Review

Antifouling technology—past, present and future steps towards efficient and environmentally friendly antifouling coatings

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Abstract

The imminent ban of environmentally harmful tributyltin (TBT)-based paint products has been the cause of a major change in the antifouling paint industry. In the past decade, several tin-free products have reached the commercial market, and claimed their effectiveness as regards the prevention of marine biofouling on ships in an environmentally friendly manner. The main objective of this review is to describe these products in as much detail as possible based on the knowledge available in the open literature. This knowledge has been supplemented by means of performance data provided, upon request, by some of the paint-producing companies. An exhaustive review of the historical development of antifouling systems and a detailed characterisation of sea water are also included. The need for studies on the behaviour of chemically active paints under different sea water conditions is emphasised. In addition, the most common booster biocides used to replace TBT-containing compounds are listed and described. It must be stressed that there is still a lack of knowledge of their potential environmental side effects.

The current interest in providing innovative antifouling technologies based on an improved understanding of the biological principles of the biofouling process is also considered in this review. From the analysis of the factors affecting the biofouling process, the interference with the settlement and attachment mechanisms is the most promising environmentally benign option. This can be accomplished in two main ways: imitation of the natural antifouling processes and modification of the characteristics of the substrate. The former mostly focuses on the study of the large amount of secondary metabolites secreted by many different marine organisms to control the fouling on their surfaces. The many obstacles that need to be overcome for the success of this research are analysed. The potential development of broad-spectrum efficient coatings based on natural antifoulants is far from commercialisation. However, exploitation of a weakening of biofouling adhesion by means of the non-stick and fouling-release concepts is at a rather advanced stage of development. The main advantages and drawbacks of these systems are presented along with a brief introduction to their scientific basis. Finally, other alternatives, which may eventually give rise to an efficient and environmentally benign antifouling system, are outlined.
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1. Introduction

Marine biological fouling, usually termed marine bio-fouling, can be defined as the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces immersed in sea water. In the case of ships, the adverse effects caused by this biological settlement are well known (see Fig. 1):

- High frictional resistance, due to generated roughness, which leads to an increase of weight and subsequent potential speed reduction and loss of manoeuvrability. To compensate for this, higher fuel consumption is needed, which causes increased emissions of harmful compounds [1,2]. It may also entail a need for heavier and less energetically efficient machinery. The increase in fuel consumption can be up to 40% [3] and in voyage overall costs as much as 77% [4].
- An increase of the frequency of dry-docking operations, i.e. time is lost and resources are wasted when remedial measures are applied. A large amount of toxic wastes is also generated during this process [4,5].
- Deterioration of the coating so that corrosion, discolouration, and alteration of the electrical conductivity of the material are favoured [6].
- Introduction of species into environments where they were not naturally present (invasive or non-native species) [7,8].

Among all the different solutions proposed throughout the history of navigation, tributyltin self-polishing copolymer paints (TBT-SPC paints) have been the most successful in

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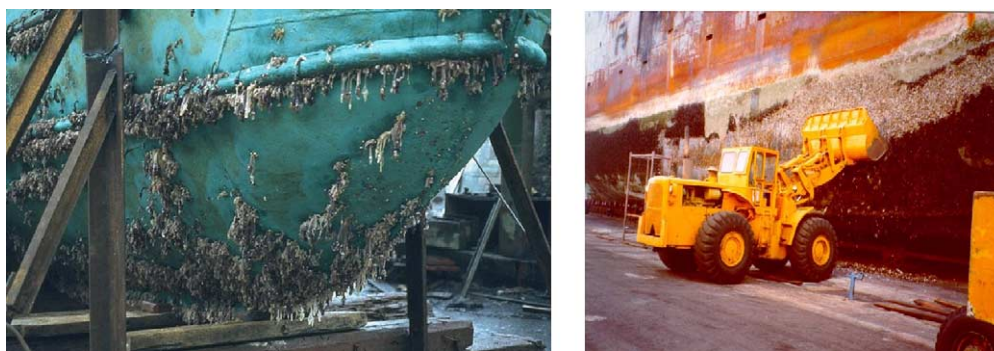*E-mail address:* sk@kt.dtu.dk (S. Kiil).

Fig. 1. Examples of heavily fouled hulls. Courtesy of Hempel's Marine Paints A/S.

combating biofouling on ships. The widespread use of these paints, estimated to cover 70% of the present world fleet in [9,10], has led to important economic benefits [3,4]. Unfortunately, the TBT-SPC systems affect adversely the environment. As an example, it has been shown that extremely low concentrations of tributyltin moiety (TBT) cause defective shell growth in the oyster *Crassostrea gigas* (20 ng/l) and imposex, development of male characteristics in female genitalia, in the dog-whelk *Nucella* sp. (1 ng/l) [11,12]. Malformations have been observed in many other species and the International Maritime Organization (IMO) also reports accumulation in mammals and debilitation of the immunological defences in fishes. These facts forced the development of national regulations in countries all over the world [3]:

- Restriction of the use of TBT-containing compounds on vessels less than 25 m in length.
- Restriction of the release rates of TBT-containing compounds from the paints.
- Elimination of the use of free TBT-holding compounds in paints.

Furthermore, after an International Convention held on 5 October 2001, parties to the convention are required to ban the application of TBT-based antifouling (A/F) paints from 1 January 2003, and the presence of such paints on the surface of the vessel from 1 January 2008 (effective dates) [10]. Although the exact dates for the global application of the resolutions of the convention are still uncertain, regional legislations have already been developed in the same direction (e.g. Amendment to Marketing and Use Directive (76/769/EEC)). Thus, the paint industry has been urged to develop TBT-free products able to replace the TBT-based ones but yield the same economic benefits and cause less harmful effects on the environment. The major antifouling paint companies (e.g. International Marine Coatings, Hempel's Marine Paints, Jotun, Ameron, Chugoku Marine Paints) have already decided to comply with the regulation by removing all TBT-based paints from their product assortment from 1 January 2003. The other party concerned, the shipping companies, has also started to react to the legislative changes by a fleet-wide conversion to tin-free paints (e.g. A.P. Møller and Leif Höegh).

In contrast to previous reviews (e.g. [1,9,11,13–23]), this paper seeks to combine all main topics related to antifouling (A/F) technology, and aims at a thorough picture of the state of art in marine biofouling prevention systems. Hence, it includes a description of sea water, an introduction to the biology of the fouling process, and a summary of the historical development of A/F paints. The latter covers not only biocide-based systems, by far the most used, but also alternative methods. This historical description leads to a discussion of tributyltin (TBT)-based systems and their tin-free biocide-based replacements, the analysis of which constitutes the backbone of the paper. Tin-free biocide-based products are described by an analysis of their binder systems, pigments, and booster biocides used to complement the biocidal action of copper. In addition, the most promising options to dominate the A/F market in the future are presented and described.

2. The marine environment

Little attention has been paid to the influence of the different sea water parameters on the performance of chemically active A/F paints. It has recently been shown that chemical reactions and diffusion phenomena are key mechanisms in the performance of biocide-based A/F paints, and that these can be markedly affected by sea water conditions [24]. The above-mentioned paints are based on the release of several biocides, which are linked or, more often, embedded in a film-forming organic matrix (see Fig. 2). Sea water has to penetrate into the paint, dissolve such biocides and diffuse out into the bulk phase again. To avoid the build-up of long diffusion paths and consequently decreasing release rates, the organic matrix is designed for slow reaction with sea water (and sea water ions) within the paint pores. Once this reaction has reached a certain conversion at the sea water–paint interface, the binder phase is released, thus controlling the thickness of the biocide-depleted layer (leached layer).

Many references to the influence of sea water parameters on the performance of A/F paints can be found in the open literature. For example, the salinity value influences
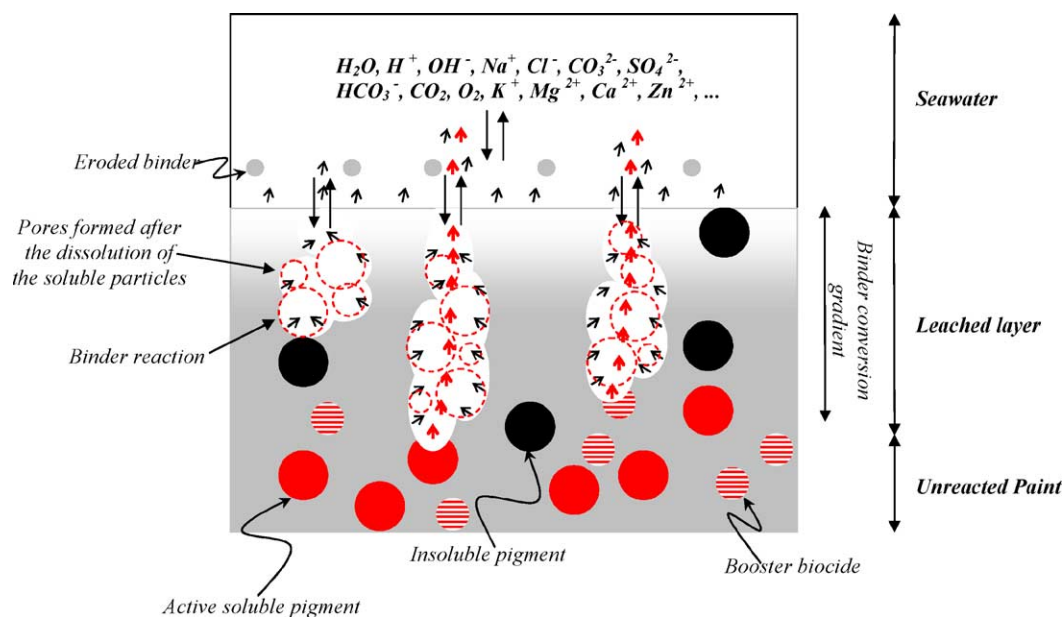
Fig. 2. Schematic illustration of the behaviour of a biocide-based antifouling system exposed to sea water.

the dissolution of the most typical biocidal pigment (Cu_2O) particles [25], the reaction of important binder components such as rosin [26] and the cleavage of the TBT groups in TBT-SPC paints [24,27,28]. The influence of temperature is also significant as it affects the rate of all chemical reactions, dissolution rates and transport processes associated with the activity of chemically active A/F paints. The effect of sea water pH on the release rate of TBT groups from TBT-SPC paints was measured by Hong-Xi et al. [29] and subsequently used by Kiil et al. [24,27,28] in the modelling and analysis of such paints. In these studies, the effect of pH on the dissolution rate of Cu_2O pigment particles, according to [25], was also considered. The influence of pH is even more important in the case of rosin-based paints, as reported by WHOI [2] and Rascio et al. [26]. The solubility of rosin is increased dramatically with increasing pH values.

It is most likely that sea water ions, pH, and temperature will also play a significant role in the reactions associated with the current tin-free biocide-based coatings because these are based on mechanisms similar to those of TBT-SPC paints. In addition, the severity of the biofouling and, consequently, the A/F requirements, and the environmental fate of the released toxicants are affected by most of these parameters. Despite these facts, most studies dealing with the development of new chemically active A/F binders or coatings lack studies on the behaviour of such systems in waters under conditions different from the "standard" or "average" ones. This could eventually lead to biocide-based paints performing excellently under certain conditions but failing in waters with different characteristics. Consequently, it is useful to characterise the environment faced by A/F coatings by determining the range of values of the most significant sea water variables.

2.1. Salinity

The most characteristic feature of sea water is its high salt content, which forms a complicated solution containing the majority of the known elements. This fact is quantified through the concept of salinity. Capurro [30] defines salinity as "the total of solid materials in grams in 1 kg of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and all organic material completely oxidised". In other words, the concentration of the dissolved salts is designated as a single solute. This definition may be obsolete due to the development of more precise measuring methods based on chlorinity and, more recently, conductivity, but it is appropriate to understand the meaning of the concept concerned. The salt content of the waters of the open sea, away from inshore influences such as melting ice, freshwater rivers and areas of high evaporation, is remarkably constant and is rarely outside the range of 3.3–3.8 wt.%. If we only consider sea water below 4000 m, the salinity values are generally between 3.46 and 3.48 wt.% [30]. There are several reasons for the higher divergence of the salinity values near the surface but, among these, rainfall and evaporation are the dominant processes [30]. This finding agrees with Fig. 3, which shows higher salinity values in the atmospheric high-pressure (high evaporation rate and low rainfall) region at around 30°N and 30°S and a local minimum close to the Equator (maximum evaporation rate counterbalanced by heavy rains). A value of 3.5 wt.% is globally accepted to describe the salinity of sea water, although large annual variations in the surface layers can be found in some regions (e.g. near ice) [30,31]. Another important feature of sea water is that the saline composition, regardless of the
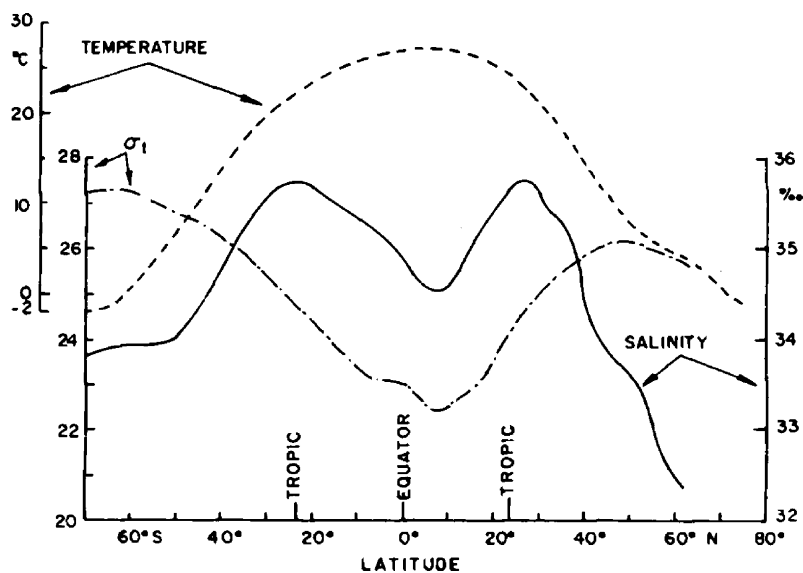
Fig. 3. Variation with latitude of surface temperature, salinity and density-average for all oceans (from [31], with permission of Elsevier).

absolute concentration, has virtually constant proportions for the different major constituents shown in Table 1.

2.2. Temperature

The temperature of the surface waters of the oceans tends to vary directly with the latitude, and the range is from about $-2\,°C$ at the poles to $28\,°C$ right on the Equator [31], although temperatures up to $35\,°C$ can be reached locally [32]. Compared to the landmass, the water temperature is less affected by the weather. In temperate zones the variations amount to around $10\,°C$ and up to $18\,°C$ in areas under continental influences (close to the continents, small Mediterranean areas, marginal seas, etc.) or $2\,°C$ in equatorial and polar regions [30]. The diurnal variations of temperature in the open sea are hardly ever bigger than $0.4\,°C$. Again, surface water shows greater changes in temperature all over the year due to solar radiation absorption, ocean surface radiation emission to the air, evaporation, rainfall and heat exchange with the atmosphere [30].

Table 1
Major ions in solution in "open sea" water at salinity 3.5 wt.% (after [32])[a,b]

Ions	g/kg
Total salts	35.1
Sodium	10.77
Magnesium	1.30
Calcium	0.409
Potassium	0.338
Strontium	0.010
Chloride	19.37
Sulphate as SO_4	2.71
Bromide	0.065
Boric acid as H_3BO_3	0.026

[a] Dissolved organic matter = 0.001–0.0025 g.
[b] Oxygen in equilibrium with atmosphere at $15\,°C = 5.8\,cm^3/l$.

