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# Need of Natural Biocides in Antifouling Paints for Prevention of Marine Pollution

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***Abstract:***
*Antifouling paints were developed to prevent marine growth on ship hulls in the middle of the 19th century. As they were designed to continuously leach biocides at the paint/seawater interface which were the predominant means of controlling fouling for a vast majority of the vessels, over a period of years in the latter part of the last century there has been a marked improvement in the effective life of antifouling paints.*

*Different types of antifouling paints came into being but after a particular breakthrough when self- polishing paints were developed in 1960s. Due to its controlled leaching rate, the self -polishing paints containing TBT was a huge success.*

*However, due to serious environmental effects, these paints have been banned since 2008 and have been replaced by copper based antifouling paints with some success. It was observed that 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. Foul release coatings are biocide-free –works on a foul release basis by providing a very smooth, low-friction surface which reduce the strength of adhesion of fouling. However, they are applicable only to high- speed, high-activity vessels, in addition to other issues such as high cost, difficult, application procedure and are easily prone to mechanical damage. Biocides from natural products appear to be the only viable alternative in the foreseeable future to protect ship hulls from fouling. This paper reviews the possible natural products that have the potential to be incorporated in to commercial antifouling paints and explores their range of activity.*

## 1. Introduction

Paint coatings or other coatings that tend to prevent or inhibit the growth of marine organisms on submerged surfaces can be broadly categorized into biocidal and non-biocidal coatings. As the name suggests, biocidal coatings release a biocide or a combination of biocides at the substrate water interface under controlled conditions. There are very few biocides that are 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. These paints were highly cost effective and efficient way to control fouling and offered up to five years of foul free hulls. However, organotins have been described as the most harmful substance introduced in to the marine ecological system and the International Maritime organization (IMO) placed a worldwide prohibition of organotin-bearing coatings on ocean-going vessels, requiring they be phased out by 2008. Copper based antifoulant coatings soon replaced TBT-based coatings following the worldwide controls on organotin (IMO 2002). In addition, to improve the effectiveness of copper based coatings a number of additional biocides also called as “booster biocides” which include cuprous thiocyanate, chlorothalonil, diuron, dichloro-octyl isothiazolin, thiram, zinc oxide, zinc and copper pyrithione, zineb, sea nine, irgarol etc all of which have varying degrees of environmental risks.

## 2. Environmental Effects of Copper

The primary advantage of using copper as an antifouling agent is that it is a naturally occurring element. Natural concentrations of copper are typically between 0.03 and 0.23 µg/L for surface seawater. In small quantities, copper is an essential micronutrient taken up by plants and animals through different mechanism. Many studies have shown that, in large quantities, copper in the aquatic environment could be harmful to a wide variety of marine organisms (Abbasi *et al,* 1995; Anderson *et al*, 1991; Carreau and Pyle 2005; Katranitsas *et al*, 2003; Negri and Heyward 2001). 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. When exposed to dissolved copper at concentrations from 3.0 to 10.0 ppb, these species showed reduced or abnormal embryo growth, development, spawning, and survival (Calabrese et al., 1984; Coglianese and Martin, 1981; Gould et al., 1988; Lee and Xu, 1984; Lussier et al., 1985; MacDonald et al., 1988; Martin et al., 1981; Stromgren and Nielsen, 1991).

In California, dissolved copper as high as 29 µg/l has been observed at Newport bay and as high as San Diego bay in California (USEPA 2002). It is estimated that 95 percent of this copper comes from pleasure craft antifouling paints due to leaching.

In Denmark, copper mean copper concentrations of 13 µg/L were observed in the pleasure craft harbour of Marselisborg (Jensen and Heslop 1997). Similar high copper concentrations were observed in the skerries of Stockholm (Bard, 1997). These elevated copper levels were observed in the proximity of pleasure craft harbours and pleasure craft traffic. Alarmingly high copper concentrations were also observed in aquatic plants. Measurements of copper performed by the French in the Arcachon bay showed an increase in copper content in oysters (Claisse and Alzieu 1993).

As a result of alarmingly high copper levels, the United States, (particularly the states of California and Washington), Sweden, Denmark, Netherlands and few other countries have begun to restrict the use of copper based antifouling paints (Swedish Chemicals Inspectorate, 2006; Danish Environmental Protection Agency, Ministry of the Environment, 2003; Netherlands Ministry of Housing, Spatial Planning, and the Environment, 2004; College Toelating Bestrijdingsmiddelen, 2004). It is likely that in the near future, many other countries would also follow suit and restrict these types of coatings. Therefore in the present scenario, alternatives for copper and tin appear to be biocides that have the following characteristics

i. The coatings must be non-toxic
ii. The biocide concentration must be such that it is effective as an antifouling agent and yet their concentrations in the aquatic environment must be such that it is not toxic to non-target organismns
iii. They must exhibit low persistence in the marine environment.

