Appendix 3C

Literature Review on the Characteristics and Potential Environmental Impacts of Non-TBT Antifouling Paints

Literature Review of TBT Free Antifouling Paints

1. Introduction

Tributyltin (TBT), which is an organotin compound based antifouling paint, has been widely used since the mid 1960s. TBT paint is an effective antifouling coating on the ship hull for preventing the marine growth, such as barnacles algae, tubeworms, hydroids and sponges. Consequently, vessels' friction and drag in the water is decreased and thus lower energy consumption is achieved. However, it was then in late 1970s proven that organotin compounds are harmful substances to aquatic environment. It was found that organotin compounds persist in water and in sediments, killing sealife other than that attached to the ship hulls and possibly entering the food chain. Specifically, TBT was shown to cause shell deformations in oysters; sex changes (imposex) in whelks; and immune response, neurotoxic and genetic affects in other marine species [1].

International Maritime Organization (IMO) in 1990s adopted an assembly resolution that called on the Marine Environmental Protection Committee (MEPC) to develop an instrument, legally binding throughout the world, to address the harmful effects of antifouling systems used on ships. The resolution called for a global prohibition on the application of organotin compounds which act as biocides in antifouling systems on ships by 1 January 2003, and a complete prohibition by 1 January 2008 [1].

As a result, alternatives of the TBT based antifouling systems have been developing and TBT free antifouling paints are widely used due to the international ban of TBT paints. This is a literature review to identify the TBT free paints commonly used on the market, their characteristics and potential impacts arising from ship servicing activities. This includes the review of a total of twelve commonly used antifouling products from five international paint suppliers.

2. Alternatives of TBT Antifouling Systems

Alternative antifouling system include TBT or tin free biocidal antifouling paints, biocide free antifouling coating, paints or coatings using natural biocide, cleaning, electricity and prickly coating [1,2,3,4]. They are briefly described as below.

<u>*TBT or Tin free biocidal antifouling paints*</u>
Biocides other than TBT are used to replace TBT in the paint formulation of this type of antifouling paint. Some common biocides and cobiocides/booster biocides found in the biocidal antifouling paints include copper (I) oxide/cuprous oxide/dicopper oxide, zinc pyrithione, SeaNine 211, Irgarol 1051, diuron, dichlofluanid, chlorothalonil, Zineb.

Before the introduction of TBT antifouling paint, copper and its compounds (e.g. cuprous oxide) were the effective antifouling agents. Due to the inability of the coatings to release constant concentrations of biocide from the copper based paint surface for extended periods of time, TBT copolymers with self-polishing mechanism, which can overcame this difficulty, replaced the conventional copper based antifouling agents. New classes of copper-based antifouling paints, which have the similar chemical properties and behavior to the TBT self-polishing polymers, have been developed and they entered the market in recent years. However, the new copper based paint does not release sufficient biocide [3]. Moreover, certain fouling organisms are resistant to copper-based antifouling agents [5]. In order to improve the efficacy of the copper-based antifouling paint, booster biocides such as Irgarol 1051, SeaNine 211, diuron are incorporated into the paint formulations [2,3].

Biocide free antifouling coating
To avoid any leaching of biocides into the sea, several paint companies have developed antifouling coatings that contain no active ingredients of biocides. Two types of biocide free antifouling coating are commonly found in the market. One is the non-stick coating and the other is fibre coating [1,2,3].

These coatings have extremely slippery surfaces preventing fouling occurring. The surface characteristics also minimize the strength of adhesion of fouling organisms and, ideally, any attached growth will be dislodged as the vessel moves through the water. The most successful non-stick coatings have been formulated using silicone polymers. The silicones have an unattractively low surface energy for most fouling organisms. These coatings have been found to perform effectively as non-stick coating and to generally remain free of macrofouling on vessels operating at speeds in excess of 15 knots [1,2,3,4].

Fibre coatings consist of short fibre applied in a dense pattern which deters settlement of fouling organisms. When the coating is submerged into water, fibres are moved by current, thus providing a spiny surface which is permanently in motion [2,4].

Natural biocide
Paint or coating contains natural substances as the biocide to prevent fouling or hinder fouling process. Although natural antifoulants have been the subject of research for more than 10 years, research on the use of natural compounds is in early stages and the development of naturally-based coatings is in its infancy. Some products have been developed to provide short-term effectiveness, but none have approached the exact requirements for large vessels [1,3].

Cleaning
This method is to carry out periodic cleaning of the ship hull. However, this method is only suitable for the ships in areas where few organisms attach to hull [1].

Electricity
Creating a difference in electrical charge between the hull and seawater unleashes chemical process which prevents fouling. This technology shown to be more effective than tin free paint in preventing fouling but this system is easily damaged and expensive. This also increases corrosion risk and higher energy consumption [1,6].

Prickly Coating
This includes coatings with microscopic prickles. The effectiveness of prickly coating depends on length and distribution of prickles, but has been shown to prevent attachment of barnacles and algae with no harm to environment. However, prickles could increase water resistance of vessel [1].