2.3. pH

Sea water is normally alkaline and the pH of the surface layers of the ocean, where the water is in equilibrium with the carbon dioxide of the atmosphere, lies between 8.0 and 8.3, and in the open ocean it is, again, a very constant property [30,32]. The presence of the carbonate system (CO_2, HCO_3^-, CO_3^{2-}) imparts a buffer capacity to sea water. In areas with considerable microbiological activity, there may be some variations due to production of hydrogen sulphide (lower pH) or removal of CO_2 by algae (rise of pH). The temperature also modifies the pH value, usually lowering it as the temperature rises unless too much CO_2 is desorbed, which leads to an increase in the pH. Slightly different pH values may be found in strongly contaminated waters or locally within the paint due to dissolution of some of the components of the A/F paint (e.g. Cu_2O).

2.4. Other sea water variables

Dissolved gases may be important to the determination of corrosion rates [32] and biological growth in sea water [2]. A basic assumption is that surface water is saturated with the atmospheric gases (mainly O_2, N_2, and CO_2), but biological processes such as respiration and photosynthesis can alter their concentrations. In fact, algal activity can lead to supersaturation of the upper layers [31]. The oxygen concentration varies from 0 to 0.8 vol.% although it is rarely outside the range of 0.1–0.6 vol.% [31]. Regarding the A/F performance, it is known that the presence of oxygen in rosin-based paints may cause oxidation of dissolved copper (I), which leads to partial re-precipitation of copper (II) carbonate, copper (II) chloride [25,33], copper (II) hydroxide [26], or even copper (II) sulphide [17,33], with the latter anion resulting from biological processes. None of

these solid compounds have been observed during tests on TBT-based paints. This may lead to the conclusion that relatively long residence times within the paint matrix, attained in the case of rosin-based paints, and deficient A/F protection, leading to the production of compounds such as hydrogen sulphide, are needed to observe such precipitations.

3. The process of marine biofouling

The organisms which take part in marine biofouling are primarily the attached or sessile forms occurring naturally in the shallower water along the coast [2]. "*Marine Fouling and its Prevention*" [2] reported that nearly 2000 species had been identified on fouled structures and [13] later increased the number to more than 4000 species. Nevertheless, it still includes a very small proportion of the known marine species. This is mainly because only those organisms with the ability to adapt to the new situations created by man can adhere firmly enough to avoid being washed off. Ships are an example of a specialised environment. Only forms which have been adapted to tolerate wide fluctuations in environmental conditions such as temperature, water flow and salinity can dominate [14]. Traditionally, the fouling process has been considered to consist of four general stages (see Fig. 4): organic molecules, such as polysaccharides, proteins and proteoglycans, and possibly inorganic compounds are rapidly accumulated on every surface, and give rise to the so-called conditioning film [34,35]. This process is essentially governed by physical forces such as Brownian motion, electrostatic interaction and van der Waals forces. Rapidly developing bacteria and single-cell diatoms settle on this modified surface. These species are first "adsorbed" reversibly, again mainly a physical process, and afterwards "adhered" [35,36] and form, together with protozoa and rotifers, a microbial biofilm [2]. This preferred disposition provides the microorganisms with higher protection from predators, toxins (10–1000-fold higher concentrations) and environmental changes, easier capture of the necessary nutrients (thanks to the gel-like polymeric matrix on which they are embedded) and the energy, carbon and nutrients provided by other microorganisms forming the biofilm [37]. That is the reason why any surface, even protected by biocides, will become covered by a biofilm or slime layer under static conditions [38]. A direct consequence of this on A/F paints is that the release rates of biocides may be modified due to extra diffusion resistances and environmental changes (e.g. alkalinity and pH). These facts stress the need for field tests to estimate the real behaviour of a coating once immersed in non-sterilised natural sea water.

The existence of adhesive exudates (extracellular polymeric substances, EPS) such as polysaccharides, proteins, lipids and nucleic acids and the roughness of irregular microbial colonies help to trap more particles and organisms. These are likely to include algal spores, barnacle cyprids, marine fungi and protozoa, some of which may be attracted by sensory stimuli. The transition from a microbial biofilm to a more complex community that typically includes multicellular primary producers, grazers and decomposers is regarded as the third stage of fouling. The fourth and final stage involves the settlement and the growth of larger marine invertebrates together with the growth of macroalgae (seaweeds) [39]. Typical characteristics of macrofoulers are fast metamorphosis, rapid growth rates, low degree of substrate preference and high adaptability to different environments.

It is widely accepted that the presence of different molecules and organisms in the film influences the settlement of subsequent organisms [40]. The reasons are that
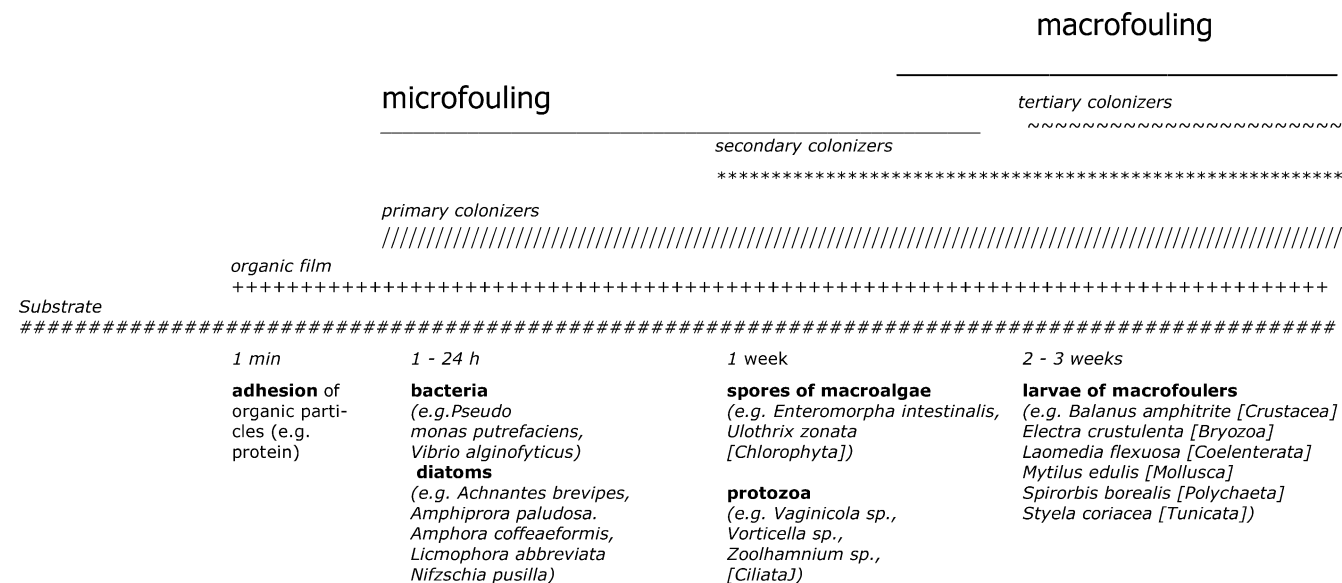

Fig. 4. Temporal structure of settlement (after [35], with permission of Inter-Research Science Publisher).

they may serve as food for very young superior organisms, discolour and dull bright surfaces (which deter the fouling) as well as increase the alkalinity of the surface, favouring the deposition of adhesives, biodegrade toxicants and influence the tenacity of the attachment through modification of the surface-free energy [41]. The assumption of this strictly successional process may inspire thoughts of the development of an efficient A/F method based on blocking of the early stages. Unfortunately, this does not seem possible as much more complex and not strictly successional mechanisms have already been proposed which describe better the biofouling process [36].

The local severity of biofouling depends upon a large number of parameters. Some of these are given by the water conditions and depend on the geographical location and the operating pattern of the vessel. Consequently, these parameters cannot be modified to control the growth of the fouling organisms. Temperature is undoubtedly one of the most important parameters. It is widely known that fouling is generally heavier in regions with high water temperatures [2]. This is clearly related to the fact that temperature appears to be the principal condition determining the breeding periods and rates of growth of marine animals. In regions where marked seasonal variations in temperature occur, the reproduction and the growth of many species are completely suppressed during the low-temperature period and only one generation can be produced in the course of the few warm months. On the contrary, in tropical climates, where the seasonal changes in conditions are relatively small, fouling may continue without interruption throughout the year. The sterilising effect of high temperatures on specific artificial systems (e.g. piping systems) has been widely studied. However, its application to the shipping industry is unfeasible [11].

According to [2], most of the common fouling forms are unable to withstand low salinities, which affects the growth rate and the maximum size attained and causes several malformations. However, slime, algae and bryozoa are commonly found in low-salinity waters, and some species do prefer such conditions [2]. The amount of solar radiation also plays a very important role in the upper layers of the oceans and, consequently, for ship's fouling. Apart from influencing temperature and salinity, it affects directly the rate of photosynthesis of the plants and thus controls the nutrition of the animals [2].

Polluted waters may be harmful either directly through toxic effects, or indirectly e.g. through depletion of oxygen or reduction of the solar radiation available for the photosynthesis. Silt and other suspended matter may asphyxiate sessile organisms or produce substrates unsuited for the attachment of many forms [2] and may also interfere with the food assimilation of animals which use water filtering. On the contrary, some contaminants may enrich the nutrient supply and thus enhance the fouling.

It is also widely known that the problem of fouling is not as pressing in deep waters as in coastal areas [2]. Marine bacteria and marine organisms in general are much less plentiful in oceanic waters compared to coastal waters. Depth is another parameter affecting the intensity of fouling, but it has no influence in the case of ships as they are always in contact with superficial waters.

Finally, the interactions between the different organisms also modify the process of fouling. Bacteria in host-associated biofilm may cause significant mortality to their hosts, produce degradation of host tissue, and increase the drag on their hosts. Bacteria and other higher species may also compete for nutrients, inhibit gaseous exchange, block incident light, and even secrete secondary metabolites which may inhibit the attachment [42]. This last phenomenon is one of the most interesting fields of study for future environmentally friendly A/F systems and will be further discussed in a later section.

Other parameters are dependent on the vessel design and could, a priori, be modified. As an example, Rascio [1] state that fouling does not take significantly place at ship's speeds higher than 6 kn. The influence of this parameter on the formation of bacterial films has also been reported by Egan [43]. Too low rates slow down the nutrient uptake, while too high flow rates increase shear (erosion) and the turbulences also hinder the capture of nutrients by the biofilm. According to [44], the biofilm formation was faster and its viscosity higher at turbulent flows compared to biofilms built up under lower water flow conditions. It may be added that a maximum in this tendency is expected, as higher speeds also involve higher biofilm detachment rates. Unfortunately, water flow (sailing speed) cannot be modified to a large extent and depends on the kind of vessel considered and its activity. However, the nature of the substrate, which clearly affects the adhesion mechanisms, depends on the coating surface properties. Hence, a coating can be optimised for A/F purposes. This constitutes the basis for the non-stick and fouling-release concepts, presently the most promising non-toxic alternative, also to be discussed in a subsequent section.

4. Historical development of antifouling systems

4.1. First attempts and lead sheathing

Some of the disadvantages of marine biofouling have been recognised and combated for more than 2000 years. Early Phoenicians and Carthaginians were said to have used pitch and possibly copper sheathing on ship's bottoms while wax, tar and asphaltum were used by other ancient cultures [2,16]. Another source [45] reports the discovery of a lead-sheathed timber Phoenician galley from about 700 B.C. In the 5th century B.C., historians report that coatings of arsenic and sulphur mixed with oil were used to combat shipworms [16]. In the 3rd century B.C., the Greeks used tar, wax and even lead sheathing. Both Romans and Greeks secured the lead sheathing with copper nails [2,16]. Plutarch

(45–125 A.D.) also mentions the scraping of weeds, ooze, and filth from the ship's sides to make them go more easily through the water [2]. Some centuries later, the Vikings (10 A.D.) are said to have used a "seal tar" occasionally [2]. From the 13th to the 15th century, pitch was extensively used to protect ships, sometimes blended with oil, resin or tallow [2]. As an example, Columbus's ships may have been covered with a mixture of pitch and tallow [2]. Hide sheathing is another material used in the 14th century [2]. Although in the early 16th century wooden sheathing, put over a layer of animal hair and tar, was a usual procedure [2], lead sheathing was much more widespread at that time, as it can be seen from its official adoption by Spain, France and England [2]. Actually, as reported by WHOI [2], lead sheathing was perhaps the most frequently tried system for the protection of ship's bottoms prior to the 18th century. Leonardo da Vinci invented a rolling mill in 1500 for making sheet lead [2]. In spite of documents certifying the poor A/F effect of such a material, lead sheathing was probably enough to protect the wooden hulls from ship worms. Unfortunately, it caused corrosion on the iron components of ships (e.g. rudders), so it was abandoned by the British Admiralty in 1682 [2]. The lead sheathing was then alternated with wooden sheathing, which was again of general use. The latter was typically painted with various mixtures, i.e. tar, grease, sulphur, pitch, and brimstone and filled with iron or copper nails with large heads, put in so closely that the heads touched and formed a kind of metallic sheathing [2].

4.2. Copper sheathing

Copper was already used in the bronze-shod rams of the Phoenician warships and as copper fastenings in the Greek and Roman boats. However, use of copper sheathing in ancient times seems improbable [2]. One of the first references to underwater use of copper was in 1618, during the reign of the Danish King Christian IV [45]. In this case, only the keel near the rudder was coppered. The first record on the use of copper as an antifoulant is in the British patent of William Beale in 1625 [2]. Beale may have used a mixture of cement, powdered iron, and probably a copper compound (copper sulphide or copper arsenic ore) [2]. More than one century later, in 1728, a method based on "rooled" copper, brass, tin, iron, or tinned plates was patented, although there is no record of its application to ships [2]. The first authenticated use of copper sheathing was reported on *HMS Alarm* in 1758 [2], and its relative success encouraged to copper of some other ships. Around 1780, copper was widely used throughout the British Navy [2]. Copper for sheathing wooden ships became of such great importance that England forbade exports of such "war materials" in the 1780s. Nevertheless, it was not until the turn of the 19th century that Sir Humphrey Davy, studying the process of corrosion of copper, clearly showed that it was the dissolution of copper in sea water which prevented fouling [2,45].

4.3. Iron ships

After the introduction of iron ships late in the 18th century, the use of copper sheathing on these boats was nearly discontinued [2,45]. The reasons were that its antifouling action was not always certain and, more importantly, its corrosive effects on iron [2]. Various alternatives were tried, including sheathings of zinc, lead, nickel, arsenic, galvanised iron and alloys of antimony, zinc and tin, followed by wooden sheathing, which was then coppered [16]. Non-metallic sheathings such as felt, canvas, rubber, ebonite, cork, paper, glass, enamel, glaze and tiles were also suggested [2]. For isolating the copper sheathing from the iron hull, felt soaked in tar was often used as well as cork, rubber, and plain brown paper [2]. Wooden sheathing, compatible with copper sheathing, over the metal hull was also tried around 1862 but it was discarded due to its high cost [2]. The most important consequence of the introduction of iron ships was the renewed interest in the use of A/F compositions.

