(BIO)FOULING AND ANTIFOULING MEASURES

Biocides based antifoulings: industrial outlook

Marine biofouling is a natural process with unwanted consequences on surfaces immersed into the seawater. A ship hull covered by fouling faces an increment in both drag and fuel consumption up to 40%, compared to a smooth and cleaned hull surface.
The aim of industry is to manufacture high performance antifouling paints ensuring a high level of protection for both human and animal health and the environment, in compliance with the enforced global legislation

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Introduction

Surfaces immersed in the seawater rapidly get covered with marine organisms, such as algae and barnacles. Their accumulation increases the ship's drag, reduces the flux in water cooling pipes and destroys protection and the equipment used in aquaculture. To protect surfaces, antifouling paints have been applied. Modern antifouling paints erode upon contact with marine water and the biocide is consequently released to the surrounding water [1]. Recent human and environmental concerns have led to legislation measures also in the European Union.

Biofouling and antifouling systems

Marine biological fouling, often called biofouling, is a natural process with unwanted consequences on manmade surfaces, which consists of the accumulation of microorganisms, plants and animals on artificial surfaces immersed in the seawater. Biofouling can be summarized as a sequence of regular steps, from the absorption of various organic compounds to the settlement of different organisms [2], as shown in Figure 1.
In the case of ships, the adverse effects caused by biofouling are well known [3]:

- High frictional resistance, which leads to an increase in weight and subsequent potential speed reduction and loss of maneuverability. Thus, the fuel consumption increases and higher emissions of harmful compounds take place [4, 5]. In the case of a ship hull covered by soft fouling (bacterial and microalgae based film), the drag force increases up to 3-10% [6]. The increase in fuel consumption can be up to 40% for ship hulls covered by hard fouling (macro algae or calcareous organism such as barnacles), if compared with a cleaned and smooth hull surface [7]. It also causes an increase in voyage overall costs of as much as 77%.
- An increase in the frequency of dry-docking operations, which leads to a large amount of toxic wastes generated during this process.
- Deterioration of the coating so that corrosion, discoloration, and alteration of the electrical conductivity of the material are favored [8].

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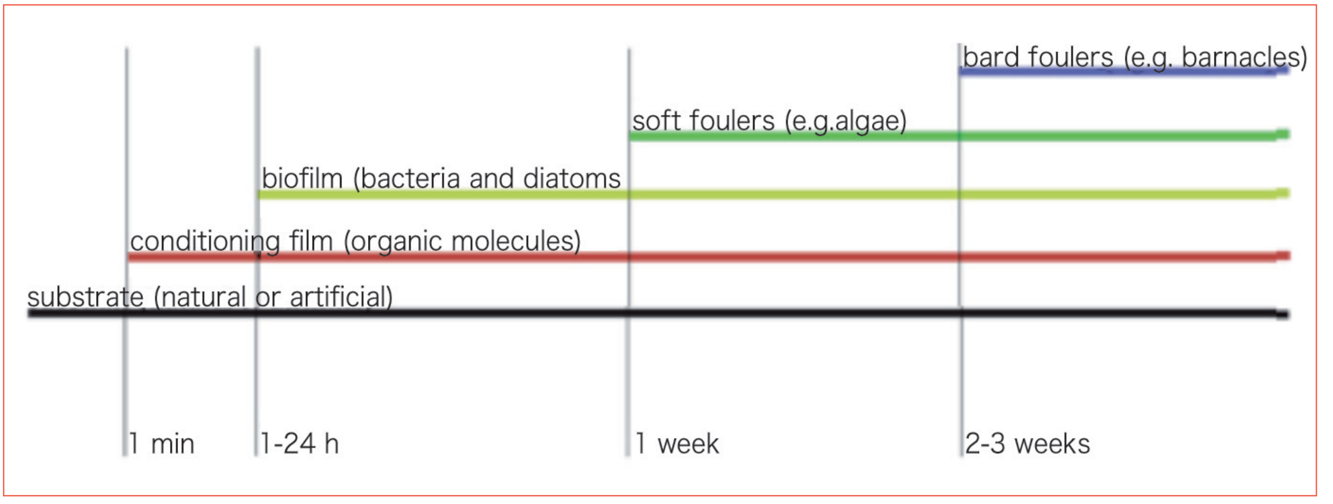

FIGURE 1 Simplified temporal succession of biofouling process
Source: E. Pinori thesis [2]

- Introduction of species into environments where they were not naturally present [9, 10].

