Chapter 6
Development of Marine Antifouling Coatings

Xiaowei Pei and Qian Ye

Abstract Antifouling coatings for underwater hulls are a very important topic in coating research. Effective hull coatings determine the performance factors including speed, fuel consumption, and weight of a vessel. Controlling fouling using an antifouling paint containing biocides is the most common way of keeping hulls as efficient as possible; however, restrictions on the use of biocide-releasing coatings have made the generation of nontoxic antifouling surfaces more important. This chapter specifically focuses on recent developments in antifouling coatings and summarizes the main types of antifouling products used through history up to the present time. Consideration is also briefly made of the main basic mechanisms by which different types of antifouling paints work. Finally, a number of current researches on antifouling technologies are presented.

6.1 Introduction

Marine biofouling is a costly, complex, and environmentally harmful phenomenon caused by the adhesion and accumulation of various marine organisms on a surface immersed in seawater. Typically, the biofouling process is divided into two main stages [1] (Fig. 6.1): micro- and macrofouling. During microfouling, a biofilm is formed and bacteria start to adhere. In the macrofouling stage, larger organisms start to attach. While each stage of fouling may colonize or dominate a surface eventually, the type of fouling that attaches is often influenced by what had settled previously [2]. The accumulation and colonization of marine biofouling have serious impacts, in particular for the ship industry, increased surface roughness and hydrodynamic drag, increased fuel consumption, and a reduction in operating speed and manoeuvrability [3]. Because of these detrimental effects on a ship's performance, biofouling costs the US Navy an estimated US$ 1 billion per year [4]. Furthermore, the adherence and subsequent release of organisms from a ship hull

---

X. Pei (✉) · Q. Ye
State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhou 730000, China
e-mail: peixl@licp.cas.cn

F. Zhou (ed.), *Antifouling Surfaces and Materials,* DOI 10.1007/978-3-662-45204-2_6

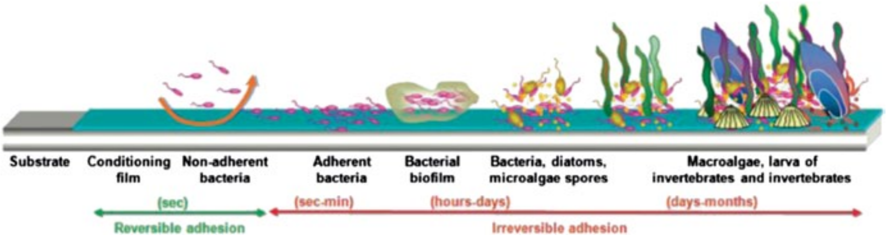

Fig. 6.1 Development processes of marine fouling. (Reprinted with permission from Ref. [1]. Copyright 2006, EDP Sciences)

poses the threat of organism transport, which can lead to non-native or invasive species introduction [5].

The best solution to the problem of fouling is treating the hull with an antifouling (AF) coating. The earliest techniques proposed were pitch, tar, wax, heavy metals (lead), or toxic (arsenic-based) coatings [6]. Ever since the 1800s, coatings with all different toxins as mentioned above have been formulated and experimented for AF till organic tin compounds came into vogue; specifically, tributyltin (TBT) self-polishing copolymer paints became widely used [7, 8]. TBT acts as a broad-spectrum biocide and can be incorporated into paints such that it is released from the coating, and effectively inhibits fouling on a ship hull up to 5 years. These paints were estimated to save the shipping industry US$ 5.7 billion during the mid-1990s in fuel and by delaying ship dry dock and repaint [9]. Although the AF performance of such systems is excellent, the amount of toxins released per ship is enormous. Leaching of TBT into the environment, even at very low concentrations, was found to have detrimental impacts on nontarget organisms. The impact of TBT on marine organisms induced many governments to restrict its use. An order was issued banning the use of this type of biocide in the manufacturing of AF paints from January 1, 2003, and the presence of these paints on ship surfaces from January, 1 2008 [10]. Thus, the paint industry has been urged to develop TBT-free products which are able to replace the TBT-based ones, but yield the same economic benefits, and cause less harmful effects on the environment.

As alternatives, copper-based paints and/or the use of new paints incorporating high levels of copper, already in use, gained popularity following the ban of TBT. These paints contain copper salts as biocidal agents and booster biocides to aid the prevention of slime fouling which can be resistant to copper salts. Although less than TBT, these systems have also shown negative effects on natural life and environment [11]. Recently, the use of copper-based coatings on recreational boats has been banned in the ports of San Diego and Washington. This drives both science and industry to evaluate other types of AF mechanisms, and there is considerable interest in developing biocide-free coatings, particularly low-surface-energy fouling release (FR) coatings that rely on surface physicochemical and bulk-material properties to either deter organisms from attaching in the first place or reduce the adhesion strength of those that do attach, so that they are easily removed by the shear forces generated by ship movement or mild mechanical cleaning devices [12].

Other alternatives are also considered for new coating designs, including enzyme-based coatings and microtopographical surfaces inspired from nature.

