

# Evolution of Antifouling Paints

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**Abstract:** *Anti-fouling paints have been around us for decades. Ever since the discovery of Anti-fouling paints there has been a large development in the composition of the paint and its diverse effect on marine life. This project helps us study the history of anti-fouling paints, its evolution, reason for evolution, effect on marine life and also its future scope.*

**Keywords:** Antifouling Paints, Antifouling Systems, Biofouling, Marine life

## 1. Introduction

### 1.1.1 What are Anti-fouling Paints?

As defined by Wikipedia, Anti-fouling paint is a category of commercially available underwater hull paints (also known as bottom paints). It is a specialized category of coatings applied as the outer (outboard) layer to the hull of a ship or boat, to slow the growth and/or facilitate detachment of subaquatic organisms that attach to the hull and can affect a vessel's performance and durability. They also act as an anti-corrosive paint in many cases.

### 1.1.2 History

In the early ages of sail, sailing vessels suffered from the growth of weed and other aquatic organisms. During this period thin sheet of metals such as copper were nailed to the bottom of the ships in order to prevent marine growth. Marine growth affects the performance of a ship in many ways:

- The maximum speed of a ship decreases as its hull becomes fouled with marine growth.
- Fouling hampers a ship's ability to sail upwind.
- Some marine growth, such as shipworms, would bore into the hull causing severe damage over time.
- The ship may transport harmful marine organisms to other areas.

Hence in the early 19's, when one of the first anti-fouling paints were tested and were found to yield a fair result, ways of preventing hull damage due to marine growth revolutionized.

## 1.2 Anti-Fouling Explained

### 1.2.1 What is fouling?

Fouling is an unwanted growth of biological material - such as barnacles and algae - on a surface immersed in water.

### 1.2.2 How much fouling does an unprotected ship get?

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.

### 1.2.3 Why do ships need anti-fouling systems?

Just a small amount of fouling can lead to an increase of fuel consumption of up to 40%, and possibly as much as 50%, since the resistance to movement will be increased. A clean ship can sail faster and with less energy.

### 1.2.4 How do anti-fouling systems save a ship owner money?

An effective anti-fouling system can save a shipowner money in a number of ways:

- Direct fuel savings by keeping the hull free of fouling organisms;
- Extended dry-docking interval, when the anti-fouling system, provides several years of use;
- Increased vessel availability - since it does not have to spend so much time in dry dock.

### 1.2.5 What makes a good biocide in an antifouling system?

A good biocide for use in an anti-fouling system has the following characteristics:

- 1) Broad spectrum activity;
- 2) Low mammalian toxicity;
- 3) Low water solubility;
- 4) No bioaccumulation in the food chain;
- 5) Not persistent in the environment;
- 6) Compatible with paint raw materials;
- 7) Favorable price/performance.

## 2. Early Trends in Marine Paints

### 2.1 Development of Ant-fouling system

In the early days of sailing ships, lime and later arsenical and mercurial compounds and DDT1 were used to coat ships' hulls to act as anti-fouling systems. During the 1960s the chemicals industry developed efficacious and cost-effective anti-fouling paints using metallic compounds, in particular the organotin compound tributyltin (TBT). By the 1970s, most seagoing vessels had TBT painted on their hulls.

With the early organotin-based anti-fouling paints, the active ingredients were dispersed in the resinous matrix - the "paint" - from which they "leached" into the sea water, killing barnacles and other marine life that had attached to the ship. But the release rate for the biocide in these "free association" paints was uncontrolled and tended to be rapid initially, with

the effect wearing off in 18 to 24 months as the biocide leached out of the paint.

## 2.2 TBT- The Problem

TBT has been described as the most toxic substance ever deliberately introduced into the marine environment.<sup>3</sup> Used as a fungicide, bactericide, insecticide and wood preservative, it is known to be harmful to a range of aquatic organism, including microalgae, molluscs and crustaceans, fish and some invertebrates.

As a biocide in anti-fouling paint, it 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. As a biocide, TBT needed to be toxic to be effective in killing off the organisms that would attach to the ship's hull. The main problem was its persistence in the marine environment.

As TBT began to be widely used in anti-fouling paints, scientists began to find increasingly high concentrations of TBT in areas with high concentrations of boats and ships, such as marinas, ports and harbours. In the open seas and oceanic waters, TBT contamination was seen as less of a problem, although later studies showed evidence of TBT accumulation in fish and mammals.<sup>4</sup> Scientists first found evidence of TBT contamination in oysters. In Arcachon Bay, on the west coast of France.

TBT contamination from boats was linked in the 1970s to high mortalities of oyster larvae and such severe malformations of the shells of adults that they were unmarketable.

In south-west England, TBT poisoning was linked to the decline of the population of the dog whelk (*Nucella lapillus*) in the 1980s. Studies showed that female dogwhelks develop the condition known as imposex in response to TBT poisoning: females develop male sexual organs and the female can become sterile.

In the 1980s, high concentrations of TBT were reported in coastal areas around the world. <sup>6</sup> As a result, a number of countries introduced controls to limit the use of TBT in anti-fouling paint on small vessels. France prohibited the use of TBT-based paints on vessels less than 25 metres in length in 1982 and other countries followed suit, including Japan, which imposed strict regulations on the use of TBT in anti-fouling paints in 1990 and prohibited the production of such paints in 1997.

### 2.2.1 Developing International Regulation on TBT

The pollution problems caused by TBT in anti-fouling paints were first raised at IMO's Marine Environment Protection Committee (MEPC) in 1988, when the Paris Commission<sup>8</sup> requested IMO to consider the need for measures under relevant legal instruments to restrict the use of TBT compounds on seagoing vessels.

By this time there was unequivocal evidence worldwide that TBT and other organotin compounds were harmful to aquatic organisms - and several countries had already, individually or under regional agreements, adopted measures to reduce the harmful effects of the use of TBT based anti-fouling paints.

It was clear, however, that international measures to regulate the use of anti-fouling systems would need to be developed and in April 1990, the Third International Organotin Symposium held in Monaco recognized that the IMO was the appropriate body to do this.

