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General Aspects of Tin-Free Antifouling Paints

Iwao Omae*

Omae Research Laboratories, 335-23, Mizuno, Sayama, Saitama, 350-1317 Japan

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1. Introduction

Organotin antifouling paints have been banned for use on small vessels in many countries, and copper and organic booster biocides blended with copolymers have been used as alternative antifoulants to organotin antifoulants for more than 10 years. In many marinas, harbors, and bays, decreases of organotin concentrations in seawater and sediments have been found as a result of the regulation. On the other hand, recently, many articles have reported the increases of concentration of the organic booster biocides. At this stage extensive damage to shellfish or very serious environmental problems caused by these high concentrations have not been reported yet. However, we should investigate and develop more environmentally friendly antifouling paints. This article reports the use of copper, organic booster biocides, self-polishing copolymers, and natural products as the antifoulants and the fouling-release coatings and electrical coatings as the antifouling systems without the use of biocidal agents.[1,2]

Iwao Omae received his B.S. (1962) degree from Japan National Defense College. He received his M.S. (1965) and Ph.D.(1968) in organotin chemistry from Osaka University, and in 1968 he became Assistant Professor and studied organotransition metal chemistry. Then he moved to Teijin Limited in 1970 and continued the study on organometallic compounds as catalysts for syntheses of polymer raw materials. He joined to Tsuzuki Integrated Educational Institute and Osaka City University as a Professor in 1997 and founded Omae Research Laboratories in 1998 for research on organometallic chemistry and environmental sciences. He has published three books, *Organometallic Intramolecular-coordination Compounds* in 1986 and *Organotin Chemistry* in 1989 with Elsevier and *Applications of Oraganometallic Compounds* in 1998 with John Wiley & Sons. He is a recipient of the Prize for the Outstanding Paper on organotin antifouling paints in The sixth International Conference for Maritime Safety and Environmental Protection for Shipping and Port Operations, Development of Ocean Resources and Offshore Energy (the Section F) in NEVA 2001.

2. Copper

Copper is used as the most important biocidal agent beside organotin compounds; therefore, copper is a main component of the tin-free alternative antifouling agents.[3,4] The copper biocidal agents are copper metal, copper alloys, and copper compounds. They act mainly as cupric ion in seawater.

2.1. Properties

Copper forms Cu^+ and Cu^{2+} ions in an aqueous solution. The Cu^{2+} ion is more stable than the Cu^+ ion. The Cu^+ ion is converted to metallic copper and the Cu^{2+} ion by a disproportionation reaction as shown in eq 1.[3] Copper metal in water, is converted to the

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* Tel: 81-42-958-1932. Fax: 81-42-958-1932. E-mail: vyq02326@nifty.ne.jp.

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Cu^{2+} ion by an oxidation with oxygen in air. Copper has been employed as a bactericide, molluscicide, and fungicide for a long time. Copper is commonly utilized at ca. 100 μg/L as an algicide. In freshwater, an acute toxicosis in fishes is unusual if the copper concentration is below 25 μg/L. Humans tolerate fairly large oral doses of copper without harmful effects, and it has been used in various therapies. Copper sulfate is a powerful emetic and has been used clinically in the treatment of intoxications:[3]

$$2Cu^{+} \rightarrow Cu^{2+} + Cu^{0} \qquad (1)$$

Copper exhibits antifouling activities against organisms such as barnacles, tube worms and the majority of algal fouling species. However, several algal species (e.g., *Enteromorpha* spp., *Ectocarpus* spp., *Achnanthes* spp.) show a marked physiological tolerance to copper. To achieve a protection against these tolerant species, various organic biocides are used in conjunction with copper to control copper-resistant fouling organisms.[5] Copper is used as an antifouling agent with a leaching rate of at least 10−15 μg/cm^2/day.[6]

2.2. Copper Agents

Both copper metal and copper compounds are used for principal biocides because these substances are able to form Cu^{2+} ion which has a biocidal activity. The following substances are used as the copper agents:

2.2.1. Copper Metal

Plate and flake powder

2.2.2. Copper Alloy

Cupronickel: Cu−Ni (90−10%, 70−30%)
Cu−Ni−M (M = Cr, Fe, Co, Ti, Zr, Nb, Ta, V, P, Ga, In, Ag)
(Cu + Ni ≥ 80%)[7]
Cu−As (As = 0.34%)
Aluminum bronze (Cu = 89.22%, Al = 7.20%)
Aluminum brass (Cu = 76.31%, Zn = 21.36%, Al = 1.99%)

Overall assessment of the antifouling performance of copper and following five kinds of copper alloys tested using the growth of copper-tolerate strain of the marine-fouling alga *Ectocarpus siliculosus* as criteria are as follows:[8]

material	antifouling performance[a]
ordinary copper	4
arsenical copper	4
cupronickel (90−10)	3
aluminum bronze	1
cupronickel (70−30)	0
aluminum brass	0

[a] Key: 4, no growth; 3, inhibited growth on <25% of surface; 2, inhibited growth on 25% to 75% of surface; 1, inhibited growth over >75% of surface; 0, normal growth, cover almost complete.

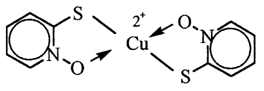
2.2.3. Inorganic Compounds

Cu_2O, a mixture of Cu_2O and CuO.[9]
A mixture of Cu_2S and CuS.[10]
CuSCN (copper thiocyanate).

2.2.4. Organocopper Compounds

PhCu, $Me(CH_2{=}CH)CuLi$, EtCu(CN)Li and $BuCuBF_3$.[11]

2.2.5. Chelate Compounds



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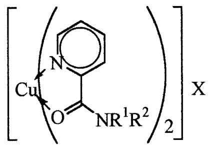
Copper pyrithione
(copper complex of 2-mercaptopyridine-1-oxide)[12]



2

R^1, R^2 = H, alkyl, aryl, aralkyl
X = $(NO_3)_2$, $(ClO_4)_2$

copper picolinic acid amide[13]

Acetylacetone copper aluminum, ethylenediamine copper aluminum.[14]

2.3. Concentrations of Copper in Seawater

Along with the growing use of copper-based paints, the monitoring of oysters in Arcachon bay (on the Atlantic coast of France) over the period 1979−1991 demonstrated an increase in the copper content of oysters in the vicinity of some marinas and mooring area. However, in 1999, Voulvoulis, et al.[5] reported that increased copper concentrations in the aquatic environment, due to the increased use of the copper-based antifoulants, do not have significant effects on marine ecosystems.

In the U.K., the concentration of current Environmental Quality Standard (EQS) for copper in seawater is ≤5 μg/L (expressed as an annual average).[5] Copper is an essential element, required for the normal growth of all plants and animals, and occurs commonly in the environment.[15−17] Copper is not lipophilic and shows only a slight tendency for bioaccumulation.[5]

In the U.K., P. Matthiessen et al. reported in 1999 that the 21.7% (30/138) of sampling locations/year exceeded EOS (5 μg/L) for copper and in six cases (4.3%(6/138)) the concentrations lay between 10 and 15 μg/L.[18] These data suggest that monitoring of concentrations of copper is important so as not to cause ecological damage in marinas and mooring areas where there are intense boating activities and poor tidal exchange.

In 2001, Vasconcelos and Leal[19] reported that marine microalgae *Emiliania huxleyi* was able to take up Cu very quickly in natural coastal seawater. For example, after 10 min exposure to a natural seawater which contained 29 nM of total initial dissolved Cu concentration, the intracellular Cu increased from 8.4×10^{-17} to 28×10^{-17} mol/cell, which corresponds to 85% of the total observed intracellular metal content after 24 h of exposure. In the future, the research on these marine organ-

Table 1. Marine Organisms to Settle on the Structures Immersed in Seawater[20]

organism	number
bacteria	37
fungi	14
diatom	111
algae	452
protozoa	99
porifera	33
coelenterata	286
annelida	108
tentaculata	139
arthropoda	292
echinodermata	19
chordata	127
other invertebrates	29
total	1,746

isms are expected to serve for decreasing the concentration of copper.

3. Organic Booster Biocides

There are 1746 species of marine organisms which attached to the marine constructions in seawater as shown in Table 1.[20] These prominent marine organisms are barnacles, algae (seaweeds), ascidians, shellfishes, seamosses, and hydrozoa. Copper as an antifoulant needs additional biocides because some of the common marine algae are tolerant to copper, as described previously. Therefore, these biocides are termed as booster biocides. Generally, these biocides are used in combination with copper.[21]

3.1. Kinds of Organic Booster Biocides

Primary organic booster biocides are shown in Table 2.[5,20,22] These biocides belong to the following compounds: heterocyclic amines, aromatic halides, carbamates, and others. These compounds contain five kinds of elements, nitrogen, oxygen, a halogen, sulfur, and boron. It is considered that the functional groups formed by bonding these elements to each other, or bonding with carbon, hydrogen, or a metal element, manifests their biocidal activities.