4.4. Antifouling paints

A variety of paints was developed mid 1800s based on the idea of dispersing a toxicant in a polymeric vehicle. Copper oxide, arsenic, and mercury oxide were popular antifoulants. Solvents included turpentine oil, naphtha, and benzene. Linseed oil, shellac varnish, tar, and various kinds of resin were used as binders [2,16]. In 1841, Mallet patented an antifouling paint in which slightly soluble coatings of poisonous materials were applied over a coat of varnish. This invention did not work because of abrasion and lack of control of the solution rate [2]. In 1847, William John Hay applied the studies by Sir Humphrey Davy and invented a successful coating based on the idea of isolating the iron hull from a coating containing copper compound powder by means of a non-conductive varnish [45]. In 1860, James McInness used copper sulphate as antifoulant in a metallic soap composition. This 'hot-plastic paint' was very similar to 'Italian Moravian' paint, the best at the time, which was a mixture of rosin and copper compound developed at the same time in Italy [2]. In 1863, James Tarr and Augustus Wonson were granted a US patent for A/F paint using copper oxide in tar with naphtha or benzene [2]. At the end of the 19th century, 'Italian Moravian' and McInness' 'hot-plastic paints', shellac type paints (rust preventive), and various copper paints were widely used. These paints were applied over a first coat of anticorrosive shellac or varnish, or of the same composition as the antifouling coating but without containing the toxicant [2]. These paints were expensive, relatively ineffective and their life span short [2].

In 1906, the US Navy tested hot-plastic and other A/F paints at Norfolk Navy Yard [2]. The manufacture of the first American ship's bottom paint started around 1908 after the success of a spirit varnish paint [2]. From 1908 to 1926 several versions of paints based on red mercury oxide suspended in grade A gum shellac, grain alcohol, turpentine,
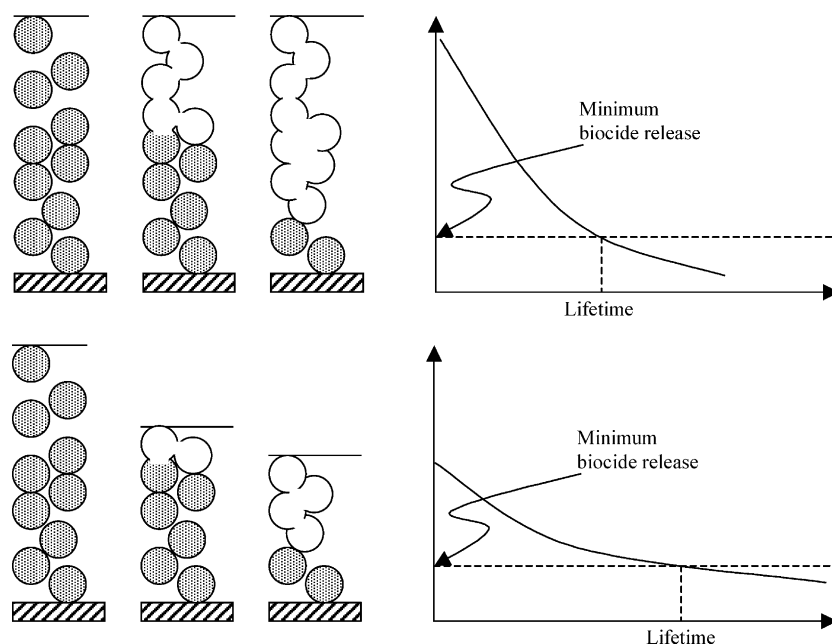
Fig. 5. Working scheme and biocide release rates of traditional insoluble and soluble matrix paints. "Minimum biocide release" indicates the limit for efficient protection against fouling (dependent on the fouling conditions).

and pine tar oil were used. Zinc oxide, zinc dust and Indian red were also added, yielding lifetimes of around 9 months [2]. About 1926, the US Navy substituted a coal-tar formulation for the shellac type A/F paints. Rosin was found to be a cheap, plentiful and successful replacement of the increasingly expensive and scarce high-grade gum shellac. Simultaneously, a hot-plastic paint (Mare Island) was developed. The use of copper or mercuric oxides as toxics improved the effectiveness of these coal-tar-rosin and shellac paints [2]. Hot-plastic paints required some heating facilities for the paint at the ship's site, which made the application difficult, so 'cold-plastic paints', easier to apply, were developed [2]. These paints already effectively decreased fouling and the period between dry-dock times (for re-painting) was extended to 18 months [2]. After the Second World War, important changes took place in the A/F paints industry. The appearance of new synthetic petroleum-based resins posing improved mechanical characteristics or the increased concern about safety and health (causing the abandonment of organo-mercurials and organo-arsenicals) and the introduction of airless spraying are examples of these changes [46]. Also during this period, the appearance of organotins improved the performance of A/F paints and seemed to solve definitively the problem of fouling.

The first report of the A/F possibilities of the broad-spectrum high-toxicity TBT-containing compounds was made in the mid 1950s by Van de Kerk and co-workers [17]. By the early 1960s, the excellent A/F properties of the TBT moiety were discovered and commercialised. Organotins were initially used as co-toxicants in high-performance copper paints, but gradually came to be used in all-organotin systems. These biocides were at first not reacted into a paint

binder, but existed in the so-called "free association form" [23]. The paints used at that time can be classified into insoluble matrix type and soluble matrix type according to the chemical characteristics of the binder and defined by their water solubility.

4.4.1. Insoluble matrix paints

In insoluble matrix paints (also termed contact leaching or continuous contact [14]), the polymer matrix is insoluble and does not polish or erode after immersion in water. A variety of commercial high molecular weight polymers can be used, and typical examples are insoluble vinyl, epoxy, acrylic or chlorinated rubber polymers [1,47]. The species dissolved by the sea water penetrating into the film have to diffuse through the interconnecting pores formed after dissolution of the soluble pigments. After a certain time in service the dissolved pigment ions have to diffuse through such a thick leached layer that the rate of release falls under the minimum value required to prevent fouling [48] as shown in Fig. 5. These types of structures are mechanically strong, not susceptible to cracking and generally resistant to atmospheric exposure in non-aqueous environments (stable to oxidation and photodegradation) [48]. The short (12–18 months [47]) lifetimes of these products have limited the number of vessels applying this kind of paints.

4.4.2. Soluble matrix paints

Soluble matrix paints were developed in order to avoid the loss of A/F efficiency with time by incorporating a binder which could be dissolved in sea water. The classical film-forming material in these systems contains high proportions of rosin. Rosin is a natural and very compatible

resin obtained from the exudation of pine and fir trees [26]. Its variable composition, which contributes to a rather unpredictable performance of natural rosin-based paints, consists generally of about 85–90% of acidic materials (resinic acids), of which the abietic (C_{30}) and levopimaric (C_{30}) acids are the most important [26]. Each of these acids contains two double bonds and a carboxyl group. These conjugated double bonds affect the stability of the rosin, and make it oxidable when exposed to air. This undesirable feature had to be taken into account during dry-docking, as the application of the paint could only be performed a short time before immersion. Once in contact with sea water, the carboxyl groups reacted with sodium and potassium ions present in the sea water, and thus gave resinates of high solubility. The resulting high dissolution rate in sea water and the brittleness of rosin forced its blending with plasticisers and co-binders [26]. These ingredients provided the binder system with the required film-forming and mechanical properties together with a suitable dissolution rate. Nevertheless, in static conditions, these compounds, and sometimes soaps formed with calcium and magnesium [26,49], were not easily released into the bulk phase, as some vessel activity was needed. Unlike other systems to be described later in this review, rosin cannot prevent sea water from penetrating into the polymer matrix through hydrophobic interactions [18,50], so relatively thick (more than 50 μm) leached layers were formed [18] due to the continuous dissolution of the copper (I) oxide pigments [51]. This unfortunate behaviour under static conditions was enhanced by the possibility of pore blocking by insoluble salts, which influenced the release of biocides. Consequently, the action of these paints at zero speed was very limited [18,52]. As a conclusion, soluble matrix paints had to find the balance between good A/F characteristics, yielded by a high rosin content [53], and good mechanical properties, attained through higher co-binder and plasticiser content. One more disadvantage of these paints was that the erosion of the paint increased exponentially with increasing vessel speed when the rosin content was above a certain value [18]. 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 the most favourable for the settlement of fouling organisms.

4.4.3. Biocides

Triorganotin derivatives were extensively used due to their wide-range activity, causing no galvanic corrosion on aluminium hulls and being colourless [23]. The preferred TBT derivatives added to both insoluble and soluble matrix paints were the bis-oxide TBTO and the fluoride TBTF, although the biological activity of TBT compounds seems to be independent of the anion [17]. The fungicide TBTO has the advantages of being an easily handled, solvent miscible liquid toxicant, compatible with many other biologically active compounds, thus perfect for fast leaching A/F paints

with good control of shell and vegetative fouling [17,23]. However, its plasticising action limits the amount that can be added [17]. Furthermore, it behaves as a solvent and migrates to the surface, leading to a rapid depletion [23]. On the other hand, the TBTF is a white, high-melting powder which is insoluble in the common paint solvents. Other used triorganotin biocides were triphenyltin derivatives, for example TPF, TPOH or TPCl. For further information, "*Fungicides, Preservatives and Antifouling Agents for Paints*" [54] cites 215 patents, many of them based on organotin derivatives.

4.5. Alternatives to the traditional biocide-based A/F coatings

The still deficient performance of both insoluble and soluble matrix technology encouraged the development of many other alternatives different from biocide-based coatings. The study of such systems was partially abandoned after the development of TBT-based paints and has been resumed after the first regulations against them. Among all the different ideas proposed, the use of electrical current is the most common and has been studied from the end of the 19th century (Bertram [22] cites an Edison patent dating back to 1891). At first, these systems based their effectiveness on the formation of toxic chemicals on the surface of the ship, mainly chlorine [2,11,55–59]. Some of these systems, especially those involving high voltages, do not have high efficiencies due to a large voltage drop across the surface, corrosion problems of the steel, cathodic chalk formation [11] and early ageing of the coating [56]. Furthermore, they lead to local pollution problems as a result of the formation of organo-chloro by-products and, very often, are not capable of achieving a uniform dispersion of the active components along the surface [22]. Electrolytically generated ozone bubble curtains [11,60], copper ions [61], hydrogen peroxide [62], Pt complexes [62,63], bromine [64], and NH_3 [65] have also been proposed as A/F methods.

As a result of the need for environmentally safe systems, many studies have come out recently using electrochemical reactions which claim no environmental risks. These systems are based on direct electron transfer between an electrode and the microbial cells, causing the electrochemical oxidation of the intracellular substance. To avoid the need for high potentials, Okochi and Matsunaga [66] proposed the use of ferrocene derivatives as redox mediators to prevent the formation of chlorine. The same principles were applied by Nakasono et al. [67] but by use of a carbon-chloroprene sheet instead. Matsunaga and Lim [62] and Nakayama et al. [68] developed titanium nitride coated plates by frequency arc spraying. The application of an alternating potential of 1 and -0.6 V against a Ag/ASCl electrode inhibited the attachment of organisms. Matsunaga et al. [69] and Okochi et al. [70] used conductive paint electrodes to apply potentials of 1.2 V saturated calomel electrode (SCE), which

completely killed the bacteria, and a negative potential to remove them from the electrode (-0.6 and -0.2, respectively). Results showed an attachment inhibition of 94 and 50%, respectively. Kerr et al. [71] used very small surface potentials (-66 mV SCE) to decrease the bacterial population to 12% of that on a reference sample. The decrease does not seem to be enough for ship's hulls, but the low costs and the lack of toxic effects could make it useful for fouling protection in medical applications. Although using toxic products, Wang et al. [72] reported that conductive polyaniline had a synergetic, although weak, effect on the A/F performance of the system. The conductivity of the polyaniline coating was found to be an important factor. Schoenbach et al. [73,74] obtained good results in their study of the effect of microsecond electric fields causing an electric breakdown of the outer cell membranes of biofouling organisms. Unfortunately, these systems are restricted to point applications (e.g. pipes).

Most of these ideas were tested on a limited amount of marine organisms, mainly marine bacteria, so their efficiency on real complex fouling scenarios is still uncertain. Furthermore, their costs are, very often, not competitive with those of chemical methods used for large structures so their usefulness may be reduced to specific applications such as fishing nets, underwater devices, medical applications, etc.

Many different types of radiations have been shown to have A/F properties. The most commonly tried form of radiation for biofouling control is acoustics [11]. It can be applied either by external vibration sources [11,16,75–78] or by means of piezoelectric coatings [79–81]. Regarding the former type, most studies have been performed on specific types of organisms [11], such as hydroids [76], barnacles [16,78] and mussels [77].

With respect to the use of piezoelectric coatings, Gerliczy and Betz [81] stated that "most marine species" (no more detail or data) have been found not to settle on these vibrating coatings. Swain [11] concluded that the power requirements of these technologies are too high and that the presence of bulkheads and other material properties impacted the distribution of energy.

Magnetic fields have been shown to have temporary effect on some organisms [11], but no attempt to apply it for A/F purposes is found in the literature. Ultraviolet radiation is widely used for sea water sterilisation in sea water pipe systems [11] but its rapid attenuation and high costs prevent its use on large external surfaces.

Some attempts to use radioactive coatings are also mentioned by Swain [11]. For example thallium 204 was shown to be extremely effective but only at levels which are not safe for human handling and therefore non-applicable. The use of technetium-95 and technetium-99 is also reported in [17,22] and considered "of questionable practicality". Finally, as pointed out earlier in this paper, heat or cryogenic treatment of ships hulls and structures were also found to be impractical [11].

5. Tributyltin self-polishing copolymer paints (TBT-SPC)

Montermoso and co-workers first suggested the possibilities of TBT acrylate esters as A/F coatings in 1958 [17]. Six years later [14], James patented the use of organotin copolymers including copolymers of TBT acrylate and methyl methacrylate. TBT self-polishing copolymer (TBT-SPC) technology, patented by Milne and Hails in 1974 [82], revolutionised the A/F paints and the shipping industries. Originally, ZnO was used as a pigment together with insoluble pigments [19]. The poor A/F 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 [19]. In 1985, the hydrophobicity of the monomers as a means of controlling the polishing rate was introduced. All these advances led to the most successful A/F system ever. An analysis of the reasons that made it such a good system may show the way towards an equally efficient substitute.

Tributyltin self-polishing A/F paints are based on an acrylic polymer (usually methyl methacrylate) with TBT groups bonded onto the polymer backbone by an ester linkage [18] (Fig. 6). The main working mechanisms of these paints were modelled by Kiil et al. [24,27,28]. After immersion, the soluble pigment particles in contact with sea water begin to dissolve. The copolymer of TBT methacrylate and methyl methacrylate in the paint is hydrophobic, which prevents sea water from penetrating the paint film [18]. Thus, sea water can only fill the pores created after the dissolution of the soluble pigment particles. The carboxyl–TBT linkage is hydrolytically unstable under slightly alkaline conditions [20]. This is usually the case of marine waters, and results in a slow, controlled hydrolysis that cleaves the TBT moiety from the copolymer (Fig. 7). This hydrolysis reaction takes place, to a varying extent, throughout the leached layer [27] (Fig. 8).

