NATURAL BIOCIDES IN ANTIFOULING PAINTS

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ABSTRACT

Since the 1970's Tributyl tin based antifouling (AF) paints were widely used to control fouling on ships hulls. These coatings offered up to 5 years of foul-free hulls and were the most effective antifouling paints ever produced. However, due to serious environmental effects, these paints have been banned since 2008 and have been replaced by copper based antifouling paints with some success. However, the extensive use of copper based antifouling paints has led to the accumulation of copper and its compounds in the marine environment particularly in the vicinity of ports and harbors and is beginning to pose a serious environmental problem. Restrictions on the use of copper based AF paints have been initiated by many western countries and it is expected that these restrictions would only grow in the years to come. In addition, these coatings are usually incorporated with "booster biocides" such as Diuron, Irgarol, Seanine, etc to improve their efficacy. The booster biocides also significantly contribute to the existing environmental concerns. The search is therefore on for a "benign AF product" that affects target organisms only and exhibits low persistence in the aquatic environment. A few natural produces fill in to these requirements. In the Indian context, Neem and Karanjin exhibit biocidal properties which could be tapped as effective AF agents. This paper reviews the various natural products that show promise as AF agents and explores the possibility of incorporating these products in AF paint formulation.

INTRODUCTION

Marine fouling is an unwanted growth of biological organisms on a surface immersed in water. Vessel bottoms not protected by anti-fouling systems may gather 150 kg of fouling per square metre in less than six months of being at sea. On a Very Large Crude Carrier with 40,000 square metre underwater areas, this would add up to 6,000 tonnes of fouling. Deleterious effects of biofouling cause Increase in fuel consumption, reduction in vessels speed, increase in green house gases, accelerated corrosion and propagation of invasive species. These biological organisms introduced accidently or Intentionally into an spread rampantly due to the lack of natural predators in different ports become leading threats to biodiversity. They impose enormous cost to fisheries, agriculture, forestry and human health.

Different strategies have been used for control of fouling but use of antifouling paints is the most widely used technique . These paints have been broadly categorized into biocidal and non-biocidal coatings. The biocidal coatings release a biocide or a combination of biocides at the substrate water interface under controlled conditions .There are very few biocides that have effective antifouling properties and at the same time have an acceptable environmental risk. In the recent past, organotin (in particular TBT) based antifouling paints were widely used by the shipping industry.

ENVIRONMENTAL EFFECT OF TRIBUTYL TIN

As a biocide in anti-fouling paints, Tributyl Tin (TBT) proved extremely effective at keeping smooth and clean the hulls of ships and boats. And when it was introduced into anti-fouling paints, it was considered less harmful than biocides used in anti-fouling systems at the time: such as DDT and arsenic. But, Extensive use in antifouling paints on ships led to the widespread distribution of TBT and its breakdown products MBT(mono-butyl tin) and DBT(di-butyl tin) in the global marine and freshwater environment, in water, sediment and biota (wildlife species) [1][2][3][4][5][6][7]. TBT has been found in marine sediments in Antarctica. The persistence of some organotin compounds means that they remain in sediments, particularly anoxic (without oxygen) sediments, for long periods of time e.g. the half-life of TBT in deep sediment has been estimated to be approximately 87+/-17 years[8]. “Hot spots” of particularly high levels of TBT in water, sediment and biota are normally associated with commercial ports, harbours, shipyards, shipping lanes, marinas and the like [9].

The damaging environmental effects of organotins released from antifoulant paints first came to light in the late1970’s and early-mid 1980’s, with two regional case histories in particular demonstrating the extent of the impacts – the collapse of oyster fisheries in Arcachon Bay, France and the phenomenon of “imposex” (the development of male sexual characteristics) in female marine snails from UK coastal waters, which led to widespread population decline[10]. Around the same time, following earlier observations of the appearance of a penis in female dogwhelks *Nucella lapillus* from Plymouth Sound, UK (which increased in prevalence with proximity to the harbour) research revealed imposex in *N.lapillus* occurring widely throughout the coastal waters of the southern UK . This phenomenon was linked with exposure to high levels of TBT in coastal waters and is due to the androgenic properties of TBT i.e. TBT acts like a male hormone.