These compounds are used mainly as agrochemicals such as pesticides, herbicides, fungicides or bactericides. In the U.K., nine booster biocides (marked *a* boosters in Table 2) were approved for use on leisure crafts as safe antifouling agents.[21] In Japan, the Shipbuilding Research Society approved 17 formulations of 15 organic booster biocides (marked *b* boosters in Table 2), used together with copper thiocyanate (CuSCN) and cupronickel (Cu−Ni alloy) as safe antifouling agents.[20,22]

The other organic booster biocides such as heterocyclic amines, aromatic halides, phenols, aryl boron amines complexes, and other amines such as alkylamines and cycloalkylamines, phosphorus compounds, sulfur compounds, and others (e.g. enzymes) which are claimed in many patents are shown in Table 3.[22−48] Many phosphorus compounds are also used as biocidal compounds, as shown in Table 3.[23−50]

3.2. Degradation and Toxicity of Organic Booster Biocides

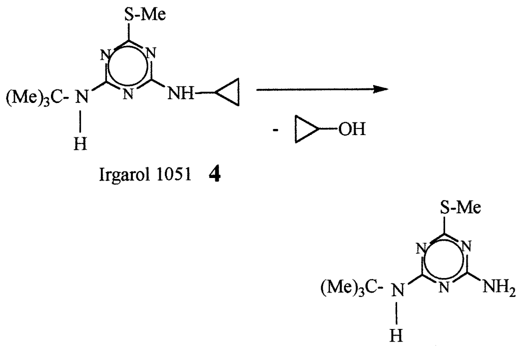
The properties related to the biocial activities of some organic booster biocides are shown in Table 4.[2,5,51−53] The table shows that generally these organic booster biocides degrade more easily in comparison with the organotin biocides.

Kobayashi and Okamura assessed the effects of eight biocides on sea urchin eggs and embryos. For these chemicals, toxicity appears to be in the order of zinc pyrithione > Sea-Nine 211 > pyridine triphenyl borate (KH101) > copper pyrithione > TBTO (tributyltin oxide) > Diuron ∼ Irgarol 1051 > M1 (a degradation product of Irgarol 1051, see eq 2).[54] The half-lives of zinc pyrithione, Sea-Nine 211, and Dichlofluanid are shorter than those of others as shown in Table 4. In particular, zinc pyrithione, which has the highest biocidal potency and a short half-life, is mainly used as the organic booster biocide component in Japanese tin-free antifouling paints.

In 2000, A. B. A. Boxall et al.[21] reported the uses of these organic biocides with copper compounds for vessels smaller than 25 m in length used in U.K. estuaries. In all biocides, copper oxide was used in the highest quantities, followed by Diuron, copper thiocyanate (CuSCN), Irgarol 1051, zinc pyrithione, and Dichlofluanid. In samples of seawater and sediments in the U.K. estuaries, the concentration of copper was the highest followed by Diuron and Irgarol 1051 as shown in Table 5.[21] In the U.K., the concentrations of zinc pyrithione and Dichlofluanid were not reported because of their low usage, etc., and the half-lives are much shorter compared with those of Diuron and Irgarol 1051. Diuron is considered to be relatively persistent in seawater, although no half-life ($t_{1/2}$) datum is available.[51]

It has been widely reported that high concentrations of organic booster biocides can be found in marinas and harbors, shown in Table 6.[52,55−65] D. Liu et al.[55] reported that Irgarol 1051 is highly toxic to nontarget marine algae, with the observable growth inhibition at a concentrations as low as 50 ng/L. This level is well within the ambient concentration levels found in some of the localities of the Seto Inland Sea in Japan and many marinas in Europe, as shown in Table 6.

Irgarol 1051 is decomposed to 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (M1 **39**) by dealkylation of cyclopropane ring in seawater as shown in eq 2.[51] Both Irgarol 1051 and its degradation product M1 were moderately toxic to marine bacteria, but in the root elongation inhibition bioassay, M1 showed a phytotoxicity at least 10 times greater than that of the Irgarol 1051.[56,66]



Irgarol 1051 **4**

M1 **39** (2)

Table 2. Primary Organic Booster Biocides[5,20,22]

organic booster biocide	trade name
1. Heterocyclic Amines	
zinc complex of 2-mercaptopyridine-1-oxide **3**[a,b]	zinc pyrithione
2-methylthio-4-butylamino-6-cyclopropylamine-*s*-triazine **4**[a,b]	Irgarol 1051
2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine **5**[a,b]	TCMSpyridine
(2-thiocyanomethylthio)benzothiazole **6**[a]	TCMTB
(4,5-dichloro-2-*n*-octyl-4-isothazolin-3-one) **7**[a,b]	Sea-Nine 211, Kathon 5287
pyridine triphenylborane complex **8**[b]	KH101
2. Aromatic Halides	
(2,4,5,6-tetrachloroisophthalonitrile)**9**[a,b]	Chlorothalonil
3-(3,4-dichlorophenyl)1,1-dimethylurea **10**[a,b]	Diuron
2,4,6-trichlorophenylmaleimide **11**[b]	
3. Carbamates	
zinc bis(dimethyl thiocarbamate) **12**[b]	Ziram
zinc ethylene bisdithiocarbamate **13**[a,b]	Zineb
bis(dimethylthiocarbamoyl)disulfide **14**[b]	Thiram
3-iodo-2-propynyl butylcarbamate **15**[b]	
manganese ethylene bisdithiocabamate **16**	Maneb
4. Others	
N,*N*-dimethyl-N′-phenyl(N′-fluorodichloromethyl-thiosulfamide **17**[a,b]	Dichlorofluanid
N-(fluorodichloromethylthio)phthalimide **18**[b]	
diiodomethyl-*p*-tolysulfone **19**[b]	

[a] Nine organic booster biocides are approved in the U.K. [b] The Shipbuilding Research Society in Japan approved above 15 organic booster biocides together with copper thiocyanate and cupronickel.

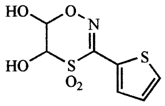
Table 3. Other Organic Booster Biocides (See Chart 1 for Structures)[23−50]

organic booster biocide	ref
1. Heterocyclic Amines	
5,6-dihydroxy-3-(2-thienyl)−1,4,2-oxathiazine, 4-oxide **20**	23, 24
5,7-dichloro-8-hydroxy-2-methylquinoline **21**	25
2,5,6-tribromo-1-methylgramine **22** (3-dimethylaminomethyl-2,5,6-tribromo-1-methylindole)	26, 27
2,3-dibromo-N−(6-chloro-3-pyridyl)succinimide **23**	28
thiazoleureas **24**	29
3-(3,4-dichlorophenyl)−5,6-dihydroxy-1,4,2-oxathiozine oxide **25**	30
2-trifluoromethyl-3-bromo-4-cyano-5-parachlorophenyl pyrrole **26**	31, 32
2. Aromatic Halides	
2-bromo-4′-chloroacetanilide **27**	33
3. Phenols	
2,6-bis(2′,4′-dihydroxybenzyl)−4-methylphenyl **28**	34
2,2-bis(3,5-dimethoxy-4-hydroxyphenyl)propane **29**	35, 36
acylphloroglucinols: 2,6-diacyl-1,3,5-trihydroxybenzene **30**	37
4. Arylboron Amine Complexes	
triphenylboron pyridine complex **8**	38, 39
alkyldiphenylboron isoquinoline complexes **31**	38, 39
triphenylboron octadecylamine complex **32**	40, 41
triphenylboron ethylenediamine complex **33**	42
5. Other Amines	
guanidines: 1,3-dicyclohexyl-2-(3-chlorophenyl)guanidine **34**	43
alkylamines: auryldimethylamine **35**	44, 46, 47
6. Phosphorus Compounds	
dialkylphosphonates: phosphoric acid di(2-ethylhexylester) **36**	45, 46
7. Sulfur Compounds	
alkyl haloalkyl disulfides: *n*-octylchloromethyl disulfide **37**	48
4,5-dicyano-1,3-dithiole-2-thione **38**	49
8. Others	
enzymes: endopeptidase	50

Under sunlight conditions, the Irgarol 1051 underwent a rapid degradation to produce M1, which remained even after the Irgarol 1051 had disappeared from the system. These compounds were persistent in any aqueous solutions tested under dark conditions, indicating their high stabilities to hydrolysis. The Diuron and M1 were more persistent than the Irgarol 1051 under sunlight irradiations.[67]

In a study investigating biodegradability in seawater, the breakdown of the Diuron, Irgarol 1051, Sea-Nine 211, and Chlorothalonil was monitored over 8 weeks by a bioassay using a ship-fouling diatom (*Amphora coffeaeformis*). The degradation of these substances in the seawater proceeds mainly by a biodegradation, although a photolysis may be significant in the upper layers of water.[5] The Irgarol 1051 and Diuron were not readily biodegraded, while the Chlorothalonil biodegradation became apparent after four weeks.[5] The Sea-Nine 211 is the most readily biodegradable compound studied and has a half-life of 8.5 days in the natural coastal seawater.[68] The highest detected concentration of the Irgarol 1051

Chart 1



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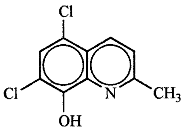

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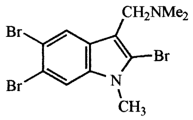

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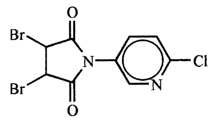

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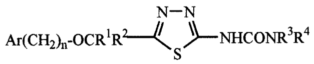

R^1-R^4 = H, alkyl, alkoxy, etc.
Ar = aryl

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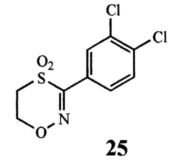

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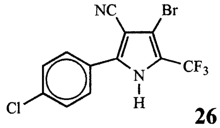

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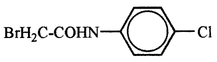

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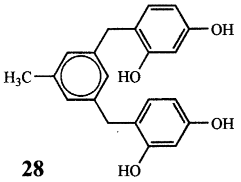

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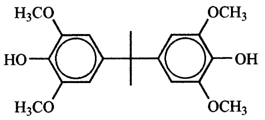

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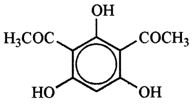

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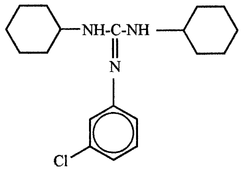
31