## 3. Foul Release Coatings

In the recent past non-toxic antifouling paints such as “Foul-release” coatings are being increasingly available in the market. This works on a foul release basis by providing a very smooth, low-friction surface which reduce the strength of adhesion of fouling. Minimum adhesion has been found to correlate with lowest value of elastic modulus tested although this did not correspond to lowest surface energy tested .These coatings are generally silicone or flouropolymer and provide “non-stick” surfaces. Those aquatic organisms that remain adhered to the hull during the voyage of the vessel could be easily washed away during dry-docking. In addition foul-release coatings provide smooth hulls that tends to reduce the drag and thereby the fuel consumption. However, there are many disadvantages of these coatings, that include high cost of paint, difficult application procedure, low mechanical strength and applicability to high-speed and high activity vessels. The most serious disadvantage of these coatings is that there is a high possibility that marine species that adhere to the vessel at a particular location could be released at different spot where it could translocate an alien species and thus turn out to be a vector for the transmigration of invasive species which is now considered a serious environmental concern.

In view of the above environmental concerns, the best alternative appears to be biocides from natural products or Natural Product Antifoulants (NPA).

## 4. Natural Product Antifoulants (NPA)

Natural antifoulants have been proposed as one of the best replacement options for the most successful antifouling agent Tri-Butyl Tin (TBT) .Research on NPAs is going on since last two decades.

Today, the search for new antifouling substances shares many of the features experienced by the pharmaceutical industry .For example , scientific knowledge in biology, development of a control release system, production costs and how to prove the product safe for the end consumer, independent of man or nature. 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 aquatic fouling organisms in seawater such as corals, sponges, marine plants, 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. Many of the antifoulants are also found in terrestrial plants. 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.

In Table 1, Potential natural product antifoulants are listed based on published literature.

| | Source | Active Ingredient | Reference |
|---|---|---|---|
| 1 | Pongamia Pinnata (karanja oil) | Karanja oil, Furan, o-flavones, pongapin, kanjone and pongaglabrin | Meher *et al (2004)* |
| 2 | Leea Indica(Burm.f.)Merr. Flowers | Essential oils(esters of phthalic acid,Di-isobutylphalate(>75%),di-n-butylphthalate(>7%)n-butylisobutylphthalate(>6%),butylisohexylphthalate(>3.5%).Monobutyl carbonotrithioate | Srinivasan *et al* (2004 |
| 3 | Pongamia glabra | polyesteramide | Sharif *et al* *(2004)* |
| 4 | Pongamia pinnata | Karanjin,a furano-flavonoid | Vismaya *et al* *(2010)* |
| 5 | Pongamia | triglycerides, flavanoids, pongamia and karanjin | John De Britto and P.Peter Baskaran (2010) |
| 6 | Pongamia Pinnata | alkaloids demethoxy-kanugin,gamatay, glabrin, glabrosaponin, kaempferol, kankone,<br>kanugin, **karangin**, neoglabrin, pinnatin, pongamol, pongapin, quercitin, saponin, β-sitosterol and tannin | Savita *et al* *(2010)* |
| 7 | Dysdercus koenigii Fab. (Hemiptera :Pyrrhocoridae) | anonin (1 %),karanjin (2 %), achook (0.15%), econeem (1%) andimidacloprid (17.8 %) | M.H. Kodandaram *et al* *(2008)* |
| 9 | Pongamia<br>glabra, azadirachta indica and Chrysanthemum cinerariifolium | azadirachtin (10 –25%) ,<br>Active ingredient :esters Pyrethin I and II,cinerin Iand II,Jasmolin I and II insect growth. | Roman Pavela *et al* *(2009)* |
| 10 | Pongamia pinnata | pongamol | Md. Abdullahil Baki *et al* *(2007)* |
| 11 | Cladiella krempfi, Sinularia kavarattiensis and Subergorgia reticulata | (l'E,5’E)-2-(2',6'-dimethylocta- l',5',7'-trienyl)-4-furoic acid 1, (-)-6-α-hydroxy polyanthellin A 2, (+)-(7R,10S)-2-methoxy calamenene 3, (+)-(7R,10S)-2,5-dimethoxy calamenene 4 and (+)-(7R,10S)-2-methoxy,5- acetoxy calamenene 5). | T.V. Raveendran *et al* *(2011)* |
| 12 | Distaplia nathensis (Chordata) | Crude extract of Distaplia nathensis | A.Murugan&M.Santhana Ramasamy *(2003)* |
| 13 | Helicoverpa armigeraHub. head polypeptides | Azadirachtin, tetranortriterpenoid | N. K. Neoliya *et al* *(2007)* |
| 14 | Lobophora variegata | lobophorolide | kubanek *et al* *(2003)* |
| 15 | French marine seaweeds | Organic extracts of the marine seaweeds | Vonthron-Senecheau *et al* 2011 |
| 16 | Ralfsia verrucosa, Petalonia fascia and Scytosiphon lomentaria (Phaeophyceae, Scytosiphonales) | Methanol and ethanol extracts of the algaes | Thabard *et al* *(2009)* |
| 17 | Capsaicin | Alkaloid capsaicin(N-Vanillylamide of trans-8-methyl-6-nonenoic acid)$(CH_2)_4CH=CHCHMe_2$ | G.Ya.Legin *et al* *(1996)* |
| 18 | Marine cyanobacterium Lyngbya majuscula | Dolastatin 16, hantupeptin C, majusculamide A, and isomalyngamide A | Bi Lik Tong Tan *et al* *(1996)* |