There are a number of alternatives of antifouling systems, however, only TBT or Tin free biocidal antifouling paints, biocide free antifouling coating and natural biocide are the technologies of paint based antifouling systems.

3. TBT Free Antifouling Paints Commonly Used on the Market

On the international market for antifouling systems many products were sold in large quantities for commercial use. There are approximately 10 international paint manufacturers currently existing [2]. In Hong Kong, Yiu Lian Dockyard uses paints mainly from the suppliers of Hempel, Jotun, International, Chugoku, Sigma, which are also the major paint suppliers internationally for the commercial ocean going vessels. More than 90% of the ocean going vessels (local or international) coated with paints from these paint suppliers.

As discussed before, TBT free antifouling paints available for replacing TBT paints on the market are TBT free biocidal antifouling paint and biocide free coating. Antifouling paints using natural biocides have also been developing, however research on the use of natural compounds is still in early stages and the development of naturally-based coatings is in its infancy.

Based on the information from *"IMO Anti-Fouling Convention: TBT Alternatives"* [4], TBT free biocidal antifouling paints are available from the aforesaid suppliers on the world market. However, silicones based non-stick coatings are only available from Hempel, Chugoku and International. Fibre coating is only available from one supplier named Sealcoat.

Most of the paint companies offer biocidal products for both recreational and commercial vessels. A variety of companies are active in the production and sale of biocide free antifouling products [2]. Large companies such as Hempel, Chugoku, International and Sigma usually offer several biocidal products along with one or two biocide free products.

Efficacy of the antifouling products is one of the most important factors for choosing suitable antifouling coatings by the ship owners. Since there is no standardized testing of biocide free products for their efficacy, ship owners would then not choose the use of biocide free products. In Germany, 99% of the antifouling products in use are biocidal products [2].

"The Status of the Treaty to Ban TBT in Marine Antifouling Paints and Alternatives" [7] lists out representative products of alternatives to TBT paints due to the ban on the use of TBT antifouling paints. TBT free biocidal antifouling paints are mainly supplied by Chugoku, Hempel, International, Jotun and Sigma. Several products of TBT free biocidal paint are supplied by each of the said suppliers. However, only one biocide free antifouling product is supplied by each of the suppliers. The number of the biocide free products as listed is much lesser than that of the TBT free biocidal paints. Moreover, some of the listed biocide free products are under development. UK Marine SACs Project [5] also indicates that silicon-based paints are less effective and they are being undergone further development.

A total of twelve antifouling paints manufactured by Hempel, Sigma, International, Jotun and Chugoku were reviewed. Paints reviewed include Antifouling Seaguardian, Antifouling SeaQueen, Antifouling Oceanic 84950, Antifouling Classic 76540, Sea Grandprix 500, Seatender 10, TFA 10, TFA Flat, Alphagen 20 series, Sigma Ecofleet 290, I/Speed 340 Tocoat and Intersmooth 460. All of these antifouling paints contain various biocides and booster biocides.

From the above, it is noted that TBT free biocidal antifouling paint and biocide free coatings are available on the market. However, only TBT free biocidal antifouling paints are commonly used on the market currently.

4. Characteristics of the TBT Free Biocidal Antifouling Paints

Like TBT antifouling paints, TBT free biocidal antifouling paints can be subdivided into two main categories:

1 "Conventional" or free association paints which is indicative of a lack of chemical binding between the paint matrix and the biocide(s):

2 Self-polishing coatings (SPCs) in which at least a part of the main biocide is chemically bound to the paint matrix.

4.1 Free association paints [2,4,6]

In free association paints, the biocide is physically dispersed and subsequently released from the paint matrix. There is no chemical binding between paint matrix and biocide. When the paint surface is immersed, seawater penetrates the paint film and interacts with the biocide, thus dissolving it and allowing its migration from the paint layer to the water via diffusion. There are three types of free association paints including soluble matrix, insoluble matrix and eroding/ablative.

The soluble matrix consists of a binder mixture of gum rosin and plasticizers or synthetic polymers in which biocides are dispersed. Rosin slowly dissolves in seawater. When the coating is immersed in seawater the biocide leaches out of the paint. In sufficient concentration this will repel, kill or impair the microscopic larvae and spores of multicellular sessile organisms before they attach to the paint surface and develop into larger adult organisms such as algae and barnacles. As the binder dissolves fresh biocide is continuously released, the rate of binder dissolution is a critical aspect for efficacy of this type of antifouling paint. Soluble matrix paints typically take on an exponential leaching rate of biocide. If binder dissolution is too slow, the coating will not provide sufficient biocidal protection; if too fast, the biocide reservoir will be too rapidly exhausted, limiting the effective life of the coating. Biocide releasing rate is high initially but after some time release rate would decrease and finally too slow to prevent fouling. The effective life of this type of paint is generally short, approximately 12 to 18 months. This type of paint is usually used on pleasure boats and for marine and fresh waster with copper as the most important active ingredient.