$Ph_3B{\cdot}NH_2(C_{18}H_{37})$

32

$Ph_3B{\cdot}NH_2\text{-}CH_2CH_2\text{-}NH_2$

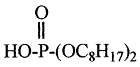
33



34

$C_{12}H_{25}NMe_2$

35



$HO\text{-}\overset{\overset{O}{\|}}{P}\text{-}(OC_8H_{17})_2$

36

$nC_8H_{17}\text{-}S\text{-}S\text{-}CH_2Cl$

37

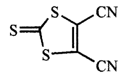


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Table 4. Properties of Common Antifouling Paint Booster Biocides[2,5,51−53]

			degradation data				
			half-life in seawater				
biocide	solubility (mg/L)	release rate[a] (μg cm^{-2} day^{-1})	$t_{1/2}$[b]	$t_{1/2}$[c] (day)	% reduction following 42 days	principal mode	other applications
Irgarol 1051	7	5.0	100 days	350 (±82.6)	4 (±22.6)		herbicide
Diuron	35	3.3			<1	biotic	herbicide
Dichlofluanid	1.3	0.6	18 hr	0.8 (±0.16)	100		fungicide
zinc pyrithione	8	3.3	<24 hr			photolysis	bactericide, fungicide
Sea-Nine 211	14	2.9	<24 h	1.9 (±0.1), 2.5[d]	100	biotic	no other applications
TCMTB	10.4		740 hr	37 (±0.8)	55 (±1.2)	hydrolysis	fungicide
TCMS pyridine		0.6					no other applications
Chlorothalonil	0.9		1.8 days	2.8 (±0.7)	100	biotic	fungicide
Zineb	0.07−10		96 hr			hydrolysis	fungicide
cuprous oxide		25−40					
TBT		1.5−4.0	several weeks to several months			hydrolysis photolysis biotic	

[a] ISO test system. [b] Ref 51. [c] Ref 52. [d] Ref 53.

(over 120 ng/L) that was observed in the study carried out in the Plymouth Sound locality significantly inhibited the growth of *Enteromorpha intestinalis* (a green seaweed) spores under laboratory conditions.[5,69]

In marinas, harbors, and coastal water of the Florida Keys, Bermuda, and St. Croix, the concentration of the Irgarol 1051 is not so high, as shown in Table 6. However, reduction in the net photosynthesis of intact coral was found at a concentration of 100 ng/L, and little or no photosynthesis was observed at concentrations exceeding 1000 ng/L after 2−8 h exposure at all tested irradiances.[64]

Diuron is considered to be relatively persistent in seawater; however, there are no half-life data available. Aerobic degradation of the Diuron is reported to result in the formation of 1-(3,4-dichlorophenyl)-3-methylurea **40** and 3,4-dichlorophenylurea **41**, while an anaerobic degradation in sediments results in the formation of 1-(3-chlorophenyl)-3,3-dimethylurea **43**, as shown in Scheme 1.[70]

The degradation properties of the Irgarol 1051, Diuron, and their degradation products are as follows:[52]

compound	half-life (days)	% reduction following 42 days
Irgarol 1051 **4**	350 (±82.6)	4 (±22.6)
M1 **39**	82 (±11.5)	26 (±8.7)
Diuron **10**	−	<1
DCPMU **40**	50 (±2.8)	65 (±3.6)
DCPU **41**	33 (±0.5)	43 (±1.5)

Irgarol 1051, Diuron, and their degradation products are relatively stable compared with the other organic booster biocides, as shown in Table 4. Therefore, the Irgarol and Diuron are not environmentally friendly organic booster biocides.

Table 5. Concentrations of Antifouling Biocides in UK Estuaries[21]

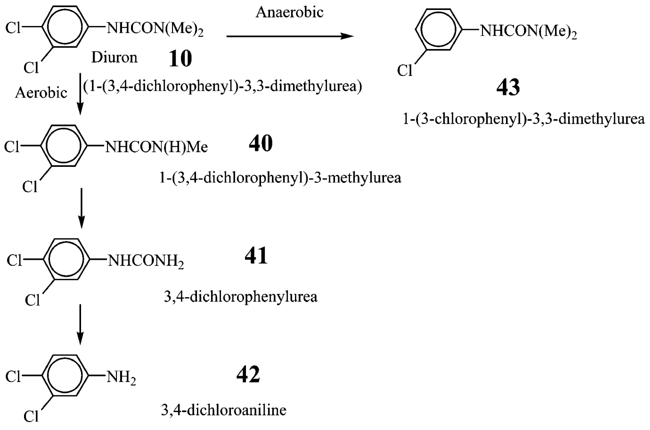
			concentrations of biocides in August 1998			
			mean estuarine		locked marina	
biocide	proportion of boats treated (%)	leaching rate ($\mu g/cm^2/d$)	dissolved (ng/L)	sediment (ng/g)	dissolved (ng/L)	sediment (ng/g)
copper	99–100		1,190	47,200	5,770	453,400
copper oxide		16.12–25.33				
copper thiocyanate		5.13–9.23				
Diuron	45–52	1.39–4.64	44.5	<12	768	395
Irgarol 1051	27–32	0.12–3.40	12.1	<10	201.4	1,011
zinc pyrithione	0.6–3.8	4.64–13.54				
Dichlofluanid	2.1–3.2	1.04				

Table 6. Concentration of Organic Booster Biocides and Their Degradation Products in Some Coastal Water and Sediment[52,55–65]

		concentration			
biocide	location	dissolved (ng/L)	sediment (ng/g)	degradation product dissolved (ng/L)	ref
Irgarol 1051	Seto Inland Sea (Japan)				55
	marinas (17/63 points =27% found)	264.2			
	Okayama	257		M1*[1] 1,870	56
	Singapore coastal	4,200			57
	Gold Coast (Australia)		118 (green algae)		58
	Southampton Water (U.K.)		110	M1[a] 99 (in surface water)	59
	Hythe Marina (U.K.)	403			60
	Hythe Marina (U.K.)	305		M1[a] 59	52
	Hamilton Harbor (U.K.)	590			61
	Baltic Sea marinas	440	220		62
	North Sea	170	25		
	Mediterranean[b] (France)	640			63
	Ely's Harbor (Bermuda)	294			64
	Elefsina (Greece)		690		65
Diuron	Hythe Marina (U.K.)		1,420 (enclosed marina)		59
	Hythe Marina (U.K.)	1,249		DCPMU[c] 14	52
	Hythe Marina (U.K.)	6,742			60
Dichlorofuanid					
	Aktio (Greece)		195		65
Chlorothalonil					
	Elefsina (Greece)		126		65

[a] M1 is 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (**38**), which is the degradation product of Irgarol 1051. [b] Côte d'Azur. [c] DCPMU is 1-(3,4-dichlorophenyl)-3-methylurea, **40**.

Scheme 1



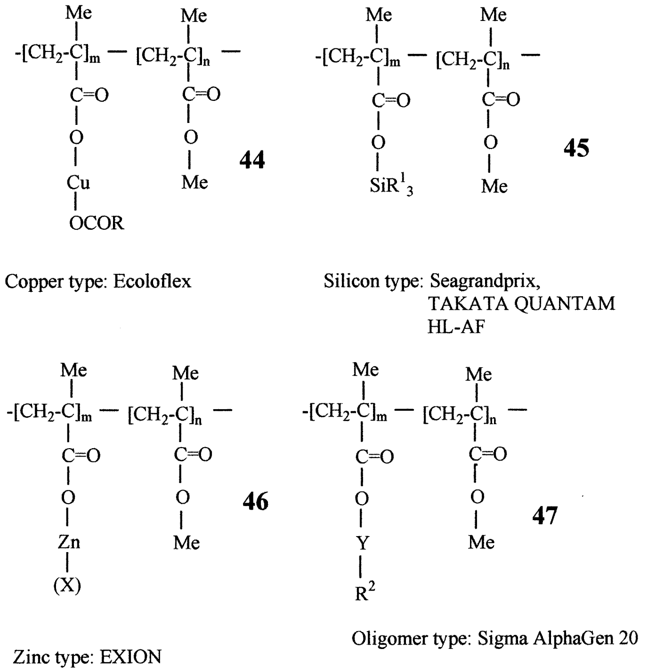
From these data, in some marinas in Europe and Japan, it was considered that some marinas were not good environments for the growth of seaweeds, at least during the boating season.

4. Self-Polishing Copolymers

4.1. Conventional Self-Polishing Copolymers

Acrylic or methacrylic copolymers are easily hydrolyzed in seawater. Fouling organisms, which attach on the surface of a paint film, are eliminated together with the copolymer film which is decomposed by the hydrolysis of the copolymers. This hydrolysis/erosion process results in a smooth surface; hence, these copolymers are called self-polishing copolymers. These copolymers blended with biocides confer a smooth surface on the copolymer and an ability of controlling/regulating biocide leaching rates.

The acrylic or methacrylic copolymers were used as the main components of the copolymers for self-polishing organotin antifouling paintings. Alternative tin-free antifouling paints also used the same type self-polishing copolymers which are used in the case of organotin antifouling paints, by bonding copper, silicon, zinc, or oligomer groups with its carboxylate side chain instead of the tributyltin groups, as shown



44

Copper type: Ecoloflex

45

Silicon type: Seagrandprix, TAKATA QUANTAM HL-AF

46

Zinc type: EXION

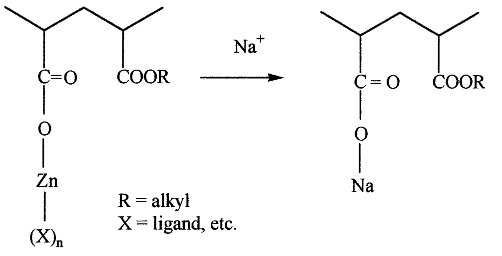
47

Oligomer type: Sigma AlphaGen 20

R = CMe_3, CH(Et)(Bu), $-(CH_2)_7CH=CH(CH_2)_7Me$, etc.
R^1 = propyl, butyl
R^2 = Me, Et, etc.
X = alkylcarboxylate group, etc.
Y = oligomer

Figure 1. Tin-free self-polishing ablative polymers.[71,74]

in Figure 1 (**44**−**47**).[71,72] In these copolymers, the hydrolysis of the zinc copolymer is explained by citing sodium as an example of an ion in seawater by an ion exchange mechanism as shown in eq 3.[73]



(3)

These copolymers bonded with metal groups or oligomers are also easily hydrolyzed by metal ions such as sodium and potassium in seawater similarly to the above zinc copolymers.