### 2.2.3 Harmful Effect of TBT

For many years tributyltin (TBT) was the favoured biocide for use in antifouling paints, although it was usually used in conjunction with other biocides such as copper. However, it became evident in the 1980s that its continued use was causing severe damage to shellfish communities and, in particular, dog whelk populations. This resulted in the implementation, in 1987, of a Europe-wide ban on the use of TBT in antifouling paints on boats under 25 meters. Its use is still permitted on craft over this length and in certain industrial and agricultural applications.

Before the widespread use of TBT, antifouling paints were commonly based on copper. The ban on TBT resulted in a shift back to paints which contain copper as the main biocide. Copper is included in antifouling paints most commonly as cuprous oxide, but also as cuprous thiocyanate and metallic copper powder. One of the main drawbacks of the return to predominantly copper based antifouling paints is that the copolymer type of paint, which was initially developed for use with TBT, is not as effective when used with copper biocides alone. Other drawbacks include its incompatibility with aluminium hulled craft and the relatively subdued colours that can be produced.

However, it is widely felt that although the performance of copper biocides cannot approach that of TBT, they remain the most effective of the alternatives for the foreseeable future. To achieve as high a performance as possible from current antifouling products, a 'booster' biocide is normally used as copper is not fully effective against all fouling species.

Pressure for a complete ban of the use of TBT in antifouling paints has been increasing with evidence that it is bio-accumulating in food chains, with particularly high levels being found in marine mammals (Iwata *et al* 1995). The reported effects of TBT in marine mammals include suppression of the immune system. Marine mammals (porpoise and grey seals) stranded along the coasts of England and Wales have been shown to be contaminated with low levels of butyl tin compounds. Whilst the levels of these tin compounds are lower than some of those reported for small cetaceans from other areas, such as Japan, the USA and the Adriatic Sea, further study is required of possible toxic effects of these compounds and the risk their accumulation poses to marine mammals in the UK (Law *et al* 1998).

It is recognised the IMO ban will need to be gradually introduced and its success depends upon the development of effective substitute paints. Paint manufacturers have been researching and developing alternative paints for some years, with varying degrees of success. At present copper antifouling paints present the best practical environmental option for a TBT alternative available to the marine industry. Phasing out TBT would be undermined if other paints were found to be more detrimental to the environment. The International Chamber of Shipping has stated that the antifouling coatings industry "seems to be seeing a way through the problem" (ENDS Report 1998), although they have warned that a full-scale switch would be at significant cost to the maritime industry. The IMO urges member states to encourage the use of alternative antifouling paint systems, pending the mandatory ban, and to set a timetable for the phasing out of TBT.

There is currently a great deal of research into alternative forms of biocides, particularly those of organic origin. These, however, tend to be less universally effective than other biocides and, in particular, may deter only specific types of fouling organism. As a result of these 'species-specific' characteristics, such biocides will almost always be used with other biocides, including copper. The organic biocides are also very expensive to develop and register. They are therefore usually developed and registered in other industries first, such as the agrochemicals industry, for use in other applications. Furthermore, although they are from organic sources there is no assumption that they are inherently less environmentally harmful than any other biocides.

Teflon based antifouling paint is also available, and has been used on racing yachts for a number of years. It is particularly suitable for racing due to its low friction surface, although it is not considered a particularly effective antifouling coating when used without a biocide. There has been some research into the use of silicon but this is at a fairly early stage and as silicon is rather soft it is not an easy material with which to work.

Antifouling paints utilising some form of copper biocide account for over 95% of the total antifouling market in the UK (personal communications) and this market share is likely to persist for a considerable time. It is on these antifoulants, therefore, that this section concentrates. This does not, however, imply that the other biocides are necessarily any more or less harmful, although there is little evidence available on their relative impacts.

#### Sources of Copper in the Marine Environment

Copper is a naturally occurring element and is essential as a trace element for metabolic processes in living organisms. However, it can also prove extremely toxic in high concentrations. Therefore if copper accumulates to a significant degree in the aquatic environment it can have a detrimental effect on marine life.

Copper is present in all human and animal wastes, and non-human activity, such as natural weathering, also leads to copper input into the environment. However, the major sources of copper contamination in inland and coastal waters

are industrial wastewater discharges and atmospheric deposition, particularly from foundries and metal plating and cleaning operations. Fungicides, wood preservatives and boat antifouling paints can also contribute to high levels of copper in the aquatic ecosystem.[1]

Tributyltin (TBT) - harmful effects on the environment	
Water and sediments	Tributyltin - organotin compound (TBT) is a broad spectrum algicide, fungicide, insecticide and miticide used in anti-fouling paints since the 1960s. TBT is toxic to humans. TBT can be broken down in water under the influence of light (photolysis) and micro-organisms (biodegradation) into less toxic di- and monobutyltin. Half-life varies from a few days to a few weeks, but decomposition is slower when TBT has accumulated in sediment - if oxygen is completely excluded, TBT half-life maybe several years. Therefore waters with heavily sedimented bottoms - such as harbours, ports, estuaries - are at risk of being contaminated with TBT for several years.
Shell malformations	TBT causes thickening of shells in sea oysters, caused by disturbance of calcium metabolism.
Imposex	Recorded in marine snails: females develop male sexual characteristics. Imposex has been recorded in 72 marine species. Concentration of just 2.4 nanograms of TBT per litre needed to produce sexual changes in dogwhelks, leading to sterility.
Marine mammals	Traces of TBT have been found in whales, dolphins and members of the seal family in the United States, south-east Asia, the Adriatic Sea and the Black Sea. The TBT is absorbed via the food chain.
Reduced resistance to infection	Research has shown TBT reduces resistance to infection in fish such as flounder and other flatfish which live on seabed and are exposed to relatively high levels of TBT, especially around areas with silty sediment like harbours and estuaries.

Ref: TBT in antifouling paints: National Institute for Coastal and Marine Management/RIZA, Netherlands: MEPC 42/Inf.10

#### 2.2.4 Copper-based antifouling paints

The ban of the use of TBT on smaller vessels has resulted in the shift back to the use of copper as the main biocide in the UK. Although copper is a naturally occurring element which is essential for metabolic processes in living organisms, it is also a widespread pollutant in industrial waters which can be one of the most poisonous heavy metals when present in excess. The main sources of copper contamination in the marine environment are from industrial discharges and atmospheric deposition, particularly from foundries and metal processing operations. Fungicides, wood preservatives and boat antifouling paints can also contribute to high levels of copper in the aquatic environment.