The insoluble matrix type free association paints have the same characteristics as the soluble matrix type, except the binding mixture of the matrix does not dissolve in water. Moreover, this type of paint needs to be removed before next application.

Eroding/ablative paints are the most advanced types of soluble matrix paints. It has the same leaching characteristics as the soluble and insoluble matrix types, except that it erodes by hydrolysis. This increases emission due to the shorter diffusion path. Seawater-soluble binders and polymeric ingredients are incorporated physically to control the dissolution rate. In theory the paint matrix and the biocides are washed or "polished" away fully over time when in contact with seawater, however, because of impurities and accumulation of various inert molecules, in practice there is usually a development of a leached layer. This leached layer reduces the effectiveness of the paint by inhibiting biocide release and for this reason eroding/ablative paints are usually limited to a life span of 36 months. This type of paint is usually used on fast racing motor boats and racing sailing boats; and for marine and fresh waster with copper as the most important active ingredient.

4.2 Self-Polishing Coatings (SPCs) [2,6]

For the past few decades, SPC technology with copolymer-bound TBT was the leading antifouling type. Roughly, 70-80% of the world fleet of deep-sea going ships were coated with TBT-SPCs. Ten years ago Japanese companies succeeded in replacing TBT with copper or zinc, and created the first TBT-free self-polishing paints. The self-polishing technology using chemically bound copper or zinc as primary biocides is now available in a variety of products.

As in TBT SPC, TBT free SPC are based on a copolymer binder. The copolymer hydrolyzes in seawater at a constant linear rate thus releasing the biocides. The binder then becomes water soluble as soon as enough of the copolymer has been hydrolyzed.

Biocide based copolymers have a unique mechanism to prevent antifouling. Because the biocide is chemically bonded to the polymer backbone, a controlled and slow chemical reaction with the seawater at the paint surface occurs and guarantees a constant but very low release rate. In the majority of products, copper is covalently bonded to the matrix. This type of paint can be used in all kind of boats.

Some of the antifouling systems use a binder that is composed of synthetic rosin resonates and different polymer co-binder systems. The synthetic rosin resonates, obtained through a hydrogenation and distillation process, eliminate impurities and double bonds. This new synthetic compound has all the benefits of natural rosin, but none of the weaknesses. It has also been reacted into zinc carboxylate binder, which during immersion in seawater undergoes a chemical ion-exchange process to form a more soluble sodium carboxylate binder.

In some paints the binder technology is used with the addition of micro-fibres. The incorporation of micro-fibres into antifouling paints provides mechanical reinforcement to the paint film and allows greater amounts of functional binder to be added to achieve full variation in the polishing rate. TBT free SPC generally can achieve life times of 36 to 60 months.

4.3 Biocides in the TBT Free Biocidal Antifouling Paints

Copper and its compound (e.g. cuprous oxide) are commonly used as the biocide in the TBT free antifouling paints. Since certain fouling organisms (e.g. Enteromorpha and Amphora) are resistant to copper based paints [5,8], booster biocides such as Irgarol 1051, SeaNine 211, Diuron are incorporated into the antifouling paints formulations. Table 1 lists some of the common biocides and booster biocides contained in the antifouling paints and their properties as extracted from various studies or literatures [2,8,9,10].

Biocide (Common name or trade name)	Chemical name	Degradability/Persistence	Toxicity to fish	Toxicity to algae	Bioaccumulation	R-phrases for aquatic environment[3]
Cuprous oxide	Copper (I) Oxide	Not biodegradable, but chelatable and/or immobilizable	10 – 10,200µg/l (Cu^{2+})	10 – 8,000µg/l (Cu^{2+})	BCF/seawater: 75-27,000/algae 10,000-20,000/macrophytes 7,000-10,000/crustacean	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Cuprous thiocyanate	Copper (I) Thiocyanate	Not biodegradable, but chelatable and/or immobilizable	10 – 10,200µg/l (Cu^{2+})	10 – 8,000µg/l (Cu^{2+})	BCF/seawater: 75-27,000/algae 10,000-20,000/macrophytes 7,000-10,000/crustacean	R52 - Harmful to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Zinc pyrithione	Zinc-2-pyridinethiol-N-oxide	Rapidly primary degradation Photolysis half life < 1hr Biodegradation 4hr	n.a.	n.a.	Considering Log P_{ow} of 0.97, a bioaccumulation potential lower than that of the other biocides can be expected	n.a.
SeaNine 211	4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one	Microcosm studies half-life ranges from 1-hr to a few days	Acute: 2 – 1,300µg/l Chronic: 0.6 – 15µg/l	n.a.	Cause for concern[2]	R50 - Very toxic to aquatic organisms
Irgarol 1051	N-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine	Not readily biodegradable[1]; photolysis half life = 273d	96hr LC_{50} for Zebra fish = 400µg/l; 96hr LC_{50} for Bluebell sunfish = 2,900µg/l	72hr EC_{50} = 1.4 – 2.4µg/l	BCF around 200 for fish; cause of concern[2]	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Diuron	3-(3,4-Dichlorophenyl)-1,1-dimethyl urea	Limited photolysis; not biodegradable[1]	96hr LC_{50} for Bluegill sunfish = 8.5 - 25µg/l	96hr EC_{50} = 0.04 – 0.12µg/l	Unlikely to significant, BCF <100	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Dichlofluanid	N-Dichlorofluoromethylthio-N',N'-dimethyl-N-phenyl-sulfamide	Not biodegradable[1]	Bluegill sunfish = 0.03µg/l	EC_{50} = 16mg/l	Cause for concern[2]	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Chlorothalonil	Tetrachloroisophthalonitrile	High persistence[1]	10µg/l	2mg/l	n.a.	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment
Zineb	Zinc ethylenebis-(dithiocarbamate)	n.a.	n.a.	n.a.	Indication of risk potential[2]	R50 - Very toxic to aquatic organisms R53 - May cause long-term adverse effects in the aquatic environment

