained only when we have done many experiments in seawater all over the world and for a long time.

Tin-free ablative polymers



R = H, Me
R^1 = Me, other acyclic alkyl, cycloalkyl groups
R^2 – R^5 = alkyl, cycloalkyl
X = alkylcarboxylate group, etc.
Y = oligomer

As discussed, there are three types of tin-free antifouling: the first is the free-association type, the second is the self-degradation type, and the third is the self-polishing type. The first type, in which copper and biocides are dispersed in a resinous matrix, that is, they are free-association paints based on copper compounds containing the organic booster biocides as shown in Table 7. These tin-free-type systems are capable of giving a relatively short-term performance. In the second, self-degradation, type, the biologically active ingredients are released by hydrative degradation of the relatively low molecular weight polymer matrices.[42] The third, self-polishing, type is a similar type to the self-polishing organotin polymers. The polymers are the same methacrylate or acrylate copolymers containing a copper, zinc, silyl moiety and oligomer groups instead of TBT moiety as shown by compounds 2–5.[42] These antifoulants have been developed largely by Japanese companies. Representative tin-free self-polishing copolymers are the copper methacrylate copolymers 'Ecoloflex' from Nippon Paints. Examples of the tin free silyl-type copolymer are 'Seagrandprix' from Chugoku Toryo and 'TAKATA QUANTUM' from Nippon Yusi BASF Coatings. 'EXION', from Kansai Paints, is a zinc acrylate copolymer. Sigma AlphaGen 20, from Shinto

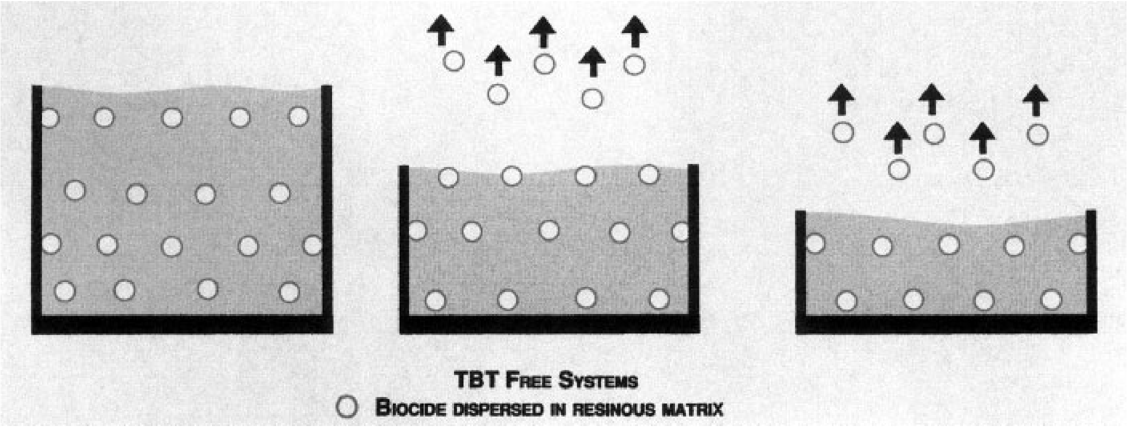


Figure 4. Tin-free systems. At seawater–paint interface, biocide leaches at a controlled rate. Reproduced from Reference 20 by kind permission of ORTEP-Association.

Shigma, is an acrylate copolymer containing its oligomer as the metal component. Some antifoulants have been reported to have achieved fouling-free high performance for 5 years.[42]

These tin-free systems are shown in Figure 4.[20] The biocides are dispersed and contained throughout the matrix but they are not necessarily chemically bonded to it (but organotin biocides bond to a polymer chain as shown in Figure 3). The biocides are copper compounds and organic boosters. At the seawater–paint interface, these biocides leach at a controlled rate; the matrix dissolves to reveal freshly available biocide, enabling a predictable performance to be achieved.[20]

ORGANOTINS IN THE ENVIRONMENT

Stability of organotin compounds

Most inorganic compounds of tin are considered to present no health hazard or environmental problem. But marked biocidal properties can be imparted by the formation of tin–carbon bonds, and triorganotins in particular derive their major applications from such biocidal activity.

Triorganotin compounds undergo degradation in the environment via the progressively less toxic di- (R_2SnX_2) and mono-organotin ($RSnX_3$) derivatives, to form harmless inorganic tin residues. This cleavage of the tin–carbon bonds may occur photolytically by UV light, microbiologically by fungi or bacteria, or by chemical attack, and a typical breakdown scheme for the TBT and TPT compounds is illustrated in Figure 5.[2,7,43] Therefore, organotin researchers did not expect the early environmental problems caused by organotin compounds.

After the environmental problems of organotin antifouling paints became evident, the stability of organotin compounds (such as TBT and TPT compounds) in terms of their half-lives have been reported in many articles. These organotins degrade by hydrolysis in water by sunlight and by microorganisms at room temperature. Hence, data for the half-life in natural seawater, in fresh water, or in pure water in the laboratory vary with the intensity of light, temperature, types or amounts of organisms, flow rates of seawater, and types or amounts of ions in seawater.

In 1983, the degradation of TBTO as a representative organotin compound in water was reported. Its aqueous solubility at 20 °C is 0.7 –7 mg l^{-1} at pH 5 –7 and the vapor pressure is estimated to be 6.4×10^{-7} mmHg. Dissolved in water, it neither volatilized nor lost butyl groups over a period of at least 2 months in the dark at 20 °C; in sunlight, however, it underwent slow ($t_{1/2} > 89$ days) photolytic decomposition, by stepwise debutylation to inorganic tin.[44]

The half-lives of organotin compounds in seawater are 6 days to several months; recently, however, those in sediments have been reported as about 1 to 9 years. These data show that the stabilities of organotins in natural seawater are surprisingly higher than the data previously indicated. In particular, in sediment the stabilities of organotins are very high. The data for half-life of organotin compounds including the above data, are shown in Table 10.[36,44–53]

Toxicity of organotin compounds

The acute oral median lethal doses (LD_{50}) of TBT compounds and TPT compounds are 112–349 mg kg^{-1} and 125–1470 mg kg^{-1} (rats) respectively, as shown in Table 4.[5,6] The acute oral toxicity of the ethyltin compounds is high and is similar to that of sodium cyanide. However, the toxicity of butyl- or phenyl-tin compounds is much lower than those of ethyltin compounds. Figure 1 shows that the toxicity of butyltin compounds to mammals is much lower than that of ethyltin compounds.