Examples of fouled hull and settlement of artificial surfaces are shown in Figures 2 and 3.

Among all the different solutions proposed throughout the history of navigation in the second half of the 20th century, an organo-tin compound, tributyltin (TBT), has been the best solution in terms of antifouling efficacy and economic profile. But, unfortunately, the TBT-SPC systems have shown unwanted environmental consequences [11]. As an example, it has been shown that extremely low concentrations of tributyltin cause defective shell growth in the oyster *Crassostrea gigas* (20 ng/l) and imposex, development of male characteri-

FIGURE 2 Example of fouled ship hull
Source: Boero Bartolomeo field tests

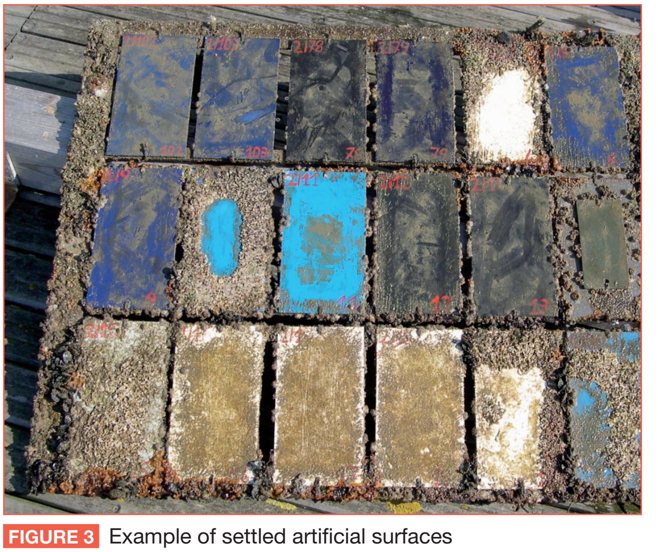

FIGURE 3 Example of settled artificial surfaces
Source: Boero Bartolomeo raft tests

stics in female genitalia, in the dog-whelk Nucella sp. (1 ng/l) [12, 13]. Malformations have been observed in many other species and also accumulation in mammals has been reported by the International Maritime Organization (IMO). These facts determined the development of national regulations in countries all over the world and TBT-containing coatings have been globally banned since 2008 after a long debate [14, 15, 16]. Thus, the paint industry has been urged to replace the TBT-based products with TBT-free ones and, in the meantime, to obtain the same economic benefits and environmentally-friendly antifouling systems, in order to have less harmful effects on the environment. Nowadays, tin-free antifouling paints are the most adopted solutions. They are paints containing copper oxide and other co-biocides, also called booster biocides, in soluble paint matrix.