The harmful environmental effects of organotin compounds were recognized by IMO in 1989. In 1990 IMO’s Marine Environment Protection Committee (MEPC) adopted a resolution which recommended that Governments adopt measures to eliminate the use of anti-fouling paint containing TBT on non-aluminium hulled vessels of less than 25 metres in length and eliminate the use of anti-fouling paints with a leaching rate of more than four microgrammes of TBT per day.

ENVIRONMENTAL EFFECT OF COPPER

The copper impregnated coatings are designed to slowly release copper, in the dissolved and most toxic form, so as to retard growth and maintain a smooth underwater surface.

Copper is a micro-nutrient that live organisms need in small doses. Higher animals like fish can regulate the content of copper in their organism and, to some extent, they can accumulate copper in the liver but not in the mussels. It has been seen that copper is very toxic with effect concentrations from only a few micrograms of copper per litre. Copper has been shown to be toxic to aquatic organisms, to accumulate in filter feeders, such as mussels and to damage larval stages of aquatic invertebrates and fish species. Dissolved copper in excess of 3.1 µg/l, is reported to be toxic to mussels, oysters, sea urchins and crustaceans [11] and it affects phytoplankton communities. Dissolved copper has been measured as high as 29.0 µg/l in Newport Bay and as high as 8.0 µg/l in San Diego Bay, according to Total Maximum Daily Load(TMDL) assessments by the USEPA (2002) and the California Regional Water Quality Control Board (CRWQCB), San Diego Region (2003).

Harbour sediments are typically anoxic and have a high content of sulfides which will bind copper. Therefore, copper is expected to be relatively strongly sequestrated in harbour sediments.

USE AS A BOOSTER BIOCIDE IN ANTIFOULING PRODUCTS

In addition to TriButyl Tin and Copper, various booster biocides have been incorporated in antifouling paints. The purpose of these compounds is to enhance the products' efficacy against a broader spectrum of fouling organisms than that achieved with copper alone. 'Booster biocides' are either organic or organo-metallic compounds which have fungicidal, herbicidal or anti-microbial actions.

Zinc pyrithione is the BSI name for Bis[1-Hydroxy-2(1H)-pyridinethionato-o,s]-T-4 zinc (IUPAC). A number of studies have been reviewed in respect of the toxicity of zinc pyrithione and two of its metabolites - pyridine sulfonic acid and pyrithione sulfonic acid to freshwater and marine aquatic organisms. The studies showed that zinc pyrithione was toxic to aquatic organisms, however the toxicity of the two metabolites was far less than that of the parent compound - often by several orders of magnitude.

Irgarol 1051(2-methylthio-4-ter.butylamino-t-cyclopropylamino-t-cyclopropylamino-striazine) was developed in recent years for use as an algaecide.
Its biochemical mode of action is by inhibition of photosynthetic electron capture transporting chloroplast.It is hydrophobic compound and is detected in sediments. Recent studies have shown that levels of Irgarol 1051 and its major degradation products'M1'&'M3'(N,N-Di-Ter-Butyl-6-methylthiol-S-triazine-2-4 diamine)are relatively stable and may pose considerable risk to primary producer community in coastal marine environment. It does not exhibit high toxicity to fish and crustacean species but exhibits extremely high toxicity to plant species.
Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a substituted urea derivative and it also inhibits electron flow in photosynthesis It is relatively persistent in sea water and considerably stable to sunlight radiation and hydrolysis. It is also found to be present in sediments[12].

Sea Nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) is highly effective against slime forming marine bacteria such as Pseudomonas Atlantica and Pseudomonas Nautica and has broad spectrum activity against marine fouling algae, Enteromorpha sp. And barnacles such as Balanus Amphitrite. When Sea Nine 211 is added to Cuprous oxide, an excellent performance against entire range of fouling organisms has been achieved. The active ingredient of Sea Nine 211 remains chemically stable at different type of coating system such as contact leaching, soluble matrix, polishing and non-stick coatings. Once it is released into environment, it rapidly bio degrades with half-life of less than one hour. Sea-nine antifoulant is an environmentally acceptable alternative to organotin antifoulants.