The chronic toxicity of organotin compounds arises from their acting as endocrine disruptors leading to disorders such as imposex, intersex and masculinization of abalone (ear shell, *Haliotis* sp.). The symptom of imposex (imposed sexual organ) is defined as a superimposition of a male

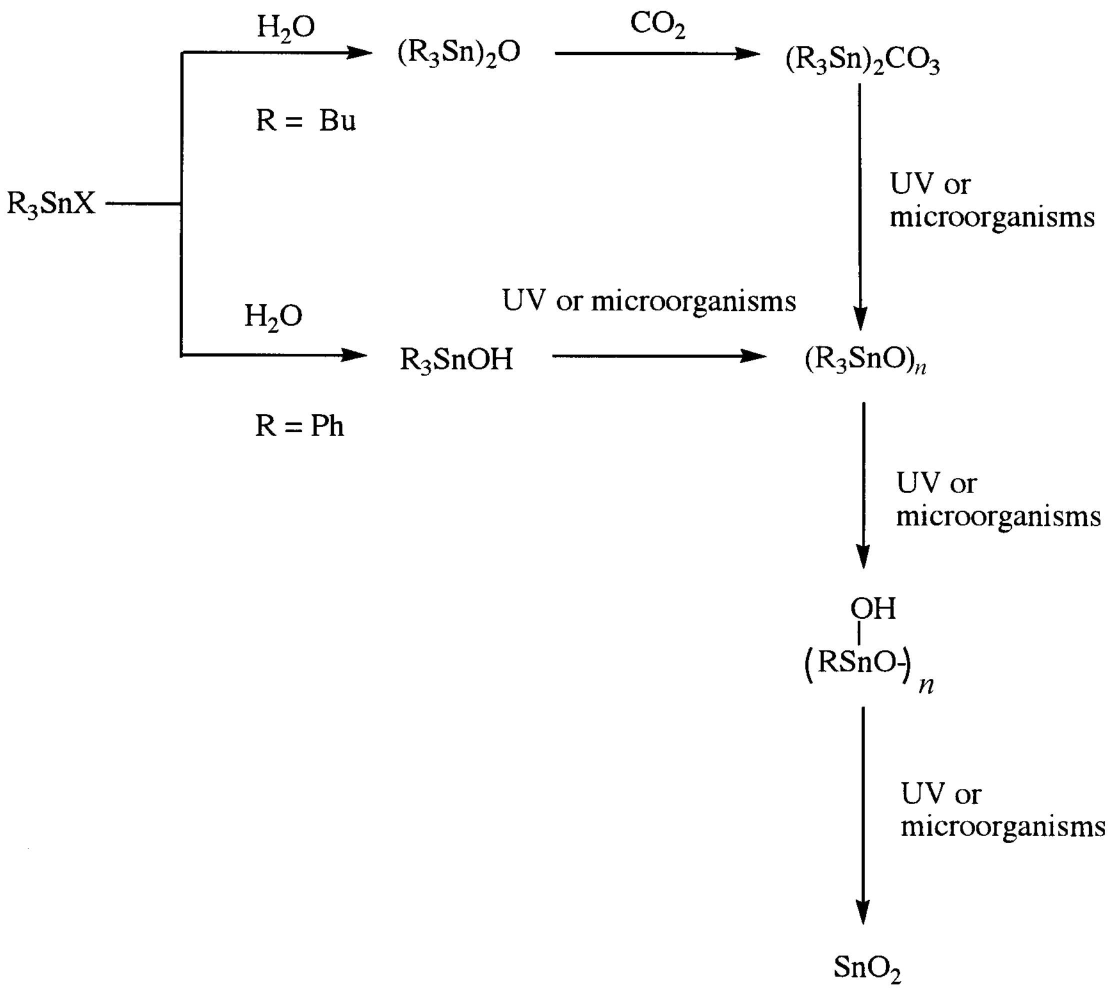
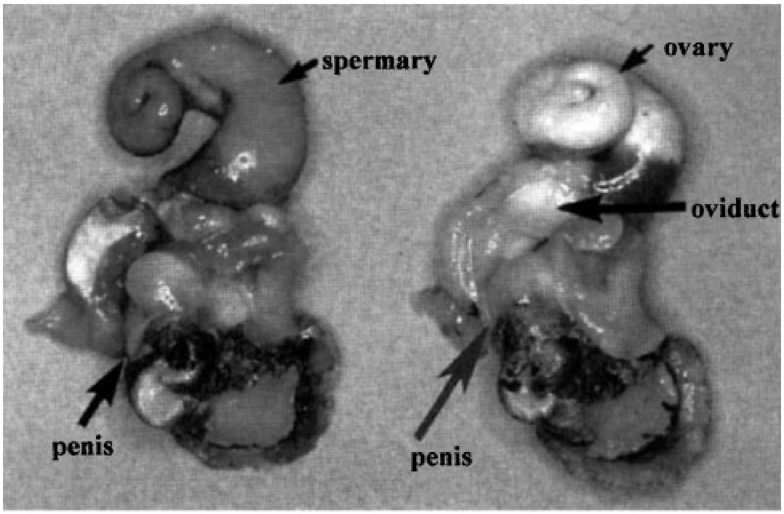


Figure 5. Environmental degadation scheme for TBT and TPT compounds.

Table 10. Stabilty of organotin compounds

Organotin	Matrix	Half-life	Date	Ref.
TBT	Seawater	4–19 days	1989	45
TBT	Seawater	Several weeks to several months	2000	36
TBT	Seawater (0.5 μg l^{-1})	6–7 days	1986	46
TBTO	Water (in sunlight)	>89 days	1983	44
TBT	River water (20 °C in the light)	6 days	1989	47
TBT	Estuarine water (28 °C)	6–7 days	1996	48
	Open seawater (28 °C)	17 days	1996	48
TBT	Sediment	About 2.5 years	1995	49
TBT	Sediment	About 8.7 years	1997	50
TBT	Sediment	2.1 years	1995	51
DBT	Sediment	1.9 years	1995	51
MBT	Sediment	1.1 years	1995	51
TBT	Bivalve *Venerupis decussata*	4–17 years	2000	53



normal male imposex female

Figure 6. Imposex in rock shell (*Thais clavigera*). Reproduced from Reference 55 by kind permission of Shokabo Co. Ltd., Japan.

characteristic, such as a penis and vas deferens, in female gastropods, as shown in Figure 6.[54,55]

Imposex was first found[56] in a *Nucella lapillus* spiral shell, in 1970, and shortly after the cause was found to be trialkyltin compounds. Then, imposex was thought to be irreversible masculinization in females and that it may bring about mass extinction by reproductive failure. As a result, females become sterile and the affected population may become locally extinct. Imposex is induced at a very low concentration of tin, as low 1 ng l^{-1} as in various neogastropod species.[57,58] Gastropods that have been observed to be affected by imposex up to December 1998 are shown in Table 11.[59] The number of gastropod species has been reported to be more than 140 (Table 11).[59] In the sea of Japan, 39 species consisting of 32 neogastropods and seven mesogastropods were found to be affected up to July 1999 (Table 11).[59]

Imposex is induced by low concentrations of organotin compounds, such as tributyltin from antifouling paints. The tissue concentrations of organotin compounds are positively related to the degree of imposex in gastropods, suggesting that imposex is a biological indicator of organotin contamination.[54]

Imposex is undoubtedly caused by organotin compounds such as a butyltin compound. However, it was found that imposex is also caused by other factors, e.g. nonylphenol, infestation of parasitic trematode larvae, etc.[60,61] Evans *et al.*[60] reported in 2000 that exposure to the estrogen-mimic nonylphenol under laboratory conditions can cause imposex in the dogwhelk *N. lapillus*.[60]

Nonylphenol was first demonstrated as an endocrine disruptor for killifish by the Japanese Environment Ministry in 2001.[62] Endocrine disruption has been reported for many substances, e.g. nonylphenol, PCBs, dioxins, DDT, bisphenol A and phthalic acid esters, etc. They generally show a feminization of the male. Therefore, the endocrine disruption property of organotin is different from the general phenomena. On the other hand, imposex caused by nonylphenol also shows masculinization of shellfish. The phenomenon of endocrine disruption such as imposex caused by organotin compounds has also been reported as intersex in the periwinkle *Littorina littorea*. Intersex is the masculinization of oviduct tissue and, in serious cases, spawning troubles are generated. Intersex was first described in the periwinkle; it is produced at a high TBT concentration (10 ng l^{-1}) and may also yield sterile females.[63–65] In Japan, the giant abalone (ear shell) *Halioti madaka* is found to show masculinization of the female, and sexual maturation varies between male and female. Consequently, their populations are declining.[58,59]