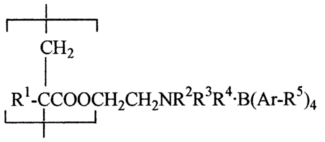
The acrylic or methacrylic copolymers were used as main components of the copolymers for the self-polishing organotin paintings. The (meth)acrylic ester groups are very easily hydrolyzed in seawater, as shown in eq 3. The leaching rate of copper and organic boosters in the self-polishing copolymer are controlled by the degree of polymerization (molecular weight) and hydrophilicity of the copolymer (depending on the ratio of carboxylic group in the molecule and kinds of copolymers).

Recently, some tin-free antifouling paint systems have been reported to have achieved a fouling free performance for five years.[71,74] The first developed tin-free antifouling paint, Ecoflex, have been used since 1990. It is a copper-type antifoulant and has been used on 6000 vessels before 2000.[74] These self-polishing copolymers are mostly acrylic or methacrylic copolymers. However, other self-polishing copolymers containing units of vinyl amides, vinyl lactams, vinylsulfonic acid esters, etc.,[75−78] have been reported.

These self-polishing copolymers including copolymers having biocidal pendant groups and biodegradable copolymers, are as follows:

4.2. Self-Polishing Copolymers Having Biocidal Groups

Copolymers having a biocidal group as a pendant group show a biocidal activity by themselves. The copolymers with copper (copolymer **44** in Figure 1) are biocidal self-polishing copolymers because the copper has a biocidal activity. However, the activity of this copolymer with copper is not so strong because the amounts of active component are much less than those of the copper component of inorganic copper compounds used as usual additives. If the carboxylic group of the polymer bonds to a biocidal pendant group, the copolymer will show biocidal activity by the hydrolysis of the pendant group in seawater. For example, a tetraalkylammonium tetraarylborate complex, **48** [79] is cited.



$$R^1\text{-}CCOOCH_2CH_2NR^2R^3R^4\cdot B(Ar\text{-}R^5)_4$$

48

R^1 - R^5 = H, lower alkyl
Ar = aryl group

The examples of biocidal pendant groups are N-methacrylimidazole of heterocyclic amines[80] and 2,4,6-tribromophenyl methacrylate of aromatic halides,[81] which are the first and the second groups of the eight groups shown in Table 3, respectively.

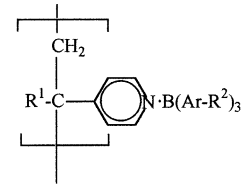
The other self-polishing copolymers having biocidal groups, besides acrylate copolymers or methacrylate copolymers, are a Schiff base type, an amide type, and a sulfoxylic acid ester type of vinyl-based copolymers.

Schiff bases are obtained by the reactions of aldehydes with primary amines. The Schiff bases are easily decomposed to form the primary amines by a hydrolysis in seawater. Many of the primary amines have biocidal activities. Therefore, the vinyl copolymers having these Schiff base groups as the pendant groups are used for self-polishing copolymers which show biocidal activities.

There are two types of Shiff bases copolymers. The monomers of the first type are formed by reacting primary vinylamines with aldehydes. The primary vinylamines are *p*-aminostyrene and N-vinylacrylamide, etc. The aldehydes are *p*-octylbenzaldehyde, *p*-hexylbenzaldehyde, and benzaldehyde, etc. Their examples are 4-(4-octylbenzylidene)iminostyrene, 4-(4-hexylbenzylidene)iminostyrene, etc., and the comonomers are an acrylate or a methacrylate.[82,83]

The monomers of the second types are formed by reacting vinylaldehydes with primary amines. The vinylaldehydes are cinnamaldehyde, methacrolein, crotonaldehyde, 4-vinylbenzaldehyde, etc. The primary amines are *p*-octylaniline, laurylamine, aniline, nonylaniline, octylamine, etc. Their examples are 4-vinyl-benzylideneaniline, 4′-vinylbenzylidene-4-*n*-octylaniline, 4′-vinylbenzyldenelaurylamine, etc.[84,85]

On the other hand, if the biocidal groups bond directly to the vinyl carbon, the rate of hydrolysis of their copolymers in seawater is not considered to be so fast. For example, 4-vinylpyridinetriphenyl-boron complex (**49**, R^1, R^2 = H) is prepared by the reaction of 4-vinylpyridine with triphenylboron.[86] Therefore, these polymers are not used as the self-polishing polymers by themselves. Thus, they are actually used together with the other self-polishing copolymers or with matrix polymers such as rosin.



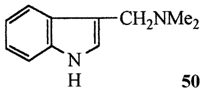
49

R^1, R^2 = H, alkyl
Ar = aryl group

4.3. Biodegradable Self-Polishing Copolymers

There are three types of biodegradable polymers. The first type of polymers (e.g., poly-3-hydroxybutyrate) are produced by organisms such as hydrogen bacterium, *Alcaligenes eutrophus*, and the blue-green algae treated with a gene manipulation. The second ones are plant products such as starch, cellulose, and lignin and animal products such as chitosan and gelatin. The third ones are synthetic polymers such as polyesters, polyamides, polyamino acids, polyimides, poly(vinyl alcohol)s, etc. Poly(vinyl alcohol), polylactic acid ester, and polybutylene succinate are used widely as general biodegradable polymers.[87]

The third synthetic polymers are used mainly for the self-polishing antifouling paints. Polyesters, poly(vinyl alcohol)s, polyamino acids, etc., are used as biodegradable self-polishing polymers for the antifouling paints. The others are celluloses and polysaccharides of the second type natural products.[88−94] For example, a polybutylene succinate as a fatty acid polyester is used as a biodegradable polymer and gramine [3-(dimethylaminomethyl)indole, i.e., donaxine] **50** is used as a biocidal agent.[88]



50

Recently many biodegradable polymers have been investigated as alternative selfpolishing antifouling polymers for conventional acrylic selfpolishing polymers of tin-free antifouling paints.[88−94]

5. Natural Products as Antifoulants

The aquatic fouling organisms in seawater are protists, animals, and plants, as shown in Table 1. Marine lives such as corals, sponges, marine plants, and dolphins, etc., prevent the surface of their bodies with antifouling substances without causing serious environmental problems. Therefore, these substances may be expected to be used, as new environmentally friendly antifouling agents, especially those having high anesthetic, repellant, and settlement inhibition properties, etc., without biocidal properties, are desired. Many of the antifouling substances are found from these marine animals, marine plants and microorganisms. Moreover, many of the antifoulants are also found in terrestrial plants such as a green tea, wasabi, and oak tree leaf.

Primary marine natural product antifoulants are shown in Table 7.[95] These antifoulants are obtained from four different animal phylum Cnidaria, Porifera, Bryozoa and Chordata and from two kinds of marine plants of Thallophyta and Angiospermae.[95] The fouling of manmade structures involves molecular bondings and biological adhesives by abiotic and biotic substances. These biotic foulings are formed by microfouling, e.g., those of bacteria and diatoms, and by macrofouling, e.g., those of algae and invertebrates. These natural antifoulants include not only toxins but also anesthetics, growth-inhibiting, attachment-inhibiting, and metamorphosis-inhibiting materials, and repelling materials as shown in Table 7.[95]

The other natural product antifoulants in 10 kinds of compounds of terpens, acetylenes, polycyclic compounds, steroids, phenols, isothiocyanates, nitrogen-containing compounds, glycerol derivatives, higher fatty acids, and enzymes are reported as shown in Table 8.[95−122] These are produced from sponges, corals, starfishes, mussels, algae, etc.

Broadly speaking, these antifoulants are classified into two types: one is terpenes, and the other is nonterpenes. The terpenes have unsaturated ligand groups and electronegative oxygen groups such as carbonyl, furan, lactone, ether and hydroxy. The nonterpenes have electronegative nitrogen, oxygen, and halogen ligand groups such as amino groups, hydroxy, carbonyl, chlorine, and bromine groups. It is considered that these compounds may give rise to the confusion of the basic metabolism because these active ligands coordinate with one or more ligand sites in place of normal ligands in enzymes, coenzymes, hormones, genes, etc.[123−125]

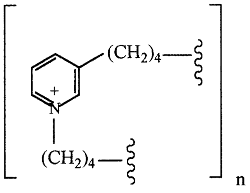
Antifouling activities against barnacles, the most troublesome fouling marine organism, are shown in Table 9.[126,127] The most potent natural product tested, bufalin (**128**), was over 100 times more toxic than TBT (tributyltin compounds) and over 6000-fold more potent with respect to antisettlement activity.[126,127] The bufalin is a steroid of toad poison, and it is one component in the secretory substance of *Bufo vulgaris*.