The participation of sea water ions in this reaction, may question the use of the term "hydrolysis". According
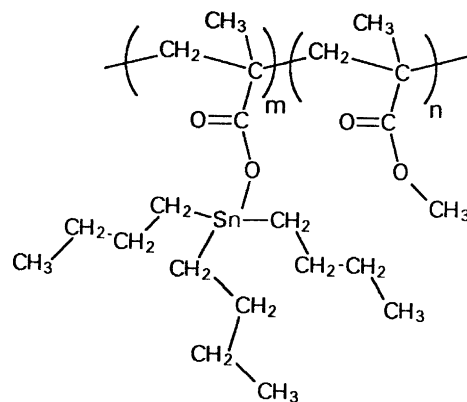

Fig. 6. Chemical formula of a repeating unit of a copolymer of tributyltin methacrylate (TBTM) and methyl methacrylate (MMA) ([27], with permission of American Chemical Society).
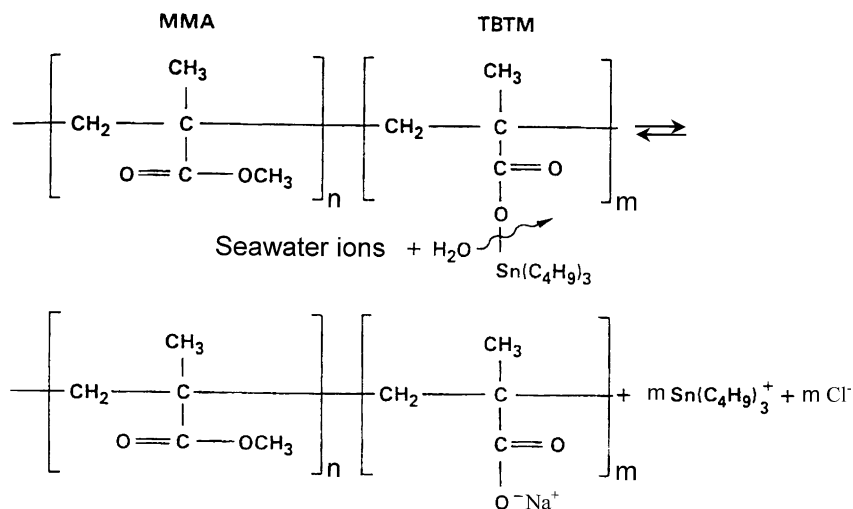
Fig. 7. Controlled release mechanism of TBT copolymer by hydrolysis (modified from [38], with permission of Kluwer).

to [83], "hydrolysis" signifies reactions catalysed by the presence of H$^+$ ions, which replace a group/atom initially bonded to the carboxylic group. In our case, the reaction would be more properly named alkaline hydrolysis or saponification. Nevertheless, "hydrolysis" will be kept due to its widespread use in the literature. The loss of the TBT moiety causes fundamental changes in the copolymer [18]:

- An increase in the glass transition temperature (from 25 to 100 °C) making it brittle.
- A change from hydrophobic to hydrophilic.

With time, the sea water slowly dissolves more pigment particles and extends the reacting zone (the leached layer). Once a sufficient number of TBT moieties have been released from the paint film surface [27], the partially re-acted brittle polymer backbone can be easily eroded by the moving sea water and exposes a less reacted paint surface (self-polishing effect):

$$\text{polymer–COO}^-\text{Na}^+ \text{ (s)} \rightarrow \text{polymer–COO}^-\text{Na}^+ \text{ (aq)} \quad (1)$$
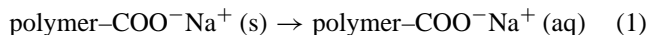
After a certain time, the movement of the pigment front resulting from pigment dissolution and ion diffusion through the leached layer is equal to the rate of erosion of the binder (related to the polishing rate), so a steady value of the leached layer thickness is reached. According to Anderson [18], this thickness has a remarkably stable and low (10–20 μm) value over the lifetime of the paint.

Regarding the polishing pattern, it was discovered that in some formulations of these new controlled release paints, the hydrolysed and removed groups were preferentially those from rough spots [14]. During operation, this self-polishing effect provides a low hull roughness (about 100 μm) [11], with consequent fuel savings and lower emissions (often called self-smoothing effect).

Typical commercial TBT-SPC paints are formulated to have a polishing rate in the broad range of 5–20 μm per month [18]. The main advantage of these systems is that it has been possible to manipulate the polymer chemistry so as to customise the rate of reaction (and thus "polishing" and biocide release rates) of the polymer in order to give a maximum effective lifetime [18]. In addition, the composition of the binder can be tailor-made through carefully controlled polymerisation conditions. This has allowed the paint industry to design different A/F paints for ships with different activities (defined by the frequency and the duration of the idle periods, the speed during sailing, etc.). High-speed vessels use slow polishing products, while slow vessels with long stationary periods apply fast polishing coatings maintaining sufficient biocide release rates for fouling control. Consequently, practically all vessels can delay dry-docking periods up to 5 years [1,20]. Further-
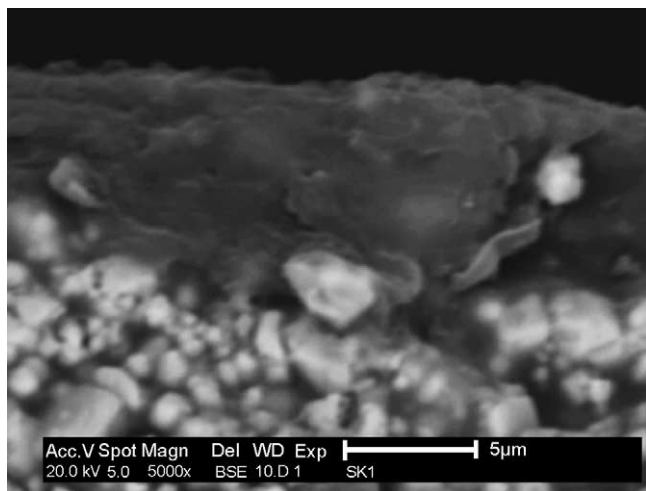

Fig. 8. SEM picture of the cross section of an SPC paint. Magnification is 5000× ([27], with permission of American Chemical Society).

more, as stated by Gitlitz [17], the toxicant release rate in TBT-SPC paints is approximately constant throughout all its active lifetime (subjected to changes in sea water conditions [27]), thanks to the thin stable leached layers. TBT-based paints also show A/F activity at zero speed unlike other traditional paints [18,27]. The A/F efficiency is very high due to the wide spectrum of fouling control achieved by the use of copper, triorganotins and booster biocides [14]. Before recoating, it is not necessary to remove any porous film residua (as it was the case of traditional soluble and insoluble matrix paints), and there is no need for a sealer coat as the remaining film is still utilisable [14,23]. It is not corrosive to aluminium and steel and it is relatively easy to blend with other paint ingredients [84]. The acrylic nature of the TBT-SPC coatings also involves short drying times, high durability and mechanical strength even after wet/dry cycling stresses [21]. An exhaustive review on the tin-based A/F products can be found in [23].

6. Tin-free technology

As stated earlier, the concern over the harmful side effects of TBT compounds on the environment has resulted in significant investment in research into and development of TBT-free systems. The products that have reached the commercial market are in the open literature classified into two main groups, see Anderson [13]:

- Controlled depletion systems (CDPs), upgrading traditional soluble matrix technology by means of modern reinforcing resins. The reaction mechanisms are assumed to be equivalent to those of conventional rosin-based A/F paints.
- Tin-free self-polishing copolymers (tin-free SPCs) (Table 2), designed for the same reaction mechanisms with sea water as TBT-SPC paints.

Nevertheless, a classification based on paint mechanisms is of very little applicability nowadays due to the evident

Table 2
Tin-free biocide-based products[a]

Company	Main products	Potential biocide (source)	Advertised mechanism
Ameron	ABC-1-2-3 and -4	Ziram (http://www.abc-3.com/)	SP. Hydrolysis
Chugoku MP	Sea Grandprix 1000/2000	Not available	SP. Silyl acrylate. Hydrolysis
	Sea Grandprix 500/700	Not available	SP. Zn acrylate. Hydrolysis
	TFA-10/30	Not available	CDP. Hydration
	Sea Tender 10/12/15	Not available	CDP. Hydration
Hempel's MP	Globic 81900-81970	Sea-Nine/Cu pyrithione	SP. Ion exchange. Fibres
	Oceanic 84920-84950	Not available	SP. Ion exchange. Fibres
	Olympic 86950/1 and HI-76600	Not available	SP. Ion exchange. Fibres HI 76600 Hydration
	Combic7199B	Not available	SP
International MC	Interclene 245	Not available	Contact leaching
	Intersmooth Ecoloflex SPC 360/365-460/465	Zn pyrithione (http://www.international-marine.com)	SP. Copper acrylate. Hydrolysis
	Interspeed 340	Zineb	CDP
	Interswift 655	Zineb or Cu pyrithione	Hybrid of CDP and SP
Jotun	SeaQuantum (Plus, Classic, Ultra, FB)	Cu pyrithione (http://www.jotun.com)	SP. Silyl acrylate. Hydrolysis
	SeaQueen	Not available	SP. "Copolymer binder"
	SeaPrince	Not available	SP. "Copolymer binder"
	SeaGuardian	Not available	SP. "Copolymer binder"
Kansai Paint	Exion	Not available	SP. Zinc acrylate. Ion exchange
	Nu Trim	Not available	SP. Hydrolysis
	Nu Crest	Not available	CDP. Hydration
Leigh's Paints	Envoy TF 400/500/600	Not available	Ablative. Copper-free (600)
	Grassline M396	Not available	Not clear
	Exion TF 700/701	Not available	Ion exchange
Sigma Coatings	Alphagen 10-20-50	Isothiazolone (http://www.sigmacoatings.com)	SP. Hydrolysis and ion exchange
	Alpha Trim	Triazine derivative (cybutryne) (http://www.sigmacoatings.com)	Not clear
	Sigmaplane Ecol (also HA)	Isothiazolone (http://www.sigmacoatings.com)	SP. "Hydrodissolving"
Transocean M.P.A.	Cleanship 2.91-2.97	Not available	Not clear
	Optima 2.30-2.36	Not available	CDP

[a] Main binder component and reported mechanism are included ([10] and companies' web sites).

lack of scientifically supported knowledge of the fundamental processes influencing A/F paint behaviour. One group claims the label "self-polishing" (SP) and is formed by companies commercialising paints based on an acrylic matrix in which different pendant groups are attached to the polymeric backbone. This pendant group is said to be released after contact with sea water in a way similar to the "hydrolysis" of TBT-SPC paints. However, developing a product with the same characteristics as TBT-based paints is no easy task. Following the introduction of organotin SPCs, many studies were aimed at the development of polymeric systems with properties similar to those of TBT-based ones but with lower costs [19], including different organotin products [14]. Apparently, none of them were really successful. The same applies to the several hundred patents granted before 1996, from which only a few commercial products have been developed [19,21]. The dramatic influence of the pendant group in the performance of the acrylic-based paints is found in [85]. This study stresses the impact of the chemical structure of the pendant group on: (1) the hydrophobic/hydrophilic balance of the matrix, (2) the change of the glass transition temperature during hydrolysis, and (3) the water absorption and possible swelling of the polymer. Furthermore, the distribution of the different units in the copolymers, the possible differentiation between the characteristics of the surface and the core of the material, and the interactions and associations between pendant groups must also be taken into account. It must be clear that even TBT-based paints with certain characteristics would not yield a sufficiently good A/F performance (e.g. a TBT monomer content less than 50% [14]). We can conclude that the achievement of a perfectly controlled release system does not rely on the simple fact of having an acrylic backbone, as steric and electronic interactions with the complex chemical neighbourhood (co-binders, additives, pigments, etc.) affect the reactivity markedly [85]. 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.

Another group of paint companies advertising their main products as "SP" commercialises a binder system based on rosin-derived compounds with a different degree of pretreatment in order to avoid the weaknesses of this natural compound (see earlier comments). These companies affirm that their products have overcome the drawbacks of the so-called "CDPs", which are mainly:

(1) Poor self-smoothing.
(2) Increasing leached layers with immersion time.
(3) Biocide release not constant.
(4) Little activity during idle periods.
(5) Short lifetimes (up to 3 years).
(6) Higher costs before applying new coats (sealer coating needed).

Regarding the first drawback, Nygren [86] provides a correlation of propulsion power as a function of the average hull roughness, in which it can be seen that "CDPs" present a worse self-smoothing behaviour than acrylic-based tin-free A/F paints. This might lead us to think that "SP" rosin-based paints could also present this characteristic. Nevertheless, Weinell et al. [87] proved that a commercial "SP" rosin-based coating led to a drag resistance similar to that of acrylic-based paints during an ageing time of 5 months. In any case, also according to [87], overlapping of sprayed applications, mechanical damage, corrosion, and, of course, fouling may have a much greater influence than the paint itself.

The next three items (nos. (2), (3) and (4)), characteristic of old rosin-based paints, cause early fouling of the coating. According to [86], the so-called "CDPs" have a good A/F performance up to 3 years in spite of the potentially increasing leached layers. Unfortunately, the companies commercialising "SP" rosin-based products provide as little information on paint performance as in the case of the acrylic-based "SP" paints. Thus, it is not known whether the paint lifetime limitation problem due to increasing leached layer thicknesses is present in modern tin-free acrylic "SP" paints and solved in rosin-based "SP" paints.

In addition to the evidences presented above, it has to be kept in mind that the different acrylic polymers and rosin derivatives currently used in modern A/F paint products are just a few of the several components of the respective binder system. Until the role of the different additives, plasticisers, retardants or pigments is elucidated, it will be impossible to predict the behaviour of the paint from the chemical composition of one of the binder components only, even if it is the one present in the greatest amount. Furthermore, proper A/F effectiveness is also only one of the different requirements an optimal A/F paint must fulfil [2] (others are e.g. good drying and adhesion characteristics). As an example, hypothetical mechanical problems associated with some tin-free "SP" acrylic A/F paints reported by Nygren [86] could make those paints ineffective.

In the light of the previous reasoning, it seems more reasonable to restructure this poorly founded classification and base it on the final performance of the paint, easier to determine and interpret. By doing this, A/F paint consumers will be able to choose the most appropriate product based on practical considerations. We have thus invited the companies to provide us with scientific data supporting the use of the term "SP" as a proper way of describing their products. This information should complement a preliminary description of the most important A/F products (extracted from [10,15]) based on the scarce scientific studies available and, more importantly, on related patents. It must always be kept in mind that it is difficult to know to what extent the cited commercial products are based on the related patents. Nevertheless, it is expected that the basic components and mechanisms of the commercial A/F paints can be properly inferred from the patent information.

As a starting point for the analysis of the different products, we may state that the following properties are characteristic of an "SP" paint:
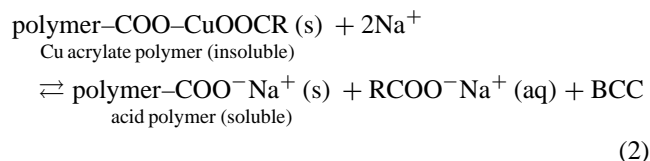
- Smooth paint surfaces during sailing.
- Thin and stable leached layers, resulting in continuous and constant biocide release rates over time (at fixed ship's speed and sea water conditions).
- A polishing rate which allows A/F activity during stationary periods and increases linearly with the sailing speed.

The fulfilment of the characteristics listed above will lead to paints with long active and efficient lifetimes (e.g. 5 years) and with a good hydrodynamic profile which gives low fuel penalties.