In general 95% of the UK recreational market is using some form of copper-based paint (UK CEED 1993). In a study commissioned by the Environment Agency, WRc estimated the amount of copper used on coastal leisure craft in the UK in one year was between 75,173 and 311,769 kg (Boxall, Conrad & Reed 1998). This study found the majority of copper in antifouling enters the marine environment through leaching, and that only a small proportion enters during the removal of antifouling paint, which occurs mostly by water blasting. However, the concentrated nature of the biocide in scrapings and cleaning residues may cause more of a localised environmental problem.

In addition to the widespread use of copper-based paints on leisure boats, they have also been tested on ocean going ships over 25m, particularly in the USA and Japan. There are potential drawbacks of the use copper-based paints, including an incompatibility with aluminium-hulled craft and the production of offensive odours. A new form of copper antifouling developed is the copper based gel coat, or epoxy, that is used widely in the United States. It is claimed that it lasts up to 15 years, but the cost is higher than the previous types of paint and it does not work as well. Certain fouling

organisms are resistant to copper-based paints and they have now been supplemented by additional biocides known as booster biocides. Trials of alternative copper-based coatings with rapidly degradable boosting biocides on ships in Japan have claimed recent breakthroughs with equivalent performance of TBT products (ENDS Report 1998).

Although at present copper antifouling paints present the BPEO available to the marine industry, 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 (Sobral & Widdows 1997). The toxicity and accumulation of copper varies 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 generalise 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 to adapt to elevated levels.

There is limited information available on the environmental impacts on non-target species, particularly algae, associated with the use of the newer booster biocides, such as the herbicides irgarol and diuron. These studies are discussed in the Recreational User Interaction report (UK CEED 1998 and 1999 in preparation 1999). Using a model to predict concentrations of antifouling in the environment, WRc have estimated that the six most common biocides used in antifouling paint for recreational craft, including copper (I) oxide, diuron, copper thiocyanate and 'Irgarol 1051', were present in marina waters in concentrations generally more than an order of magnitude higher than levels required for toxic effects on marine algae and fish (Boxall, Conrad & Reed 1998). However, it should be noted that these estimated concentrations were generally higher than levels actually measured in the marine environment and are likely to be an overestimate. An improved model is currently being developed for the HSE and the Environment Agency, which should provide information that will help to determine whether further control options are necessary.

### **2.2.5 The Effects of Copper in the Marine Environment**

Due to its complex nature and the uncertainty over its level of interaction with other substances, it is difficult to establish the precise effect of elevated levels of copper in the marine environment. Furthermore, although it may be possible to detect the presence of copper concentrations in sediments by sampling, it is rather more difficult to identify the source of such concentrations. Depending on the location, sediments can be highly mobile and resuspension of copper in the water column can result in the transportation of the metal to areas away from the main sources.

Therefore, before assumptions can be made concerning the impact of copper-based antifoulant on the marine

environment, it is vital that further research is carried out. This should be focused on identifying the sources of elevated levels of copper found in the marine environment and establishing the exact nature of any subsequent environmental impact.

In 1984, a UK government commissioned report on copper, concluded that due to problems of quantifying the exact environmental effect of differing copper concentrations, it is difficult to generalise about the toxicity of copper to marine organisms.

There is, however, evidence to show that certain species of fish and other marine organisms are sensitive to quite low levels of copper even though other species are relatively tolerant of much higher levels. Marine invertebrates are thought to be slightly more sensitive to copper than fish.

Furthermore, evidence suggests that marine organisms have some capacity for adaptation to higher than normal levels of copper although sudden high inputs of the metal are likely to cause adverse effects in otherwise unexposed populations.

Significant copper accumulation is unlikely to occur in fast flushing open coastal areas, but can accumulate in the sediments of low flushing waters including streams, rivers and bays. The US National Oceanic and Atmospheric Administration found that between the late 1970s and 1990, levels of copper in marine organisms have steadily increased (World Resources 1992-93). This is an indication of increasing copper concentrations in the aquatic environment.

There are relatively few studies that specifically relate to the effect of copper based antifouling paints on the marine environment and none which examine the potential impact on the mSAC designated features. Those that do exist point to evidence of elevated levels of copper in the vicinity of shipyards and dry docks, whilst others found that marine organisms in the vicinity of a marina had higher levels of copper than those in an adjacent undeveloped bay.

The only research identified which specifically assesses the concentrations of copper in the vicinity of marinas is an undergraduate research project carried out at the University of Southampton (Newbold, 1993). This involved sampling sediment from several sites around Southampton Water to determine whether marina environments were associated with elevated concentrations of copper. The research found some evidence that copper based antifouling paints have an effect on copper concentrations on the surface sediment in the vicinity of the marinas sampled. However, due to the mobility of copper in the water column, it concluded that more research was required to determine whether the effluent from industrial processes in the area is contributing to such concentrations.

Some studies have been carried out into the effects of particular substances contained within copper-based antifoulants. For example, research into Irgarol 1051, a trizine herbicide used to boost the effectiveness of antifoulant paints, has suggested that it can result in reduced plant growth and a reduction in photosynthesis.

Some European countries including Denmark have now banned the use of certain biocides in antifouling paints. The bans have been based on evidence that such substances do indeed have a negative impact on the marine environment. However, this evidence is disputed by industry and other EU countries have been slow to follow suit.

### 3. Modern Trends in Marine Antifouling Paints

#### 3.1 Advances in Antifouling Coating Technology

Marine coating systems are applied to ships and offshore structures both in sea and fresh water environments. They serve the dual purpose of protecting the structure from deterioration and keeping the ships looking good. The world merchant fleet is comprised of bulk carriers, tankers, container ships, cargo ships, and passenger and cruise ships, among others.

Marine coatings have specific functional properties that provide superior corrosion protection to the surfaces on which they are applied. The coatings protect submerged materials such as vessels, ships, or yachts from sea water. Marine coatings also protect materials from corrosion and abrasion. The application of such coatings improves the durability and overall performance of the vessel.