The antifouling properties of various known biocides are summarized in Table 1 below.

Table 1

Sl No	Known antifoulig compound	Bactericidal	Insecticidal/pesticidal	Fungicidal	Antialgal	Activity against brine shrimp	Activity against cyprid larvae	Activity against daphnia magna
1	tributyltin chloride [13,14]	Y	Y	Y	- [22,23]	Artemia franciscana Y	Y	Y
2	zinc pyrethione	Y	Y	Y	-	Artemia	Y	Y

	[15]					selina. Y		
3	Irgarol 1051 [16]	Y	herbicide-Y	-	low	Y(A. Selina)	Y	Y
4	sea-nine 211 [17]	Y	_	_	_	_	Y- moderate to strong	_
5	Zineb [18]	Y	Y	Y	Y	_	Y	Y
6	Medetomidine [19]	_	_	_	_	_	Y	_
7	Tolyfluanid [20]	Y	_	Y	_	_	Y	Y
8	Thiram [21]		Y	Y	_	_	Y	Y
9	Chlorothalonil [22]	Y	Y	Y	Y		_	Y
10	Cu Pyrethione [23]	Y	Y	Y	Y	Y Artemia franciscana	Y	_
11	dichlofluanid(N-dichlorofluoromethylthio-N0-dimethyl-N-phenylsulphamide) [24,25,26]	Y	Y	Y	Y	Y	Y	Y
12	TCMS(2,3,5,6-tetrachlora-4-methyl sulphonyl)pyridine[27]	Y	Y	Y	_	_	Y	Y
13	ziram [28]	Y	Y	Y	Y	_	Y	Y
14	Maneb [29,30,31]	Y	Y	Y	Y	Y	Y	Y
15	Captan [32]	Y	Y	Y	Y	_	_	_

Note : Y indicates Yes.

NATURAL PRODUCT ANTIFOULANTS(NPA)

Environmental concerns about the long–term effects of leachable antifouling biocides have led to increased interest in the development of environmental friendly alternatives. Research activities are centered on biodegradable toxic compounds, non-toxic adhesion inhibitors, electro-chemical systems and cleaning devices.

Today extensive research is going on natural antifoulants. All organisms, benthic and pelagic, must maintain a foul free hull. The rationale is reflected in the types of organisms that have been investigated for the elucidation of their antifouling mechanisms. Antifouling strategies of sessile organisms have been subject of several research projects [33][11].

The usual approach adopted has been to extract the tissues using solvents and subsequently employ bioassays to assess the antifouling potential of the extracts. The first groups of organisms to be investigated were corals and sponges which were known to maintain a foul-free surface. Red algae extracts have been found to contain halogenated furanones which show biocidal activity comparable to,and sometimes better than that observed with commercial biocides. . Natural antifoulants have been proposed as one of the best replacement options for the most successful antifouling agent, tri-n-butyl tin(TBT). The NPAs are advantageous over conventional toxic biocides in that they are less toxic, effective at low concentrations, biodegradable, have broad spectrum antifouling activity and their effects are reversible. The natural product antifoulants in 10 kinds of compounds of terpenes, acetylenes, polycyclic compounds, steroids, phenols, isothiocyanates, nitrogen containing compounds, glycerol derivatives, higher fatty acids, and enzymes is reported. Various NPAs have been tested for potential industrial applications including halogenated furanones, triterpinoids. Data has been collected on many natural products which seem promising as a natural antifoulant as they show bactericidal/insecticidal/pesticidal properties. Many of the antifoulants are also found in terrestrial plants.

POTENTIAL ANTIFOULING AGENTS

Search is on for natural biocides which will affect target organisms only and exhibits low persistence in the aquatic environment.

Macroalgae:Marine macroalgae have developed chemical cues to deter settlement of organisms involved in biofoulin [34]. The localization and surface quantification of these antifouling compounds has been studied to understand their ecological roles and the chemical defence strategies of seaweeds[35][36].