Notes:

1. Overall persistence categories resulting from the combination of the criteria: (a) primary degradation, (b) mineralization, and (c) bound residues [2].

2. Bioaccumulation overall assessment, derived from the combined criteria (a) bioconcentration factor BCF, and (b) elimination (or depuration, expressed as half-life clearance time CT50) [2].
3. R-phrases (risk phrases) as assigned by the European Economic Community (EEC) which first created a List of Dangerous Substances in 1967, classifying substances according to health hazards; or referred to CEPE (European Council of the Paint, Printing Ink and Artists' Colours Industry) hazard classification.

Table 1 Common Biocides and Their Properties

In UK, almost all the registered antifouling products under the UK Health & Safety Executive are copper based [11]. Only some of the registered TBT based antifouling paints does not contain copper or its compounds. Federal Environmental Protection Agency of Germany and European Commission [2,12] carried out comprehensive surveys on the registered antifouling products in some countries including Australia, New Zealand, Canada, United States and UK. Again, almost all the TBT free antifouling paints contain copper or its compound. Moreover, it is found that cuprous oxide is the most common active ingredient contained in the copper based antifouling paints. In Netherlands, all the admitted antifouling products also contain copper or its compounds. Over 80% of the products use cuprous oxide as one of the active ingredients [12]. In United States, copper based biocides became the primary antifouling coating option for recreational boats as the use of TBT based paints was phased out in the late 1980's since USEPA restricted the use of TBT based antifoulants. Cuprous oxide has been formulated by 11 manufacturers into 157 marine antifouling products that are registered for sale in California [13]. Moreover, all twelve reviewed antifouling products contained cuprous oxide.

European Commission [12] summarised the concentrations of some common biocides in some antifouling products. It is found that the concentrations range from 10-25%w/w to 50-100%w/w for cuprous oxide, 5-10%w/w to 10-25%w/w for copper thiocyanate, 1-2.5%w/w to 2.5-10%w/w for diuron, 0-2.5%w/w to 0-50%w/w for Irgarol 1051, 2-10%w/w to 10-25%w/w for zinc pyrithione and 1.35%w/w to 1.53%w/w for dichlofluanid in the antifouling products.

In view of the twelve antifouling products reviewed, all of them contain cuprous oxide and its concentrations range from 10-25%w/w to 40-50%w/w. For the antifouling paints registered for sale in California, cuprous oxide concentrations range from 26 to 76%, most paints are in the 40-70% range. Typical cuprous oxide marine antifouling paints in California contain 36-62% copper by weight [13]. These indicate that cuprous oxide not only is the most common biocide contained in the antifouling paints, and also the primary biocide and major component in the antifouling products. Other biocides or booster biocides contained in the antifouling paints are only in trace amount.

4.4 Other Major Ingredients in the Antifouling Paints

From the twelve reviewed antifouling products, it is found that other ingredients with more than 10%w/w commonly found containing in the paints is Xylene. Zinc oxide is other chemicals commonly found in the antifouling products. All the antifouling paints reviewed contain Xylene. The concentrations of Xylene range from 0-2.5%w/w to 20-30%w/w and 11 out of 12 antifouling paints contain Xylene with the concentration above 10%w/w. 9 out of 12 antifouling paints contain zinc oxide. The concentrations of zinc oxide range from 1-10%w/w to 10-25%w/w and 3 antifouling paints contain zinc oxide with the concentration above 10%w/w.

5. Characteristics and Properties of Antifouling Biocides

5.1 Copper

There are a number of potential environmental impacts that may occur from using copper antifouling paints. Copper present in the water and sediments can be accumulated by benthic animals causing, for example, reduced respiration rates and impaired growth in mussels, clams and other shellfish. Table 1 also shows that copper based biocides have the highest toxicity and bioaccumulation potential among the other common biocides. The toxicity and accumulation of copper vary greatly depending on concentration levels, exposure, temperature and salinity, the presence of other metals and the type, size and age of the marine organism. It is therefore difficult to generalize about the toxicity of copper to marine organisms, there is evidence that certain species of fish are sensitive to quite low levels of copper even though other species are tolerant of much higher levels. Benthic marine organisms are thought to be slightly more sensitive to copper than fish, although some species demonstrate a capacity able to adapt to elevated levels [5].