The latest survey report on the global antifouling paint market, published by Markets and Markets, projects the market to grow from U.S. \$5.61 billion in 2015 to U.S. \$9.22 billion by 2021 at a CAGR (Compound Annual Growth Rate) of 8.6 percent between 2016 and 2021. High demand for antifouling coatings from the shipping industry is expected to drive the growth of the market in the near future, the report states.

Asia-Pacific dominates the global distribution of marine coatings for both new shipbuilding and repairs. China is fast becoming the world's largest shipbuilding nation and has set a goal of becoming number one in the industry by 2017.

As per record from 'The Shipbuilders Association of Japan' the New Shipbuilding share for 2015 is: Japan 19.2%, South Korea 34.4%, China 37.2%, Europe 1.4%, and the rest of the world 7.7%.

High demand for marine coatings in Asia-Pacific, especially due to the emergence of China as a major player in the shipbuilding industry, is driving the marine coatings market in the region.

Need for fuel-saving and low emission coatings are factors that have driven the growth of the marine coatings market over the past few years. Growth in the shipbuilding industry in India, Vietnam and the Philippines is expected to provide large opportunities for players in the marine coatings market during the forecast period.

The global marine coatings market is heavily consolidated, with 80% of the market shared by five companies—

AkzoNobel (through its International Paint business), Chugoku Marine Paints, Hempel's Marine Paints, Jotun and PPG.

#### 3.1.1 What Are Antifouling Coatings?

Antifouling coatings are specialized paints applied to the ship's hull to slow the marine growth on the underwater area which can affect the vessels performance and durability. In addition to preventing marine growth, the hull coating can also act as a barrier against hull corrosion that will degrade and weaken the metal. It also improves the flow of water passing the hull of a fishing vessel or high-performance racing yacht.

#### 3.2 Prevention of Marine Growth (Biofouling[2])

Antifouling paint, applied to the underwater hull of ships, discourages or prevents the growth of organisms that attach to the hull. Its self-polishing resin and biocide, such as cuprous oxide along with a booster biocide, help to prevent biofouling organisms.

A self-polishing copolymer (SPC) antifouling paint will release biocide at a nearly constant rate throughout its life. The diffusion of the biocide on the hull surface is primarily due to a chemical reaction between the paint and seawater. The self-polishing mechanism of an antifouling paint film ensures a consistent renewal of paint film and release of biocide on the surface to prevent settlement and attachment of biofoulants.

The self-polishing activity is very dependent on the speed and activities of the vessels. Based on various studies, the polishing rate of anti-fouling paint reduces almost by half when it is stationary as compared to when the vessel travels at 14 knots. Hence, the duration of the vessel staying stationary will enable the colonizing of micro- and macrofouling as explained below.

#### 3.3 Mechanism of Marine Growth (Biofouling)

Marine biofouling can be defined as the unwanted deposition or accumulation of microorganisms, plants and animals on the ship hull immersed in sea water. Fouling of the ship's hull will result in speed reduction, increased fuel consumption, loss in time and money and a higher frequency of dry-dockings.

The process of biological fouling is often grouped into key growth stages as shown in Figure 1 which illustrates the accumulation of adsorbed organics, settlement and growth of bacteria creating a biofilm matrix and subsequent succession of micro- and macrofoulers.

Biofouling consists of two main components: microfouling and macrofouling. Microfouling refers to the formation of biofilm and adhesion to the surface, and macrofouling refers to the attachment of organisms such as barnacles, diatoms and sea weed to produce a fouling community. The growing bacteria and the chemicals they secrete make up microfouling, also referred to as 'slime', which develops within hours of an object's immersion in water. Within a few

days, macrofouling develops as unicellular eukaryotes, such as protozoa and diatoms, that colonize the surface. Multicellular eukaryotes begin colonizing the surface within several weeks and include settlement of meroplankton larvae and algal spores.

### 3.4 New Technology Growth

Marine environment is a harsh environment in terms of corrosion and biofouling. Biofouling generates huge operational losses for the shipping industry. A high degree of fouling on the ship's hull significantly increases drag, reducing the overall hydrodynamic performance of the vessel and increasing the fuel consumption. Due to these reasons, it is in the best interest of the ship owners to use high-performance coatings that prevent corrosion and antifouling growth on the ship's hull.

Reduced fuel consumption and increasingly stringent environmental regulations have prompted the development of new antifouling technologies. Marine coatings manufacturers are generally cautious in adopting new technologies. However, increasingly stringent environmental legislation, paralleled by customer preference for more eco-friendly products, is pushing innovation in the market.

The need to lower fuel consumption and to reduce CO<sub>2</sub> emission has become a strong driving force for paint companies to develop new technologically-advanced antifouling coatings for ship's hulls which reduces the fuel consumption.

Foul-release technology, which also results in substantial fuel savings, is particularly useful for large cargo ships, which consume a lot of fuel. Many companies are investing time and money in developing eco-friendly products such as low friction coatings, metal-free antifouling coatings, etc. Most recent participants now offer silicone- or fluororesin-based foul-release products.

### 3.5 Regulations Force New Developments

The present working principle for most of the marine paint systems is based on a slow release of toxins (self-polishing coatings). Although the antifouling performance of such systems is excellent, the amount of toxin released per ship may be quite substantial. The impact of such toxins on nature can be detrimental. Because of this impact, the use of organotin, such as tributyltin (TBT), on ship hulls was completely banned in 2001. In addition, the use of other toxins in antifouling coatings is restricted by law.

Although the use of copper-based paints is not yet prohibited it may be banned in the near future. Recently, the use of copper-based coatings for recreational boats has been banned in the ports of San Diego and Washington. This drives both science and industry to evaluate new types of antifouling mechanisms.

### 3.6 Alternatives to Self-Polishing Coatings[3]

The following systems are commonly suggested and are also applied as alternatives to self-polishing coatings. Hydrophilic antifouling coatings prevent or slow down adherence of marine organisms to ship hulls. (The latest solutions that are provided by a marine coating manufacturer formulates anti-fouling paint based on hydrogel technology which is comprised of a network of advanced polymer chains that absorb high amounts of water to create a water-like boundary layer. This water-like layer misguides the fouling organisms into believing that the hull is a liquid and solid surface and this minimizes protein and bacterial adhesion to the hull.)