This chapter provides an overview of the technologies developed for use as AF coatings, seeks to combine all main topics related to AF technologies, and aims at a thorough picture of the state of art in marine biofouling prevention systems. In addition, the latest developments of novel approaches currently being explored by materials scientists in marine AF applications will be discussed, and emphasis will be given to interdisciplinary studies in which the structure and surface properties of coatings are correlated with their AF properties. Finally, the chapter focuses on interesting cases that would then allow the reader to understand the main trends that emerge from this field, and indicate future and promising directions of research.

6.2 AF Technologies and Types

AF coatings and other surface treatments used to prevent or inhibit the settlement and growth of marine organisms on underwater surfaces can be broadly categorised according to their mode and mechanism of action. An understanding of these different AF types is considered necessary to the development of AF technologies. Historically, humans have explored a variety of methods for preventing the fouling of ship hulls. Currently, AF strategies can be divided into two main categories: (i) biocidal coatings, which act on the marine organisms by inhibiting or limiting their settlement using chemically active compounds, and (ii) nontoxic coatings, which inhibit the settlement of organisms or enhance the release of settled organisms without involving chemical reactions [13]. A growing interest in enzyme-based coatings and engineered topographical surfaces as "promising" coatings has appeared in marine applications since the early 2000s, with a number of scientific papers, which doubles over the period 2000–2010 for the enzyme-based technology.

6.2.1 Historical Development of AF Systems

The history of development of AF methods for protection of engineered structures dates far back to the ancient times but is the topic which still continues to remain as an important issue for research. In early times, wooden hulls were protected with coverings of lead, copper, pitch, tar, wax, asphalt, oil, tallow, and other available materials [14, 15]. Most of these ancient methods were partially effective in protecting the surfaces of ships and resulted in huge losses in property and lives. The sheathings were difficult to structure and cast and left defects or holes which led to drastic corrosion and failure. When iron ships were introduced, the development of different systems was necessary. It was the use of iron ships which eventually led to the development of AF coatings after attempts of sheathing with many other metals, and wooden, rubber, or cork sheathing covered with metals, were unsuccessful.

Table 6.1 Main and new candidate biocides used in antifouling coatings

Biocide	Alternative name	CAS number
Copper		7440-50-8
Dicopper oxide (cuprous oxide)		1317-39-1
Copper thiocyanate		1111-67-7
Bis(1-hydroxy-1H-pyridine-2-thionate-O,S) copper	Copper pyrithione	14915-37-8
Zinc complex of 2-mercaptopyridine-1-oxide	Zinc pyrithione	13463-41-7
N-dichlorofluoromethylthio-N′,N′-dimethyl-N-phenylsulfamide	Dichlofluanid, preventol	1085-98-9
N-dichlorofluoromethylthio-N′,N′-dimethyl-N-p-tolylsulfamide	Tolylfluanid, Preventol	731-27-1
4,5-dichloro-2-n-octyl-4-isothazolin-3-one	Sea-Nine211,Kathon287T	64359-81-5
Zinc ethylene bisdithiocarbamate	Zineb	12122-67-7
N′-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamie	Irgarol 1051, Cybutryne	28159-98-0
Triphenylboron pyridine complex[a]	TPBP	971-66-4
2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoro-methyl pyrrole[a]	Tralopyril, Econea	122454-29-9
N-[(4-hydroxy-3-methoxyphenyl) methyl]-8-methylnon-6-enamide[a]	Capsaicin	404-86-4
4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole[a]	Medetomidine, Selektope	86347-14-0

[a] New candidate biocides

TPBP triphenylborane pyridine

6.2.2 *Biocidal Coatings*

6.2.2.1 Biocides

Few biocides have the necessary combination of characteristics to make them safe and effective AF agents. Mercury, arsenic, and their compounds, and also now the organotins, are examples of effective AF agents that have been deemed unacceptable due to adverse environmental or human health risks. The potential of biocidal compounds to cause adverse effects has received major attention, and biocide-containing AF coatings are currently regulated and approval is required. The number of “acceptable” AF agents is now a rather short list. Table 6.1 gives a list of the main biocides currently used in AF coatings as well as new candidate biocides not yet mentioned in the Biocidal Products Directive [13]. All these compounds vary in terms of their mode of action, environmental persistence, and toxicological properties. Generally, the organic biocides are only used as booster biocides to improve the active spectrum of copper compounds.

Environmentally benign alternatives to control surface colonization have been investigated. They exploit natural marine product antifoulants utilized by marine organisms to prevent themselves from colonization by other marine organisms (e.g. sponges, corals, and macroalgae) [16–18]. The challenge of finding a natural product, which fulfils the required criteria of low toxicity, broad-spectrum activity, and ease of production has yet to be realized and is the main reason why they have not been so far successfully commercialized [13].