6.1. International Marine Coatings and Nippon Paint

These companies have published by far the largest amount of data on the performance of their paints. The three main A/F products of these companies are Interclene 245, Interspeed 340, and Intersmooth Ecoloflex SPC. Very recently, a new hybrid product between a "CDP" and an "SP" has been launched by International Marine Coatings with the name Interswift 655. International's Intersmooth Ecoloflex SPC is patented as a self-polishing copolymer technology based on an acrylic matrix bearing copper salts of an organic moiety of unknown composition. In the first Nippon Paint European patent related to metal salts (which were not exclusively carboxylates) [88], the poor resistance to cracks and peelings showed by the low molecular weight metal-containing hydrolysable resins patented in Japan by Nippon Paint a few years earlier was addressed. Such weaknesses could not be solved by increasing the molecular weight of the polyester film-forming resin as the rate of the hydrolysis reaction would be reduced. If it was tried to balance the latter by an increase in the metallic side chains, the resin would not be soluble in the common organic solvents and it would swell in sea water. Subsequently, patent [88] reported the development of a resin with good film-forming characteristics and, similar to TBT-based systems, with metal-bearing side chains providing a hydrophilic group through "hydrolysis" (see earlier comments on TBT-based paints) at an appropriate rate. One year later, the possibility of using a bioactive moiety as a pendant group was included in a new patent [89]. Apparently, such improvement could not be applied to the final commercial product, in which only the hydrolysed copper could have some biocidal effect [21,90]. Some problems in the synthesis method proposed in the previous patents, eventually leading to blistering of the coating after immersion, undesirable reactions during storage and base plate corrosion, were solved in patent [91]. Patent [92], deals again with some undesired effects such as ion association and reaction with A/F agents leading to gelled or viscous paints upon storage observed in their products. In 1997, a new patent [93] points out that the addition of a (meth)acrylic ester monomer with an appropriate ester residue in the copolymer chain yields enhanced an-

ticracking, adhesive and self-polishing properties. The latest patent consulted [94], from 2001, focuses on lowering the VOC content of the acrylic coatings described above. Of all the possibilities covered by the patent, copper acrylates (CA) are actually used. The reaction undergone by that binder system in contact with sea water can probably be written as
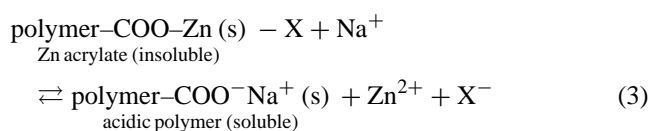
$$\text{polymer–COO–CuOOCR (s)} + 2\text{Na}^+$$
$$\underset{\text{Cu acrylate polymer (insoluble)}}{}$$
$$\rightleftarrows \text{polymer–COO}^-\text{Na}^+ \text{ (s)} + \text{RCOO}^-\text{Na}^+ \text{ (aq)} + \text{BCC}$$
$$\underset{\text{acid polymer (soluble)}}{}$$
$$\tag{2}$$

where "BCC" is an abbreviation for basic copper carbonate (see [23,90] for further details) and "R" is a monobasic acid. It should be mentioned that [9,20,90] seem to disagree somewhat with respect to the sea water reaction of the copper acrylate copolymer. However, this is probably a consequence of the lack of experimental evidence available in the literature on the chemical mechanism, and presently reaction (2) is used. According to [13,18,90] the "basic copper carbonate" shows no bioactivity. The chemical structure of the acid, "R", was not mentioned by any of the authors. Preferred examples used in patent [94] are cyclic organic acids such as rosins, which are described as "inexpensive, readily available, easy to work with and desirable in terms of long-term antifouling effect". At a certain surface conversion the partially hydrolysed CA is probably released to sea water in a way similar to that of the TBT-SPC system (reaction (1)).

The Cu-acrylate coatings have been reported to be active for up to 3 years in several early papers [21,90], but they have apparently been further improved to reach 5 years of interval between dry-dockings [13,20], although performance data is only found for up to 42 months in the open literature [13,20]. "Relative performance data" up to 60 months are now available on International's web site (http://www.international-marine.com) claiming similar A/F efficiency to TBT-SPCs. In addition, photographic record of two vessels coated with Intersmooth Ecoloflex SPC dry-docked after 5 years in-service is available. Non-scientifically supported data are provided showing the linear behaviour of the polishing rate of Cu-acrylate paints (no further details) with changing sailing speed up to 20 kn [90]. Thin leached layers and smooth paint surface after 15 months of static immersion (unknown water characteristics) are claimed and proved by means of SEM pictures available on International's web site. It has to be pointed out that International Marine Coatings provided active help during the elaboration of this manuscript [95], although scientific data on the behaviour and performance of their A/F products could not be facilitated due to confidentiality reasons.

6.2. Kansai Paint

The main product of this company is named "Exion", which is derived from the reaction mechanism assumed for the release of the zinc-containing pendant group bonded to

an acrylic backbone: ion exchange. A few details on the mechanism can be found in [96,97]. While in the more scientific paper [96], the reaction mechanism presented is very similar to that of copper acrylate paints, Anon. [97] proposes that several zinc ions from the same polymeric chain need to be exchanged by Na^+ prior to polishing of the paint. According to a definition of ion exchange [98], the ions exchanged must neutralise the charged, or potentially charged, groups attached to a fishnet-like structure or, in other words, must be exchanged without collapse of the solid structure. In the case of the mechanism proposed by Anon. [97], the use of the term "ion exchange" is not realistic, as the exchange of Zn^{2+} for Na^+ cannot be performed without releasing the pendant group as a result of the different ionic charges. Thus, the following reaction is assumed [96]:
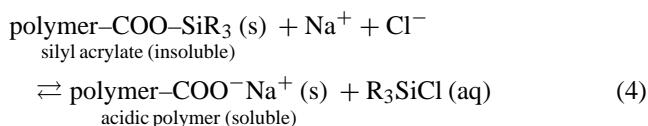
$$\text{polymer–COO–Zn (s)} - X + Na^+$$
$$\underset{\text{Zn acrylate (insoluble)}}{}$$
$$\rightleftarrows \underset{\text{acidic polymer (soluble)}}{\text{polymer–COO}^-Na^+ \text{(s)}} + Zn^{2+} + X^- \qquad (3)$$

If this hydrolysis reaction, undoubtedly influenced by the sea water ions, is assumed, the label "ion exchange" could only be used to distinguish this product from the similar copper acrylate. In any case, the term "ion exchange" will be used in this paper in accordance with the patents of the company.

The polishing of the Zn-acrylate films depends on both the zinc acrylate content, influencing the binder reaction, and the hydrophobicity of the co-monomers (influencing the water uptake) [96]. As an increase of the amount of zinc acrylate led to less flexible paints [96] (which shows again the difficulties of achieving "true SP" paints), it was opted to modify the hydrophobicity of the co-monomers. For this purpose, several zinc acrylate/zinc methacrylate ratios, different types of alkyl acrylate co-monomers and distinct fractions of methoxy ethyl acrylate monomers (hereafter called MEA), were tested. From this information, an approximate composition of these paints can be inferred. In the results obtained in [96], the major influence of the mentioned variables on the paint parameters (water absorption, solubility of the copolymer, copper release in static conditions and erosion rate) compared to the slight variations derived from changes in the content of zinc acrylate monomers has to be stressed. The latter variable only influences significantly the release rate of copper in dynamic tests. This different behaviour in static and dynamic tests is not explained, but the influence of the "ion exchange" reaction on the paint performance is, in any case, not very clear. In addition, this study provides no information about the performance after long immersion times (experiments took only few days). According to this study, the release rate of copper in static conditions is 20 µg/cm^2 per day, after very few days of immersion. Although higher than 10 µg/cm^2 per day, a value often used as the lower limit to yield A/F action, the release rate after long immersion times is not known as well as it is not known whether this rate is enough to prevent fouling in every fouling scenario.

6.3. Jotun

The SeaQuantum series is based on silyl acrylate (SA) polymers to attain the controlled release of the biocides. This structure was first patented in 1986 [99] and further improved by Nippon Oil & Fats' (NOF's) scientists in [100,101]. According to [100], the paints patented in [99] showed no erosion in the rotary tests, did not exhibit satisfactory A/F properties and had poor mechanical properties and substrate adhesion. The solutions proposed in [100] were not able to prevent fouling during the out-fitting period, which is usually as long as 3 months. To solve this problem, patent [101] claimed that organosilyl copolymers could be successfully blended with rosin derivatives and thus compensate for the drawbacks of these substances. Furthermore, no residue layer is formed after the dissolution of rosin over long immersions and no physical defects are observed.

Gerigk et al. [9] and Anderson [20] have mentioned aspects of the proposed sea water chemistry of SA-SPC. In the leached layer of this paint type, sea water slowly reacts with the active polymer and thus release R_3SiCl:

$$\text{polymer–COO–SiR}_3 \text{(s)} + Na^+ + Cl^-$$
$$\underset{\text{silyl acrylate (insoluble)}}{}$$
$$\rightleftarrows \underset{\text{acidic polymer (soluble)}}{\text{polymer–COO}^-Na^+ \text{(s)}} + R_3SiCl \text{(aq)} \qquad (4)$$

The binder system itself does not give any A/F effect. Probably, this paint type also polishes by a mechanism similar to that of the TBT-SPC system, reaction (1). According to [9] the alkyl group, R, can be e.g. isopropyl or butyl. A more complete list of possible radicals can be found in [101]. From the information provided by Jotun's web page, it seems that the SeaQuantum series still contains some rosin in their formulation.

6.4. Chugoku Marine Paints

Apart from the 3-year Sea Grandprix 500/700 systems based on zinc or copper acrylates, the main product of this company is the silyl acrylate-based Sea Grandprix 1000/2000 series. Patents [102,103] are likely to be the origin of this product. According to [102,104], silylated acrylate binders presented in the previous patents show cracks and flake formation after long exposure to sea water/sunlight cycles. The problem is particularly relevant to self-polishing paints where a certain degree of water absorption occurs after immersion in sea water as the film swells and dries out again cyclically. Furthermore, the mechanical resistance to the application of pressure on the coating could be improved. For this purpose, patent [102] proposed the use of a binder system based on trialkylsilyl ester of polymerisable unsaturated carboxylic acid (mainly tributylsilyl and tripropylsilyl methacrylates) and, more importantly, high amounts of chlorinated paraffin (18–65 parts by weight
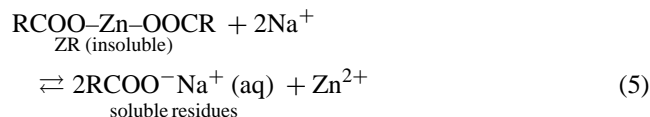
of the film-forming copolymer). This component is said to contribute to the improvement of the cracking and peeling resistance of the coating. The addition of a dehydrating agent to the A/F coating composition involves a better storage stability. In the more recent patent [103], improved mechanical properties, adhesion characteristics, and erosion/antifouling performance are claimed on the basis of the use of a modified organosilyl composition, probably based on triisopropylsilyl acrylate and methyl methacrylate or triisopropylsilyl acrylate, tri-*n*-butylsilyl acrylate and methyl methacrylate. There is no evidence to propose a reaction mechanism different from Eq. (4), for hydrolysis, and Eq. (1), for erosion. In a personal communication [105], Chugoku provided marketing information in which the superior performances of the "3rd Generation" organosilyl acrylates compared to the "1st Generation gum rosin-based eroding type paints" and the "2nd Generation" metal acrylates are claimed. Sea Grandprix is described therein as an A/F product having all the distinguishing properties of SP coating, but the plots provided, part of a commercial brochure, lack information on the experimental procedure, conditions, uncertainty, etc.

6.5. Hempel's Marine Paints

This company is now focusing on the patented idea of applying fibres to the paints [106,107], as it is the case of the Globic series, Hempel's main A/F product. In these two patents, the addition of fibres to rosin-based binders resulted in a reinforcement of the mechanical properties of the intrinsically weak rosin compounds. As a result of this, it is no longer necessary to add large amounts of insoluble co-binder systems, which are expected to be responsible for the formation of large leached layers and consequent deficient performance of traditional rosin-based systems. This problem has often been used to illustrate the advantages of acrylic systems (e.g. [21]) but it may not be applicable to the advanced fibre technology. Prolonged sunlight exposure periods or immersion/sunlight cycles were used to test the mechanical reinforcement. Furthermore, the patents claim that the paint system retains the crucial A/F properties. According to the patents, mineral fibres are the easiest to incorporate into the binder, and they seem to be the ones actually used. The preferred fibres could be those of a length between 50 and 300 μm and an average thickness of 2–10 μm with a ratio between the average length and the average thickness of at least 15 (it has to be taken into account that some reduction of length may occur during manufacture). The concentration of fibres would normally be 2–10% by solids volume of the paint, although the patent covers the range 0.1–30%.

Referring to the rosin compounds, the Globic series avoids the use of natural rosin for the reasons given earlier. Instead, it uses a synthetic substitute of natural rosin (subjected to a hydrogenation and distillation process) which is more consistent, less sensitive to oxidation (low carbon–carbon double bonds) and has a suitable sea water solubility. This rosin derivative is further reacted to form zinc carboxylate

(which is sometimes called zinc resinate, e.g. [15]), which gives rise to the controlled release properties through an "ion exchange" reaction in addition to increased hardness and faster drying times. There is no scientific evidence supporting the assumption of the ion exchange mechanism, so the most likely reaction can be written as follows:

$$\underset{\text{ZR (insoluble)}}{\text{RCOO–Zn–OOCR}} + 2\text{Na}^+$$

$$\rightleftarrows \underset{\text{soluble residues}}{2\text{RCOO}^-\text{Na}^+ \text{ (aq)}} + \text{Zn}^{2+} \tag{5}$$

In addition, the patents mentioned use complementary polymeric binder components (plasticisers) to provide the final paint with certain characteristics (e.g. suitable T_g). Thus, these components should have a T_g higher than 25 °C (oils, saturated polyester resins, alkyd resins, hydrocarbon resins, chlorinated polyolefines are mentioned as possible options). The thixotropic agent bentonite was reiteratively used in the examples. Finally, non-crystalline polymeric flexibiliser components are added. By adjusting the hydrophilicity of this flexibiliser and the amount of the rosin derivatives, different paints can be tailor-made to fulfil different polishing requirements. In the more recent patent, ethyl acrylate, acrylamide-based terpolymer and vinyl and oil resins are used as examples. Finally, it has to be pointed out that how the addition of fibres influences the relation between sailing speed and polishing rate is not mentioned in any of the patents.