#### 3.6.1 Low energy, hydrophobic foul-release coatings facilitate an easy release of marine organisms.

Traditional fouling release coatings consist of a silicone elastomer (PDMS) which relies on low surface tension (hydrophobic) and low modulus of elasticity, usually with a good initial foul-free performance. Over time, the coatings ability to self-clean is lowered, which results in a higher hull skin friction. The technology behind the third generation fouling release coatings is a unique blend of silicone polymers which maintains a more hydrophobic surface, with fouling release performance that lasts. The foul-free period is longer, and required speed for self-cleaning is lower. This results in a lower hull skin friction over time with potentially lower fuel consumption

#### 3.6.2 Enzyme-based coating systems.

Current antifouling technologies for ship hulls are based on metals such as cuprous oxide and co-biocides like zinc pyrithione. Due to the adverse effect of these biocides on the environment, enzyme-based antifouling paints are proposed as a bio-based, non-accumulating alternative. Scientists tested a hydrogen peroxide-producing system composed of hexose oxidase, glucoamylase and starch for the chemical and physical functionalities necessary for successful incorporation into a marine coating. The activity and stability of the enzymes in seawater was evaluated at different temperatures, and paint compatibility was assessed by measuring the distribution and activity of the enzymes incorporated into prototype coating formulations. The scientists used a biomimetic encapsulation procedure for HOX through polyethylenimine-templated silica co-precipitation. Silica co-precipitation significantly improved the stability and performance of the antifouling system in marine-like conditions.

#### 3.6.3 New biocide free, two-component, fouling release coating

Non-stick fouling release coatings are based on a technology which prevents the adhesion of fouling organisms by providing a low-friction, ultra-smooth surface on which organisms have great difficulty in adhering. The coatings do not inhibit the fouling settlement, but provide self-cleaning when sailing at a certain speed at a certain activity, typically minimally 15 knots at minimum 75 percent of the time. Fouling release coatings have their origin in the desire for a biocide-free system and have been in existence for 30 years. On these types of coatings fouling is not prevented from settling, as in the case of traditional antifouling, but in

practice the bond between the fouling organisms and the coating surface is so weak that it breaks by the weight of the organism itself or by the water pressure and current to which it is exposed.

### 3.6.4 Copper-Free Antifouling coating

The January 3, 2003, International Maritime Organization deadline for application of organotin coatings is now past, and the industry is shifting to the next generation of antifouling coatings. The most promising candidates are self-polishing coatings based on copper, zinc, and silyl acrylate polymers filled with cuprous oxide and U.S. Environmental Protection Agency-approved booster biocides. Unfortunately, these technologies are unproven and may not meet the demands of today's oceangoing fleet (more than 5 years of service life), 80 percent of which is coated with organotin antifouling coatings.

Copper has been the principal biocide in antifouling coatings for more than 150 years. The question is not if this is a problem, but where.

Although proponents of the continued use of copper compounds as antifoulants cite the fact that copper is a naturally occurring micronutrient, there is concern about the long-term effects of copper when the concentrations from the combination of natural and anthropogenic sources greatly exceed required micronutrient levels. This Phase I research project sought to develop durable, biologically active antifouling coatings without the use of copper-based compounds or other toxicants that persist in the environment and affect nontarget species.

CuO is a still a very effective biocide but it requires a high concentration to give fully effective protection against most types of marine fouling. Paints that contain less copper metal, or use less powerful ingredients such as copper thiocyanate, often contain extra biocides such as zinc pyrithione or organic algaecides to cope with slime and weed growth. It is these organic boosters that are currently causing a stir, as some people think they could cause similar problems to TBT.

One of the latest biocides to be authorized is Selektop (generic name medetomidine), made by the pharmaceutical giant AstraZeneca. Instead of killing off marine growth, it is said to temporarily stimulate the octopamine receptor in the larvae of molluscs, causing them to be harmlessly repelled from the hull. Various research has apparently proved that it works at extremely low concentration levels (3 g/L) in any paint, and needs no other biocide for a barnacle-free hull. Sadly it's not as effective on weeds, so paint formulations will also have to contain approved algaecides to be effective.

Copper-free coatings that are biologically active with antifouling properties were developed. Unfortunately, biological activity of these coatings is short-lived, with activity diminishing after only 1 month of exposure. Based on results from Phase I, and problems associated with synthesis of the proposed starting materials, E Paint Company does not intend to seek additional funding to support this research.

### 3.6.5 Self-adhesive /fouling-release coatings.[4]

The 'eSHaRk' (eco-friendly Ship Hull film system with fouling Release and fuel-saving properties) project aims to bring to the market a fouling-protection technology which not only maintains the current state-of-the-art fouling-protection standards, but is superior to existing paint-based solutions in terms of eco-friendliness, ease of application, robustness and drag-reduction effects, all of which will lead to fuel savings and the reduction of GHG (greenhouse gas) emissions.

The aim of the eSHaRk project is to finalise the development of an innovative new fouling protection system for commercial vessels, and to accelerate its market entry.

Fouling, defined as the settlement and growth of marine plants and animals on submerged structures, is a constant challenge for the shipping industry. Fouling results in higher hydrodynamic drag of vessels, which in turn translates into higher fuel usage and greenhouse gas emissions. A number of fouling protection technologies exist on the market, the most widely used being paint-based anti-fouling and fouling release coatings. However, these existing solutions face a number of challenges concerning their environmental impact, the efficiency of their application on ship hulls, and their effectiveness in protecting vessels against fouling.

The eSHaRk project aims to bring a new and innovative solution to the market, which will lead to a paradigm shift in the fouling protection business. This solution is based on self-adhesive foil technology, which not only maintains the current state-of-the-art fouling protection standards but is superior to existing paint-based solutions in terms of eco-friendliness, easiness of application, robustness, and drag reduction effects leading to fuel savings and reduction of GHG emissions.