Guidelines for Managing Water Quality Impacts within UK European Marine Sites [8] indicates that the potential effects of the copper in the marine environmental include acute toxicity to invertebrates, and to a lesser extent fish, at concentration of dissolved copper above the environmental quality standard (EQS) of 5μg/L (annual average). Accumulation in sediments can pose a hazard at concentrations above 18.7mg/kg according to Canadian interim marine sediment quality guidelines; and bioaccumulation in organisms poses a potential hazard to marine organisms.

Although it is well known that copper is toxic to marine organisms, Batley [14] indicates that despite the replacement of TBT with antifoulants based on copper in association with common pesticides since the banning of TBT, oysters are no longer affected and oyster copper levels are in compliance. It also indicates that copper/pesticide formulations continue to be widely used, however, no adverse environmental consequences have been reported. Both IMO [1] and Greenpeace [17] also point out that copper is much less harmful than TBT.

5.2 Toxicity of Booster Biocides to Aquatic Environmental

European Commission [9,15] had carried out an assessment on some of the booster biocides including Irgarol 1051, Diuron, SeaNine 211, Chorothalonil, Dichlofluanid and zinc pyrithione. Toxicity of all six substances to phytoplankton communities and toxicity of three of the substances to periphyton were tested. With the already available data of the remaining substances, the EC_{50} values for all these substances established are shown in Table 2.

Biocides	EC_{50} Phytoplankton	EC_{50} Periphyton
Irgarol 1051	2-3nM	4.7-5.5nM
Diuron	9-12nM	15-23nM
SeaNine 211	25-28nM	200-800nM
Chorothalonil	76-187nM	6,203-17,579nM
Dichlofluanid	23-36nM	1.4-734nM
Zinc pyrithione	9-30nM	37-84nM

Table 2 EC_{50} Values for the Selected Substances

Toxic effects of antifouling biocides including TBT, SeaNine, Diuron, Irgarol 1051, chlorothalonil, dichlofluanid and TCMTB on Vibrio fischeri (luminescent bacterium), Daphnia magna (microalga) and Selenastrum capricornotum (microscopic crustacean) have also been evaluated by *Fernandez-Alba et al* [16]. Results indicate that the sensitivity of the organisms towards the antifoulants in most cases in descending order is S.capricornotum > D.magna > V.fischeri. TBT and SeaNine 211 are the most toxic to the organisms. TBT and SeaNine 211 have similar toxic effects on the organisms tested. However, the half-life of SeaNine 211 is much lower than that of TBT and this reduces the bioaccumulation potential of SeaNine 211. Chlorothalonil, dichlofluanid and TCMTB show toxic effects on non-target organisms.

An ecotoxicological assessment of antifouling biocides has been conducted by Danish Environmental Protection Agency [18]. The assessment indicates that SeaNine 211 and zinc pyrithione are very toxic for marine organisms. However, both types of biocides rapidly breakdown into substances that are much less toxic than that of the original substances. The assessment also shows that the risk coefficient for SeaNine 211 and zinc pyrithione is higher than 1 in a marina with many pleasure boats but lower than 1 outside the marina area. This indicates that there is probably a risk of chronic effects on animals and plants in the marina area but there is only a low risk of these substances having an impact on animals and plants outside the marina area.

Within the Eorupean Commision's Assessment of Antifouling Agents in Coastal Environments (ACE) project [9,14], endocrine disruption was also assessed. None of the assessed antifoulants, Irgarol 1051, Diuron, SeaNine 211, Chorothalonil, Dichlofluanid and zinc pyrithione, showed a strong estrogenic response. Diuron, dichlofluanid and Irgarol 1051 were, however, shown to have a limited anti-estrogenic potency although levels in the marine environment. They are generally 1000 times less than the levels that may cause such an anti-estrogenic response in in-vitro systems. Experiences undertaken in ACE project show that endocrine disruption is not a problem with the antifouling booster biocides.

5.3 Leaching Rates of Biocides in Antifouling Paints

Biocides in antifouling paints may enter the marine environment through leaching. The emission of biocides in antifouling products from ships is normally determined using the leaching and the total antifouled underwater area [6]. The amount of biocide released to the biosphere is a first indicator of a potential damage [10]. The leaching rate of antifouling agent is a critical parameter in an environmental risk assessment. An accurate biocide release rate value is essential. There has been much debate over experimentally derived release rate data. ACE project has reported the leaching rates for a number of antifouling agents using ISO laboratory test and field simulated flume systems. Table 3 summarizes the results [9]. It can be seen that cuprous oxide has the highest leaching rate, more than 5 times of the other booster biocide.