According to Hempel, this technology presents extraordinary mechanical properties, controlled polishing tailor-made for different requirements (see Fig. 9), good recoating characteristics (at least on the top of other Globic layers), low VOCs content and microroughness similar to that of tin-based paints. Regarding this last point, Hempel has completed the information supplied in [87] by providing the results of well-documented rotary experiments (30 kn, 30 °C) using artificial sea water (ASTM D-1141). In those experiments, a decrease in the macro-roughness with ageing time in their main tin-free fibre-containing A/F paint can be observed (see Fig. 10). This involves that the addition of fibres does not seem to involve different paint surface roughness (and drag resistance consequently) from acrylic-based paints (see [87] for details on the experimental procedure). Furthermore, the initial surface roughness is reduced during activity imitating TBT-based paints (self-smoothing effect). Thin (below 22 μm) leached layers were developed by the different Globic products after long-term (470–590 days) rotary experiments in natural seawater (Barcelona, Spain) (pictures not shown; conditions detailed in Fig. 9). Slightly higher values (below 35 μm) were measured on ships sailing during less than 1 year at speeds ranging from 13 to 20 kn and activity from 65 to 75% (pictures not shown). The uncertainty in the measurement of such values was not provided. A satisfactory A/F performance at static conditions comparable to TBT-SPCs is proved by means of several pictures of rafts immersed during a confidential period of time (blanks
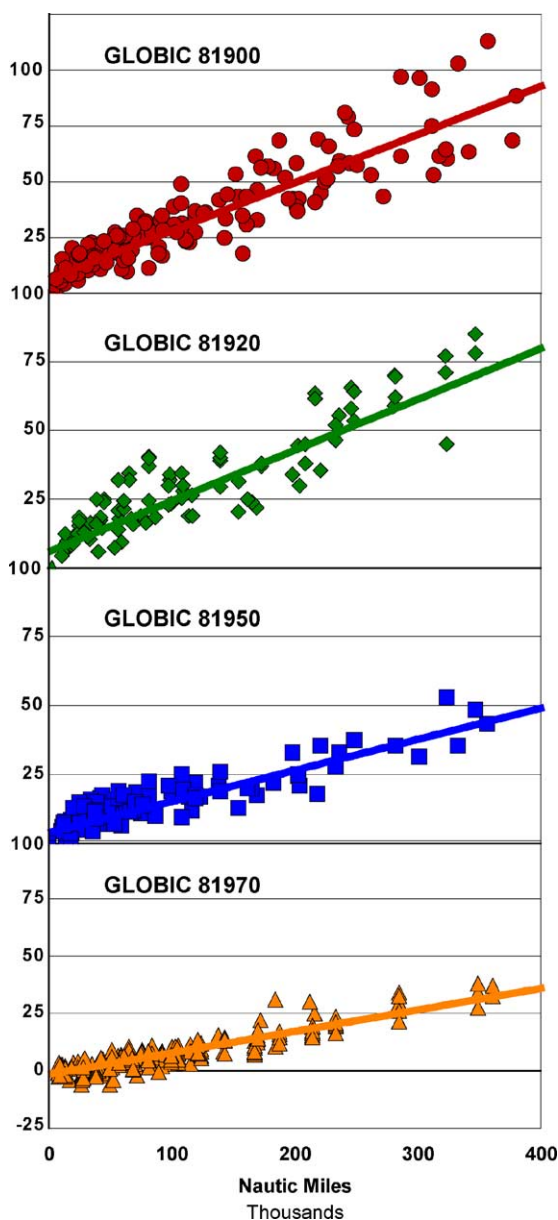
Fig. 9. Relative dry-film thickness reduction (DFT) of the different Globic products after rotary experiments in natural sea water (pH: 8.1–8.2, salinity 3.8‰, and temperatures 10–27 °C, 14–14.2 kn and activity 98%). The data have not been corrected for temperature (influencing the scattering). Confidential values of the DFT reduction have been replaced by relating the data to those of Globic 81900 (fastest polishing). Courtesy of Hempel's Marine Paints A/S.

heavily fouled) in the Mediterranean sea (Barcelona, Spain) and tropical waters (Singapore) (pictures not shown).

6.6. Sigma Coatings

The last product analysed in this section is named Alphagen. The technology of Alphagen is based on a unique resin developed and produced by Sigma. The composition resulting from the use of this resin together with other paint in-
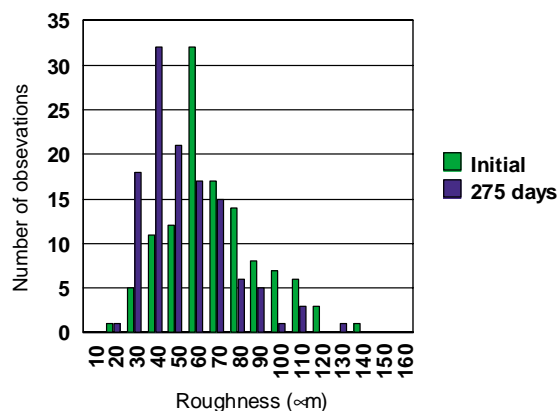

Fig. 10. Roughness distribution of an aged commercial Globic paint compared to the values of the freshly applied paint. The samples were attached to a rotor rotating at 30 kn in artificial sea water ASTM D-1141 at 30 °C. Courtesy of Hempel's Marine Paints A/S.

gredients is the responsible for the claimed "SP" behaviour [108]. To prove such a statement, Sigma has provided a polishing rate curve of one of the different Alphagen products (see Fig. 11). A completely linear polishing rate could be observed during more than 500 days, similar to a Sigma's TBT-based paint (Simaplane HB). The polishing rate of such products is claimed to be of 5–6 μm per month [108]. In contrast to this, one of the Sigma's ablative paints (Sigmaplane Ecol) showed a more irregular polishing rate. The uncertainty in the experimental data was not provided. Sigmaplane Ecol also developed a 2- to 3-fold thicker leached layer and a more irregular surface compared to Alphagen and Sigmaplane HB according to SEM pictures taken from paint samples attached to vessels sailing in different areas of the world after an unspecified time (pictures not shown). The speed of such vessels was around 20–22 kn while the frequency and the duration of the idle periods are not known. Finally, a picture of a fouling-free raft panel exposed to natural sea water in Holland during 57 months was provided to prove the long-term effectiveness of Alphagen at static conditions.

6.7. Promising ideas for the short-term future

Hempel's patented idea of incorporating fibres into the paints might also be applied to improve the mechanical properties of other binders such as metal acrylates ([109] based on International/Nippon and Chugoku Paints), nitrogen compound-blocked acid functional groups (e.g. sulphonic) copolymers ([110] based on Courtauld's patents) and silylated acrylate binders ([104] based on NOF and Chugoku's patents). In patents [111,112], Sigma presents new silylated acrylate products. Akzo/International has recently patented a binder based on a copolymer of an olefinically unsaturated sulphonic acid blocked by amine salts [113].

Other interesting studies worth mentioning are the acrylic systems described by Vallée-Rehel et al. [114], which use biocompatible α-hydroxyacids, Camail et al. [115]
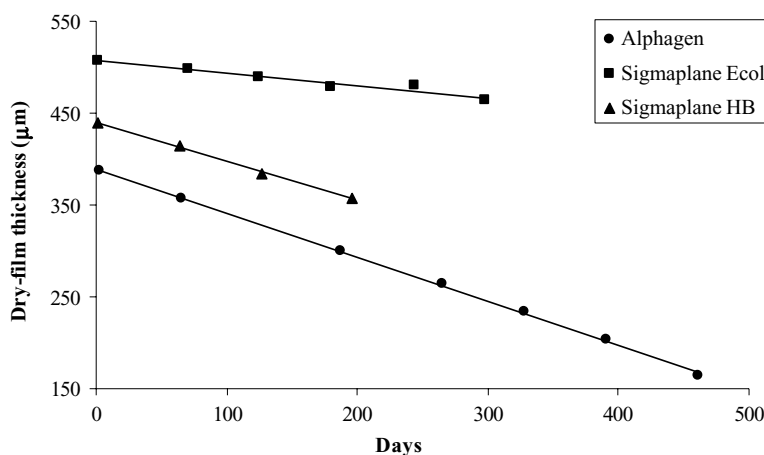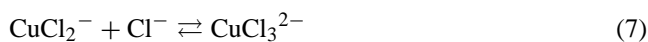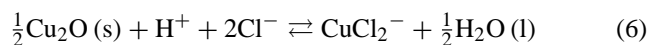
Fig. 11. Evolution of the dry-film thickness of three different coatings applied on discs rotating in natural sea water (pH: 8.2, salinity 3.1%, T: 19–23 °C) at 19 kn. Each experimental point (symbols) is obtained by averaging 20 measurements on different defined spots in the disc. Data courtesy of sigma coatings.

synthesising acrylic titanium polymers, and Kuo et al. [116] which describes a surface fragmenting polymeric system containing cupric carboxylate groups.

6.8. Pigments

All of the mentioned chemically active paint systems rely on the use of sea water soluble Cu_2O pigment in combination with various organic boosting co-biocides for fouling control. The solution of Cu_2O in sea water is given by the following reactions [2,25,27]:

$$\tfrac{1}{2}Cu_2O\,(s) + H^+ + 2Cl^- \rightleftarrows CuCl_2^- + \tfrac{1}{2}H_2O\,(l) \qquad (6)$$

$$CuCl_2^- + Cl^- \rightleftarrows CuCl_3^{2-} \qquad (7)$$

Reaction (6) is reversible and influenced by kinetics, whereas reaction (7) is reversible and instantaneous and can be considered in equilibrium at all times. When dissolved O_2 is present in sea water, the copper complexes are oxidised to Cu^{2+}, which is the main biocidal species formed from Cu_2O. Copper is an essential element, required for the normal growth of all plants and animals and occurs commonly in the environment. As reported by Pidgeon [117], it is estimated that the load of copper released from A/F paints into sea water is only 3000 t per year compared to 250,000 t per year from natural weathering. However, high concentrations can be deleterious to algae and other aquatic biota [118]. Copper is not lipophilic and shows only a slight tendency for bioaccumulation [118], and its low solubility makes it precipitate rapidly and thus decrease greatly its toxicity. According to [119] the adsorption of copper onto the sediment is rapid and dependent on the characteristics of the sediment. The most bioavailable form, and thus the most toxic of ionic, unbound copper, is the free hydrated ion, $Cu(H_2O)_6^{2+}$ [118]. Copper speciation is governed by pH, salinity and the presence of dissolved organic matter [118].

Biological indicators differ widely with respect to copper sensitivity and a general decreasing order of sen-

sitivity would be: microorganisms > invertebrates > fish > bivalves > macrophytes [118]. The presence of water-soluble ligands that bind copper reduces toxicity, probably by decreasing the concentration of free ionic copper. Binding of the cationic species with organic ligands results in the formation of anionic hydrophilic and chemically inert copper chelates [118]. Speciation studies carried out indicate that more than 99% of the total copper is strongly bonded or chelated with organic ligands, leaving the concentration of free Cu^{2+} at levels that are non-toxic to most microorganisms. In addition there is evidence that strong copper chelators are synthesised and excreted by microorganisms in response to increases in copper concentrations [118]. Finally, the formation of the slightly soluble malachite green ($CuCO_3 \cdot Cu(OH)_2$) further decreases the concentration of biologically active cupric ions [23].

Despite these chelation reactions, there is some concern about the harmful effects of high copper concentrations in the marine environment. As Voulvoulis et al. [118] pointed out, copper has a synergetic effect with some of the currently used booster biocides (e.g. thiocarbamates), as they form lipophilic complexes, which enhance the bioaccumulation of copper. These reactions are also found with other organic compounds present in sea waters. In the same study, high concentrations of copper in waters and oysters are reported as a result of its use in A/F paints in France and Sweden [120]. In general, copper concentrations above the Environmental Quality Standards are expected to cause a range of sub-lethal effects in several invertebrate phyla, and even lethal effects in early life stages [118]. In spite of all these doubts, in a recent study [121] the low bioavailability of the cupric ion after release from the A/F coating is stressed, which suggests a good enough environmental profile.

Other widely used pigments are copper (I) thiocyanate, zinc (II) oxide, titanium (IV) oxide and iron (III) oxide. The first was studied in [122] where this pigment is described as a substitute of copper oxide (I) when another paint colour is desired. Cuprous thiocyanate is, in this sense, more

appropriate than cuprous bromide (too soluble), cuprous iodine (too expensive) and cuprous cyanide (too insoluble and toxic). The result of [122] showed that this pigment led to similar concentrations of $CuCl_2$ at a pH close to that of sea water (about 8.43). According to the same source, a reduced rate of oxidation of Cu^+ to Cu^{2+} may lead to higher toxicities. Oxidability data was given in the range of days, so it is not clear what the difference of oxidability will be in the short diffusion times within the pores. Furthermore, biological tests were only performed by use of two organisms. No data is provided regarding the dissolution rate of this pigment.

Concerning the soluble pigment zinc (II) oxide, there is a total lack of studies on its behaviour in sea water (e.g. dissolution rate) and its consequent effect on A/F paint performance. The same is true for the influence of insoluble pigments such as the very common titanium (IV) oxide or iron oxides.

6.9. Biocides

6.9.1. Booster biocides

After the ban of TBT-based products, marine paint companies are urged to find an appropriate substitute able to complement the biocidal action of copper, ineffective against some widespread algal species tolerant to copper (e.g. *Enteromorpha* spp.) [118], and to yield good A/F protection. The most commonly used booster biocides are listed by Gerigk et al. [9], Omae [23], Voulvoulis et al. [118], and Thomas [123] and shown in Table 3. Other chemicals currently used as active compounds in A/F paints are copper pyrithione, benzmethylamide, fluorofolpet, polyphase, pyridone-triphenylborane, TCMS, TCMTB, and tolyfluanid [123]. They can be classified into non-metallic and metal-based compounds.

From the first group, the herbicide Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) has caused many doubts about its environmental effect. Irgarol 1051 is effective mostly against freshwater and sea water algae and less against animal organisms. It has low water solubility and partition coefficient (log K_{oc}) compared to other booster biocides (see Table 4). Compounds with low partition coefficients will predominantly exist in the dissolved phase. This means that they will be rapidly dispersed and diluted in the aquatic environment, although it can also involve a higher bioavailability and, thus, a wider contamination area. On the other hand, substances with high partition coefficient will lead to high-localised concentrations in the sediment [119]. According to [124], Irgarol is likely to be found in significant concentrations in both the water column and in the sediment. Its mode of action consists on inhibiting the photosystem-II (PSII) by interfering with the photosynthetic electron capture transport in chloroplasts [118]. It has been proved that the degradation of Irgarol 1051 in sea- and freshwater sediment is rather slow, with half-lives of about 100 and 200 days, respectively [125].

Under anaerobic conditions, the degradation in sediments is considerably slower. The modified Sturm test shows that Irgarol 1051 is not readily biodegradable [123,125,126]. It has been reported to be highly toxic to non-target marine algae, with growth inhibition from 50 ng/l [126]. Evans et al. [120] report that low concentrations can damage micro- and macroalgal communities, endosymbiotic corals, sea grasses and indirectly, herbivorous mammals, such as dugongs. Irgarol 1051 has been detected in the UK [118,127,128], France, the Netherlands, Spain, Sweden [126], Switzerland [125], Japan [126,129], Denmark [120], Germany [123], and Australia [130]. Little is still known about the long-term exposure and degradability of Irgarol 1051, although a large number of studies have been carried out to characterise the fate of this biocide in the environment. It has been proved that Irgarol can be degraded via different pathways such as slow biodegradation [123,125,126,129,131] (not bacterial [131]), hydrolysis catalysed by mercuric chloride [131], and sunlight photodegradation [132–135]. The major stable degradation product from these processes is M1 (2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine), which retains the heterocyclic ring of Irgarol 1051 [123,129]. This by-product has been found to be quite toxic, although less than Irgarol itself [129], and it has already been detected in Japan, Spain, and UK [123]. As a conclusion, it is clear that Irgarol 1051 gives rise to much doubt about its environmental convenience [120,136].

Something similar is true of Diuron. Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a substituted urea-based herbicide employed principally for the control of vegetation in non-crop areas since the 1950s, although it is now used as booster biocide in A/F paints. Diuron is a non-ionic compound with moderate water solubility working as a photosynthesis inhibitor [137]. Its hydrolysis rate is negligible at a neutral pH but increases under strongly acidic or alkaline conditions. It is stable to oxidation and breakdown [137]. Diuron is reported not to bioaccumulate to any great extent [118,123] despite the fact that high concentrations in the dissolved phase are predicted by Voulvoulis et al. [124] due to its slow degradation in sea water [120,136]. Aerobic degradation products of Diuron are 1-(3,4-dichlorophenyl)-3-methylurea and 1-(3,4-dichlorophenyl)-urea, whereas 1-(3-chlorophenyl)-3,1-dimethylurea is formed in the absence of oxygen [123]. Diuron was not found in water or sediment samples in the study by Voulvoulis et al. [138], performed in a commercial estuary in the UK, although it is the most used biocide after copper oxide (I) in this country [127]. This is not in good agreement with the findings in [127], where high concentrations of Diuron in other estuaries of the same country were measured. Denmark [120], Sweden, and Spain [123] have also been reported to be contaminated by Diuron.