In 2003, Faimali et al.[128] reported that polymeric 3-alkylpridinium salts **133** from a Mediterranean sponge, *Reniera sarai*, was less effective at inhibiting cyprid larvae settlement compared with the organic booster biocides, copper pyrithione **1**, or zinc pyrithione **3**, and their effects were non toxic and reversible, as measured by very low toxicity bioassays. Future efforts are expected to focus on chemi-

Table 7. Marine Natural Product Antifoulants (See Chart 2 for Structures)[95]

basibiont	antifoulant	activity
	Cnidaria	
Leptogorgia virgulata, L. setacea	homarine **51**	growth inhibition
Pseudopterogorgia americana	furanogermacrene **52**	growth inhibition
Renilla reniformis	renillafoulins **53**−**55**	settlement inhibition
Leptogorgia virgulata	pukalide **56**	settlement inhibition
	epoxy pukalide **57**	
Lobophytum pauciflorum	14-hydroxycembra-1,3,7,11-tetraene **58**	growth inhibition
	15-hydroxycembra-1,3,7,11-tetraene **59**	
Muricea fruticosa	muricins **60**−**63**	inhibition of diatom growth
Sinularia sp.	(−)-*β*-bisabolene **64**	repellant
Sinularia sp.	13α-acetoxypukalide **57**	antimussel
	(9*E*)-4-(6,10-dimethylocta-9-11-dienyl)-furan-2-carboxylic acid **65**	antibarnacle
	Porifera	
40 sponge spp	terpenoids **66**−**80**	general antibacterial variable antifungal settlement inhibition
Aplysina fistularis	aerothionin **81**	inhibition of metamorphosis
	homoaerothionin **82**	
Aplysilla glacialis	1-methyladenine **83**	antibacterial
Phyllospongia papyracea	furospongolide **84**	settlement inhibition
Dysidea herbacea	herbacin **85**	settlement inhibition stimulation
Crella incrustans	lyso-platelet aggregating factor **86**	settlement inhibition
	Bryozoa	
Zoobotryon pellucidum	1-methyl-2,5,6-tribromogramine **22**	settlement inhibition
	Chordata	
Eudistoma olivaceum	eudistomins G **87** (H **88**)	settlement inhibition
Halocynthia roretzi	lysophosphatidylinositols **89**, **90**	antifungal
	Thallophyta	
Delisea pulchra	halogenated furanones **91**−**96**	inhibition of barnacle, algal settlement, bacterial growth, and germling development
	Angiospermae	
Zostera marina	*p*-(sulfooxy)cinnamic acid **97**	settlement inhibition

cally synthesizing these polymer analogues for further tests.[128]



133

On the other hand, the activities of the other antifoulants which are higher than that of copper are shown in Table 10,[98,113,129] in which the activity of copper is set as 100.

Some natural product antifoulants having higher activities compared with those of organotin compounds and copper compounds are found, as shown in Table 9 and Table 10. Generally, most natural products are not easily synthesized; however, some compounds such as nicontineamide **123** and 2,5,6-tribromo-1-methylgramine **22** are simple compounds. In particular, 2,5,6-tribromo-1-methylgramine from *Zoobotryon pellucidum* shows 3−6 times of settlement inhibition property to TBTO. It acts only to inhibit the settlement action to barnacle larvae without killing them.[130]

Some of these active antifoulants of 2,5,6-tribromo-1-methylgramine **22** and nicotinamide **123** have been claimed in a patent.[131] The paint, consisting of these antifoulants and silicone as the matrix polymer component, was coated on the surface of acryl board, and the board was found to be fouling free after 2 months in seawater.[131] Therefore, we might expect to find some environmentally friendly natural product antifoulants for actual uses in near future.

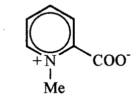
6. Antifouling Systems without Biocidal Agents

6.1. Fouling-Release Coatings

The major organosilicon compounds are silicones, which are polymeric compounds having Si−O bonds. Silicones are used in various industrial fields such as the electric and electronic industries, business machinery and tools, constructions, foods, medical treatments, fibers, plastics, papers, pulps, paints, rubbers, etc.[125]

The characteristics of silicones are a result of two properties, a strong Si−O bond (428 kJ/mol, 101 kcal/mol) and a low intermolecular force. The low intermolecular force is caused by a highly polarizable state, that is, the state between covalent bonds and ionic bonds because of a large difference in the electronegativities of Si and O in the Si−O bond.[125] On the other hand, the SiC−H bond has small ionic property. By both the properties of small intermolecular force and small ionic property of the methyl

Chart 2



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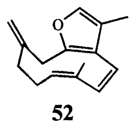

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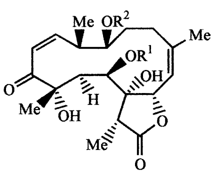
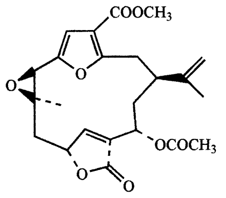


53 $R^1 = R^2 = Ac^-$

54 $R^1 = Ac, R^2 = C_2H_5CO^-$

55 $R^1 = Ac, R^2 = n\text{-}C_3H_7CO^-$



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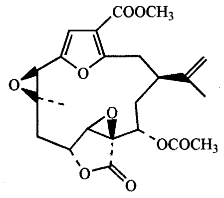

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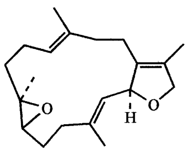

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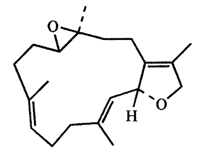

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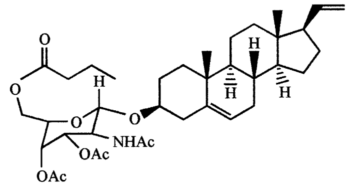

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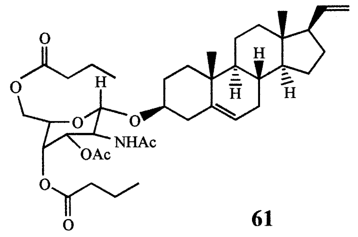

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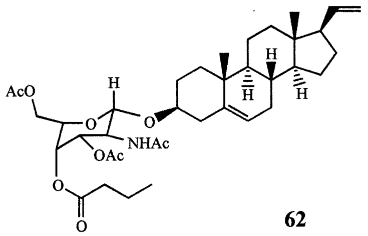

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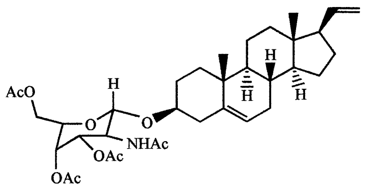

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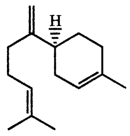

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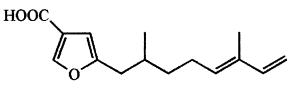

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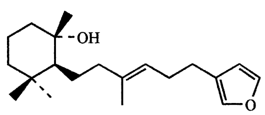

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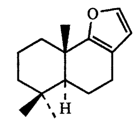

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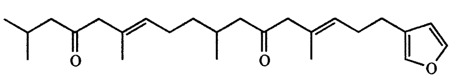

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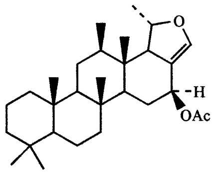

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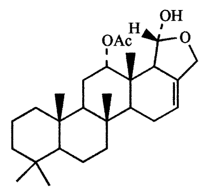

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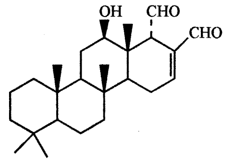

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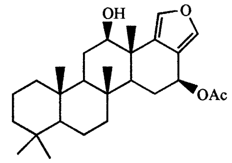

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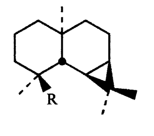
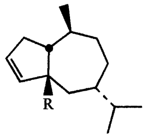


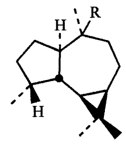
73 R = NC

74 R = NCS



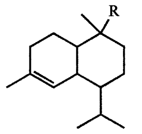
75 R = NC

76 R = NCS



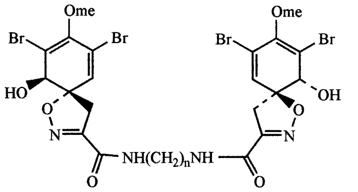
77 R = NC

78 R = NCS



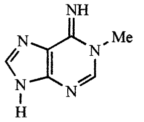
79 R = NC

80 R = NCS



81 n = 4

82 n = 5



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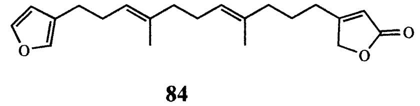

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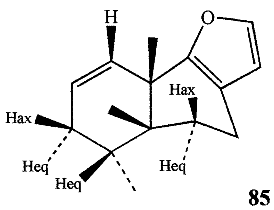

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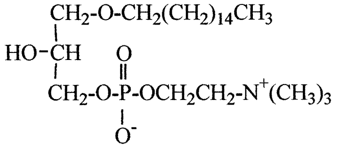
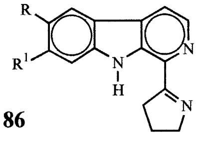


$$\begin{array}{l}\mathrm{CH_2\text{-}O\text{-}CH_2(CH_2)_{14}CH_3}\\ \mathrm{HO\text{-}CH}\\ \mathrm{CH_2\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}\text{-}OCH_2CH_2\text{-}N^+(CH_3)_3}\end{array}$$

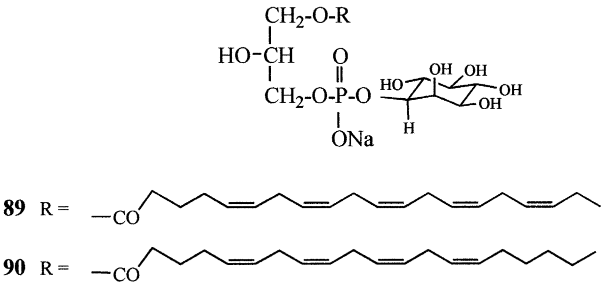


86

87 $R = H, R^1 = Br$

88 $R = Br, R^1 = H$

Chart 2 (Continued)



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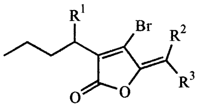
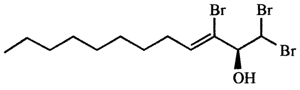


	R^1	R^2	R^3
91	H	Br	Br
92	H	H	Br
93	OAc	H	Br
94	OH	H	Br
95	OAc	H	I



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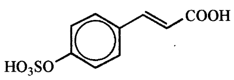

97

groups, the silicones show a high water repellency, water resistant qualities, weather resistance, mold releasing, and lubricating properties.[125,132]

Silicon coatings are called "fouling-release coatings" to differentiate them from the self-polishing antifouling paints containing biocidal components. Ideally, these "nonstick" coatings should completely prevent the hull from the attachment of the fouling. Actually the silicon coatings get fouled only weakly. They significantly limit the strength of the joint between fouled and the hull to make the bond so weak that it can be broken by the weight of the fouling or by the motion of the ship through the water.[133]

The fouling-release property correlates with a low surface energy, a low elastic modulus, the microphase separation structure of hydrophilic and hydrophobic layers, and a nonfixed surface layer containing oil materials.