Concentrations of organotin compounds in the environment

Many articles have reported on the concentrations of organotin compounds in seawater from all over the world after observations of the deformities shellfish caused by the organotin compounds were noted. In Japan, fishing production of ear shells and ivory shells (*Babylonia japonica*) has recently decreased drastically. The cause is thought to be organotin compounds.[59]

The Tokyo Metropolitan Research Laboratory of Public Health has published the concentrations of TBT and TPT

Table 11. Gastropod species affected by imposex up to December 1998[59]

Mesogastropoda	
Ampullariidae	*Ampullaria (Packylabra) cinerea*
	Ampullaria gigas
	Ampullaria polita
	Marisa cornuarietis
	Pila globosa
	Pomacea canaliculata
Viviparidae	*Campeloma rufum*
Hydrobiidae	*Hydrobia ulvae*
Rissnidae	*Rissoa auriscalpium*
	Rissoa ventricosa
	Rissoa violacea
	Rissoina allanae
	Rissoina boucheti
	Rissoina bruguierei
	Rissoina nivea
Cypraeidae	*Trivia aperta*
	Trivia arctica
	Trivia costata
	Trivia millardi
	Trivia monacha
	Trivia verhoefi
Lamellariidae	*Lamellaria perspicua*
Pterotracheidae	*Pterotrachea coronata*
Approphoridae	*Aporrhais pespelecani*
Oocorythidae	*Galeoocorys leucodoma*
Cassidae	*Galeodea tyrrhena*
Cymatiidae	*Fusitriton oregonensis*
	Monoplex echo
	Charonia sauliae sauliae
Strombidae	*Strombus luhuanus*
Naticidae	*Neverita didyma*
Tonnidae	*Tonna luteostoma*
Neogastropoda	
Galeodidae	*Buscycon carica*
	Buscycon contrarium
	Melongena corona
Muricidae	*Calotrophon ostrearum*
	Ceratostoma burnetti
	Ceratostoma foliatum
	Cronia margariticola
	Cronia pothuauii
	Dicathais orbita
	Drupella fragum
	Drupella ochrostoma
	Drupella rugosa
	Ergalatax contractus
	Eupleura caudata
	Eupleura caudata etterae
	Eupleura caudata sulcidenta
	Forreria belcheri

Table 11. Continued

Neogastropoda	
Muricidae	*Haustrum haustorium*
	Lepsiella albomarginata
	Lepsiella scobina
	Lepsiella vinosa
	Morula granulata
	Morula marginalba
	Morula marginatra
	Morula musiva
	Murex (Trunculariopsis) trunculus
	Murex brandaris
	Murex florifer dilectus
	Murex pomum
	Naquetia capucina
	Nucella canaliculata
	Nucella emarginata
	Nucella freycineti
	Nucella heyseana
	Nucella lamellosa
	Nucella lima
	Nucella lapillus
	Ocenebra erinacea
	Ocenebra lumaria
	Ocenebra lurida
	Ocinebrina aciculata
	Plicopurpura patula
	Rapana venosa venosa
	Thais bronni
	Thais clavigera
	Thais haemastoma
	Thais kieneri
	Thais luteostoma
	Thais mancinella
	Thais orbita
	Thais savignyi
	Urosalpinx cinerea
	Urosalpinx cinerea follyensis
	Urosalpinx perrugata
	Urosalpinx tampaensis
	Vasum turbinellus
	Xymene ambiguus
Coralliophilidae	*Coralliophila abbreviata*
	Coralliophila lamellosa
Buccinidae	*Babylonia japonica*
	Buccinum middendorffi
	Buccinum opisthoplectum
	Buccinum undatum
	Colus gracilis
	Colus halli
	Cominella virgata
	Japeuthria ferra
	Kelletia lischkei

Table 11. Continued

Neogastropoda	
Buccinidae	*Neptunea arthritica arthritica* *Neptunea phoenecia* *Pisania tinctus* *Pusiostoma mendicaria* *Searlesia dira* *Searlesia fuscolabiata* *Volutharpa ampullacea perryi*
Melongenidae	*Hemifusus tuba*
Nassariidae	*Bullia rhodostoma* *Cyclope neritea* *Hinia incrassata* *Hinia reticulata* *Hinia trivittata* *Hinia vibex* *Ilyanassa obsoleta* *Reticunassa festiva*
Columbellidae	*Anachis avara*
(Pyrenidae)	*Mitrella lunata*
Fasciolariidae	*Fasciolaria hunteria* *Fasciolaria lilium* *Fusinus perplexus perplexus* *Fusinus syracusanus* *Pleuropoca gigantea* *Taron dubius*
Cancellariidae	*Sydaphera spengleriana*
Marginellidae	*Marginella apiciana*
Olividae	*Amalda (Baryspira) australis* *Olivella biplicata*
Conidae	*Conus anemone* *Conus coronatus* *Conus dorreensis* *Conus klemae* *Conus lischkeanus* *Conus marmoreus bandanus* *Conus mediterraneus* *Conus sponsalis* *Kurtziella cerina* *Lora (Propebela) turricula* *Raphitoma reticulata* *Viriconus lividus* *Virrroconus ebraeus* *Virrroconus fuigetrum*
Terebridae	*Terebra dislocata* *Terebra protexta*

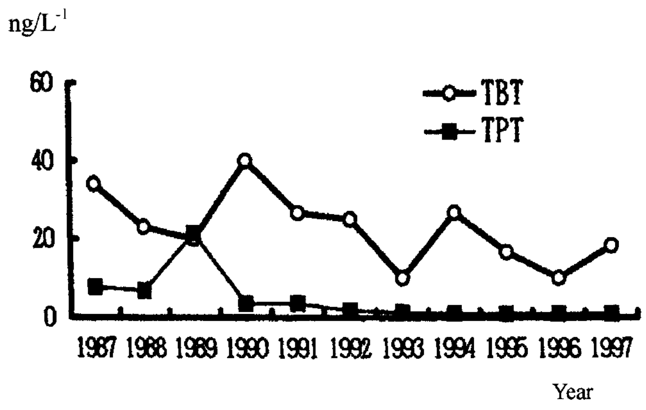


Figure 7. Concentration of TBT and TPT in surface seawater of Tokyo Bay. Reproduced from Reference 66 by kind permission of The Chemical Society of Japan.

found in the seawater of Tokyo Bay (Fig. 7), and the concentrations of TBT and TPT in fish and shellfish in Japan are shown in Fig. 8.[66] Restrictions on the use of TPT and TBT started in 1989 and 1990 respectively. Therefore, the decrease of concentration of TPT began 1 year before that of TBT. The concentration of TBT in seawater was found to be about 40 ng l^{-1} in 1990, and it decreased to about 20 ng l^{-1} in 1997. In contrast, the concentration of TPT in seawater was about 20 ng l^{-1} in 1990, and had decreased to be almost undetectable in 1997.[66] In a recent report,[67] the average concentrations of both TBT and TPT in fish and shellfish are almost the same (0.01 ppm (10 ng g^{-1})), although the concentration of TPT in seawater is very much lower than that of TBT, as shown in Fig. 7. Therefore, the report[67] shows that the disappearance of TPT is considerably slower than that of TBT. Accumulations (concentration ratio of tissue organotin to seawater organotin) of TBT and TPT in Tokyo Bay in fish and shellfish were 5500 and >170 000 in 1996 respectively.[66,67]