6.2.2.2 Insoluble Matrix Paints or Contact Leaching Paints

These types of AF paints consist of high-molecular-weight polymer backbones such as epoxy, acrylates, chlorinated rubber, etc., which are insoluble and do not polish or erode after immersion in water [14]. In view of their good mechanical strength characteristics, due to which these coatings are also known as hard AF paints, high amounts of toxicants can be incorporated. These active molecules or particles can be in direct contact with each other and, consequently, can be released gradually. Since the binder is not soluble in seawater, as the pigment/toxicant is penetrating through interconnecting pores, and diffuse out similarly to generate AF action. Although these are mechanically robust and resistant to cracking and atmospheric degradation, they lose their pigment/toxicant release capacity due to the build-up of thick leached layers, and have a very short life span (rarely exceeding 18 months) [19].

6.2.2.3 Soluble Matrix Paints

Soluble matrix paints, also known as ablative/erodible paints, are paints in which the biocide is mixed through the paint matrix/binder/resin. These paints, with binders based on rosins and their derivatives, incorporate toxic pigments, such as copper, iron or zinc oxides, and previously also arsenic and mercury. In soluble matrix paints, the paint binder is sparingly soluble and slowly dissolves to allow biocide to be released. To be effective, the biocide must be continuously released at the paint surface at a rate necessary to generate a toxic concentration within the surface boundary layer. Limitations in the dissolution process prevented these paints from remaining effective for periods beyond 18 months to 2 years. Their main advantage is that they can be applied on smooth bituminous-based primers. Their main disadvantages are related to the sensitivity of the binders to oxidation and oil pollution. This means that ship hulls coated with these paints need to be refloated as soon as possible after dry-docking, in order to avoid oxidation in contact with the atmosphere. Furthermore, their relatively weak biocidal activity in stationary conditions makes them unsuitable for slow-speed vessels or ships that remain idle for long periods [20]. In summary, these products were depleted over time in an imprecise and inadequate manner, as the minimum biocidal activity was observed during stationary periods, which are most favourable for the settlement of fouling organisms.

6.2.2.4 Ablative Paints

Ablative paints are essentially soluble matrix paints with improved mechanisms of solubility that enable effectiveness for periods up to 36 months. Controlled depletion polymer (CDP) technology is one example of this paint type. Their binder is reinforced by synthetic organic resins, which are more resistant than rosin derivatives, and control the hydration and dissolution of the soluble binder. In contact with seawater, the biocides dissolve together with the soluble binder, and the dissolution process-controlling ingredients are “washed” from the surface [21]. The key difference between ablative paints and true self-polishing paints is that the ablative mechanism is still hydration and dissolution, not hydrolysis.

6.2.2.5 Self-polishing Copolymer Paints

Compatible with both steel and aluminium hulls, self-polishing copolymer (SPC) paints are based on acrylic or methacrylic copolymers which are easily hydrolysable in seawater. These copolymers, blended with biocides, confer a smooth surface of the coating and an ability of controlling/regulating biocides leaching rate through controlling the binder erosion rate [22].

TBT Self-polishing Paints Organotin copolymer paints, based on TBT methacrylate, were the first true SPC–AF coatings. Montermoso et al. first suggested the possibilities of TBT acrylate esters as AF coatings in 1958 [23]. As the carboxyl–TBT bond is hydrolytically unstable in slightly alkaline conditions, like those found in seawater, slow and controlled hydrolysis of the coating takes place, which corresponds to the “wear” of the polymer. These paints differ to all previous types, in that the copolymer acts as both the paint matrix and biocide.

With correct application, organotin SPC coating systems could provide AF effectiveness for 5 or more years. However, it should be noted that the polishing rate of SPC coatings can be varied to maximise the effectiveness on vessels with different operating speeds and activity. Fast vessels which are especially sensitive to increase in fuel consumption, require much more efficient AF protection and harder (slow polishing rate) systems have been formulated, while for slow vessels or those that spend long periods in port, softer (fast polishing rate) systems have been formulated, in order to assure the most suitable rate of release for the adequate control of marine fouling [21].

Tin-Free Self-polishing Paints As stated earlier, the concern over the harmful side effects of TBT compounds on the environment has resulted in significant investment in research and development of TBT-free systems. Tin-free self-polishing coatings are now available based on copper, zinc, and silyl acrylate which are designed for the same reaction mechanisms with seawater as TBT–SPC paints. Unlike the organotins SPCs, these copolymers do not generate sufficient biocide to be effective. Therefore, besides the toxicants that react inside the copolymer, these paints include toxicant pigments, and thus present highly efficient AF properties in any service conditions at sea. Originally, ZnO was used as a pigment together with insoluble pigments. The poor AF activity of zinc ions was compensated for by high polishing rates. The shift to cuprous oxide made it possible to reduce the polishing rates and attain a better efficiency against algal fouling.

In time, seawater dissolves more pigment particles, causing the releasable area to grow and making the copolymer film brittle and easily erodible by seawater, leaving a new fresh area of the coating uncovered for subsequent release (self-polishing effect). This process not only generates a continuous and predictable release of biocide but also the paint surface actually smoothes in service which improves ship performance. However, developing a product with the same characteristics as TBT-based paints is no easy task. In any case, none of the existing acrylic-based tin-free alternatives can fully mimic the activity of the TBT–SPC technology since none of them involves the same biocide release mechanisms; strictly speaking only the polishing and Cu leaching rates of the tin-containing products can be imitated by these tin-free technologies. Furthermore, 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 service lives of 5 years have been reported.