Other biocides seem to present better environmental profiles. Sea-Nine^TM 211 Biocide is a member of the 3(2H)-isothiazolone class of compounds which has demonstrated high microbial activity against a wide spectrum of bacte-

Table 3
Nomenclature and structures of booster biocides currently used in antifouling paints (adapted from [118], with permission of Wiley)

Type	Commercial and chemical names	Structure
Non-metallic	Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine)	
	Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea)	
	Sea-Nine 211 (4,5-dichloro-2-*n*-octyl-3(2H)-isothiazolone)	
	Kathon 5287 (4,5,dichloro-2-*n*-octyl-4-isothiazolin-3-one)	
	Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile)	
	Dichlofluanid (*N*′-dimethyl-*N*-phenylsulphamide)	
	Thiram (bis(dimethylthiocarbamoyl)disulphide)	
Metal-based	Zinc pyrithione (zinc complex of 2-mercaptopyridine-1-oxide)	
	Ziram (zinc bis(dimethylthiocarbamates))	

Table 3 (*Continued*)

Type	Commercial and chemical names	Structure
	Maneb (manganese ethylene bisdithiocarbamate)	$\left[\begin{array}{c} H_2C-NH-\overset{\overset{S}{\|\|}}{C}-S^{\cdot} \\ \| \\ H_2C-NH-\underset{\underset{S}{\|\|}}{C}-S-Mn^{2+} \end{array}\right]_x \ (x>1)$
	Zineb (zinc ethylene bisdithiocarbamate)	$\left[\begin{array}{c} H_2C-NH-\overset{\overset{S}{\|\|}}{C}-S^{\cdot} \\ \| \\ H_2C-NH-\underset{\underset{S}{\|\|}}{C}-S-Zn^{2+} \end{array}\right]_x \ (x>1)$

ria, diatoms, fungi, and algae [139–141]. It is miscible in most organic solvents and its reported solubility ranges from 4.7 mg/l in synthetic sea water [141] to 14 mg/l [123] (conditions not known). It is practically non-volatile. It binds strongly to sediment and, once bound, it is essentially immobile and thus reduce the bioavailability [140,141]. According to [140], it has shown an excellent performance in laboratory tests, raft trials and ship's hulls. Moreover, it is degraded much faster than TBT compounds and its concentration is rapidly reduced below toxic levels (<24 h [123,141] or 8.5 days according to [136]) in good agreement with [120]. Slightly higher photodegradation half-lives in sea water (more than 13 days) were measured by Sakkas et al. [142]. Although Thomas [123], Jacobson and Willingham [140], and Guo and Jacobson [143] state that all its degradation products are ring-opened structures with a reduction of toxicity of 4–5 orders of magnitude, Sakkas et al. [142] reported recently the identification of a phototransposition by-product retaining a ring structure (toxicity not stated). Finally, little bioaccumulation of this compound was predicted by Thomas [123], and Jacobson and Willingham [140]. All these promising characteristics are in accordance with the results of the comparative study carried out in [136], where it is stated that this biocide shows a much better environmental profile than other frequently used biocides. Nevertheless, new studies may reveal still unknown side effects as it is the case of [144], which shows the high toxicity of Sea-Nine to non-target sea urchin eggs and embryos. Larsen et al. [145] may as well be referred to regarding adverse effects of Sea-Nine on phytoplankton communities. In spite of the absence of Sea-Nine in Danish and British waters [123], significant concentrations of this biocide are now being reported [23,142,146].

Regarding the metal-based biocides, probably the most interesting products are the polyvalent metal salts of pyrithione, mainly zinc and copper salts [147]. These products have gained acceptance for use in marine paints and coatings to decrease or minimise soft-fouling. These salts are known to be effective biocidal agents, for which reason they are widely used as algaecides, fungicides and bactericides in paints and personal care products such as anti-dandruff

shampoos (Zn pyrithione). Generally, these salts are only sparingly soluble in water and show favourable environmental chemistry [147]. The latter is a result of apparently rapid degradation in sunlight to form less toxic photodegradation products [120,147–149], biodegradation [119], and low sediment accumulation due to facile reduction of a critical functional group under anaerobic conditions [147]. Nevertheless, it has been hypothesised that pyrithiones may accumulate in the sediment in polluted or deep waters where UV light is non-existent, either as a stable manganese complex or as a copper pyrithione complex (when copper concentrations are high) [120]. Furthermore, it was found to be the most toxic product to the sea urchin [144]. Boxall et al. [127] studied the occurrence of zinc in UK estuaries, finding high concentrations of zinc. This fact, however, is thought to be due to other sources such as industrial discharges, sewage effluents, run-off and sacrificial anodes in boats.

Copper pyrithione offers several advantages over zinc pyrithione for many applications, notably a lower solubility and short half-lives [123]. The former, as compared to zinc pyrithione, increases its effective availability as a biocidal agent over a longer period of time, when exposed to marine environments, and makes it particularly desirable against soft-fouling [150]. However, copper pyrithione is not as effective as regards the prevention of hard-fouling as might be desired. To address this shortcoming, combinations of soft-fouling and hard-fouling agents are being manufactured [150].

According to the studies performed so far, the predicted environmental concentrations of these compounds are usually well below the acute toxicity value. However, it is widely recognised that death is insufficiently sensitive as an endpoint in environmental bioassays, and much attention must be paid to potential long-term, sub-lethal impacts of pollutants [120] (e.g. hormone-like effects at the reproductive level). As Evans et al. [120] points out, very few toxicity studies have been carried out on these alternative biocides compared to TBT-based ones and, moreover, most of these studies focus on acute toxicity (e.g. [151,152]). In addition, single-component toxicity studies may not reflect the real effects due to synergetic effects. Voulvoulis et al. [118]

Table 4
Some important parameters characterising the environmental profile of selected booster biocides

	Other applications[a]	Effects on living organisms[a]	$\log(K_{oc})$		$\log(K_{ow})$	$t_{1/2}$ (natural SW)	Solubility (mg/l)	Toxicity[b]
Diuron		Inhibition of photosynthesis in plants	3.18–5.20[c]	1 g/l SS	2.6–2.85[d,e,f]			4
	Herbicide	Carcinogenic	2.28–3.45[c]	20 g/l SS		–	35[e]	
		Deformed growth in fish larvae	2.74–3.28[c]	200 g/l SS				
			3.14–4.89[c]	1 g/l SS				
Irgarol 1051	Herbicide	Inhibition of photosynthesis in plants	2.92–3.39[c]	20 g/l SS	2.38[f], 3.95[e,g]	100 days[e,g]	7[g]	5
			2.41–3.65[c]	200 g/l SS				
		Allergic contact dermatitis in humans					8[e]	
Zn pyrithione	Bactericide, fungicide, shampoos	Inhibition of cell growth in mammals	4.03[e]		0.9–0.97[e,h]	<24 h[e], 4 days[h]		2
		Paralysis in rabbits, mutagenic potential						
Cu pyrithione	Bactericide, fungicide	–	–	–	–	0.5 h[e]	–	1
		Eye irritation, sensation, toxic					4.7[i], 14[e]	
Sea-Nine 211	–	on inhalation in humans	3.75–4.19[i]		2.8[e], 4.5[i]	<24 h[e,i], 8.5 days[j]		3
TCMTB11	Fungicide					740 h[k]	10.4[k]	
Zineb	Fungicide					96 h[k]	0.07-10[k]	
Chlorothalonil	Fungicide					1.8 days[k]	0.9[k]	
Dichlofluanid	Fungicide					18 h[k]	1.3[k]	

[a] From [120].

[b] Toxicity ranking (1 the most toxic) from in vitro acute toxicity test on *Oncorhynchus tshawytscha* embryos [152].

[c] From [119]. SS: suspended solids.

[d] From [137].

[e] From [123].

[f] From [124].

[g] From [125].

[h] From [147]; $t_{1/2}$ in absence of light.

[i] From [139].

[j] From [136]; $t_{1/2}$ in absence of light.

[k] From [23].

reports the synergetic effects of dithiocarbamates (Maneb, Zineb, Ziram, Thiram, etc.) and copper, while Fernández Alba et al. [151] studied the effects of the combined action of Irgarol and other biocides.

In summary, there are still many uncertainties about the environmental parameters associated with all these booster biocides [120]:

- Environmental profiles of booster biocides.
- Acute and chronic toxicity.
- Validation of analytical methods for biocides, monitoring and fate and toxicity in the environment.
- Synergistic interactions between pollutants.
- Accumulation in the environment.
- Evaluation of the performance of alternative antifoulants.

All these uncertainties question the results of the very interesting study performed by Voulvoulis et al. [153], which tried to find the most environmentally benign biocide from the analysis of several parameters (multicriteria analysis, MCA). It is expected that this study may provide some qualitative knowledge of the performance of these alternative biocides. According to [153], zinc pyrithione and Zineb seem to be the most environmentally friendly, while Irgarol and, even more, Diuron do not present very good profiles. In any case, all these biocides performed better than TBT-based ones. Sea-Nine and copper pyrithione were not included, but they are also expected to yield good results.

6.9.2. Natural biocides

While the fouling of man-made surfaces is well known, marine organisms face similar problems in that fouling can interfere with vital processes such as respiration, nutrient absorption and sensing. In nature some organisms may be heavily fouled on much of their surfaces while others can be totally fouling-free [154]. This has generated interest in identifying the secondary metabolites that might repel or inhibit fouling organisms. According to [35,155] these compounds can act enzymatically by dissolving the adhesives, interfering with the metabolism of the fouling organisms (e.g. nervous pathway interference), inhibiting the attachment, metamorphosis or growth, promoting negative chemotaxis, altering the surface of the organisms [155,156], as repellents, or finally acting as biocides.

The identification of active compounds is just one of the steps required before they can be incorporated in A/F coatings. A mechanism must be found by which they can be combined with the coating matrix and supplied to the surface at a rate sufficient to prevent fouling but without wasting the compound [157,158]. Natural sources or synthetic analogues must be found to ensure supply at a reasonable cost. In addition, the compounds must pass rigorous scrutiny from environmental regulation agencies [155]. In Fig. 12 the steps and the estimated time needed to develop a novel A/F system based on natural compounds are summarised from [159].

The secondary metabolites under scrutiny include mainly terpenoids, steroids, fatty acids, aminoacids, heterocyclics (furans, lactones), acetogenins, alkaloids, and polyphenolics [160–162], some of them halogenated compounds with chemical structures that are unprecedented among terrestrial organisms. As an example of the chemical diversity that may occur in marine organisms, members of the red algal genus *Laurencia* produce over 500 different terpenes presenting at least 26 different structural classes, more than 16 novel and found only in *Laurencia* [162]. Again, it would be impossible to cite all the studies available in the open literature on the isolation of secondary metabolites from different organisms.
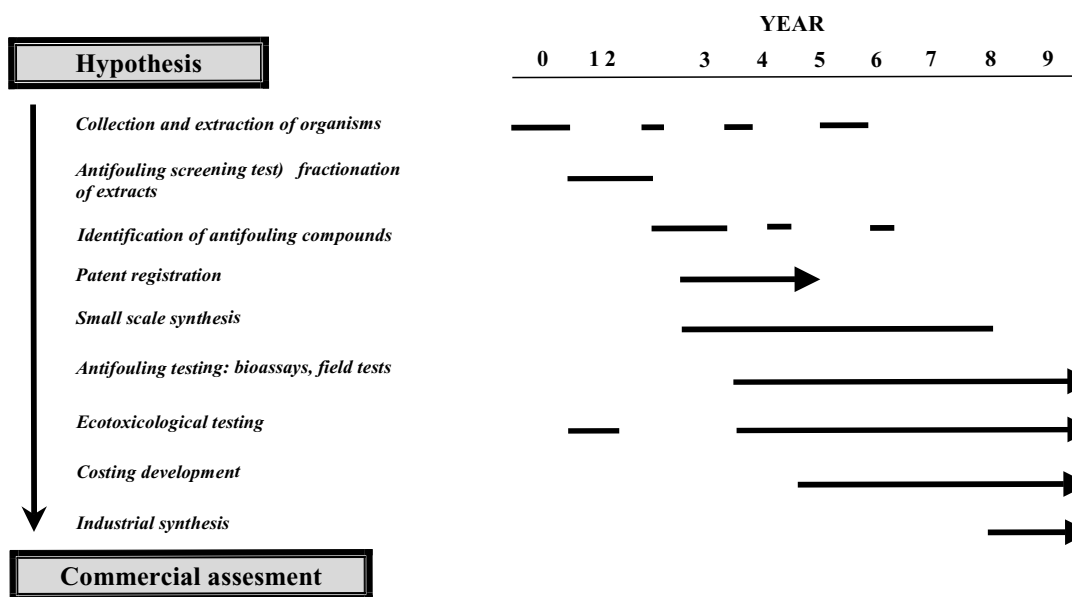

Fig. 12. A possible research management schedule for the development of a novel antifouling system based on natural antifouling compounds (after [159], with permission of Surfex Limited).

The paper [161] summarises most of the Japanese attempts before 1997 and deals with metabolites extracted from a variety of species such as sponges, nudibranches, red and brown algae, corals, gorgonians, etc. All the studies reviewed by this research group show one of the most common deficiencies of this kind of studies: testing of the antifoulants on only one species, in this case, a very common barnacle, instead of field experiments. A metabolite able to interfere with the attachment mechanisms of algae may not be as effective against the adhesion of mussels, barnacles, bacteria, etc. due to the widely recognised variety of adhesion mechanisms and chemical sensitivity to toxins found in fouling organisms [42,156,160,163–166], which are, furthermore, poorly known. Thus, some authors claim that more studies should be aimed at analysing the structure–activity relationships for the most promising secondary metabolites [155,156,160] and their location and quantification in the organisms to understand better their ecological role [42,155,156,167]. Although not only the metabolites concentrated on the surface of the organisms inhibit settlement, the localisation of the metabolites could indicate their potential to be used in surface-mediated interactions [167], once proved that the settlement on artificial and natural surfaces involves similar mechanisms [42]. All these studies may determine whether the action of these products involves a non-toxic interference with a specific component of the signalling pathway of settlement or metabolic processes, as it seems to be the case of furanones [42,156,160,167], which explains their broad-spectrum activity. Once identified which properties of the compound lead to the desired effects, it will be possible to screen products according to their potential applicability to A/F coatings or even modify them in order to improve their effectiveness [160]. However, if this is the case, it will be necessary to examine if the improved products can be degraded by the existing bacteria and thus discard any possible environmental risks of non-target organisms [160].

As stated before, the discovery of the antifoulant is only one step to the development of an A/F system. Firstly, it must be proved that the incorporation of the bioactive substance into a paint matrix does not affect its biocidal or repellent effect as it has been observed in some attempts [168]. This is no easy task as, even by use of compatible matrixes, the natural compounds may be degraded too rapidly and their efficiency thus decreased [169]. Secondly, the compatible matrix must fulfil the same requirements as the rest of the paints regarding mechanical properties, stability and release characteristics. On the other hand, the production of the compound on a large scale is another challenge for this technology. Unless a synthetic derivative of the natural biocide with similar properties is developed (as it is the case of [170,171]), only the use of bacteria, either for the production of biocides or immobilised in hydrogels (mimicking natural mucous surfaces) [172,173], can yield a sufficient amount of active compounds [168]. Finally, the cost must as well be equal to or lower than that of other tin-free environmentally friendly paints of a similar efficiency to be commercially competitive.