In Japan, the Environment Ministry has reported that the concentrations of organotin compounds in seawater, sediment, fish, shellfish and birds from 1991 to 1999 have been decreasing. The data for seawater, sediment, fish and

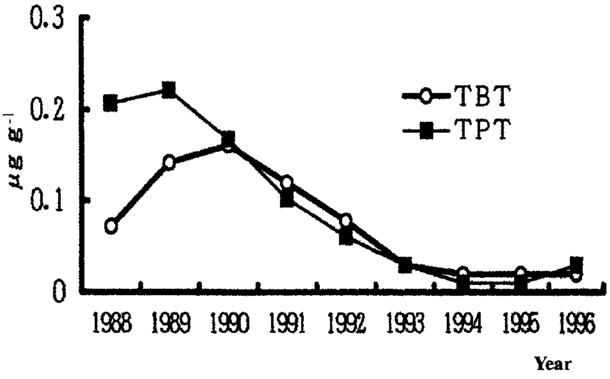


Figure 8. Concentration of TBT and TPT in fish and shellfish. Reproduced from Reference 66 by kind permission of The Chemical Society of Japan.

Table 12. Concentrations of organotin compounds in seawater, sediment, fish and shellfish[68]

	TBT		TPT	
Year[a]	Ratio of detection points[b] to investigaton points	Minimum and maximum data	Ratio of detection points[b] to investigaton points	Minimum and maximum data
Seawater ($\mu g\ l^{-1}$)				
1999	19/105	nd–0.0098	3/102	nd–0.0040
1998	20/76	nd–0.0080	4/102	nd–0.0015
1997	21/107	nd–0.009	0/108	nd–trace
1996	27/105	nd–0.014	0/108	nd–trace
1995	31/105	nd–0.042	0/87	nd
1994	35/99	nd–0.03	4/92	nd–0.01
1993	42/99	nd–0.049	2/90	nd–0.011
1992	52/99	nd–0.084	10/90	nd–0.044
1991	60/93	nd–0.067	5/87	nd–0.014
Sediment ($\mu g\ g^{-1}$ *dry*)				
1999	85/103	nd–0.45	45/99	nd–0.062
1998	86/105	nd–0.73	54/94	nd–0.065
1997	85/105	nd–0.24	36/91	nd–0.28
1996	94/108	nd–0.93	41/99	nd–0.22
1995	87/104	nd–0.57	48/93	nd–0.11
1994	87/102	nd–0.44	47/88	nd–0.26
1993	85/102	nd–1.6	59/96	nd–0.15
1992	88/102	nd–0.42	57/95	nd–0.09
1991	85/95	nd–0.42	55/89	nd–0.34
Fish ($\mu g\ g^{-1}$ *wet*)				
1999	9/70	nd–0.12	10/70	nd–0.048
1998	17/70	nd–0.09	14/70	nd–0.05
1997	13/70	nd–0.14	19/70	nd–0.12
1996	23/70	nd–0.24	20/70	nd–0.27
1995	13/70	nd–0.54	21/70	nd–0.25
1994	15/70	nd–017	28/70	nd–0.28
1993	23/70	nd–0.37	38/70	nd–0.34
1992	22/70	nd–0.43	40/70	nd–0.26
1991	21/65	nd–0.59	34/65	nd–0.59
Shellfish ($\mu g\ g^{-1}$ *wet*)				
1999	0/30	nd–trace	0/30	nd–trace
1998	10/30	nd–0.11	0/30	nd–trace
1997	18/30	nd–0.24	5/30	nd–0.07
1996	15/30	nd–0.09	0/30	nd
1995	20/30	nd–0.35	0/30	nd
1994	6/30	nd–0.1	5/30	nd–0.04
1993	15/30	nd–0.78	5/30	nd–0.07
1992	17/30	nd–0.45	10/30	nd–0.11
1991	18/30	nd–0.38	22/30	nd–0.09

[a] 'Year' is the Japanese financial year, i.e., from 1 April of one year to 31 March of the next year.

[b] Detection points: points where TBT or TPT > detection limit.

shellfish are shown in Table 12;[68] the concentrations in birds are at undetectable levels. The ratios of detection points (i.e. TBT or TPT > detection limit) to all investigation points of TBT and TPT in seawater and sediment in Japan are shown in Fig. 9.[68] The concentrations of TBT and TPT in seawater show the same tendency as the data for Tokyo Bay shown in

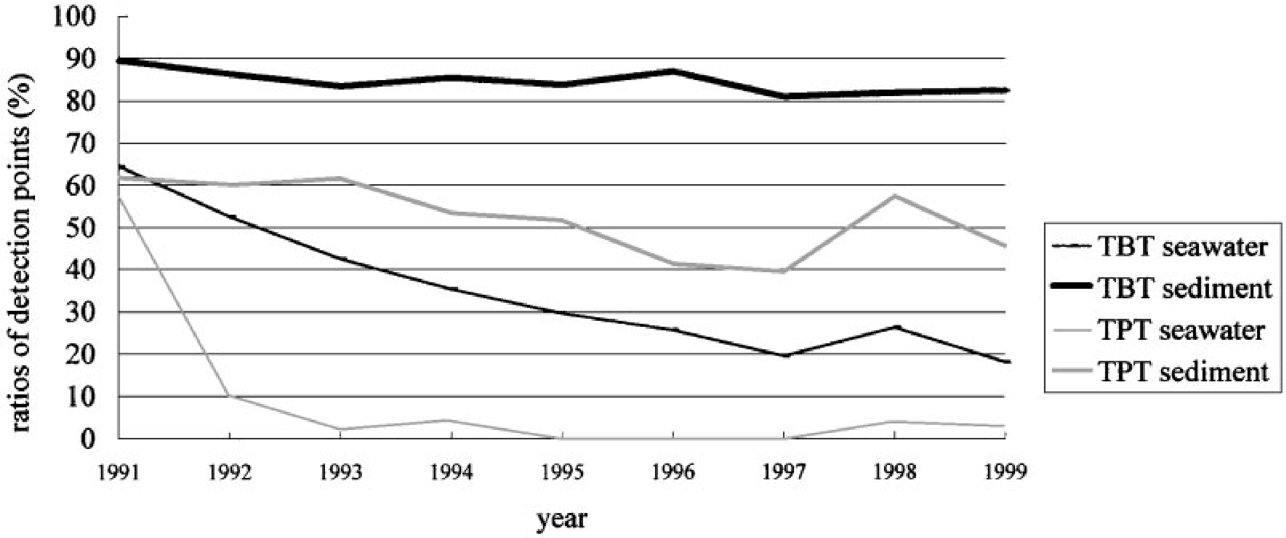


Figure 9. The ratios of the numbers of detection points to all investigation points of TBT and TPT in seawater or sediment in Japan.[68]

Figs 7 and 8, i.e. both concentrations decrease. Recently, however, the concentration of TPT has been remarkably low. The decreasing tendency of concentrations in fish and shellfish shown in Table 12 are similar to the data in Fig. 8. However there is a decreasing tendency in reductions in the concentrations of organotins in the sediments; in particular, the variation in the ratios of the number of detection points to that of all investigation points on TBT is very small for the period from 1991 to 1999. These data show that TBT in the sediment is stable for a long time, i.e. it decomposes very slowly.[68]