Biocide	**Leaching Rate (μg/cm²/day)**	
	ISO Test System	**Flume System**
Cuprous oxide	25-40	18.6±6.5
Irgarol 1051	5.0	2.6
Diuron	3.3	0.8
Dichlofluanid	0.6	1.7
Zinc Pyrithione	3.3	n.a.
SeaNine 211	2.9	3.0

Table 3 Leaching Rates of Antifouling Agents

5.4 Environmental Fate and Bioaccumulation of the Biocides in Aquatic Environment

Apart from the toxicity and leaching rate of the biocides, environmental fate and bioaccumulation are the other factors of concern for the impact or risk imposed on the aquatic environment.

Chemical, photolytic and biological degradation of biocides was assessed under experimental and semi-field conditions. Irgarol 1051 and diuron were found to be comparatively resistant to degradation whereas the half-life of SeaNine 211 was found to be in the order of approximately two to nine days [15]. Information on the degradability/persistency of other common biocides is shown in Table 1.

Bioaccumulation, describing bioconcentration from the surrounding media as well as biomagnification along the food chain, reflects the internal exposure of biota in relation to a given external exposure. As most ecotoxicological effects conceptually depend on internal exposure, bioaccumulation is a further indicator of a potential environmental damage [10]. Bioconcentration factor (BCF) is commonly used to express the affinity of a chemical substance to organisms for describing the bioaccumulation of a chemical substance. Some BCF values are shown in Table 1. It is found that cuprous oxide has the highest bioaccumulation accumulation potential among the other biocides or booster biocides.

5.5 Environmental Risk of Antifouling Biocides

Ranke [10] used five indicators including releasing rate, bioaccumulation, spatiotemporal range, biological activity and remaining uncertainty to carry out the risk evaluation of some biocides including copper and its compound, Irgarol 1051, SeaNine 211 and zinc pyrithione. The releasing rate and bioaccumulation have been discussed before. The spatiotemporal range was determined by a combination of the expected equilibrium distribution and the persistence in water and sediment. The main parameter for biological activity evaluation was aquatic NOEC (No-observed-effect concentration) values. The evaluation results show that copper and its compounds have the highest releasing rate; copper and its compounds, SeaNine 211 and Irgarol 1051 have high bioaccumulation potential; copper and its compounds, SeaNine 211 and zinc pyrithione have high spatiotemporal range and biological activity. However, the remaining uncertainty for zinc pyrithione is the highest. Copper and its compounds impose highest risk to the environmental as compared with Irgarol 1051, SeaNine 211 and zinc pyrithione.

6 Other Ingredients in the Antifouling Products

From the reviewed twelve antifouling products, zinc oxide and xylene are two ingredients in addition to the biocides and booster biocides commonly found in the paint formulation, and are further discussed in the following.

6.1 Zinc Oxide

Zinc oxide is the industrially most important zinc compound. It is used variously including in paints. Zinc is insoluble in water but reacts readily with non-oxidising acids, forming zinc (II) and releasing hydrogen. Zinc ions found in aquatic environments are in the (II) oxidation state. It is rarely encountered as the free zinc (II) ion due to its strong tendency to form complexes with inorganic and organic compounds freely available in nature. Zinc oxide is practically insoluble in water [19]. According to the EEC dangerous substances classification, zinc oxide is classified with R-phrases

R50 and R53, very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

Zinc is likely to build up in fish and other organisms, but unlikely in plants. The toxicity of zinc in water is affected by water hardness and pH, with lower toxicity encountered in waters with higher water hardness and lower pH, and vice versa. Generally, zinc and its salts have high acute and chronic toxicity to aquatic life in polluted waters. Fish can accumulate zinc moderately [19].

Guidelines for Managing Water Quality Impacts within UK European Marine Sites [8] indicates that potential effects of zinc in marine environment include acute toxicity to algae, invertebrates and fish above the EQS of 40μg/L (annual average) for dissolved zinc. Accumulation in sediments and can pose a hazard to sediment-dwelling organisms at concentration above 124mg/kg according to Canadian interim marine sediment quality guidelines. Bioaccumulation in marine organisms poses a potential threat to fish, birds and sea mammals.

6.2 Xylenes

Xylene occurs in three isomers (o-, m- and p-) which vary in the site of attachment on the benzene ring of the two methyl groups. Xylenes are commonly used as solvent in paint manufacturing. Xylenes are flammable liquids and fire hazards. Xylenes are moderately soluble in water. When xylenes release into water, they quickly evaporate. It also has high chronic (long-term) toxicity to aquatic life. Xylene is expected to moderately bioaccumulate in fish [19].

Guidelines for Managing Water Quality Impacts within UK European Marine Sites [8] indicates that potential effect of xylenes in marine environment is toxic to invertebrates and fish at concentrations above EQS of 30μg/L (annual average) of total xylene.

However, xylenes are not classified with any environmental risk phrases under the EEC dangerous substances classification.