The surface energy and elastic modulus of silicones are very low. Brady, Jr. et al.[133,134] found that the relative adhesion data correlate with the square root of the product ($(\gamma E)^{1/2}$) of the surface energy (γ) and elastic modulus (E). By this relation, the silicones show a relatively low adhesion property (the ratio of the silicones to poly(tetrafluoroethylene) is1/26.6; elastic modulus (E): poly(tetrafluoroethylene) = 3.3×10^9 dyn/cm^2, silicones = 3.6×10^6 dyn/cm^2)[22] as compared with that of poly(tetrafluoroethylene), although poly(tetrafluoroethylene) has a lower surface energy (18.5 dyn/cm) than that of silicones (24 dyn/cm.).[6]

Singer et al.[135] have studied on barnacle release mechanisms and the durability of silicone coatings. Both pseudobarnacles and barnacles (*Balanus improvisus*) are separated by a peeling process, although differences in peeling modes were observed. Release forces from both coatings are decreased as coating thickness is increased. The durability of coatings is increased with increasing coating thickness. The critical removal force of pseudobarnacles from both single and duplex coatings suggested that three parameters must be considered in the design of foul releases coatings, namely, the surface energy, elastic modulus, and thickness. In particular, coatings should have a low elastic modulus and preferably, be thicker rather than thinner. Scratch tests on duplex coatings also supported thicker coatings for increased tear resistance.

In 1972, silicone elastomers were tested during a nine-month fouling seasons in South Devon, England. The silicone elastomers were derived from dimethylsiloxane, including room-temperature vulcanizing (RTV) and moisture-curing elastomers. The RTV elastomer permitted only small amounts of fouling and very low adhesion of the fouling species was observed.[136]

In 1987, Brady et al.[137] reported on the experimental application of the silicone elastomer coatings on US Naval vessels. After nine months in the seawater, the coating showed some slight damage from abrasion, but the adhesion of the system was excellent and delamination of the coating did not spread from the abraded sites. Some seagrass and a few barnacles had attached to the coating, but they were easily removed by bare hand or by brush.

In two-year exposure experiments in the harbor of Ischia in Italy, the silicon fouling-release coating proved to be unsuitable for colonization by organisms, due to low surface energy of the coatings. Once a fouling organism attached to the surface of the silicone coating, the fouling was removed easily by a water jet pressure $^1/_4$ or less than that used in the case of the conventional self-polishing copolymers such as poly(methyl methacrylate). The use of silicone fouling-release coating technology represents an alternative to the use of biocidal antifouling coating.[138]

Some commercial silicon coatings contain silicon oil that migrates from the bulk of the coating to the surface and into the water. Fouling organisms settle on the oil rather than the surface of the coating. The joint between oil and coating is weak and fails readily; the oil migrates into the water taking early stages of fouling with it. Thus antifouling systems by the release of mucous materials seems to be similar to the system of dolphins which resists fouling on the surface of their skin. The oil also plasticizes the coating.[133]

Less than 1.1 wt % of the incorporated oil, polydimehtyldiphenylsilicone oil, was lost from the coating over a year. The toxicity of these coatings were shown to be minimal to shrimp and fish.[139] In the test of aquatic environments in Florida over a period of 1.5−2 years, it was demonstrated that the oil incorporation decreased barnacle and oyster adhesion.[140]

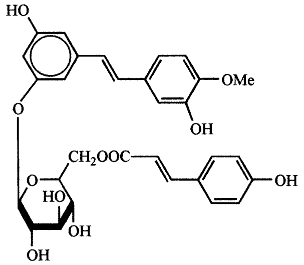

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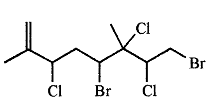
Table 8. Antifouling Agents of Natural Products (See Chart 3 for Structures)[27,96−122]

	compound, living thing	species	ref
	1. Terpens		
monoterpenes	1,4-dibromo-2,3,6-trichloro-3,7-dimethyl-7-octene **98**		96
	temperate red alga	*Plocamium costatum*	
susquiterpens	3-acetoxy-E-γ-bisabolene **99**		97
	marine red alga	*Laurencia rigida*	
	isocyanosesquiterepene alcohol (1S*,4S*,7R*10S*)10-isocyano-5-cadinen-4-ol) **100**		98
	nudibranch	*Phyllidia pustulosa*	
	2-hydroxy-9,11-dimethyl-10-methylene-3-oxatricyclo[7.3.1.$0^{2,6}$]tridec-5-en-4-one **101**		99
	palauan marine sponge	*Dysidea herbacea*	
diterpenes	*epi*-agelasine C **102**		100
	marine sponge	*Agelas mauritiana*	
	eleganolone **103**		101
	common brown alga	*Bifurcaria bifurcata*	
	renillafoulins **55**		102
	Atlantic sea pansy	*Renilla reniformis*	
	kalihinenes (Kalihinol A **104**)		103
	marine sponge	*Acanthella cavernosa*	
sesterterpene	22-acetoxy-16β-hydroxy-24-methyl-24-oxoscalarano-25,12β-lactone **105**		104
	palauan marine sponge	*Lendenfeldia chondrodes*	
terpene glucosides	pittosporanoside A_2 **106**		105
	pittosporum	*Pittosporum tobira* Ait	
	2. Acetylenes		
polyacetylenes	callytetraynetriol **107**		
	marine sponge	*Callyspongia truncata*	106
	3. Polycyclic Compounds		
solenoide	bis(deacetyl)solenoide D **108**		
	marine sponge	*Psammaplysilla purpurea*	107
	4. Steroids		
epidioxy sterol	5-α,8α-epidioxycholest-6-en-3β-ol **109**		104
	Palauan marine sponge	*Lendenfeldia chondrodes*	
seco-steroids	12α-actoxy-13,17-seco-chlolesta-1,4-diene-3-ones **110**		108
	octocoral	*Dendronephthya* sp.	
	3-methoxy-19-norpregna-1.3,5(10),20-tetraene **111**		109
	octocoral	*Alcyonium gracillimum*	
steroid lycosides	$\Delta^{9(11)}$3β,6α-diydroxysteroidal aglycon **112**		110
	starfish	*Henricia downeyae*	
	5. Phenols		
tannins	epigallocatechingallate **113**		111
	green tea		
phloroglucinols	3,5-diformyl phloroglucinols **114**		112
	blue mussel	*Eucalyptus* sp.	
kaempferol glucopyranosides	kaempferol coumaroylglucopyranoside **115**		113
	leaves of oak tree	*Quercus dentata*	
stilben glucoside	polydatin coumarate **116**		113
	eucalyptus	*Eucalyptus rubida*	
monophenols	capsaicin **117**		114
	pepper		
	6. Isothiocyanates		
alkyl isothiocyanates	phenylethylisothiocyate **118**		113
	wasabi	*Wasabi japonicas* Matsum	
	7. Nitrogen-Containing Compounds		
pyrroles	pseudoceratidine **119**		115−117
	marine sponge	*Pseudoceratina purpurea*	
	mauritiamine **120**		
	marine sponge	*Agelas mauitiana*	118
indoles	2,5,6-tribromo-1-methylgramine **22**		27
	zoobotryon	*Zoobotryon pellucidum*	
amides	N-docosanoyl-*D*-*erythro*-(2S,3R)-16-methyl-heptadecasphing-4(E)-enine **121**		119
	marine sponge	*Haliclona koremella*	
	nicotinamide **122**		113
	mallotus	*Mallotus japoinicus* Mueller-Arg.	
carbamates	ethyl N-(2-phenylethyl)carbamate **123**		107
	marine bacteria	*Cytophaga* sp.	
primary amies	ceratinamine **124**		120
	marine sponge	*Pseudoceratina purpurea*	
	8. Glycerol Derivatives		
glycoylglycerolipids	digalactosyl diacylglycerol **125**		113
	wakame(sea weed)	*Undaria pinnatifida*	
	9. Higher Fatty Acids		
	arachidonic acid **126**, palmitoleic acid **127**		121
	marine sponge	*Phyllospongia papyracea*	
	10. Enzymes		
	phenoloxidase		122
	blue mussel	*Mytilus edulis*	

Chart 3



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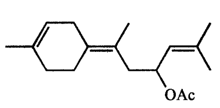

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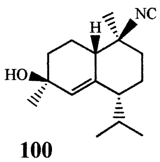

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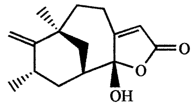

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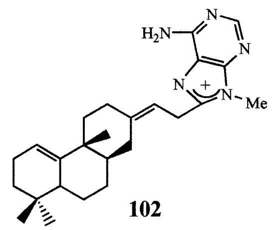