Antifouling paints technology

Following the ban of TBT-based antifouling paints, a lot of improvements have been done and good results have been achieved by using antifouling systems containing copper compounds, and toxins or active ingredients will hereby called biocides to harmonize our terminology to the newly introduced regulations. Some regulatory aspects for the modern antifoulings will be described in the following.
The general principle of antifouling paints is to create a protective layer around the ship hull, working as control delivery system for biocides. In order to reach good performance and to be environmentally-friendly, an antifouling paint should have the following basic features: anticorrosion properties, efficacy, environmental compatibility, long-life properties, economic feasibility, compliance with the enforced legislation, abrasion and biodegradation resistance, no surface roughness, very low environmental toxicity, very low environmental persistence, low costs, chemical stability. To achieve this goal, several components are demanded in the paint formulation, in order to control and maintain the release rate of biocides. These components are: binder (that defines the matrix type), pigments, extenders, additives, solvents, and biocides. Biocides have to be active to both hard and soft fouling (typically barnacles and algae, respectively). The released biocides have to be bioavailable to the target organisms at the surface.
The release rate of biocides from the paint matrix, called leaching rate, has to be kept above a limit threshold in order to reach and maintain a minimum inhibition concentration of the biocide at the exposed surface [17, 18]. The leaching rate is usually expressed in micrograms per square centimeter per day [19].
Different types of antifouling paints have been developed in the second half of the 20th century. These paint products, systematically based on the dispersion of toxicants in different types of polymeric binders, have become differentiated over recent decades according to the mechanisms they use to release the toxicants in the sea water. These mechanisms determine the application, behavior and duration of the antifouling coatings obtained. In the following, the main types of antifouling paints are described according to their behavior mechanisms and to the release rate of their toxicants over time [20].
Soluble matrix paints, with binders based on rosins and their derivatives and incorporating biocide such as copper, started to be developed in the 1950s. They are soluble in the sea water, present poor mechanical strength, and only allow the inclusion of low concentrations of biosoluble materials and the application of relatively fine films [21, 22]. Their leaching rate decreases with time quickly and they do not assure protection for more than 12–15 months (see Figure 4).
Insoluble matrix paints use high molecular mass binders, which are insoluble in the sea water. As the biocide particles are deeper in the paint film, the leaching rate gradually decreases in time, and the protection afforded becomes increasingly less efficient [23]. The lifetime of these paints is between 12 and 24 months, depending on the exposure conditions, which limits their application on some types of ships [24].
TBT self-polishing paints are based on an acrylic copolymer with TBT groups bonded to the main polymer chain by ester bonds [25, 26], in which the polymer is soluble in the seawater. Since this dissolution can be controlled at molecular level, it is possible to obtain a well-known self-polishing effect in these paints. Unlike insoluble matrix paints, in these type of products, the water is prevented from penetrating the film [27]. Thus,

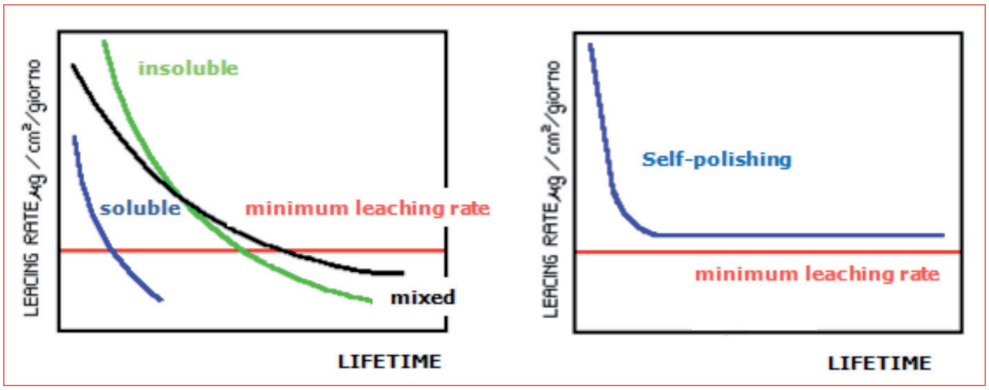

FIGURE 4 Biocide release rates of traditional insoluble and soluble matrix paints and self-polishing ones. "Minimum leaching rate" indicates the limit for efficient protection against fouling (dependent on the fouling conditions)

the sea water barely manages to fill the pores created by the dissolution of the soluble pigment particles, as represented in Figure 5.

As previously mentioned, due to the environmentally harmful action of the well known, efficient and versatile TBT self-polishing paints, and the consequent total worldwide