6.3 Ingredients which are Toxic or Harmful to Aquatic Environment

According to the safety data sheets of the twelve antifouling paints reviewed, some of the substances apart from the active ingredients (biocides or booster biocides) are found to be toxic or harmful to the aquatic environment according to the “risk phrases” (R-phrases) assigned by the EEC. The ingredients, their concentration ranges and assigned R-phrases in environmental dangerous are listed in Table 4. Most of the substances shown in Table 4 are in trace amount in the antifouling paints. Only solvent naphtha (light aromatic) has a relative higher concentration range in the paints. Although all of these substances are toxic to aquatic environment, the toxic effects due to these substances would be insignificant as they are only in trace amount.

Ingredient	Concentration Range	Risk Phrases	Remark
Solvent naphtha (light aromatic)	2.5-10%w/w to 10-25%w/w	R51- Toxic to aquatic organisms R53 – May cause long-term adverse effects in the aquatic environment	3 out of 12 antifouling paints contain solvent naphtha (light aromatic)
Solvent naphtha (heavy aromatic)	1-2%w/w	R51- Toxic to aquatic organisms R53 – May cause long-term adverse effects in the aquatic environment	Only 1 out of 12 antifouling paint contain solvent naphtha (heavy aromatic)
Solvent naphtha (petroleum), medium aliphatic (White spirit)	0.1-0.15%w/w to 0.15-0.2%w/w	R51- Toxic to aquatic organisms R53 – May cause long-term adverse effects in the aquatic environment	2 out of 12 antifouling paints contain white spirit
Tricresylphosphate	0.5-1%w/w to 1-2.5%w/w	R51- Toxic to aquatic organisms R53 – May cause long-term adverse effects in the aquatic environment	3 out of 12 antifouling paints contain tricresylphosphate
Bis (1-hydroxy-1h-pyridine-2-thionato-o,s) copper	1-2.5%w/w	R50 – Very toxic to aquatic organisms	Only 1 out of 12 antifouling paint contain Bis (1-hydroxy-1h-pyridine-2-thionato-o,s) copper
4-nonylphenol, branched	0-2.5%w/w	R50 – Very toxic to aquatic organisms R53 – May cause long-term adverse effects in the aquatic environment	Only 1 out of 12 antifouling paint contain 4-nonylphenol

Table 4 Ecotoxicity of the Ingredients other than Biocides

7 Impact due to the Release of Antifouling Agents during Ship Servicing Activities

Toxic antifouling biocides would have potential to release to the surrounding environment and causing impact on the environment during the ship servicing activities. Antifouling biocides may enter the marine environment through leaching. Only small portion enters marine environment during the removal of antifouling paint by water blasting [5,12]. However, the concentrated nature of the biocide in scrapings and cleaning residues may cause more of a localized environmental problem.

As indicated in Table 1 and discussed in the previous sections, most of the biocides are toxic to aquatic environment and may cause adverse effect to aquatic environment.

During the application of antifouling paint on ship hull, emissions of antifouling agents to air and surface water may occur. The routes of the antifouling agents releasing to air or water from painting activity are listed below [6]:

1. During mixing and stirring of the antifouling paint, spillage on a hard standing area within paint cells, docks or slipway, etc. may occur. Thus, spillage of antifouling paint may be flushed to water.
2. During painting, overspray may end up through the air into the water.

During drying, mainly solvents will evaporate. Due to low volatility it is unlikely that emission of antifouling agents would take place.

The amount of antifouling biocide emitting during painting is dependent on [6]:

- characteristics of the facility including the working practice and control measures to prevent emissions;
- characteristics of the active ingredients of the antifouling product and the matrix;
- application method (brush/roller or spraying);
- average hull surface of a ship that is to be painted; and
- amount of ships that is painted in a certain time period.

During the removal of antifouling on ship hull, emissions of antifouling agents to air and surface water may also occur [6]. High pressure water washing and abrasive blasting or hydroblasting will take place for the paint removal. During the high pressure water washing and hydroblasting, water with the antifouling biocides may enter into the water. During abrasive blasting, abrasives together with the antifouling biocides may travel via the air into the water due to wind blowing. Generally, wastewater generated from water washing and hydroblasting is often treated with filtration and separation. Spent abrasive is cleaned from dock bottom and handled as hazardous waste.

The amount of antifouling biocides emitting during paint removal is dependent on [6]:

- characteristics of the facility including the working practice and control measures to prevent emissions;
- regulation in force;
- age and type of the antifouling coating;
- removal methods (abrasive blasting or hydroblasting);
- average hull surface of a ship to be treated; and
- amount of ships that is treated in a certain time period.

By adopting proper environmental control measures and practices, release of antifouling biocides into the marine environmental would be minimized or avoided during ship servicing activities. Examples of such control measures and practices are listed below [20]:

During application of antifouling paint:

- Treating spillage with a suitable absorbent and disposed of as chemical or hazardous waste;
- Not performing paint spraying in high winds;
- Sheeting for preventing spray drift;

During removal of antifouling paint:

- Containing wash waters and segregating wash waters from non-contaminated flow;
- Treating the paint scrapings as the chemical or hazardous waste;
- Avoid washing residues into the sea.