As part of the eSHaRk project, the surface morphology of the foil will be optimised to enhance its drag reduction, fuel savings and emissions reduction benefits. In addition, a robotised laminator will be finalised to apply the foil on large commercial vessels in an automated way. A cruise vessel will be equipped with the foil to ensure full-scale testing and validation in operational conditions before market entry. The technology will then be ready for commercialisation immediately after project end, in late 2018.

The system incorporates a fine-tuned fouling-release system based on PPG's 100% silicone binder technology and a self-adhesive film designed by MACtac for underwater use. As part of the 'eSHaRk' project, new, robotized application technology is being developed by VertiDrive that will be used to automate application of the film on large commercial vessels. Furthermore, the surface morphology of the film will be optimized to enhance drag-reduction, fuel-savings and emission-reduction benefits to previously unattainable levels.

### 3.6.6 Nano antifouling coating

A number of manufacturers have come up with some sensible and effective alternative coatings, but none of them has solved the problem completely. But some interesting new products are on trial at the moment, which could well come to fruition within the next decade.

Among these are Teflon- and silicone-based nanotech coatings, using technology already found in marine gel coat polish. Cornwall-based Nanotech Marine is working on a self-cleaning nanotech antifoul and the first three-year test results look promising. It's only intended for motorboats at the moment, but the company is looking into ways of applying the same principles for sailing boats.

Nanotech Marine's antifoul is a silicone-based product, said to create a surface so slippery (at a molecular level) that no weed or mollusc can get a grip on the hull.

Research has shown it does indeed work, but only on boats capable of high speed (10 knots or more), which are used regularly, as the coating relies on the boat's motion through the water to wash off biofouling. They're not so effective for a boat left on a mooring or in a marina for weeks on end, so even if one has a fast yacht, a nanotech coating may have to be used in conjunction with another product, such as an 'ultrasonic' bio-deterrent system.

Progress in materials science is associated with the development of nanomaterials in terms of energy-saving, environmentally friendly, and low-cost methods. Since the use of tributyltin compounds in antifouling coatings was banned in 2003, the search for ecofriendly alternatives has been promoted. Foul-release (FR) nanocoatings have been extensively investigated because of their non-stick, ecological, and economic advantages. Such nanocomposite systems are dynamic non-stick surfaces that deter any fouling attachment through physical anti-adhesion terminology. Instead of biocidal solutions, several functional FR nanocomposite coatings have been developed to counter biofouling and biocorrosion with ecological and ecofriendly effects.

Selected inorganic nanofillers have been incorporated because of their enhanced interaction at the filler-polymer interface for nanocomposites. Metallic nanoparticles and their oxides have also been widely explored because of their unique morphological characteristics and size-dependent, self-cleaning properties. In modeling a novel series of FR nanocoatings, two modes of prevention are combined: chemical inertness and physical microfouling repulsion for maritime navigation applications. Long-term durability and self-cleaning performance are among the advantages of developing effective, stable, and ecofriendly modeling alternatives. This review provides a holistic overview of nano-FR research achievements and describes recent advancements in non-stick marine nanocoatings for ship hulls. This review highlights the key issues of nanocomposite structures and their features in improving the biological activity and surface self-cleaning performance of ship hulls. This review may also open new horizons toward futuristic developments in FR nanocomposites for maritime navigations.

### Conclusion

Companies are investing a lot in research and development to expand the efficiency of antifouling coatings which, in turn, is expected to increase the demand from end-users. Technology advancement worldwide is one of the trends

expected to add to the growth of the global antifouling coatings market.

Increased demand for oil and gas, increasing population and urbanization are drivers for the growth of the antifouling coatings market. These are also widely used for the protection of structural infrastructure and machinery in rigs. One of the major challenges faced by the antifouling coatings market is predictable decline in the shipbuilding industry. The market has also been witnessing the growing consumer preference for eco-friendly products due to which strict environmental regulations have been imposed that pose a challenge to the growth of this market.

## 4. Effect on Aquatic Life

### 4.1 Introduction

According to the Biocides Directive (98/8/EC), biocides are active substances or preparations that are intended to destroy, deter, render harmless and exercise control or prevent the action of any other harmful organism through chemical or biological means. Biocides are classified into 23 different product types, each of which is comprised of multiple subgroups. Biocides are used because of their potential to destroy a wide range of organisms and for their relatively easy applicability to vessels and aquaculture systems. The settlement of microorganisms, plants and animals is a natural phenomenon that occurs continuously and vigorously on immersed surfaces. This process is called biofouling. Biofouling is a problem for any structure placed in the aquatic environment. It can be controlled through the use of both chemical biocides and non-biocidal technologies.

Aquaculture in general, and the fish farming industry in particular, suffer significantly from the effects of biofouling. The aquaculture industry makes periodic discharges of wastes from farm activities. These waste products include detergents, effluent from net washing, antifoulants, heavy metals and even chemicals, such as drugs. The chemicals are essential for aquaculture as they help increase and control the production of seeds in hatcheries, increase feeding efficiency, improve survival rates, control pathogens and diseases and reduce transport stress.

Nevertheless, despite the beneficial effects of the chemicals to aquaculture, they may also cause potential harm to aquatic organisms and even to humans. The chemicals may be ingested by farmed fish and shellfish, which are, in turn, consumed by humans. Ingestion of the contaminated fish and shellfish can pose a great risk to human health. The conditions and locations of the aquaculture farms play a significant role on the spread of these chemicals and heavy metals into the environment.

Marine pollution caused by the chemicals utilised in aquaculture activities, however, is not yet well documented. In addition, available information indicates low concentrations (low ng L<sup>-1</sup> level) of these compounds in the environment. This is due to factors, such as the complexity of the matrix, the high dilution factor, and degradation



phenomena. Nevertheless, the health risk in animals and humans may increase when bacterial resistance to antibiotics and heavy metals caused by the use of biocides occurs. The aim of this study is to review the main effects and risks of using antifouling biocides in aquaculture on aquatic systems, shellfish, fish and humans.

#### 4.2 Present Situation of Biocides Used in Aquaculture [5]

Aquaculture is the farming of aquatic organisms, including fish, molluscs, crustaceans and aquatic plants, using techniques designed to increase the production and productivity of these organisms beyond the natural capacity of the environment. Since wild fish stocks are reaching the limits of exploitation, we have to rely to a far greater extent on products produced from aquaculture. However, the practice of aquaculture has become so widespread that it has begun to have significant impact on the environment and on natural resources. A number of concerns have been expressed by both environmental activists and scientists regarding this practice.