The concentrations of TBT in open sea and in deep sea (500–2500 m) locations are generally lower (a maximum of 0.1 ng l^{-1}) than those on the surface of areas of restricted water exchange.[69]

Bioaccumulations and sediment accumulation on organotin antifoulants

Many reports on the environmental problems of organotin compounds have been published. The degradation rates of organotin compounds are not very high in the environment; actually, Morita[70] reported in 1989 that the bioaccumulation in fish and shellfish is to about 5000 times that of the concentration in seawater. The organotins were first used commercially in the 1960s, owing to their high acute toxicity with regard to the target organisms.[5,6] In the mid 1970s, concern over the effects of organotins used in antifouling paints first arose in France, where severe problems such as incidences of oyster deformity and a sharp decrease in the production of commercial fisheries were encountered in areas where there was intense boating activity and poor tidal exchange.[28] In many areas of the UK, USA and Canada, extensive damage to crabs and shellfish have been reported.[70]

In New Zealand, the use of antifouling paints containing organotin compounds was banned in 1989.[71] The restrictions that were introduced were said to have decreased the flux of TBT to the marine environment. In a 1996 report, the imposex level in the dogwhelk (*Lepsiella scobina*), except for one point in a harbor area subject to both pleasure craft and commercial vessels, showed no decline in the percentage of imposex. However, a significant decline in the relative penis size index (ratio of mean penis length in female to male (RPSI)) in female dogwhelks was observed.[72] The report showed that the intensity of the deformity became much smaller.

If the organotin is always released at a constant rate from the hulls of vessels, then the surface sediments show the highest concentration. However, if the amounts released then become much less or none, then the surface sediments also show a lower concentration partly because the decomposition rate of organotin below the surface layers is much slower than for outside layers.

Marine cores showed the maximum in TBT concentration is at 8 cm depth, indicating clearly that the retail ban on organotin-based paints to craft less than 25 m in length has successfully reduced the flux of TBT to surface sediments. However, as larger vessels still use TBT, no such trend was visible in harbor cores, with the highest concentration of TBT in superficial sediments.[50]

In 1982, France first took regulatory measures to limit the use of organotin compounds in antifouling paints for the protection of boat hulls. The TBT concentrations in water were 4.6 ng l^{-1} on average, but in ten stations (10/237

= 4.2%), contaminations were above 100 ng l^{-1} (English Channel, Mediterranean).[73]

The Strait of Malacca and Tokyo Bay are areas having heavy shipping activity via tanker routes, and the mean concentrations of the various butyltins (monobutyltin (MBT), dibutyltin (DBT), and TBT) in these waters in 1996 were as follows:[74]

	MBT (ng l^{-1})	DBT (ng l^{-1})	TBT (ng l^{-1})
Strait of Malacca	1.7	1.1	2.2
Tokyo Bay	38.8	18.1	3.0

The TBT concentration in seawater in the Strait of Malacca is slightly lower than that in Tokyo Bay. The high ratio of TBT/DBT observed in the Strait of Malacca suggests that recent inputs of TBT have occurred there. Lower ratios were observed for that in Tokyo Bay. These data suggest that the release of TBT from large vessels is the major source of butyltins in seawater. The amounts of MBT and DBT in Tokyo Bay are considerably higher than those in the Strait of Malacca. Pollution caused by the butyltin compounds in Tokyo Bay is considered to come from waste water.[74]

In the open water area of Hamilton Harbour in the UK[30] the TBT concentrations are falling due to legislated changes in antifouling treatments, from 220 ng l^{-1} in 1990 to <20 ng l^{-1} by 1995. However, offshore of a boatyard the concentration is found to be >600 ng l^{-1}, indicating a continued release due to painting operations and sediments in the area. The concentration of Irgarol 1051 was found to be up to 590 ng l^{-1}.[30]

In the German North Sea and Baltic Sea marinas, the concentrations of Irgarol 1051 and TBT are as follows:[31]

Antifoulant	Concentration (ng g^{-1} dry weight)	
	Baltic Sea marinas sediments (restricted water exchange)	North Sea marinas sediments (higher water exchange rates)
Irgarol 1051	220	3–25
TBT	570–17 000	80–720

This study shows parallel contamination patterns of Irgarol and organotins in North Sea and Baltic Sea marinas and the persistence of several organotins in the sediments about 8 years after the ban (1989). The data in areas of restricted water exchange show that the concentrations of TBT were still high and that some kinds of organic booster were also high.[31]

The concentrations of TBT in seawater, sediments and fish are shown in Fig. 10.[75] The concentrations are different (10^3–10^5 times) between the seawater or freshwater and sediments or fish. These data show that TBT is stable in sediments, sludges and living organisms, such as algae and fish.

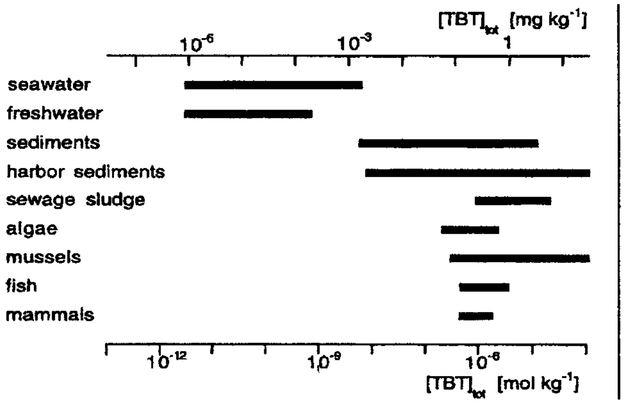


Figure 10. Range of measured TBT concentration in different compartments of aquatic environments. Reprinted with permission from Ref. 75. Copyright 1997 American Chemical Society.

The main ingredients of the sediments are oxygen in the form of metal oxides, and those of fish and shellfish are proteins containing the nitrogen elements of amino acids. Organotin compounds easily form a five- or six-coordination state by which the tin element is coordinated by electronegative atoms such as nitrogen, oxygen, sulfur or phosphorus.[2] In particular, the organotin compounds very easily form the five-coordination state by coordination of three sites with alkyl or phenyl groups and two sites with oxygen or nitrogen atoms of metal oxides or proteins ($R_3SnL^1L^2$). Therefore, organotin compounds show a high affinity to those substances containing nitrogen or oxygen atoms. Hence, the data in Fig. 10 are considered to show that organotin compounds show bioaccumulation in fish and shellfish and sediment accumulation in seawater. However, their accumulations are quite difference from that of the PCBS (which are very stable compounds) because the organotin compounds easily degrade photolytically, biologically and chemically. Therefore, organotin compounds do not show bioaccumulation via food chains, which require higher stabilities for transfer from one living organism to another. However, the relatively stable phenyltin compounds show a tendency for accumulation in the food chain. The accumulations of TBT are also different from those of the PCBs regarding their accumulation spots and the difference of their sex according to their high affinity to tissues containing proteins. Females lose PCBs by giving birth and feeding. Accumulation of TBT is mainly in muscles, liver and kidney, and the accumulation of TBT in males is almost the same as that in females. However, the accumulation of PCBs is mainly in subcutaneous fat and it is much different according to the sexes of marine animals.[76]