Table 1 Continue….

| | | | |
|---|---|---|---|
| 19 | Marine algae | Fatty acids, lipopeptides, amides, alkaloids, terpenoids, lactones, pyrroles and steroids | Bhaduri P,Wright PC(2004) |
| 20 | Canistrocarpus cervicornis,Richardo Rogers,Valeria Laneuville Teixeira and Renato Crespo Pereira | Antifoulant diterpenes | Bianco *et al* *(2009)* |
| 21 | Haliclona koremella | ceramide N-docosanoyl-d-erythro-(2S,3R)-16-methyl-heptadecasphing-4(E)-enine (C22 ceramide) | Hattori *et al* *(1998)* |
| 22 | Mediterranean Seagrass Posidonia oceanica (L.) Delile | Aqueous and lipid extracts from the rhizomes of Mediterranean sea grass | P. Bernard and D. Pesando *(1989)* |
| 23 | Palauan Sponge, Haliclona sp. | hexapeptide, waiakeamide ,<br>and a new sulfone derivative | Dahms *et al* *(2003)* |
| 24 | Haliclona | new peptides, Haliclonamides C, D, and E. | Yutaka *et al* *(2002)* |
| 25 | Phyllogorgia dilatata Esper(octocorollia,Goroniidae) | diterpene 11β,12β-Epoxypukalide | Mora *et al* *(2006)* |
| 26 | Chili pepper | capsaicin ,zosteric acid | XuQ *et al* *(2005)* |
| 27 | dictyota sp.(brown algae) | cyclic diterpenes and a carotenoid | Armstrong *et al* *(2005)* |
| 28 | Mediterranean Brown Alga Dictyota sp. | Diterpenoids | Camps et al *(2009)* |
| 29 | Red Alga Sphaerococcus coronopifolius | Terpenes | Veronica et al *(2000)* |
| 30 | marine sponge Acanthella cavernosa | Terpenoids | Hirotaa et al *(1996)* |
| 31 | Andrographis paniculata | Terpenoids | Sarala et al *(2011)* |
| 32 | Root of Ceriops tagal | Diterpenoid | Chen et al *(2011)* |
| 33 | Azadirachta indica | Nortriterpenes | Nicoletti et al *(2010)* |
| 34 | Azadirachta indica | azadirachtin | G K Karnavar *(1987)* |
| 35 | Azadirachta indica | Neem Triterpenoids | Rob J. Aerts and A. Jennifer Mordue (Luntz) *(1997)* |
| 36 | Azadirachta indica | azadirachtin | Mondal et al *(2007)* |
| 38 | mediterranean sponge Reniera Sarai(Pulitzer-Finali) | 3-alkylpyridinium salts (poly-APS) | Fainali et al *(2003)* |
| 39 | Pongamia glabra | Triterpenes, flavonoids | Nirmal et al *(2007)* |
| 40 | Pongamia pinnata | pongamol and karanjin | Tamrakar et al *(2008)* |
| 41 | Pseudognaphalium robustum | Flavonoid | Cotoras et al *(2011)* |
| 42 | Pongamia glabra | Isopongaglabol and 6-methoxy isopongaglabol | Talapatra et al *(1982)* |
| 43 | Azadirachta indica | azadirachtin | A. Mordue *(2004)* |
| 44 | Azadirachta indica | 2',3'dehydrosalannol,nimbolide,salanin & azadiradione | S Gunasekaran and B.Anita*(2010)* |
| 45 | Anacardium Occidentale | cashew nut shell liquid or (CNSL)-Anacardic acid | Asogwa et al *(2007)* |
| 46 | Azadirachta indica | Azadiracthin | Xie et al *(1995)* |
| 47 | Pongamia pinnata | 70% ethanol extract of Pongamia pinnata leaves | Srinivasan et al *(2003)* |
| 48 | Pongamia pinnata | Karanjin | Akanksha et al *(2011)* |
| 49 | Azadirachta indica | azadirachtin | Schaaf et al *(2000)* |
| 50 | Azadirachta indica | azadirachtin | Wana et al *(1997)* |

*Table 1*

From above table, we can see that most of the active ingredient are terpenoids, flavonoids, polyphenolic ,halogenated polyketides compounds.