As mentioned before, release of antifouling biocides due to the ship servicing activities is much less than leaching. In UK, the estimated quantities of copper releasing due to water blasting and leaching during ship navigation are 26,294kg/yr and 109,502kg/yr respectively [12]. Thus, the environmental impact of antifouling biocides leaching to the marine environment would be the key concern rather than through blasting during ship servicing.

8 International Legislative Control

Due to the persistence and ecotoxicity of the biocides and booster biocides contained in the antifouling products, legislative control on the import, sale and use of the antifouling product is enforced in different countries in order to minimize any potential impact from these substances to the environment.

Within European Union (EU) countries, the Biocidal Product Directive 98/8/EC is coming into effect. Although there is a debate on the criteria for classifying biocidal and non-biocidal products, according to the 2nd Review Regulation 44 antifouling biocides have been notified [2]. Directive 98/8/EC defines the biocides and biocidal products. All biocidal products must be labeled according to the EC-Guideline 1999/45/EC.

Generally, registration, approval or permit is required for the manufacturing, import, sale or use of antifouling products in many countries such as UK, Demark, Sweden, Finland, The Netherlands, Malta, Switzerland, United State, Canada, Australia and New Zealand. However, no restriction or registration is required for the antifouling products in China, India, Japan and South Korea. In Japan, although there is no registration procedure required, there is regulation for the control and restriction on the tin compounds in certain antifouling products. In South Korea, certification of non-TBT containing product is required to be provided by the paint companies [2].

In Canada, only the antifouling paints with a maximum daily copper releasing rate of 40μg/cm^2/day are acceptable for registration [21]. In Demark, import, sale and use of biocidal antifouling paint, for which the release of copper exceeds 200μg/cm^2 within the first 14 days and 350μg/cm^2 within the first 30 days counted from the application of registration, shall be prohibited on pleasure crafts of more than 200 kilograms used primarily in salt water. After 1 January 2006, Denmark will also prohibit the import, sale and use of biocidal antifouling paint on pleasure boats which would release substances of risk phase R53.

In Hong Kong, antifouling paints with the active ingredients concentrations above the permitted limits should be registered with AFCD. Only registered products may be distributed or used in Hong Kong. The permitted active ingredients, concentrations limits and formulations of the antifouling paints are listed in Table 5.

Common Name	Concentration Limit
Copper (I) oxide	65% w/w
Copper (I) oxide/Copper pyrithione	52% / 4% w/w 39% / 4.2% w/w
Copper (I) oxide/Dichlofluanid	45% / 3% w/w
Copper (I) oxide / 4,5-dichloro-2-n-octyl- 3(2H)-isothiazolone	40% / 2% w/w
Copper (I) oxide/Diuron	50% / 5% w/w
Copper (I) oxide/Irgarol 1051	50% / 5% w/w
Copper (I) oxide/Zinc pyrithione	48.19% / 4.29% w/w
Copper (I) oxide/Zineb	65% / 15% w/w
Copper (I) thiocyanate/Dichlofluanid	20% / 4% w/w
Copper (I) thiocyanate/Diuron	30% / 5% w/w
Copper (I) thiocyanate/Irgarol 1051	25% / 5% w/w
Copper (I) thiocyanate/Zinc pyrithione	21% / 5% w/w

Table 5 Permitted Active Ingredients, Concentration Limits and Formulations of Antifouling Paints in Hong Kong

9 Conclusion

Due to the international ban of TBT antifouling paint, TBT free antifouling paints have been developed and are now available on the international market. The most commonly and widely used TBT free antifouling paint is copper based antifouling paint. This type of paint commonly contains cuprous oxide as the primary biocide for the provision of antifouling function. Booster biocide(s) may also be contained in the antifouling paints to enhance the antifouling. Nowadays, biocide free antifouling coating is available on the market but not being commonly used. Antifouling fouling paints using natural biocides to serve as the antifouling function are still being developed.

Properties of the common biocides and booster biocides, including toxicity, leaching rate, bioaccumulation potential and environmental fate, have been reviewed. Most of the biocides or booster biocides commonly found in the antifouling paints are classified as EEC r-phrase of R50 – very toxic to aquatic environment. Copper and SeaNine 211 are found to be the most toxic. However, SeaNine 211 would rapidly breakdown into substances that are much less toxic than that of the original substances. Although copper and its compounds can impose highest risk to the environment as compared with those commonly used booster biocides, oysters are no longer affected by the copper based biocides. Both IMO and Greenpeace concluded that copper is less harmful than TBT.

Ingredients, which are toxic or harmful to aquatic environment, other than biocides or booster biocides, are also found in the antifouling paints but they are in trace amount. Potential impact from these substances would be insignificant.

Releasing TBT free antifouling paints into marine water during the ship servicing activities would pose potential impact on the aquatic organisms. However, proper environmental control measures and practices would reduce or even avoid releasing toxic antifouling substances into the marine environment during ship servicing activities. However the antifouling biocides leaching into marine environment during ship navigation would be the key environmental concern.

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