6.2.3 Nontoxic Coatings

An awareness of the harmful effects of biocides used for AF divert the attention to develop nontoxic alternatives as it was realized that the best possible approach in controlling biofouling would be not to rely on the release of toxic biocides to control the problem. Thus, keeping in mind the environmental perspective three general (non-exclusive) strategies including FR coatings, engineered microtopographical surfaces, and marine natural antifoulants are typically followed in the design of novel, non-biocidal, non-fouling surfaces.

6.2.3.1 Fouling Release Coatings

FR coatings are biocide-free coatings, and their AF performances rely on a dual mode of action, i.e. nonstick properties and an FR behaviour. These coatings do not completely eliminate attachment of fouling forms but prevent strong adhesion of the latter due to smooth low-energy surface so that the hydrodynamic forces of water are sufficient in washing off the attachments [24]. The self-cleaning properties of FR coatings are illustrated in Fig. 6.2, where an initially fouled FR coating-coated surface is able to self-clean at different velocities [13]. Moreover, the smoothness of FR coatings enables them to reduce the drag of the vessel and therefore reduce fuel consumption and greenhouse gas emissions. However, the limitation is that FR coatings are efficient only when the speed of the ship produces the hydrodynamic shear needed for the loosely attached macrofouling organisms to fall off [14].

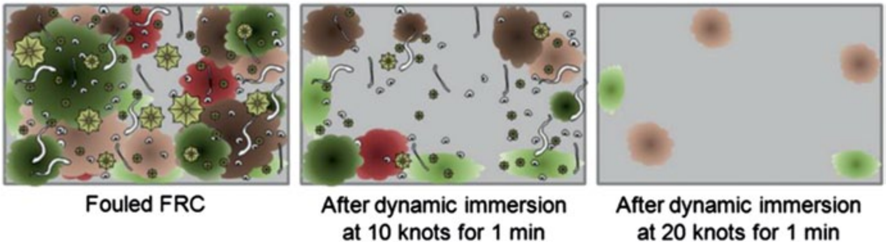

Fig. 6.2 Schematic illustration of the self-cleaning ability of FR coatings. FR fouling release. (Reprinted with permission from Ref. [13]. Copyright 2012, American Chemical Society)

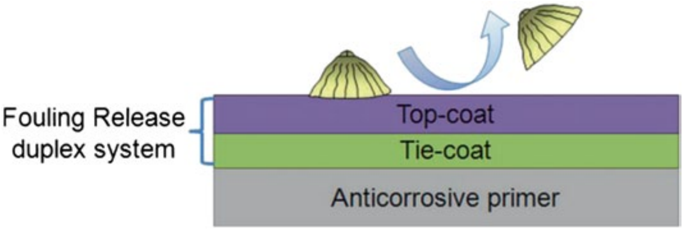

Fig. 6.3 Schematic illustration of FR systems. FR fouling release. (Reprinted with permission from Ref. [13]. Copyright 2012, American Chemical Society)

On static or slow-moving structures, the efficacy is limited to the initial stages of fouling which remain easy to remove [25].

In the patented and scientific literature, FR coatings mainly based on fluoropolymer and elastomeric silicone binders. PTFE (Teflon®)-based systems were the first FR coatings developed, but silicone-based systems have since been found to perform more effectively due to their low-surface energy and modulus. Both of these properties are important in determining the release from a surface, as surface energy influences initial attachment to a surface and low modulus influences organism release by allowing peeling from the surface [26]. However, the elastomeric coatings that have been developed on this premise are soft and mechanically weak, which leads to their easy damage in the marine environment [27]. Moreover, their performance is often enhanced by the addition of nonreactive silicone slip agents which leach from the coating over time, into the marine environment [28]. While these slip agents are released at very low levels and known to be typically nonhazardous, their gradual release from coatings can lead to the decrease of performance over time. Additionally, these coatings also do not adhere well to marine primers and often require the use of a tie coat to achieve satisfactory adhesion [14]. The top coat is based on cross-linked polydimethylsiloxane (PDMS) elastomers and usually contains additive oils to enhance their slippery nature. The tie coat is required to promote the adhesion between the nonstick FR top coat and the epoxy primer (Fig. 6.3) [13].

6.2.3.2 Engineered Microtopographical Surfaces

Some nontoxic AF strategies are mainly based on controlling the surface physicochemical, mechanical, and topographic properties that have significant impacts on the interactions between marine organisms and the surface [29–31]. The study of AF surfaces with special microtexture have gained momentum [32–34]. Brennan et al. investigated the effect of surface structure features on marine biofouling [32]. Several design patterns, including channels, ridges, pillars, pits, and ribs, were fabricated, and they concluded that an effective coating should possess topographical features that are smaller than either the dimension of marine organisms or the parts of organisms that explore the surface while settling. However, as different fouling organisms respond to topographies of different length scales, hierarchical patterning may be required. Efmenko et al. suggested that coating with a topographical pattern with a single length scale could not prohibit marine biofouling since there are a very diverse range of marine organisms. So they reasoned a coating with a hierarchically wrinkled surface topography with patterns of different length scales ranging from tens of nanometres to a fraction of a millimetre can be employed as AF coating for underwater applications [34].