### *4.1. Potential Antifouling Agents Available Locally*

Some of the natural products that have potential for being used as a biocide and have not been fully investigated are listed below

#### 4.1.1. Pongamia Pinnata (Karanj) Seed Oil

Pongamia Pinnata (Karanj) is widely spread all over tropical Asia, Australia, India and locally distributed throughout the state of Maharashtra ( India) along the bank of rivers, very common near sea coast in tidal and beach forests in Konkan, along Deccan rivers. Mature seeds of Karanja have recently gained a great commercial relevance owing to their high oil content, which is used as an alternate source of fuel and energy .It has a rare property of producing seeds of 25-40% lipid content of which nearly half is oleic acid. Oleic acid is found in various animal and vegetable fats.

Pongamia Pinnata (Karanj) seed oil contains karanjin , a bioactive molecule with important biological attributes

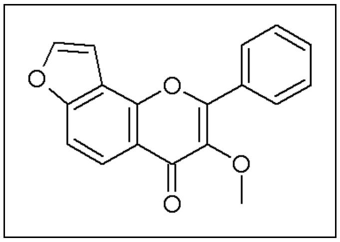

*Figure 1: Karanjin*

Antibacterial activity of this oil was demonstrated against Bacillus, E.Coli, Pseudomonas,Salmonella, Staphylococcus and Xanthomonas.

#### 4.1.2. Azadirachta Indica (Neem)

The Neem tree (Azadirachta indica) of the family Meliaceae is native to India and Myanmar but now found throughout the Indian subcontinent. Products of the neem tree have a wide variety of uses including the provision of medicines, pesticides, fuel wood, timber and food .Neem based insecticides have been developed for pest management applications in agriculture, horticulture and forestry in Thailand and many countries (Ascher, 1993, Tran and Perry, 2003; Schulte et al., 2006). Commercial neem-based biopesticides such as Margosan-O®, Neemix®, Bioneem®, and Azatin-EC® are available globally under a varied registration status .

The primary active ingredient of the neem tree is azadirachtin A which is the biologically active limonoid of the tetranortriterpenoid type extracted from seeds of the neem tree (Azadirachta indica) with many reactive functional groups in close proximity to each other

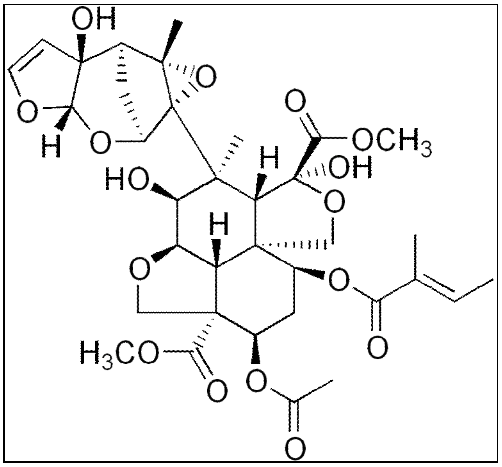

*Figure 2: Azadirachtin molecule*

The $LD_{50}$ value of Azadirachtin is found more than 5000mg/kg both in male and female rats if a single oral dose of Azadirachtin(5000mg/kg)was given to male and female rats.(Raizada et al 2001)

### 4.1.3. Cashewnut Shell Oil

Cashew nut shell oil contains anacardic acid which acts as repellent to pest insects. It is traditionally used by fishermen to protect the hulls of country boats and is claimed to have antifouling properties

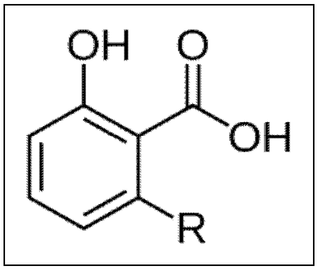

*Figure 3: Anacardic acid*

Cashew nut shell oil contains anacardic acid which acts as repellent to pest insects. Work is being done to determine antifouling property for these terrestrial natural products.

## 5. Conclusions

Utilization of metallic based biocidal antifouling coatings is becoming a serious environmental issue due to their high persistence in the marine environment and their toxicity to non-target aquatic organisms. Restrictions are beginning to appear on the use of these coatings in many countries and there could be even more restrictions in the near future. Foul-release or non-stick coatings have as yet a limited applicability and are potential vectors for the transmigration of invasive species. Therefore, the best alternative for antifouling coatings appears to be natural product antifoulants and a number of potential such products have been identified. However, before they could be commercialized there are a number of areas that have to be addresses which include availability in sufficient quantities, standardization, durability, cost, etc. If these issues could be resolved, a severe environmental pressure would be relieved and would contribute significantly to the sustainable growth of the shipping industry.

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