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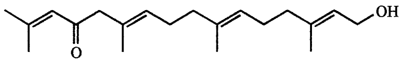

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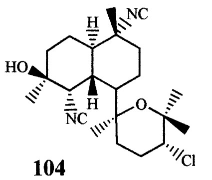

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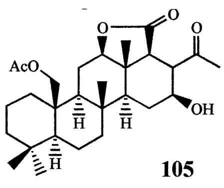

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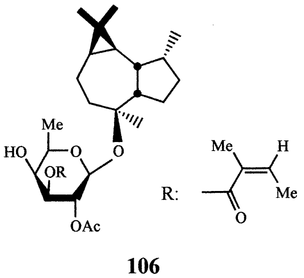

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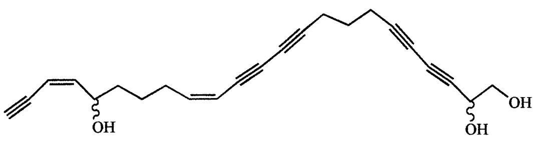

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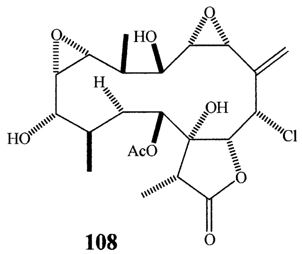

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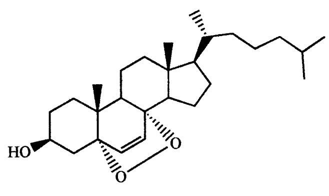

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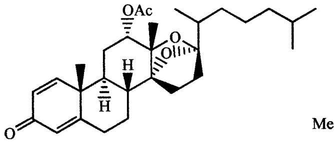

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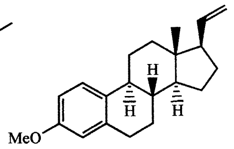

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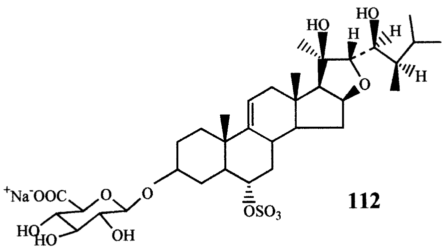

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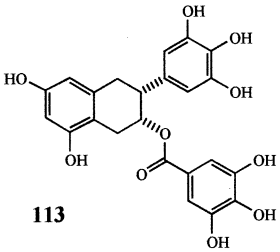

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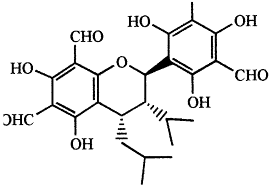

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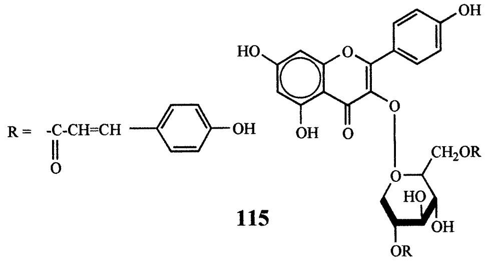
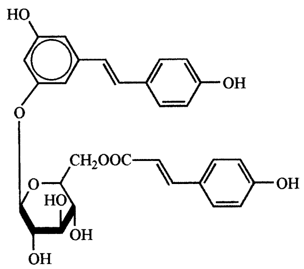


115

Kaempherol 3-*O*-(2",6"-di-*O*-(*E*)-*p*-coumaroyl-β-*D*-glucopyranoside



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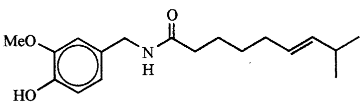
Polydatin 6"-*O*-(*E*)-*p*-coumarate



117

Ph-CH$_2$-CH$_2$NCS

118

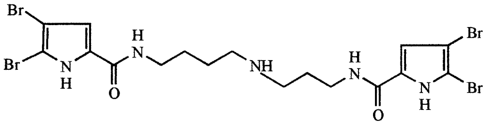


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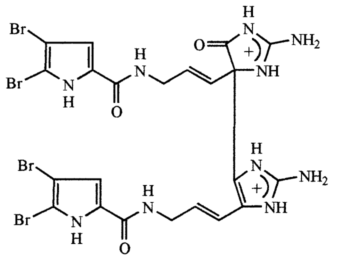
Chart 3 (Continued)



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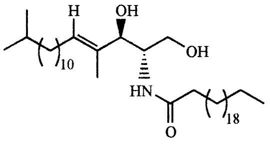

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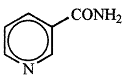

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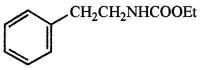

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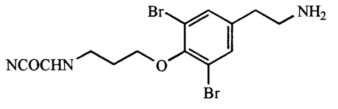

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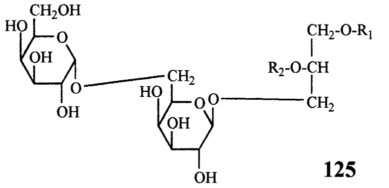
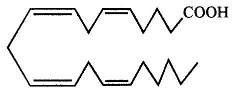


125

R_1, R_2 = mixtures of saturated and unsaturated acyl groups



126

$CH_3(CH_2)_5$-CH=CH$(CH_2)_7$COOH

127

Table 9. Antibarnacle Activity of Bufodienolids and Tributyltin Chloride (See Chart 4 for Structures)[126,127]

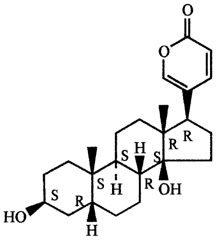
	naupliar toxicity		cyprid antisettlement	
antifoulants	LD_{50}, ng/L	relative potency	EC_{50}, ng/L	relative potency
bufalin[a] **128**	27	100.0	10	100.000
cinobufagin[b] **129**	37	73.0	162	6.000
cinobufatalin[c] **130**	837	32.0	2600	0.380
TBT Cl (n-Bu_3SnCl)	3400	0.8	66000	0.001
digoxigenin[d] **131**	4720	0.6	>50000	0.002
digoxin[e] **132**	5450	0.5	6300	0.150

[a] Bufalin = 3,4-dihydroxybufa-20,22 dienolide. [b] Cinobufagin = 16-(acetyloxy)-14,15-epoxy-3 hydroxybufa-20,22-enolide. [c] Cinobufatalin = 16-(acetyloxy)-14,15-epoxy-3,5-dihydroxybufa-20,22-enolide. [d] Digoxigerin = 3,12,14-trihydroxycard-20(22)-enolide. [e] 3-[(O-2,6-dideoxy-β-D-ribo-hexopyranosyl((1→4)-O-2,6-dideoxy-β-D-ribo-hexopyranosyl-(1→4)-2,6-dideoxy-β-D-ribo-hexopyranosyl)oxy]-12,14-dihydroxycard-20(22)-enolide.

Other fouling-release coating utilize microphase separation structures of hydrophilic and hydrophobic layers. The best ratio of hydrophobic layers to the total of hydrophilic and hydrophobic layers in the silicone polymers is 15−20%. The surface energy of these polymers showed the lowest value, and fouling was prevented in test environments.[22,141]

Fluorosilicones are silicone polymers which incorporate fluorine atoms.[142−144] They may be expected to have a lower surface energy because a poly(tetrafluoroethylene) as the representative fluorine polymer shows the lowest surface energy described above. Therefore, fluorosilicone polymers are expected to have lower surface energy than that of silicone polymers. However, silicone polymers showed much higher fouling release properties than that of the fluoropolymers. For example, the polymers of fluorosilicone **135** have been investigated on its prolonged immersion in seawater on the poly(methacrylate) controls. The antifouling property of these polymers were found to be better than that of poly(methyl methacrylate); however, they were worse than that of polysilicones.[142]

Chart 4



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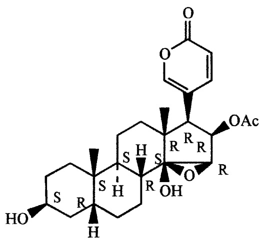

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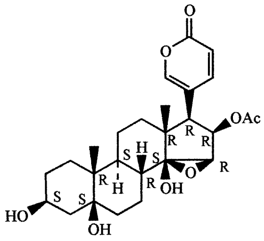

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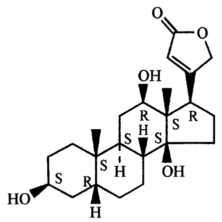

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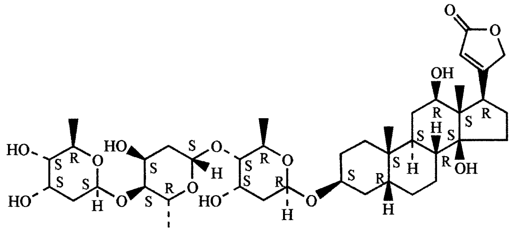

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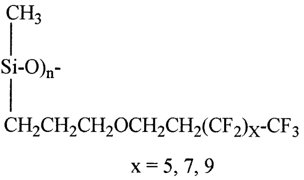
Recently, some fluorosilicone polymers showed better fouling release properties than that of the simple silicone polymer in seawater test. In 2001, the US Navy reported some fluorinated silicones **136** in the US Patent.[144]