In fact, structural anti-biofouling coatings are inspired by nature since the skin or shells of many marine organisms do not have biofouling at all along the lifetime because of their special surface topography [35]. The surfaces of many marine animals ranging from shells of molluscs to the skin of sharks and whales have a complex surface topography, and by analogy with the “self-cleaning” lotus-leaf effect, it is often speculated that this surface roughness may have a role in either deterring fouling organisms from attaching or promoting their easy release. Artificial surfaces which were inspired from natural microtextures such as gorgonian echinoderms, marine mammal skin, and sharklet skin, and these biomimic surfaces provided promising fouling resistance [36]. Scientists have developed methods to reproduce these microtextured surfaces (laser abrasion, photolithography, moulds and casting, and nanoparticles)[37] and performed tests for their AF efficacy in the laboratory and in the field. Figure 6.4 gives some examples of engineered topographies on a PDMS surface [32]. Carman et al. presented a biomimetically inspired surface topography (Sharklet AF$^{\text{TM}}$) containing 2-mm-wide rectangular-like (ribs) periodic features (4, 8, 12, and 16 mm in length) spaced at 2 mm that can reduce *Ulva* settlement by 86 %. This represents a typical example of a topographic inhibition of settlement of marine alga [38]. Herein, it should be pointed out that to be successful, bioinspired technologies will require multiple attributes (topography, modulus, and chemistry) to be effective in the marine environment. This research area is very prolific and is progressing considerably through large consortium project such as the Advances Nanostructured Surfaces for the Control of Biofouling (AMBIO) project which aims at linking various scientific experts (chemists, engineers, and biologists) with the aim of designing new wide range nanostructured coatings [39].

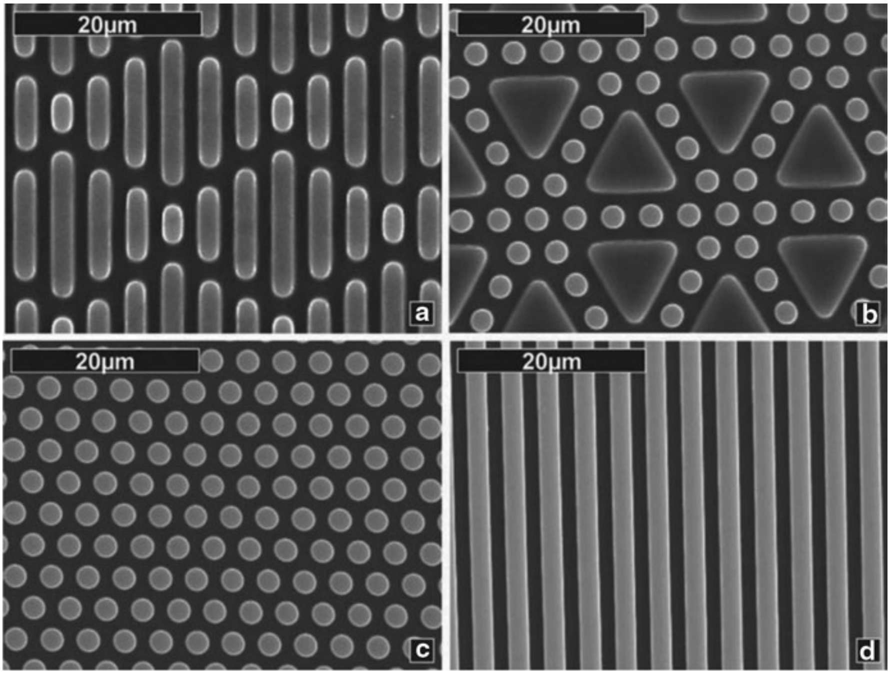

Fig. 6.4 SEM images of engineered topographies on a PDMS surface. **a** 2 μm ribs of lengths 4, 8, 12, and 16 μm combined to create the Sharklet AF™. **b** 10 μm equilateral triangles combined with 2-μm-diameter circular pillars. **c** Hexagonally packed 2 μm diameter circular pillars. **d** 2-μm-wide ridges separated by 2-μm-wide channels. *PDMS* polydimethylsiloxane; *SEM* scanning electron microscopy; *Sharklet AF™* biomimetic topography inspired by the skin of fast moving sharks. (Reprinted with permission from Ref. [32]. Copyright 2007, Taylor & Francis)

6.2.3.3 Marine Natural Antifoulants

Studies on AF mechanisms in marine organisms suggest that some secondary metabolites act as fouling deterrents rather than biocides and AF treatments based on these "natural" products are under development. The discovery of naturally occurring bioactive agents is based on bioassay-guided fractionation and purification procedures. The choice of the test organisms for bioassays is crucial and has to be ecologically relevant. In the previous years, most of the screening were conducted against *Ulva intestinalis* [40] and *Balanus amphitrite* [41]. But, nowadays, the trend is to increase the number of organisms used in bioassays to draw a wider picture of the activity spectra of a specific compound as well as of its mode of action [42].