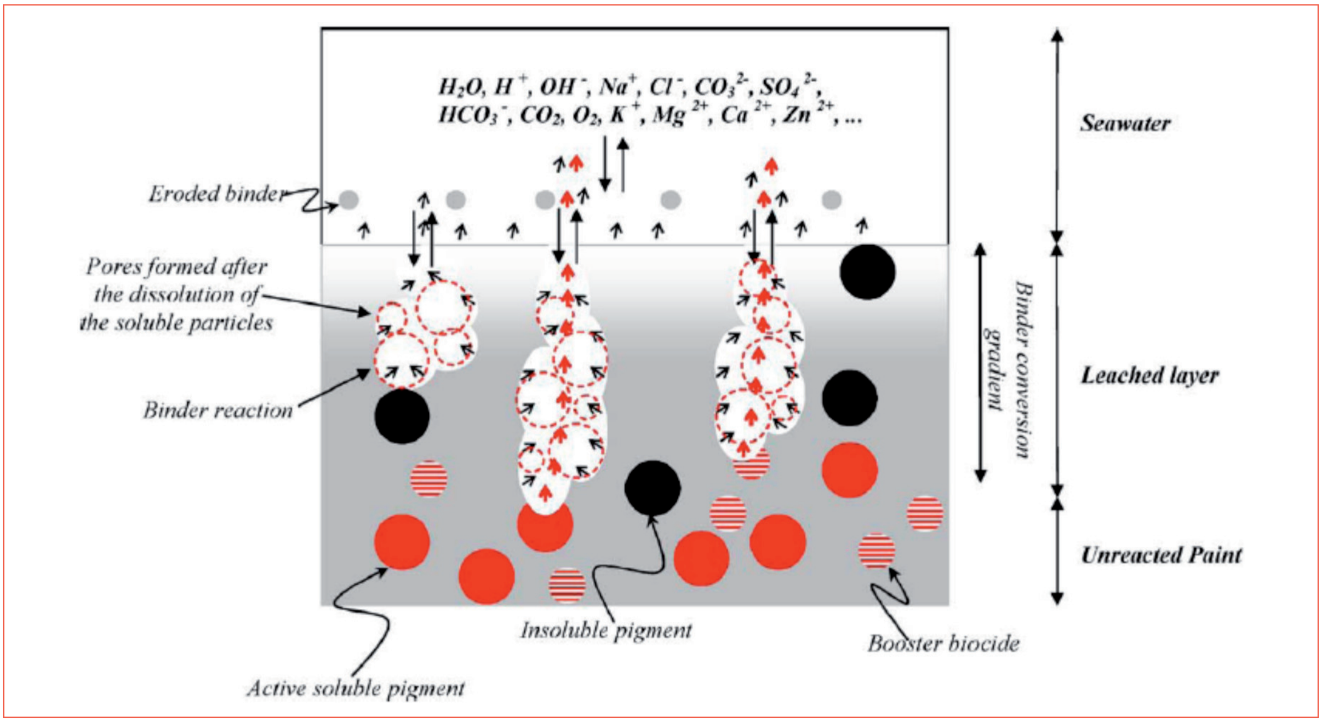

FIGURE 5 Schematic illustration of the behavior of a biocide-based antifouling system exposed to the sea water
Source: [3]

prohibition of their application and presence on ship surfaces following 1st January, 2008 [28, 29], paint manufacturers have been forced to urgently study and develop new more environmentally-friendly antifouling paints.
Among the products with biocides that have recently been marketed for this purpose, tin-free, biocide-containing, self-polishing paints (TF-SPCs) are very common. In this type of paints, products are integrated in an acrylic matrix to which different pendent groups of the main chain are added, however without tin. Like in self-polishing paints containing tin, the pendent groups are considered to be released when in contact with the sea water. Nevertheless, and despite the high number of patents registered in this domain until 1996, these groups are in no case as effective as TBT [30]. These polymers interact with the sea water, and their self-polishing effect is seen with the controlled release of biocides [31]. Due to their relatively high polishing rate, the maximum service life of this type of paint is normally around 3 years, although in some cases 5-year service lives have been reported [32, 33, 34]. However, according to various authors, they do not achieve the same level of efficiency as TBT-based self-polishing paints.

Regulations and industrial developments

The active ingredients in antifouling paints are regulated under the Biocide Products Regulation (BPR, Regulation EU 528/2012 – formerly the Biocides Products Directive, 98/8/EC).
This Regulation concerns the making available on the market and use of biocidal products and its purpose is to improve the functioning of the internal market through the harmonization of its rules, whilst ensuring a high level of protection of both human and animal health and the environment. It aims to improve the EU market by the harmonization of the various local legislation, breaking down barriers of trade between countries. It covers 22 very different product types; biocides for antifouling paints belong to the Product-type 21 – "Antifouling product: Products used to control the growth and settlement of fouling organisms (microbes and higher forms of plant or animal species) on vessels, aquaculture equipment or other structures used in water".
The approvals of active ingredients have to be based on scientific risk assessments and best practice, products do not pose any unacceptable risks to humans, animals and the environment and safe use must be demonstrated. In the meantime, as the products work as claimed, efficacy must be demonstrated. Among the many data requirements in order to obtain the approval of an active ingredient belonging to a specific product type, the main ones are: physical, chemical, technical properties (e.g., storage stability), toxicological and eco-toxicolo-