With the rapid expansion of the aquaculture industry and with the tightening of the legislation on the use of antifouling (AF) biocides, the problems of aquaculture biofouling have increased. The herbicides or fungicides currently used in aquaculture were originally developed for use in agriculture or as additives for boat anti-fouling paints. As such, the published data regarding their occurrence in marine waters are mainly related to such activities. Accordingly, many studies have investigated and demonstrated the presence of pesticides and biocides in surface waters.

With the gradual elimination of triorganotin-based formulations (e.g., tributyltin (TBT)), copper has become the principal biocidal component of most AF paints. It usually comes in the form of copper oxide (Cu<sub>2</sub>O). Inorganic zinc is often used in combination with copper to increase the overall toxicity of the formulation or to facilitate the leaching process. Organic booster biocides, such as Irgarol 1051®, Sea Nine 211®, dichlofluanid, chlorothalonil, zinc pyrithione, and Zineb are also added to the paint to enhance its effectiveness. Nevertheless, these alternatives to TBT are also toxic and their contamination of the aquatic environment has been a topic of increasing importance in recent years. Several studies have evaluated the toxicity of booster biocides on non-target species and have found most of them to be growth inhibitors for freshwater and marine autotrophs, influencing key species, such as sea grasses and corals. Therefore, there is increasing interest in the impact of these compounds on the aquatic ecosystems.

In the aquatic environment, fishes have been found appropriate to be used as a model for the immunotoxicity testing because they are representatives of aquatic organisms and, therefore, bioindicators of aquatic animal health. As vertebrates that have immune systems strikingly similar to those of mammals, they can also be used to identify potential threats to terrestrial wildlife and humans. The risk to predators and humans through the consumption of fish is very low, especially for humans, since the latter are less exposed to the dangers of contamination due to the fact that

fish constitutes only a small part of their diet. However, the risk may be increased by mechanisms of resistance.

## 5. Conclusion

### 5.1 Main Type of Antifouling Used and its Effect on Aquaculture

#### 5.1.1 Chlorothalonil

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is a pesticide used widely in agriculture, silviculture and urban settings. This pesticide can enter surface waters through rainfall runoff, spray drift or atmospheric deposition, subsequently impacting aquatic biota. It is used as a booster biocide in marine paints as one of the chemicals replacing the widely banned organotin fungicides, such as tributyltin, resulting in greater potential for chlorothalonil contamination of marine waters and sediments. Chlorothalonil is a broad-spectrum fungicide with a  $K^{ow}$  of 2.64–4.28 and a water solubility of 0.9 mg L<sup>-1</sup>.

Chlorothalonil can be acutely toxic (50% lethal concentration, LC<sub>50</sub>) to fish following 96 h exposures ranging from 8.2 to 76 µg L<sup>-1</sup>, depending on the species and the exposure conditions. Chlorothalonil can accumulate in the tissue of fish. Bioaccumulation factors have been reported to be 18 for willow shiner (*Gnathopogon caerulescens*) and 25 for carp (*Cyprinus carpio*) following sublethal exposures (1.1–1.4 µg L<sup>-1</sup>). It has been suggested that leukocytes may be a potential target of toxicity because significant decreases in leukocyte values were found in the Australian freshwater fish *Pseudaphritis urvulii*, which was exposed for 10 d to 4.4 µg L<sup>-1</sup> chlorothalonil. *In vitro* studies have demonstrated that the exposure of fish (*Morone saxatilis*) macrophages and oyster hemocytes to chlorothalonil (10 ± 500 µg L<sup>-1</sup>) suppressed immunostimulated ROS (reactive oxygen species) and baseline NADPH (nicotinamide adenine dinucleotide phosphate) concentration but did not inhibit phagocytosis. There are numerous toxicity studies for chlorothalonil on marine animals, such as crustaceans, molluscs, tunicates and teleosts.

#### 5.1.2 Dichlofluanid

Dichlofluanid (*N*-dichlorofluoromethylthio-*N*0-dimethyl-*N*-phenylsulphamide) has been commonly used as a herbicide on crops (Lee *et al.*, 2010). Dichlofluanid has a lower toxicity compared with other AF agents, although some studies have identified its toxic effects, such as embryotoxicity in sea urchin, *Glyptocidaris crenularis*.

#### 5.1.3 DCOIT (Sea Nine 211®)

One of the new alternative biocides is 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOIT), the active ingredient of the Sea Nine 211® AF Agent manufactured by Rohm and Haas Company. Aquatic microcosm and marine sediment studies demonstrate that the predominant route of DCOIT dissipation in the marine environment is its rapid biodegradation. DCOIT predominantly undergoes biotic degradation under both aerobic and anaerobic conditions with biological degradation over 200 times faster than hydrolysis or photolysis. Biodegradation is a very effective mechanism for

the detoxification of the compound since the resulting metabolites are five orders of magnitude less toxic than the parent compound. However, Sea-Nine antifoulant is acutely toxic to a wide range of aquatic organisms although no chronic toxicological effects have been observed in the extensive toxicology tests conducted on it. DCOIT has a log  $K_{OW}$  of 2.8 and an aqueous solubility of 14 mg L<sup>-1</sup>.

There are numerous studies that have investigated the toxicity and effects of DCOIT on marine animals. These studies demonstrated the following: larval mortality in crustaceans: embryo-larva immobility and embryotoxicity in molluscs, embryotoxicity in echinoderms, embryotoxicity and inhibition of larval settlement in tunicates and mortality in teleosts.

#### 5.1.4 Diuron

Diuron (1-(3,4-dichlorophenyl)-3,3-dimethylurea) also persists in seawater, but it is less persistent in marine sediments with a half-life of 14 days. Diuron is relatively soluble in water (35 mg L<sup>-1</sup>) and has a reported log  $K_{OW}$  of 2.8. Diuron is present at high concentrations in marine surface waters but it has only been detected at low concentrations in sediments. Diuron is persistent in the marine environment and partitions poorly between water and sediments. It can remain suspended and available for uptake by marine organisms.