Previous reports have suggested that the best sources for AF compounds are organisms such as sponges, corals, and macroalgae and/or their associated microflora and/or symbionts. The active ingredients isolated and their performances against representative fouling organisms have been recently reviewed [43]. To date, purification of active products from marine organisms has yielded to around 200 mol-

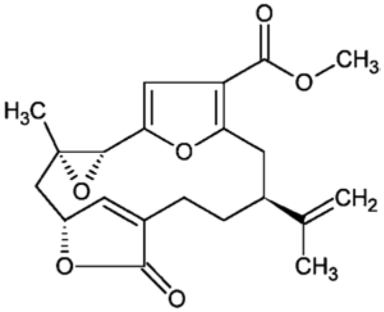

Fig. 6.5 An example of a natural product with antifouling activity. (Reprinted from Ref. [45]. Copyright 1975, with permission from Elsevier)

ecules with variable degrees of AF activities against a wide range of marine fouling organisms, and the discovery of new compounds has been improved through the continuous advances in technical innovation [44]. Figure 6.5 gives an example of a natural product with AF activity. The molecule depicted is Pukalide, a sesquiterpene isolated originally from a Hawaiian soft coral in the 1970s [45].

When a lead compound is discovered from the laboratory screening, field assays and paints formulation require large quantities of marine natural products and the difficulties of mass production becomes a serious constraint [43]. Moreover, compatibility of natural products with coatings is unlikely as compatibility requires specific chemistries that are unrelated to natural product synthesis pathways. In practice, most natural products are oils that modify the composition of coatings to the extent that they interfere with polymer film formation and properties, alter the physical properties of the coating, and/or cannot be effectively released from the coating [46]. Encapsulation is often a basic research strategy of choice for effective molecules with chemistry that is incompatible with the polymer film chemistry. Although encapsulation may solve chemical incompatibility and enable delivery, it does not address synthesis, environmental fates and effects, and registration hurdles. To date, no commercial AF coatings use encapsulation technology [46].

6.3 Other Systems and Future Directions

Based on the level of toxicity of different compounds, different concepts were used to prevent and inhibit biofouling. The most widely practiced ideas include applying alternating current on the surface to repel and kill attaching species. In the 1990s, an interesting innovation was made in AF paints, with the introduction of fine fibres in their formulation. This technology was initially based on the use of relatively short fibres (e.g. 1.0 and 1.3 mm in length) in a dense profile (close to 200 fibres/mm^2). After the application of an epoxy adhesive, the fibres were electrostatically charged and applied by spraying, in order to assure their orientation perpendicular to the surface before the drying of the adhesive. When the coating was submerged, the fibres moved with the action of the current, giving rise to a movement on the coating surface which prevented the attachment of marine organisms [21].

Mechanical cleaning is one of the oldest methods for biofouling control. Underwater cleaning, which avoids the necessity of frequent dry-docking, can maintain high-level ship performance with attendant reductions in fuel consumption. One potentially environmentally benign fouling management strategy is robotic cleaning. The application of UV, ultrasonics, laser beams, etc., could be used by such an automated system. The potential price of underwater cleaning could be lower than that of the high-pressure water cleaning in a dry-dock, and underwater cleaning could be used jointly with FR systems provided it does not damage the weak coating. Once a robot that can clean a large portion of a ship hull in an environmentally benign way is developed, problems such as cost and versatility can be addressed.

The idea of using enzymes for AF coatings emerged during the 1980s, and the concept has received increased interest in recent years [47, 48]. Enzymes are catalytically active proteins and are omnipresent in nature. They have been shown to be effective in reducing settlement and adhesion strength of a range of fouling organisms, algal spores, diatoms and barnacle cyprids, due to dissolution of adhesive [49]. A variety of commercially available enzymes have been explored as nontoxic AFs, such as Alcalase, a commercial preparation of the serine endopeptidase Subtilisin A. This enzyme has the advantages of being readily available, nontoxic, and biodegradable. However, the challenge for enzyme technology will be to achieve controlled release and stability of enzymes when incorporated into a coating [30, 50].

Conductive coatings like polyaniline have also been reported to possess weak but synergistic AF performance by virtue of their conductivity.[14] Another set of ideas for AF include radioactive coatings (e.g. those containing thallium compounds), piezoelectric coatings, and application of external vibrations—glass-flake coatings have also been attempted with some success and deserve a mention. Most of these techniques are limited to practice on a very small scale to limited marine organisms so that uncertainties about real-scenario performance exist. The greatest drawback of most of these concepts is that the set-up and application requirement of them are very expensive and outweigh the benefits obtained.