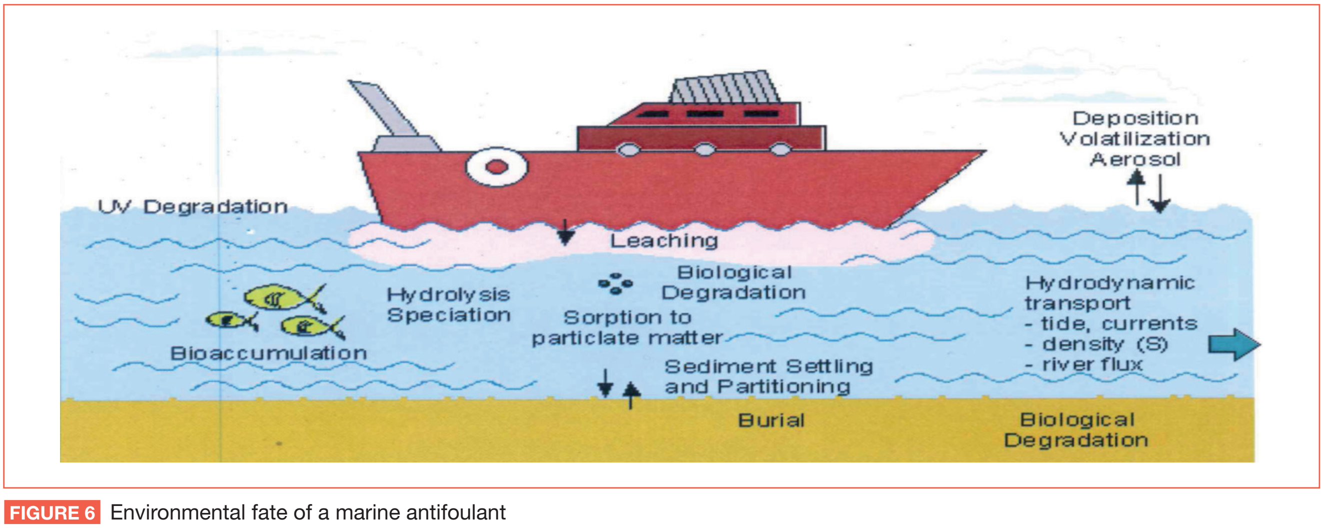

FIGURE 6 Environmental fate of a marine antifoulant
Source: A. Jacobson [35]

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gical profile, and effectiveness of the products, which have to combine the label claim with the efficacy, environmental fate and behavior. Regarding the last one, it is very interesting because the environmental fate of a marine antifoulant involves very different processes. Many complex and interacting processes that can be of a biological, chemical or physical nature determine the chemical fate of contaminants in the marine environment. Some of the major transport and transformation processes have been summarized in Figure 6.
Especially in energy-rich marine environments the hydrodynamic transport and mixing processes of water masses tend to have a major impact for most compounds. For compounds with a high affinity to particulate matter or sediment, sediment transport phenomena will be of dominant importance. Stable dissolved compounds are likely to be affected most by river discharges or tidal currents. In specific marine environments with low exchange rates or pseudo stagnant conditions the chemical and biological processes will become more important. The relative importance of each of these processes is highly compound- and habitat-specific and may vary between seasons. Biodegradation processes are highly temperature dependent and may be the dominant removal process in tropical water, while in temperate or polar zones this may be less. Photolysis may have a prominent role in the open sea even at greater depths in warm and transparent waters, while in turbid estuarine environment in temperate zones this only may be of importance in the upper water layers [36].
Stringent environmental regulations is pushing the innovation developments. As above mentioned, in UE the coatings industry is heavily regulated and hence it is strictly controlled in many ways. Also in the US there are a series of Regulations governing the substances that can be used in the marine sector together with rules for VOC's and biocides. In addition, new countries are regulating in these areas such as Far East. Due to the global impact of the regulatory drivers, the coating industry is investing in developing eco-friendly products such as metal-free, anti-fouling coatings or silicone- or fluororesin-based, foul-release products at worldwide level. New biocides issues are added day by day to the already treated articles obliging companies to invest on and develop new eco-friendly and less environmental impacting solutions to keep their marine business and their leadership in the specific market segments.