Biomethylation proceeds by microorganisms such as

Table 13. Amounts (ng g^{-1} dry weight) of organotin compounds in silt and sand samples in Arcachon Harbor (France)

	TBT	DBT	MBT	Me_4Sn	Me_3SnBu	Me_2SnBu_2	$MeSnBu_3$
Silt	600	530	2460	0.0193	0.0085	0.0212	0.0514
Sand	3340	2030	2720	0.0100	0.0249	0.0191	0.0381

bacteria with a methylating capability.[77–83] The principal naturally occurring methylating agents are (a) methylcobalamin (vitamin B_{12}), (b) *S*-adenosylmethionine (methyl-group donor, active methionine) and (c) methyl iodide (probably formed by the methylation of the iodide ion by *S*-adenosylmethionine).[77] Biomethylation is known for methylation of metal such as mercury, arsenic, lead, chromium, tin, palladium and thallium. For, example, methyl mercury compounds are produced from inorganic mercury in sediments by anaerobic bacteria through the action of the methlylating agent, methylcobalamin.[77]

Recently, Amouroux *et al.*[78] reported on volatile organotin compounds in Arcachon Bay (southwest France). These compounds, formed by the biomethylation of organotin compounds, were found both in silt and sand, as shown in Table 13.[78] The methylation products are the mono-, di-, tri- and tetra-methyl derivatives. The tetraorganotins do not generally have highly physiologically active properties; therefore, they are used mainly as intermediates for the production of other organotin compounds. The amount of monomethyltin compounds is about half of that of the total methyltin compounds in the silt sample and it is about 1/10000 of that of TBT. Hence the total amount of these products is very small compared with that of the TBT compounds. At present, the volatile methyl derivatives are considered to be of little concern in causing environmental problems.

Volatile butylmethyltin compounds formed by biomethylation were reported in the 1980s by Maquire and coworkers[84,85] and Rapsomanikis and Harrison,[79] and more recently by Yonezawa *et al.*[83] and Vella and coworkers.[82,86–88] In 1994, Yonezawa *et al.*[83] reported that these biomethylations are one of degradation of the triorganotin compounds by microbial activities in the sediment. The degradation of triorganotin compounds proceeds by two reactions of methylation with sulfate-reducing microbial activity and debutylation with nitrate-reducing microbial activity.

LEGISLATIVE ASPECTS

The first use of organotin-based antifouling boat-bottom paints began in the early 1960s. In 1974, oyster growers first reported the occurrence of abnormal shell growth in *Crassostrea gigas* (the Pacific oyster), along the east coast of England. However, it was not until the mid 1980s that researchers in France and the UK began to suggest that the use of TBT in antifouling paints was adversely impacting a number of marine species other than the fouling organisms.[89–91]

Legislation to ban the use of organotins on small boats was first introduced in France in 1982 and followed by the UK in 1987. Similar legislations have been introduced worldwide, leading to a significant fall in organotin concentrations. A US federal law was introduced early in 1989, banning the use of organotins on small boats and allowing use of organotins paints on commercial vessels that comply with a release rate equal to or less than $4\ \mu g\ cm^{-2}\ day^{-1}$. Interim US Navy results showed that, as a consequence, by 1990 the water concentrations of organotins had deceased to below the EPA-proposed water-quality criteria level of $0.01\ ng\ cm^{-3}$ and federal and state regulations have had a significant impact on reducing TBT levels, generally to well below the provisional water-quality standard of $10\ ng\ l^{-1}$ in the US coastal zone and in bivalve tissues.[89]

The International Maritime Organization's (IMO's) Marine Environment Protection Committee (MEPC), at its 30th session in November 1990, adopted the resolution on 'Measures to control potential adverse impacts associated with the use of tributyltin compounds in antifouling paints'. The MEPC agreed a recommendation that governments promote legislation along the following lines:[20]

1. Elimination of usage on non-aluminum vessels less than 25 m in length.
2. Elimination of usage of paints having an average release rate greater than $4\ \mu g\ cm^{-2}\ day^{-1}$.
3. Development of alternative systems.

In November 1999, a draft Assembly Resolution prepared by the MEPC of the IMO proposing a global ban on the use of organotins in antifouling paints, was approved by the IMO at its 21st regular session. The Assembly agreed that a legally binding instrument be developed by the MEPC that should ensure: (i) by 1 January 2003, a ban on the application of TBT-based antifouling paints; and (ii) that 1 January 2008 is the last date for having TBT-based antifouling paint on a vessel. In addition, the MEPC has also proposed that the IMO promotes the use of environmentally safe antifouling technologies to replace TBT.[89]

Countries and regions that have banned the use of organotin for antifouling boat-bottom paints include France, the UK, the USA, the Netherlands, Sweden, Norway, Switzerland, Austria, Germany, Ireland, Finland, other EC countries Canada, Australia, New Zealand, South Africa, Europe (non-EC members), Hong Kong, and Japan.[71,89,91]

In 1990, Japan banned the use of TPT and TBT as antifoulings; the production of TPT was prohibited in May 1989. By then, the use of TPT had already decreased to 15% of that of 1988. In 1997, Japan completely banned use of all organotin compounds as antifouling paints.

The other total ban countries are Switzerland and Austria (land-locked countries) and New Zealand, which does not possess major drydock facilities capable of receiving large vessels exceeding 100 m.[90]

On 5 October 2001, the final act of the proposed ban on TBT in November 1999 was adopted in the conference at the headquarters of the IMO in London, with the representatives of 75 states and with many observers from intergovernmental organizations, non-governmental international organizations, etc. Under the terms of the new convention, parties to the convention are required to prohibit and/or restrict the use of harmful antifouling systems on ships flying their flag, as well as ships not entitled to fly their flag but which operate under their authority, and all ships that enter a port, shipyard or offshore terminal of a party.

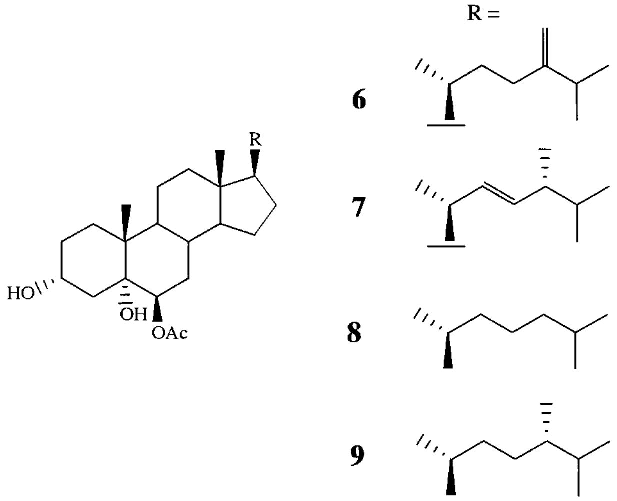
However, the alternatives that are used instead of TBT are largely untested for their long-term biocidal properties.[92] Some articles have reported on the high concentrations of these organic booster biocides in areas such as Italy, France, Spain, the UK, Australia and Japan.[30–34,93–97] In particular, Irgarol 1051 already appears to cause some environmental harm.[92] On the other hand, the regulation of TBT for small ships yields better results. The concentrations of organotin compounds have declined in seawater, sediments and tissues of mollusks. Therefore, recoveries of populations of marine organisms have been observed in areas such as France, the UK, USA, Mexico and Australia.[98,99] Hence, some articles have pointed out that the TBT ban was likely to be introduced prematurely and that introduction should be delayed until the alternatives have been proved to be at least similar to the organotin compounds in environmental and economic cost/benefit analyses.[61,92,98]