Overall, while efforts continue to be made in the development of coatings suitable under all environments, application conditions, surfaces, and organisms, the copper-based systems continue to dominate the market and can be foreseen to do so till superior nontoxic replacements surge the market. It is unlikely that non-biocidal solutions based on coating designs incorporating a single attribute will solve the problem. One way forward will be to design "multifunctional coatings", incorporating a range of attributes, for example, an appropriate topography combined with a suitable amphiphilic or zwitterionic surface chemistry and environmentally benign compounds that deter settlement or enzymes to target their bioadhesives.

6.4 Conclusions

AF coatings are essential for preventing the growth of fouling on immersed structures. There is a long history behind their development involving tremendous technological progress and research. Although the list of accomplishments in the field of AF is significant, the Environmental Protection Agency (EPA) regulations are being tightened in response to the environmental hazards and inefficiencies of the current AF technology. The present scenario is that non-tin alternatives have been able to support the AF industry but only at the cost of being more expensive, low in life span and durability, and unable to deliver the same satisfactory AF performance.

While biocide-based AF coatings still represent the main part of market, FR coatings are expanding, as they do not contain biocides and, moreover, enable savings in fuel costs. FR coatings already yield good results on fast-moving vessels. Further studies on the influence of the surface properties on the adhesion phenomena will orientate the search for a material, which could release the fouling organisms at lower speeds. Furthermore, the development of an efficient product entirely based on natural biocides seems still far away in time. Again, the still incomplete understanding of the working mechanisms of these products may be slowing down the identification of truly interesting compounds.

In the future, we expect more research on environmentally benign, marine AF coatings. There is an ongoing need to constantly improve the performance of AF coatings and to raise environmental awareness. Conversely, the ever tighter legislation regarding safety and environmental protection is driving the development of an ecofriendly marine coating solution.

References

1. Haras D (2006) Biofilms et altérations des matériaux: de l'analyse du phénomène aux stratégies de prevention. Mater Tech 93:27–41
2. Roberts D, Rittschof D, Holm E et al (1991) Factors influencing initial larval settlement: temporal, spatial and surface molecular components. J Exper Mar Biol Ecol 150(2):203–221
3. Schultz M, Bendick J, Holm E et al (2011) Economic impact of biofouling on a naval surface ship. Biofouling 27(1):87–98
4. Callow ME, Callow JA (2002) Marine biofouling: a sticky problem. Biologist 49(1):10–14
5. Piola RF, Dafforn KA, Johnston EL (2009) The influence of antifouling practices on marine invasions. Biofouling 25(7):633–644
6. Callow M (1990) Ship fouling: problems and solutions. Chem Ind 5:123–127
7. Evans S, Birchenough A, Brancato M (2000) The TBT ban: out of the prying pan into the fire?. Marine Poll Bull 40(3):204–211
8. Milne A, Hails G (1976) International paint. GB Patent 1,457,590
9. Rouhi AM (1998) The squeeze on tributyltins. Chem Eng News 76(17):41–42
10. Pereira M, Ankjaergaard C (2009) Legislation affecting antifouling products. In: Hellio C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodshead Publishing, Cambridge, pp 240–259