Screenings of crude extracts of whole organisms offer one route to identify putative natural product antifoulants if used in a bioassay –guided purification strategy.Most research on purifying natural product antifoulants has been carried on Rhodophyta species and to a lesser extent on Phaeophyta.

Sponges:They are among the oldest groups of multi-cellular animals and more than 10000 species have been described[37].

A significant number of sponge metabolites have been shown to exhibit a wide array of bioactivities including antitumour/cytotoxic,enzyme inhibitory,receptor antagonist,antiviral and antifungal [38].

Pure compounds and extracts with antifouling properties have been obtained from sponges.
Cnidarians: Corals communities are known to be rich sources of natural products that are often implicated in allelochemical interactions.These biologically active compounds have different functions according to the types of natural pressures that coral encounter, e.g.,antimicrobial and antifungal activities and the feeding detererrence [39].
Among the pure compounds tested, it is of interest to note that none of them showed any antimicrobial activity, despite the fact that numerous crude extracts inhibited the growth of bacteria and microalgae.

The potential of some of these natural products to be effectively utilized as antifouling biocides is summarized in Table 2.It gives us information about some natural extracts which may have potential for antifouling.

Table 2

S.No	Parts	bactericidal	insecticidal/ pesticidal	fungicidal	antialgal	some additional information
A.	**Compounds of Pongmia Pinnata**					
1	Karanjin	Y	Y	Y-moderate	acaricide	major flavones of seeds associated with non-glyceride portion of oil and have bitter taste,highly toxic to fishes
2	Pongapin	-	Y-	-	-	-
3	Pongamol	moderate	Y-	-	_	safe to human beings
4	Pongaglabrone	Y	-	-	-	
5	Lanccolatin-B	-	-	-	-	-
6	2-methoxy furanoflavone	-	-	-	-	-
7	pongol	-	-	-	-	-
8	Karanjachromene	-	-	-	-	-
9	Isolonchocarpin	-	-	-	-	-
10	Isopongaflavone	-	-	-	-	-
11	Glabrin	-	-	-	-	-
12	Glabrachalcone	-	-	-	-	-
B.	**Compounds of neem(Äzadirachta indica)**					
1	Azadirachtin (triterpenoid)	Y	Y	Y	-	-
2	nimbidin	Y		y	-	-
3	Nimbin	Y	Y - moderate antifeedent activity	y		It's a triterpenoid(limono ids)
4	Gedunin	-	-	Y	-	-
5	14-Epoxy Azaradion	-	-	-	-	-
6	Diacetyl salanin	-	-	-	-	-
7	Salannol acetate	-	-	-	-	-

8	Salannol	-	-	-	-	-
9	Salannin	-	Y - moderate antifeedent activity	-	-	It's a triterpenoid
10	Mellantriol	-	Y -in v.low conc.show antifeedent activity	-	-	-
C.	**Cashew shell oil (non-isoprenoid phenolic lipids)**					
1	Anacardic acids	3-unsat.side chain showed activity against bacteria (Streptococcus mutans)	provides resistance to pest insects	-	-	-
2	Cardol	-	-	-	-	Cardol is a resorcinol derivative havg a long unsat.hydrocarbon chain.It is a naturally occuring substituted phenol whic h can take part in a variety of reactions.It is a cheap and renewable subs and can be employd for manufacture of many usefl industrial products .
3	cardanol	-	-	-	-	-
D.	**Walsura Piscidia**					
1	Piscidinol	-	Y	-	-	It’s a tetracyclic triterpenoid(C30H 50O4)

CONCLUSIONS

Metallic antifouling coatings are of serious environmental concern. Since the banning of TBT based AF coatings, copper is widely used in AF formulations. However, there is growing evidence that copper released from these coatings is highly detrimental to the marine environment. Natural antifoulants have been proposed as one of the best replacement options for the metallic based AF coatings due to the fact that that they are less toxic, effective at low concentrations, biodegradable, have broad spectrum antifouling activity and their effects are reversible. Several of these products have been identified for the Indian context. High priority must therefore be given to bring these NPA to the shipping industry.

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