Fortunately, tin is a safer element for humans compared with the other heavy metals, such as mercury or lead, because tin is the an important indispensable element in the human body.[3] The tissue of a human or mouse contains tin at 2.0–12.8 ppm (10^3 ng g^{-1}, 10^6 ng kg^{-1} or 10^6 ng l^{-1}) and tin is not accumulated over this level in the human body even if one ingests more than 130 mg day^{-1}. Tin compounds have been investigated or used as pharmaceuticals, such as in anticancer drugs and as a remedy for hyperbilirubinemia.[3]

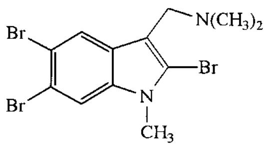
ANTIFOULING CHALLENGES

The tin-free antifoulants described above have used higher amounts of copper and organic boosters as the biocide ingredients because of their lower performance compared with those of organotin compounds. Following the small-boat TBT ban, and the increased usage of tin-free systems, current monitoring data, already in 1995, identified a significant increase of the copper and organic biocides, e.g. Irgarol 1051, in some marine coastal waters, although the environmental significance of such data is, as yet, unknown in detail.[27] However, developing more effective and environmentally free antifouling agents should always be encouraged.

The antifoulants exhibit biocidal properties in order to resist fouling organisms. These antifoulants should resist fouling without themselves causing environmental problems by the use of artificial biocidal materials or they should resist fouling by systems that do not use biocidal materials. However, it cannot be denied that the artificial biocides have a potential to cause the abnormalities to non-target organisms.



6 = 6-β-acetoxy-24-methylenecholestane-3β,5α-diol
7 = 6β-acetoxy-24(*s*)-methylcholesta-22-ene-3β,5α-diol
8 = 6β-acetyoxycholesta-3β,5α-diol
9 = 6β-acetoxycholesta-24(*s*)-methyl-3β,5α-diol



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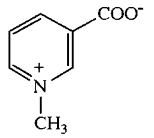


11

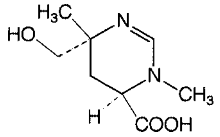
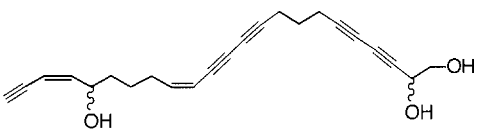
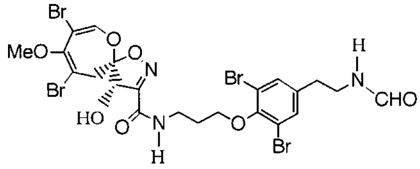
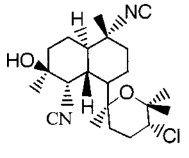
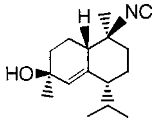
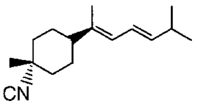
We new describe two new types of antifoulants and antifouling systems.

Natural products

There are two types of natural product used as antifoulants: the first type is an antifoulant in which the living organisms use their own products to protect their bodies and prevent them from being settled with fouling species. The second type of antifoulant is obtained from land plants and marine plants by separation processes such as extraction and distillation. In particular, the first type of antifoulant has been used only to target specific organisms and may not lead to any environmental problems in the natural world for a long time. Hence, some natural products may build our hopes up as being ideal antifoulants not likely to cause any disasters.[100–102]

The first types of antifoulant are obtained as products from marine sponges, corals and ascidians (e.g. *Halacynthia*

Table 14. Antifouling activities of natural products from the marine sponge against barnacles[a]

Natural products	Sponge	Antifouling activity against barnacles (*Balanus amphitrite*)	Ref.
 Pyrimidinecarboxylic acid	*Protophlitaspongia aga*	IC_{50} 5.0 ppm (24 h) ($CuSO_4$ = 4.0 ppm)	103
 19-Hydroxysiphonodiol	*Callyspongia truncata*	ED_{50} 0.24 μg ml^{-1}($CuSO_4$ = 0.15 μg ml^{-1})	104
 Ceratinamide	*Pseudoceratina purpurea*	ED_{50} 0.10 μg ml^{-1}($CuSO_4$ = 0.15 μg ml^{-1})	105–107
 Kalihinol A	*Acanthella cavernosa*	IC_{50} 0.087 μg ml^{-1}($CuSO_4$ = 0.15 μg ml^{-1})	108
 Isocyanosesquiterpine alcohol	*Phyllidia pustulosa*	EC_{50} 0.17 μg ml^{-1}($CuSO_4$ = 0.15 μg ml^{-1})	109
 3-Isocyanotheonellin	*Phyllidiiae pustulosa*	IC_{50} 0.13 μg ml^{-1}($CuSO_4$ = 0.15 μg ml^{-1})	111

[a] Figures in parentheses are antifouling activities in seawater of the $CuSO_4$ standard.

roretzi and *Ciona savignyl*), or as products secreted from the skin of marine animals such as dolphins and whales. It is well known that many marine invertebrates, such as marine sponges and corals, remain remarkably free from settlement with fouling organisms. It has been suggested that they produce compounds that prevent the settling and attaching of other marine organisms to their bodies.

For example, four kinds of steroids 6–9 obtained from corals (*Sinularia* sp.) around the Palau Islands resist the adhesion of blue mussel (*Mytilus edulis* L.). 2,5,6-Tribromo-1-

Table 15. Antifouling natural products from land plants and marine plants[101,102]

	Compound	Name of plant	Activity[a]
Sesquiterpenes	Xanthatin	*Xanthium strumarium*	19
Isothiocyanate	$C_6H_5(CH_2)_6NCS$	*Wasabi japonicas* Matsum *Cochlelia amoracia*	10
Catechins	(+)-Catechin	*Prunus jamasakura*	6
	(−)-Epicatechin		14
Sugar acylated terpenes	Pittosporanoside A_2	*Pittosporum tobira* Ait	10
Sugar acylated flavonols	Kaempferol oleuropeic acid ester	*Eucalyptus resinifera*	46
	Kaempferol glucopyranoside	*Quercus dentata*	227
Sugar acylated stilbenes	Polydatin coumarate	*Eucalyptus rubida*	185
	Raponticin coumarate		179
	Trihydroxystilben glucopyranoside		8
Conjugated lipids	Glucopyranosyl palmitoylsphinga diene	*Prunus jamasakura*	50
	6-Sulfoquinovosyldiacylglycerol	*Undaria pinnatifida, Costaria costata*	44
	Digalactosyldiacylglycerol		29
	Monogalactosyldiacylglycerol		29
Nicotinamides	Nicotinamide	*Mallotus japonicus* Mueller–Arg.	313

[a] $CuSO_4 = 100$.

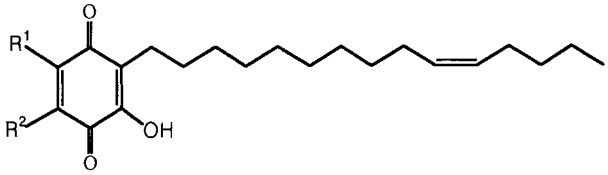
methylgramine (10), obtained from sea moss (*Zoobotryon pellusidum*), shows very high antifouling activity to the attachment of barnacles by blocking their attachment without killing them.[100]

The natural product homarine (*N*-methyl-4-picolinic acid) (11), also obtained from corals (*Dendronephthya* sp.) around the Ogasawara Islands in Japan, resists the adhesion of barnacles. Its activity is the same as that of copper sulfate.[100]

Other recent representative products, obtained from various sponges, and their antifouling activities are shown in Table 14.[103–111] The activity of kalihinol A is higher than that of copper sulfate.