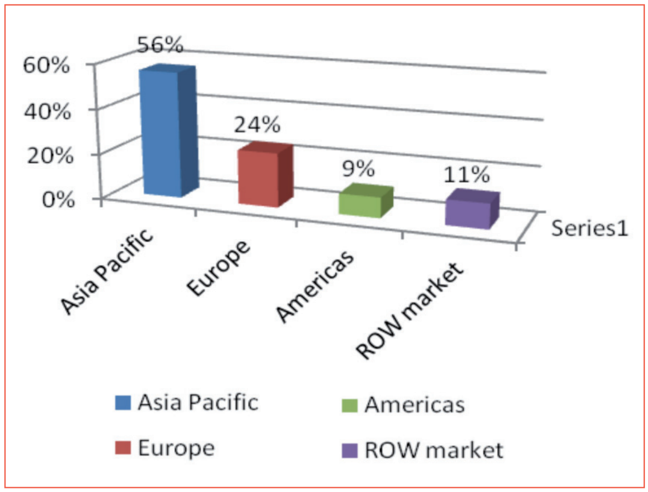

FIGURE 7 Marine coating market distribution

Marine coatings market

The Marine Coatings Global market size was about $ 4.8 billion in 2012. The end markets are new-building, repair and maintenance of deep sea, coastal and navy vessels. In the past the market especially depended on new-building activity, while maintenance and repair were a less cyclical business. On the contrary, in the last few years the new ship building market continues to be in decline and the market for marine coatings benefitted from an increase in ship repair and maintenance.
It seems that in 2013 the market for marine coatings has continued to show signs of improvement and this trend can go on beyond, especially as Asia Pacific continues to lead the way in new shipbuilding and dry-docking. As a consequence the Asia Pacific region remains the most important area for marine coatings manufacturers, with China, South Korea and Japan representing nearly 80% of world's new building capacity, and China now leading in the number of dry docks and dry dockings, Asia is growing two or three times faster than any other region. Concerning the European region, tank coating

work in Europe will be the main segment (Figure 7). Within the total marine coatings market value, the dimension of the market for antifouling paints in 2012 was around $ 1.4 billion, of which 80% of the market is ocean-going ships, 20% leisure boats & offshore structures.

Conclusion

Since remote times Man has been fighting a never-ending battle against the fixing of marine organisms on surfaces immersed in the sea water in general, and on ship hulls in particular. Even when the problem seemed to have been solved, thanks to the boom in the development of TBT-based antifouling paints, with their well-known technology in which, by suitably controlling the molecular composition of the binder, it was practically possible to tailor-make antifouling paints to meet the needs of each particular type of ship, it was soon to become an issue once again. Its harmful effect for marine organisms has lead to the total ban of TBT-based antifouling paints after 1st January, 2008. Meanwhile, the numerous alternative techniques to antifouling painting which have been tested over time have either not proven to be sufficiently efficient nor are so expensive and/or difficult to apply on ship hulls, so that they have not been applied with the hoped-for success. Thus, in a first attempt to address the problem, antifouling paint manufacturers replaced TBT in self-polishing polymers with other chemical ligands of their main chains, such as copper, and reinforced the biocidal effect of copper with artificial biocides, such as certain known herbicides and pesticides. However, many of the latter have also proven to be highly harmful to the environment, and the long-term effect of many others has not been fully clarified yet. Moreover, the implementation of the European legislation on biocide, EU Regulation 528/2012, imposes certain requirements for the acceptance and registration of new biocide products, which encourage the abandonment of this type of products in the sea water. In these conditions, antifouling paint manufacturers have no alternative but to intensify their research in the quest for biocide-free products that prevent the attachment of marine organisms. For the purpose of both efficacy and safety for human health and the environment, the future developments of the antifouling paint systems are designed to use biocides at very low concentrations and very high and quick biodegradation, Smart technology, green Chemistry, nanotechnologies.

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