In these compounds, the nonafluorohexyl group (*n* = 3) resulted in fewer barnacles, and less encrusting bryozoans, settling on the fluorosilicone panel than on the polydimethylsilicone. However, the level of



$$-(\overset{CH_3}{\underset{CH_2CH_2CH_2OCH_2CH_2(CF_2)_X\text{-}CF_3}{Si}}\text{-}O)_n\text{-}$$

x = 5, 7, 9

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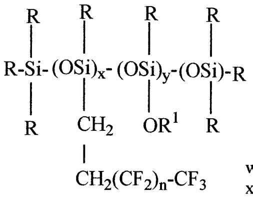
algae fouling was greater for the fluorosilicone. All fouling was easily removed from both panels by wiping with a damp sponge.



$$R\text{-}\overset{R}{\underset{R}{Si}}\text{-}(O\overset{R}{\underset{CH_2CH_2(CF_2)_n\text{-}CF_3}{Si}})_x\text{-}(O\overset{R}{\underset{OR^1}{Si}})_y\text{-}(O\overset{R}{\underset{R}{Si}})\text{-}R$$

R = alkyl
R^1 = H or alkyl
n = 2 - 10
x = at least 1
y = at least 2
wherein, preferably n is 2 or 3,
x + y = 20 - 50, x = 75 - 90%,
y = 10 - 25%

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In Japan, Intersleek, SigmaGlide LSE and Bioclean SPG are already used as commercial fouling release paints. On the Intersleek, an article[145] and catalogues[146,147] reported as follows: A patent was awarded in 1976 to International Coatings Ltd. It was coated on large vessels at first in 1987. It was specifically designed for deep sea, high activity-scheduled ships such as container vessels, LNG/LPG carriers, cruise liners, and vehicle carriers, which travel at 15−30 knots. It works by providing an ultrasmooth, slippery, low friction, hydrophobic surface, onto which the fouling organisms have difficulty settling. Usually, any settled organisms are easily removed by pressurized water hosing or by a light wiping with a sponge or soft cloth. Its slippery and ultrasmooth surface provides an easily cleanable surface with a potential reduction in hull roughness via careful applications, increasing fuel efficiency, and prolonging the drydocking schedule up to 60 months. Recoating should not be required during subsequent drydocking, after the cleaning of the hull, usually only spot repairs of mechanical damages are necessary. At the end of September 2002, 230 vessels have been coated by this silicon polymer. The results after 61 months of application is shown in Figure 2.[146]

A silicone elastomer “Bioclean SPG, which was developed by Chugoku Marine Paints Co. Ltd. in Japan in 1985, over a period of 4 years up to 1993. It has been used for cooling water pipes for an electric generator as an antifouling paint.[148]

Although the cost of the silicone coating materials is not low, the application and removal costs are less than those of other systems.[133] This silicon coating is used mainly for circulation water pipes or aqueduct pipes for power plants, but recently, a large number of large high-speed vessels, military vessels, and nonferrous pleasure boats have used such coating materials,[22,133]

6.2. Electrical Antifouling Systems

Electric current has been used as antifouling systems. These systems consist of two types of antifouling systems. One is an electrical disinfection system.[149−153] The surface of marine bacterial cells are usually negatively charged. Therefore, a positive electrode draws the cells on its surface and is able to kill them by electric current at a low electric potential of around 1−1.5 V. The prevention of bacterial cell accumulation on the surface of the electrode for a long time can be performed by applying alternating potentials. This electrical control system does not generate chlorine or change pH by seawater electrolysis[152] as the other electrical system because seawater electrolysis needs higher electrical potential as described below.

Marine bacteria were killed electrochemically by applying a potential of 1.2 V [versus saturated calomel electrode (SCE)] using a conductive coating and a TiN film electrode. Most of cells on the electrode were desorbed within 30 min by applying a potential of −0.6 V versus Ag/AgCl. The prevention of bacterial cell accumulation can be performed by applying alternating potentials. Therefore, the electrochemical control of bacterial cell accumulation for a long time was achieved by applying an alternating potential of 1.2 and −0.6 V.[151]

This alternating potential of 1.2 and −0.6 V was applied to a fishing net made from nylon yarn, and the surface of the nylon yarn was coated with an electroconductive paint approximately 50 μm thick, which was used as a working electrode. The counter electrode was an iron bar. The Ag/AgCl electrode was used as a reference electrode. An alternating voltage of 1.2 V vs Ag/AgCl for 60 min and −0.6 V vs Ag/AgCl for 10 min was applied to the electrode for an experimental period of 158 days from July to December 1995. No increase of weight by attachment of biofouling organisms to the net was observed.[153] The electroconductive polymer consists of a urethane resin and graphite particles. This antifouling preventive system would be an environmental friendly system. Use of this system in the pipes of a power plant over one year prevented marine fouling.[152] Many patents on these electrical disinfection systems have been published.[154−160]

Other electrical systems are electrolytic antifouling systems.[161−163] Seawater contains about 35 g/kg of salts with Cl^- and Na^+, accounting for about 86% of the salts. The major electrolytic reaction in seawater (a weak alkaline aqueous solution at pH 8) is as follows:

Anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{4}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{5}$$

$$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^- \tag{6}$$

Cathode:

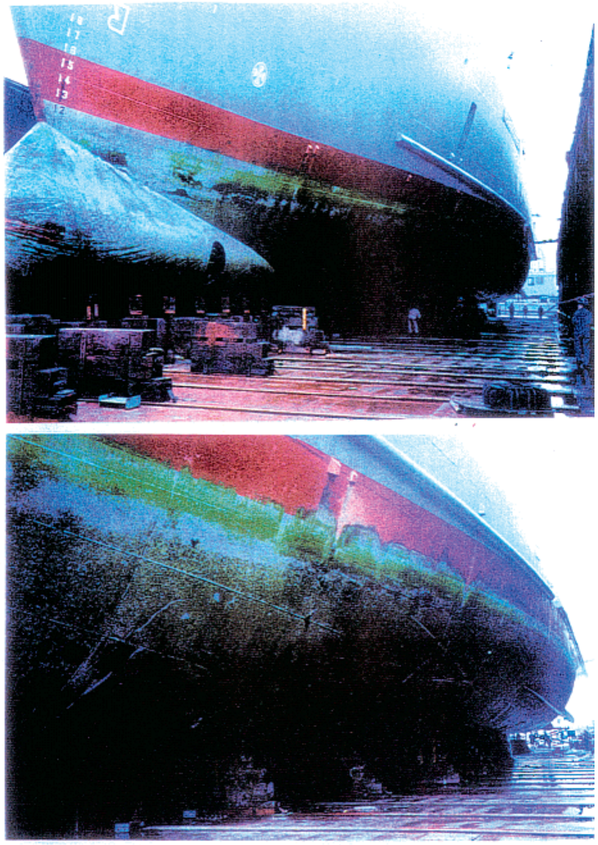
$$2H_2O + 2e^- \rightarrow OH^- + H_2 \tag{7}$$

At an anode, chlorine, hypochlorite, and oxygen are generated, and at a cathode, hydrogen is generated,

Table 10. Antifouling Agents of Natural Products[98,113,129]

compound	living things	activity unit	ref
nicotinamide **122**	*Mallotus japonicus*	313	113, 129
kampferol glycoside **115**	*Quercus dentata*	227	113, 129
polydatin coumarate **116**	*Eucalyptus rubida*	185	113
raponticin coumarate**134**	*Eucalyptus resinifera*	179	113
isocyanosesquiterpene alcohol **100**	*Phyllidia pustulosa*	ca. 100	98

Before washing with water



After washing with water

Figure 2. An American ro-ro ship (2,563 ton, 15 knot) coated with the silicone elastomer antifouling paints "Intersleek". Before and after simply washed with water after 61 months voyage.[146]

chlorine, and hypochlorite show biocidal activities. In a weak alkaline solution, the chlorine changes to sodium hypochlorite, as shown in eq 8:

$$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O \quad (8)$$

Hence, two electrochemical equivalents generate one hypochlorite ion. The minimum electrolysis decomposition voltage is 1.766 V. The theoretical electrical power that generates 1 ton of chlorine is 1320 kWh.[161]

The electroconductive coatings utilizing the seawater electrolysis resist fouling by substances generated by the electrolysis reactions. The hull is first coated with an insulating material, and then coated with electrocondutive coatings containing metals such as copper powder. The conductive layer as the cathode is charged with electricity by making a part of the hull the anode. Hypochlorite ions and chlorine are generated by the electrolysis of seawater with a very small amount of electric current on the surface of the electroconductive layer. The transmission of electric current of 0.3 $A/m^3/h$ prevents sticking of marine organisms. The hypochlorite ion together with chlorine acts as a fungicide. The hypochlorite ion is easily decomposed by ultraviolet light in seawater to form chloride ions. Hence, this system does not cause the environmental problems. The consumption of electricity is only 100 W h for 40−100 ton ships. These systems have been investigated for an application to small ships or aqueduct pipes for the power plants.[161,162]

Other antifouling systems without using biocidal agents, such as ultrasonic waves[164] and laser irradiation[165] have been investigated, however these systems have many problems for applications for large vessels.

7. Conclusions

Copper compounds and organic booster biocides blended in self-polishing copolymers have been used as tin-free antifouling paints since the regulation to prohibit the use of organotin antifouling paints was enforced at the end of 1980s. Usually, Irgarol 1051, and Diuron have been the most commonly used as an organic booster biocide because they are the most cost-effective. However, these antifoulants and their degradation products are more stable than the other biocides; therefore, such antifoulants have the potential to cause environmental problems due to increasing concentrations. High concentrations have been found in many marinas. Therefore, safer and better organic booster biocides should be selected as soon as possible before new serious environmental problems are found.

The better organic booster biocides are required to have higher biocidal activities, shorter half-life in seawater, and higher cost-effectiveness than those of the Irgarol 1051 and Diuron, and above all, their degradation products should be environmentally safe.

Furthermore, it should be encourage to investigate and develop natural products, silicone fouling-release coatings and electrical coatings as environmentally friendly antifouling coatings.

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