Antifoulants from land plants and marine plants are shown in Table 15.[101,102] These antifoulants are obtained from land plants such as wasabi (Japanese horseradish), green tea, the bark of the wild cherry tree, the leaves of the oak tree, and from marine plants such as wakame seaweeds. The activity level of copper sulfate, set as 100, is used as the basic value for the activity of an antifoulant. The activities of kaempferol glucopyranoside, polydatin coumarate, raponticin coumarate and nicontinamide from land plants are of much higher activity than those of copper sulfate, as shown in Table 15.

Recently, a screening of antifouling activity from plant extracts led to selection and further study of Myrsinaceae (*Maesa lanceolata* Forssk). Two *p*-benzoquinone compounds (maesanin (12), maesanol (13)) were isolated from the fruits. They were found to be active against representative marine crustaceans *Artemia salina* as shown in Table 16.[112] Maesanin and maesanol showed the highest activity against *Artemia salina* among all the fractions, and they were more active than 6-pentadecylsalicylic acid (PSA) isolated from *Ozoroa insignis*, although were less potent than TBTO. Hence, they are active against marine fouling organisms. Chemical modifications of these compounds were undertaken in order to obtain more active derivatives.[112]



12 Maesanin: $R^1 = OCH_3$, $R^2 = H$
13 Maesanol: $R^1 = OH$, $R^2 = CH_3$

Physical systems

Ablative resin systems are one of several physical systems. These systems are used for both the previous organotin

Table 16. Activity[a] of maesanin and maesanol against marine crustaceans *Artemia salina* larvae

	Test concentration (mg l^{-1})						
	50	25	10	5	2.5	1	0.5
Maesanin	3	3	3	2	2	1	1
Maesanol	3	2	2	1	1	1	1
PSA	3	2	2	1	1	1	1
TBTO	3	3	3	3	3	2	1

[a] Evaluation criteria: 3: >90% kill; 2: 10–90% kill; 1: <10% kill; TBTO was used as the reference compound.

systems and tin-free systems. The ablative coatings require a constant water flow passing over their surface. They are most effective at consistently high water velocities. The lifetimes of these coatings are determined by the initial thickness of the coating and by the temperature of the seawater. In temperate water, their ablations are on the order of 75 μm year^{-1}. Thus, a new coating applied at a thickness of 375 μm would be expected to give 5 years of service.[27] However, the ablative systems are not used alone as the physical systems because they require additional biocidal antifouling agents' for ships to be able to sail with slow speeds or for anchorage. Physical systems without biocidal ingredients are used only in the two systems discussed below.

Fouling-release coating

Marine foulings are resisted by using the following physical properties:[113]

(i) low surface energy;
(ii) low elastic modulus;
(iii) microphase separation structures of hydrophilic and hydrophobic layers;
(iv) smooth surface;
(v) low coefficient of friction;
(vi) non-fixed surface layer containing oil materials.

Silicone coatings are called 'fouling-release coatings' to differentiate conventional antifoulants from poisonous precursors. The fouling release correlates with the square root of the surface energy and elastic modulus. Both the surface energy and elastic modulus of silicone are very low. Some commercial non-toxic silicone coatings contain a silicone oil that migrates from the bulk of the coating to the surface and into the water. Fouling settles on the oil rather than on the surface of the coating. The joint between the oil and coating is weak and fails readily; the oil migrates into the water, taking the early stages of fouling with it. Thus, these antifouling systems work in the same way as the release of mucous materials used by dolphins to resist fouling on the surface of the skin. The oils are nonbonded and migrate to the coating surface, and the surface structure increases its slipperiness.[27,100]

As for the other fouling release coatings, there are coatings that use the microphase separation structures of hydrophilic and hydrophobic layers. These are similar to the structures of the inner walls of blood vessels. The inner walls of the blood vessels resist adhesive proteins, i.e. those of platelets and lipoproteins.[100,113] The best ratios of hydrophobic layers to the total of hydrophilic and hydrophobic layers in the silicone polymers is 15–20% (which have lowest surface energy). The surface energy of these polymers shows the lowest values and the fouling in such an area shows as zero in the fouling test on a test piece in seawater.[100]

Although the cost of the silicone coating materials is not low, the application and removal costs are less than those for other systems.[27] This silicone coating is used mainly for circulation water pipes or aqueduct pipes for power plants, but, recently, a large number of big high-speed vessels, military vessels and non-ferrous pleasure boats have used such coating materials.[27,100]

Electroconductive coatings for seawater electrolysis

Electroconductive coatings for seawater electrolysis resist fouling by substances generated by electrolysis reactions. The hull is first coated with an insulating paint; it is then coated with an electrocondutive paint containing metals such as copper flake powder. The conductive layer forms the cathode and is charged with electricity to make a part of the hull as the anode. Hypochlorite ions and chlorine are generated by electrolysis of seawater with very small amount of electric current on the surface of the electrically conductive layer (Eqns (3)–(6)).

Anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \tag{4}$$

$$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^- \tag{5}$$

Cathode:

$$2H_2O + 2e^- \longrightarrow OH^- + H_2 \tag{6}$$

The application of a current concentration of 0.3 A m^{-3} h^{-1} resists the adhesion of marine organisms. The hypochlorite ions, together with the chlorine, act as a fungicide. The hypochlorite ions are easily decomposed in seawater by ultraviolet light to form chlorine ions. Hence, this system does not cause environmental problems. The consumption of electricity is only 100 Wh for 40–100 ton ships. These systems have been investigated in applications to small ships or aqueduct pipes for power plants.[114,115]

CONCLUSIONS

Organotin antifouling paints have been used for most vessels for about 40 years because of their high performance. However, in the late 1980s many countries started to ban their use for small vessels, since many incidences of deformity problems (considered to be caused by them in marinas, harbors and the other poor tidal-exchange areas) have been found. For these small vessels, tin-free alternative antifouling paints containing copper compounds and organic booster biocides have begun to be used since then.

In 2001, the IMO decided that the application of organotin antifoulants would be totally banned from the year 2003 and that these coatings on ships would be prohibited from 2008 onwards. However, it has already been reported that high concentrations of the alternatives have been found in seawater and in sediments in some coastal areas, although the useage of the alternatives is still much smaller in comparison with those of the organotin antifoulants. In particular, one of the alternatives, Irgarol 1051, appears to cause some environmental harm. On the other hand, the regulation of tin antifoulants for small vessels was found to be effective in reducing organotin contamination. The recovery of oyster farming has also been reported in several countries. Therefore, some recent articles have pointed out that the proposed ban on organotin from 2003 may be premature because the safety of alternative antifoulants is still questionable and requires much more long-term environmental testing.

In considering the prevention of a new catastrophe in the future and the conservation of the world marine environment for a long time, a complete ban may not provide a simple solution and the availability of a proven safer alternative satisfying many tests in seawater is an urgent necessity. We also expect to develop more useful antifouling systems, such as a fouling-release coating without using biocidal substances, and to develop environmentally friendly antifoulants related to safer natural products.

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