11. Ytreberg E, Karlsson J, Eklund B (2010) Comparison of toxicity and release rates of Cu and Zn from anti-fouling paints leached in natural and artificial brackish seawater. Sci. Total Environ 408(12):2459–2466
12. Callow JA, Callow ME (2011) Trends in the development of environmentally friendly fouling-resistant marine coatings. Nat Commun 2:244 doi:10.1038/ncomms1251
13. Lejars M, Margaillan A, Bressy C (2012) Fouling release coatings: a nontoxic alternative to biocidal antifouling coatings. Chem Rev 112(8):4347–4390
14. Yebra D, Kiil S, Dam-Johansen K (2004) Antifouling technology–past, present and future steps towards efficient and environmentally friendly antifouling coatings. Prog Org Coat 50(2):75–104
15. Hellio C, Yebra D (2009) Advances in marine antifouling coatings and technologies. Woodshead Publishing, Cambridge, pp 1–15
16. Clare AS (1996) Marine natural product antifoulants: status and potential. Biofouling 9(3):211–229
17. Clare AS (1998) Towards nontoxic antifouling. J Mar Biotechnol 6(1):3–6
18. Rittschof D (2000) Natural product antifoulants: one perspective on the challenges related to coatings developments. Biofouling 15(1–3):119–127
19. Marson F (1969) Anti-fouling paints. I. Theoretical approach to leaching of soluble pigments from insoluble paint vehicles. J Appl Chem 19(4):93–99
20. del Amo B, Giúdice CA, Rascio VJD (1984) *Influence of binder dissolution rate on the bioactivity antifouling paints*. J Coat Technol 56(719):63–69
21. Almeida E, Diamantino TC, de Sousa O (2007) Marine paints: the particular case of antifouling paints. Prog Org Coat 59(1):2–20
22. Omae I (2003) General aspects of tin-free antifouling paints. Chem Rev 103(9):3431–3448
23. Gitlitz MH (1981) Recent developments in marine antifouling coatings. J Coat Technol 53(678):46–52
24. Schultz MP, Kavanagh CJ, Swain GW (1999) Hydrodynamic forces on barnacles: implications on detachment from fouling-release surfaces. Biofouling 13(4):323–335
25. Terlizzi A, Conte E, Zupo V et al (2000) Biological succession on silicone fouling release surfaces: long term exposure tests in the harbour of Ischia, Italy. Biofouling 15(4):327–342
26. Brady R (2001) A fracture mechanical analysis of fouling release from nontoxic antifouling coatings. Prog Org Coat 43(1–3):188–192
27. Bennett S, Finlay J, Gunari N et al (2010) The role of surface energy and water wettability in aminoalkyl/fluorocarbon/hydrocarbon-modified xerogel surfaces in the control of marine biofouling. Biofouling 26(2):235–246
28. Brady R, Singer I (2000) Mechanical factors favoring release from fouling release coatings. Biofouling 15(1–3):73–81
29. Weinman C, Finlay J, Park D et al (2009) ABC triblock surface active block copolymer with grafted ethoxylated fluoroalkyl amphiphilic side chains for marine antifouling/fouling-release applications. Langmuir 25(20):12266–12274
30. Tasso M, Pettitt M, Cordeiro A et al (2009) Antifouling potential of Subtilisin A immobilized onto maleic anhydride copolymer thin films. Biofouling 25(6):505–516
31. Leroy C, Delbarre-Ladrat C, Ghillebaert F et al (2008) Effects of commercial enzymes on the adhesion of a marine biofilm-forming bacterium. Biofouling 24(1):11–22
32. Schumacher J, Carman M, Estes T et al (2007) Engineered antifouling microtopographies—effect of feature size, geometry, and roughness on settlement of zoospores of the green alga Ulva. Biofouling 23(1):55–62
33. Banerjee I, Pangule R, Kane R (2011) Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. Adv Mater 23(6):690–718
34. Efimenko K, Finlay J, Callow M et al (2009) Development and testing of hierarchically wrinkled coatings for marine antifouling. Acs Appl Mater Interfaces 1(5):1031–1040

35. Cao X, Pettitt M, Wode F et al (2010) Interaction of zoospores of the green alga ulva with bioinspired micro- and nanostructured surfaces prepared by polyelectrolyte layer-by-layer self-assembly. Adv Funct Mater 20(12):1984–1993
36. Scardino A, de Nys R (2011) Mini review: biomimetic models and bioinspired surfaces for fouling control. Biofouling 27(1):73–86
37. Scardino AJ (2009) Surface modification approaches to control marine biofouling. In: Hellio C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodshead, Cambridge, pp 664–692
38. Carman M, Estes T, Feinberg A et al (2006) Engineered antifouling microtopographies correlating wettability with cell attachment. Biofouling 22(1):11–21
39. Callow J, Callow M (2009) Advances nanostructured surfaces for the control of marine biofouling: the AMBIO project. In: Hellio C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodshead, Cambridge, pp 647–663
40. Fletcher R (1989) A bioassay technique using the marine fouling green alga Enteromorpha. Int Biodeterioration 25(6):407–422
41. Branscomb E, Rittschof D (1984) An investigation of low frequency sound waves as a means of inhibiting barnacle settlement. J Exp Mar Biol Ecol 79(2):149–154
42. Mokrini R, Ben Mesaoud M, Daoudi M et al (2008) Meroditerpenoids and derivatives from the brown alga *Cystoseira baccata* and their antifouling properties. J Nat Prod 71(11):1806–1811
43. Hellio C, Maréchal J, Da Gama B et al (2009) Natural marine products with antifouling activities. In: Hellio C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodshead, Cambridge, pp 572–622
44. Maréchal JP, Hellio C (2009) Challenges for the development of new non-toxic antifouling solutions. Int J Mol Sci 10(11):4623–4637
45. Missakian MG, Burreson B, Scheuer P (1975) Pukalide, a furanocembranolide from the soft coral *Sinularia abrupta*. Tetrahedron 31(20):2513–2515
46. Rittschof D (2009) Trends in marine biofouling research. In: Hellio C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodshead, Cambridge, pp 725–748
47. Olsen S, Pedersen L, Laursen M et al (2007) Enzyme-based antifouling coatings: a review. Biofouling 23(5):369–383
48. Kristensen J, Meyer R, Laursen B et al (2008) Antifouling enzymes and the biochemistry of marine settlement. Biotechnol Adv 26(5):471–481
49. Aldred N, Phang I, Conlan S et al (2008) The effects of a serine protease, Alcalase on the adhesives of barnacle cyprids (*Balanus amphitrite*). Biofouling 24(2):97–107
50. Tasso M, Cordeiro A, Salchert K et al (2009) Covalent immobilization of subtilisin A onto thin films of maleic anhydride copolymers. Macromol Biosci 9(9):922–929