While the toxic effect of the antifoulant herbicide diuron to the photosynthetic aquatic biota has been widely studied, its sublethal effects on the different life stages of fish have been under-reported. Diuron has been proven to be very toxic for the reproduction of the green freshwater alga *Scenedesmus vacuolatus*. It has also been proven to affect planktonic and periphytic microalgae by reducing the chlorophyll *a* levels. Moreover, it has been proven to be toxic to certain bacterial species.

#### 5.1.5 Irgarol-1051®

Irgarol-1051 (2-methylthio-4-terbutylamino-6-cyclopropylamino-s-triazine) is a slightly soluble and moderately lipophilic triazine herbicide used in concert with copper to control fouling on boat hulls. Irgarol inhibits electron transport in the photosystem II (PSII) by binding to the D1 protein. Irgarol may affect non-target photosynthetic organisms, such as phytoplankton, periphyton and aquatic macrophytes when leaching into the marine environment.

Only a few studies have addressed the possible effect of Irgarol on marine non-target algae. The effect of Irgarol on green alga *Dunaliella tertiolecta*, *Synechococcus sp* and *Emiliania huxleyi*, natural phytoplankton communities, periphyton colonization and phytoplankton species has been investigated and the results showed a decrease in growth, inhibition in cell number and a decrease in the photosynthetic activity of these organisms. These effects have been seen in many different marine plants and algae, such as the eelgrass *Zostera marina*, the brown macroalga *Fucus serratus*, the green macroalga *Enteromorpha intestinalis* and the green macroalga *Ulva intestinalis*.

#### 5.1.6 TCMS Pyridine

TCMS (2, 3, 5, 6-tetrachloro-4-methylsulphonyl pyridine), which was used in both the textile and leather industries, is one of the more recent AF compounds introduced to the market. The toxicity of TCMS towards living organisms has already been evidenced and substantiated in *in vitro* studies. TCMS has been found to cause immunotoxic effects at concentrations higher than 10 µM in haemocyte cultures of the colonial ascidian *Botryllus schlosseri*, causing oxidative stress in the process.

Both diuron and TCMS pyridine exerted immunosuppressant effects on the *Botryllus* hemocytes when used at concentrations higher than 250 µM and 10 µM, respectively, causing (i) deep changes in the cytoskeleton that irreversibly affect cell morphology and phagocytosis; (ii) induction of DNA damage; and (iii) leakage of oxidative and hydrolytic enzymes due to membrane alteration. Unlike organotin compounds, diuron and TCMS pyridine do not inhibit cytochrome-c-oxidase and only TCMS pyridine triggers oxidative stress.

#### 5.1.7 Zinc Pyrithione

Zinc pyrithione (ZnPT) (bis(1hydroxy-2(1H)-pyridethionato-o,s)-(T-4)zinc), one of the most popular surrogate AF biocides, has long been widely used as algacide, bactericide and fungicide. ZnPT was found to be highly toxic to aquatic plants and animals, but it was assumed to be environmentally neutral because it could easily photo-degrade to less toxic compounds. ZnPT is toxic to Japanese medaka fish (*Oryzias latipes*) and also causes teratogenic effects, such as spinal cord deformities in embryos and on the larvae of zebra fish (*Danio rerio*) at very low sublethal concentrations. However, there is a lack of data on the toxicity of ZnPT.

#### 5.1.8 Zineb

Zineb (zinc ethylenebis-(dithiocarbamate)) is a widely used foliar fungicide with prime agricultural and industrial applications. Zineb has been registered for use on fruits, vegetables, field crops, ornamental plants and for the treatment of many seeds. It has also been registered as a fungicide in paints and for mould control on fabrics, leather, linen, painted and wood surfaces, and so on. The occurrence of the dithiocarbamates in coastal environments was not reported until 2009 although it is known that these compounds exhibit teratogenicity in fish embryos at relatively low concentrations.

#### 5.2 Bioaccumulation

The bioconcentration of pesticides and other chemicals into aquatic organisms mainly proceeds by passive diffusion through gills, epithelial tissues, or the gastrointestinal tract. Bioconcentration factors (BCFs) are available for certain biocides in specific tissues. They represent the concentration of a biocide in the tissue per concentration of the biocide in water (L kg<sup>-1</sup>). DCOIT has been shown to bioaccumulate in fish at very low levels following exposure to radiolabelled DCOIT. There are no reports of the bioaccumulation of diuron with BCFs of 75 and 22 L kg<sup>-1</sup>, suggesting that its accumulation in aquatic organisms is unlikely. Irgarol 1051 accumulates in freshwater macrophytes and marine

macrophytes with BCFs of up to 30,000 L kg<sup>-1</sup>. It also accumulates in the green alga *Tetraselmis suecica* under laboratory conditions with BCFs of up to 150,000 mL g<sup>-1</sup>. In addition, the accumulation of Zineb in trout (*Salmo gairdneri*) is reported to be low with a BCF of <100 L kg<sup>-1</sup>.

### 5.3 Resistance

Scientific evidence from bacteriological, biochemical and genetic data indicate that the use of active molecules in the biocidal products may contribute to the increased occurrence of antibiotic resistant bacteria. The selective stress exerted by biocides may favour the existence of bacteria expressing resistance mechanisms and their dissemination. Some biocides have the capacity to maintain the presence of mobile genetic elements that carry genes involved in cross-resistance between biocides and antibiotics. The dissemination of these mobile elements, their genetic organisation and the formation of biofilms, provide conditions that could create a potential risk of development of cross-resistance between antibiotics and biocides.

### 5.4 Conclusions

Biocides are used as components in paints to coat the structures of vessels, as a means of disinfecting aquaculture facilities and cages, as well as in controlling the biofouling phenomenon (antifouling). The use of biocides is not as well-regulated as drug use in aquaculture because the information available on the effects of these agents to the marine ecosystems is still limited. Hence, it is important to know the risks associated with the existence of those biocides in the marine environment. It is also important to evaluate the effects of these compounds through the continuous monitoring of biocide concentration profiles in water, sediment and biota to provide information that could lead to concerted action to ban or regulate their use.

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