All this reasoning, together with the fact that it is not clear whether all the attachment mechanisms include chemosensory inputs [174], leads to the conclusion that attainment of natural metabolites with broad-spectrum activity seems an extremely difficult goal if not unfeasible. According to [42], attempts to eliminate completely fouling bacteria by means of these natural metabolites should be abandoned and focused on the selective regulation of bacterial communities on synthetic surfaces (e.g. attracting grazers [175]). Apparently, the future of natural metabolites for A/F purposes will rely on the joint use of synthetic biocides [174], unless new studies, in the same line as [170], prove the contrary.

Something similar may apply to the use of enzymes incorporated into polymeric matrixes. The fact that most known adhesive mechanisms include proteinic compounds led to the idea of using proteolytic enzymes [19,176–180] as part of the paint system. However, it is also known that the proteins used by the barnacles to adhere show a great degree of adaptability [165]. Future studies will show whether scientists have been able to create an enzymatic system capable of succeeding against such a complex and adaptable process.

7. Non-toxic technologies

In the short term, no alternative seems able to reach a sufficient degree of development to replace biocide-based A/F coatings. Thus, improved products derived from the current ones and new binder systems and booster biocides will, very likely, dominate the A/F market during the coming years. However, there are already some lines of investigation that deserve special attention due to their promising characteristics as effective systems and because they involve more environmentally friendly modes of action.

7.1. Non-stick fouling-release

Non-stick, fouling-release coatings are an attempt to prevent the adhesion of fouling organisms by providing a low-friction, ultra-smooth surface (see [47,105]), on which organisms have great difficulties in settling (Table 5). Fouling-release coatings were conceived almost simultaneously with self-polishing copolymers. However, the latter proved to be much more effective as well as cheaper, so the development of fouling-release systems did not take off until the 1990s after the first bans of TBT-based products. Many studies have been performed to elucidate the properties that a coating should possess to resist adhesion [163–166,181–185]. The main ones are summarised by Brady [164]:

- A flexible, linear backbone which introduces no undesirable interactions.
- A sufficient number of surface-active groups which are free to move to the surface and impart a surface energy in the desired range.

Table 5
Key features and benefits of foul release coatings (after [20], with permission of IBC UK Conferences Ltd.)

Features	Benefits
Non-biocidal	No release of biocides into the sea
	No toxic waste (in dry-dock)
	Not affected by biocidal legislation
Smooth, glossy surface	Maximum speed
	Minimum fuel consumption
Extended fouling control	Long in-service periods (5 years)
	Reduced maintenance costs
Chemically durable	Surface stays smooth
Copper-free	Lower weight than standard antifoulings
	Safe to use on aluminium
High-solids	Low solvent content
	2-Coat system (for 5 years)

- Low elastic modulus.
- A surface which is smooth at the molecular level to avoid infiltration of a biological adhesive leading to mechanical interlocking.
- High molecular mobility in the backbone and surface-active side chains.
- A thickness which can control the fracture mechanics of the interface.
- Molecules which combine all of the above factors and are physically and chemically stable for prolonged periods in the marine environment.

These properties are mainly possessed by two families of materials: fluoropolymers and silicones. Fluoropolymers form non-porous, very low surface-free energy surfaces with good non-stick characteristics [183]. This low tendency to adhesion on fluoropolymers is optimised by assembling closely packed, oriented perfluoroalkyl groups on the surface, exposing CF_3 moieties [183,186], and permanently cross-linking them in this arrangement to minimise surface molecular diffusion or rearrangement when exposed to a marine adhesive [183,186]. With this disposition, very low values of surface-free energy are achieved [183,186]. Nevertheless, a drawback of these materials is the limited mobility due to the stiffness added by the F atoms, which hinder the rotation about a backbone bond [182]. A higher critical stress is also needed to make the adhesive–substrate joint fail due to a higher bulk modulus compared to elastomers. Thus, the fouling which does accumulate on the surface is not easily released [11].

Silicones, which are applied in thick (6 mm) layers [183], markedly improved the non-stick efficiency of fluoropolymers. Poly(dimethylsiloxane)-based fouling-release coatings (see Fig. 13) are the most used today due to their low surface energy, low microroughness, high elastic modulus and low glass transition temperature [11]. These surfaces present "moving targets" to the functional groups of marine adhesives due to their conformationally mobile surfaces
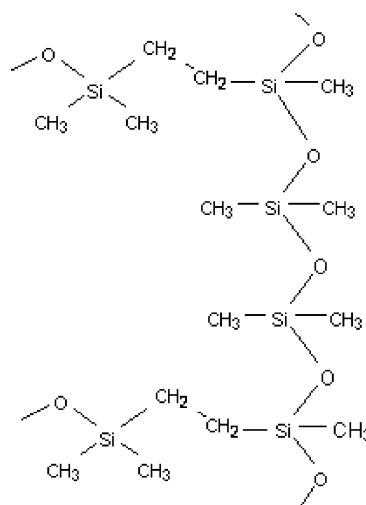

Fig. 13. Molecular structure of a cross linked poly(dimethylsiloxane).

[163]. The application of a force to the joint deforms the rubbery silicone and the resin peels away from the marine adhesive in a process which is slower than for fluoropolymers (which have lower surface-free energy) but requires less energy [183]. The mechanical locking of biological glues is minimised and slippage and fouling-release are enhanced.

Polysiloxanes substituted by fluorine might seem to be attractive candidates for surfaces with low bioadhesion. This could lead to polymers with the main advantages of each type, such as low surface-free energy and the elastic properties of silicones [183,187]. To improve the performance of the coatings, most commercial poly(dimethylsiloxane)-based coatings also contain fluid additives, and it is suggested that these migrate to the coating surface where they create weak surface layers that further promote fouling-release [11,188,189]. According to [183], these oils bring early stages of fouling with them and plasticise the coating. One drawback of this technology is that once the reservoir of oil has been depleted, the coating becomes brittle, cracks and fouls. The service life limit of the present coatings is approximately 2 years [183]. Furthermore, studies should assure that the released oils pose no threat to the environment.

Currently available fouling-release coatings are listed by Swain [11]. Their performance has been tested in several papers such as [190–192]. The results of [190] are of direct application as the tests were performed on real ships operating under different conditions. The conclusion of the study is that most coatings could prevent a fouling coverage greater than 20% of the total surface for 3 years. These modest results highlight the still deficient fouling-release properties of the coatings, which need 22 kn as a minimum to remove attached fouling organisms [183] (Ryle [15] reported minimum speeds of 7 kn to remove barnacles and 18 kn to wash weeds off), while speeds even above 30 kn cannot remove the slime film [20,185]. In addition, this technology is still

expensive [11,15,20,158], the coatings exhibit poor adhesion to the substrate [11,158,183], are easily damaged (cutting, tearing and puncturing) and have poor mechanical properties [11,15,158,183]. Furthermore, after repair they need to have a tie coat before recoating [15], there is a risk of contamination by silicone of other coatings after deficient cleaning of spray equipment [15], and some new kind of hull cleaning is required as none of them can prevent the abrasion of the coating [11,158,183].

Recent studies aiming at improved coatings are investigating the addition of biocides to these elastomeric surfaces. The attempt reported by Clarkson and Evans [193] was not successful but left room for improvements in the same direction. Thus, the joint use of fouling-release systems and fouling deterrent natural biocides could give rise to a wide spectrum of efficient and environmentally friendly A/F system [36]. The already active research in the field will show whether the advantages of this technology will be limited to fast-moving vessels or will spread to the rest of the world fleet.

7.2. Other systems

Some recent studies focus on the investigation of the surface properties of marine organisms with respect to bio-fouling control. As an example, Swain [11] reports that the non-fouling condition of porpoise and killer whale has been attributed to the outermost surface being composed of a glycoproteinaceous material with low surface energy. Baum et al. [194] studied the skin of the pilot whale, which showed a hydrated jelly nanorough surface characterised by a pattern of nanoridge-enclosed pores, of a pore size below the average value for the skin of most of the marine biofouling organisms. This high elasticity and high energy dissipative film are, in addition, rich in various hydrolytic enzymes. Nevertheless, it is known that many other mechanisms may contribute to the A/F protection of living animals [42]. In this case, the high shear water flow and air bubbles during jumping may also play an important antifouling role. Consequently, it is not clear whether the mentioned characteristics of the substrate are enough to prevent fouling. Similarly, use of microtextured silicones as a way of preventing settlement was proposed by Andersson et al. [195]. Apparently, it is not probable that surface microroughness can prevent the attachment of all the different types of foulants [196]. The results of [195] are modest in relatively cold waters, so the efficiency of these systems in warmer regions will probably be insufficient.

Another innovative solution consists of a layer of adhesive onto which a large number of microfibres are sprayed. Each fibre is microstatically charged to create the furry surface effect that is said to prevent hard biofouling from settling [197]. No good control of soft-fouling is achieved and the fouling-release properties of these coatings are doubtful as it is seen from the previous sections. Furthermore, the rough surface may contribute to some drag. Doubtful results of

this technology on ship's hulls are reported in [190]. For vessels moving at 8–11 kn, the best results showed a fouling coverage of 55% after 17 months. The same idea was studied by Phillippi et al. [198], again with poor results after only 1 month of exposure.

Mechanical cleaning is one of the oldest methods of biofouling control. Underwater cleaning, which avoids the necessity of frequent dry-docking, can maintain high-level ship performance with attendant reductions in fuel consumption [199]. This paper reports that long dry-docking intervals could be achieved even without any A/F coating, if a hard and smooth anticorrosive coating was regularly cleaned. Nevertheless, in practice, it would be better to coat the hull with a non-toxic fouling deterrent (to avoid toxic discharges), and thus achieve more flexibility for the timing of the underwater cleaning, and to protect some areas which could be difficult to clean by means of an automatic remote-controlled vehicle areas such as bilge keels, rudder and the stern arch [199]. The application of UV, ultrasonics, laser beams, etc. could be used by such an automated system. Robot technology, already applied to aircraft cleaning, is being investigated on sea vessels and small boats in Germany [199]. The potential price of underwater cleaning could be lower than that of the high-pressure water cleaning in a dry-dock [199], and underwater cleaning could be used jointly with fouling-release systems provided it does not damage the weak coating.

Finally, Hoffman [200] and Galaev [201] introduced the multiple types of stimuli and responses associated with existing "smart" polymers. As an example, these author mention that some substances can control the permeation rate of a polymeric matrix when the pores of the latter are coated with them. Will it some day be possible to create a coating capable of selectively releasing bioactive substances after artificial (electricity, sound, etc.) or natural (water temperature, pH, fouling adhesives) stimuli or, in other words, a coating active only when foulants are settled or during stationary periods?

8. Discussion

Shipping companies will very soon be forced to discontinue completely the use of TBT-based products and rely on the new tin-free biocide-based A/F products. The latter have traditionally been classified into two groups depending on the characteristics of their binder system. In principle, it could be expected that the most appropriate substitute for TBT-SPC products could be found from paints relying on similar chemical characteristics. This is the basis for what is here called acrylic-based tin-free "self-polishing" paints. However, we have shown in this paper that achieving the same performance as TBT-based paints is not as simple as binding a hydrolysable pendant group to an acrylic backbone. In addition, it is widely recognised that the presence of co-binders, additives, pigments and other potential paint components affects markedly the performance of chemically

active A/F paint systems. Following the evolution shown in the patents, it is seen that the companies which commercialise acrylic-based "SP" paints have needed to improve progressively their products to overcome different problems observed in their paints. It is not known if the currently commercialised products have succeeded in solving all the defects of the paints. These doubts are nourished by the lack of scientifically supported data offered by the different companies. Something similar applies to the so-called rosin-based tin-free "SP" paints, improved traditional rosin-based systems, which are claimed to have solved all the drawbacks associated with both the traditional soluble matrix technology and the modern CDP systems and achieved an "SP mechanism".

As a result of this and the fact that there is no scientific evidence on the relation between reaction mechanisms (also uncharacterised) and antifouling performance in the commercially available tin-free A/F paints, it is more reasonable to classify the existing products according to performance parameters which are, at the end, the important ones. As a first step towards the characterisation of the A/F performance of current commercial products, all of the larger companies commercialising tin-free "SP" A/F coatings were asked to provide data supporting the self-polishing behaviour of their products. In general, very few detailed data have been provided by the different companies due to confidentiality reasons and the figures shown in this paper are often lacking scientifically desirable features (e.g. experimental uncertainty).

Although the performance of A/F paints could be sufficiently inferred by experiments similar to those used for the elaboration of the figures shown in this paper, the attainment of fundamental knowledge of their mechanisms under different conditions would ease the product optimisation process greatly. The studies [24,27,28] show that profound knowledge of a particular system (TBT-SPCs) can lead to the development of mathematical models which can describe the performance of such a system with a high reliability. Once the model has been verified to capture the main mechanisms of the paint, it can be used to optimise the coating performance by analysis of the effects of changes in e.g. the pigment type and content, retardant concentration and biocide type on polishing rates, biocide release rates, and leached layer thickness. The attainment of such a model could also help to cut down on the long times used by the traditional empirical methods to develop new A/F products. This could for instance be brought about by the joint use of short-time rotary experiments and reaction engineering studies to provide empirical inputs for the model, which could then subsequently simulate the whole lifetime of the paint in just a few minutes.

It is evident that reliable A/F paint performance models would also constitute a powerful tool for a more rational screening of new ideas based on similar mechanisms of action. The model could be used to identify the characteristics to be possessed by the new A/F product to attain the desired performance (e.g. [157]). As an example, systems too sensitive to environmental changes, which have also been shown to affect the performance of A/F paints, could be discarded at early stages of the development process. Short experiments could be performed under different sea water conditions in order to feed the model, which would then be capable of estimating the A/F performance of the paint in any potential fouling scenario in a short time. A brief summary of the most usual ranges for the values of the sea water variables is presented in this paper to give an idea of the high variability and importance to the A/F performance of the sea water conditions. In the near future, potential tighter restrictions on the release rate of active compounds from A/F products could stress the advantages of having reliable paint models for the design and optimisation of coatings with perfectly controlled biocide release mechanisms. The same applies to the commercial implementation of A/F products based on chemically active non-toxic products, e.g. isolated from marine organisms, undoubtedly one of the main research interests in the A/F field nowadays, as discussed below.

The need for increasingly environmentally friendly substitutes for TBT-based products has also encouraged a profounder study on the adhesion mechanisms and biological characteristics of the fouling process. From the short summary given in this paper, the biological basis for the two most promising alternatives to synthetic biocide-based systems (fouling-release and natural biocide-based coatings) can be understood.

While many commercial fouling-release systems are already available in the market, 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. The latter has already caused a change from a blind and massive screening of organisms to a more rational study to determine which compounds have actually a role in deterring the growth of epibiota on marine organisms and to identify the common functional groups. Still, the broad-spectrum activity of these compounds is questioned by the huge diversity of organisms, behaviours and attachment mechanisms found in the oceans. Thus, some authors already state that no system entirely based on natural products will ever prevent the fouling of a surface totally. Unfortunately, some "external" factors (e.g. lack of industrial/academic interaction, slow testing times, costly and time-consuming environmental assessments, government registration and, more importantly, the existence of highly efficient toxic methods [155]) may never allow scientists to prove that it is indeed possible to attain such a coating. On the other hand, fouling-release 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. This should be achieved at the same time that other problems, inherent in these systems, are solved. The next years will help to elucidate whether the goal will be achieved.

This review is completed by an exhaustive review of past A/F attempts and the presentation of some innovative ideas which could, someday, lead to an efficient and environmentally friendly A/F system. In summary, the past, present and most likely future steps of the A/F technology have been presented.

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