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Research review paper

Current and emerging environmentally-friendly systems for fouling control in the marine environment

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ABSTRACT

Following the ban in 2003 on the use of tributyl-tin compounds in antifouling coatings, the search for an environmentally-friendly alternative has accelerated. Biocidal TBT alternatives, such as diuron and Irgarol 1051®,[1] have proved to be environmentally damaging to marine organisms. The issue regarding the use of biocides is that concerning the half-life of the compounds which allow a perpetuation of the toxic effects into the marine food chain, and initiate changes in the early stages of the organisms' life-cycle. In addition, the break-down of biocides can result in metabolites with greater toxicity and longevity than the parent compound. Functionalized coatings have been designed to repel the settlement and permanent attachment of fouling organisms via modification of either or both surface topography and surface chemistry, or by interfering with the natural mechanisms via which fouling organisms settle upon and adhere to surfaces. A large number of technologies are being developed towards producing new coatings that will be able to resist biofouling over a period of years and thus truly replace biocides as antifouling systems.

In addition urgent research is directed towards the exploitation of mechanisms used by living organisms designed to repel the settlement of fouling organisms. These biomimetic strategies include the production of antifouling enzymes and novel surface topography that are incompatible with permanent attachment, for example, by mimicking the microstructure of shark skin. Other research seeks to exploit chemical signals and antimicrobial agents produced by diverse living organisms in the environment to prevent settlement and growth of fouling organisms on vulnerable surfaces. Novel polymer-based technologies may prevent fouling by means of unfavourable surface chemical and physical properties or by concentrating antifouling compounds around surfaces.

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[1] Irgarol 1051® — registered trademark no. 2195791, Ciba Specialty Chemicals Corp., US.

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1. Introduction

Biofouling of material surfaces is a major problem in the marine environment, particularly to shipping where it can cause substantial costs due to increased fuel consumption. Traditionally, biocides have been used in antifouling coatings to prevent the build-up of biofouling by killing potential fouling organisms such as bacteria, fungi, algae, plants and molluscs. However, biocides are problematic because they can leach into the environment and cause harm to living organisms other than the ones they were intended to kill. For this reason world-wide legislation is imposing increasing limitations on the use of biocides to combat biofouling and in this respect alternative, biocide-independent technologies must be developed to meet this challenge. In this review, we first give an overview of the biofouling process and the problems associated with the use of biocides and then discuss biocide-free strategies that are currently available or at the development stage.

1.1. The process of biofouling

Biofouling describes the establishment of a macroscopic community of living organisms on a submerged surface, which is generally preceded by the formation of a biofilm of microorganisms. As early as 1889, V B Lewes remarked in the *Transactions of the Institute for Naval Architecture* (Lewes, 1889) (UK):

> "of some protective and anti-fouling compositions in use by the Navy, it is no exaggeration to say that, as far as speed is concerned, one half of our fleet would be useless before one year had elapsed, from the accumulation of rust, weed and shell"
>
> [Quoted by Townsin (2003).]

The impact of biofouling on fuel consumption can be estimated by applying a formula detailed by Schultz (2007), which models the effect of varying degrees of fouling, derived from data obtained using a laboratory-scale model of a frigate, on frictional resistance and increased propeller power (required to keep the vessel at a comparable speed to a 'clean' control). The consequence of heavy calcareous fouling on the frigate resulted in an increase in required propeller power of 86% in comparison to a non-fouled 'clean' control (Schultz, 2007). Such analysis typically indicates that if no antifouling treatments are used on vessels there may be a 40% increase in the use of fuel and a reduction in speed that may exceed 10% (Kohli, 2007; Schultz et al., 2011).

Common fouling organisms can be divided into three groups;

- Microorganisms, including bacteria e.g. sulphate-reducing bacteria (SRB), fungi, and diatoms (unicellular algae such as *Navicula*) (Bernbom et al., 2011; Landoulsi et al., 2011; Xu et al., 2012)
- 'Soft' fouling — such as sponges (e.g. *Cladosporium* sp.), bryozoans (de Messano et al., 2009) multicellular algae (e.g. *Ulva* (Egan et al., 2000; de Messano et al., 2009)), and brown algae (de Messano et al., 2009; Hellio et al., 2001)
- Shell or 'hard' fouling — such as barnacles (e.g. *Balanus improvisus*) (Andersson et al., 2009), mussels (e.g. *Mytilus galloprovincialis*) (Marcheselli et al., 2011), and polychaete worms (e.g. *Hydroides*) that produce hard tubes (Wang and Qian, 2010). Barnacles and oysters may also initiate pitting and crevice corrosion on steel substrates (Blackwood et al., 2010).

Although biofouling is typically observed over a period of months or longer, the initial stages of the fouling process usually occur on a much shorter timescale. Compere et al. (2001) found that biofilm formation and macrofouling are usually preceded by the formation of a conditioning film comprised of adsorbed polysaccharides, proteins and polypeptides, which form on surfaces within 1 min of immersion in a potentially fouling environment. The composition of the conditioning film is influenced by the properties of the substrate on which it forms. For instance, solvent cleaning procedures can have an effect on the compounds found on stainless steel after subsequent immersion in seawater (Compere et al., 2001). It may be that future antifouling strategies may target the formation of the conditioning layer as a way to prevent subsequent colonisation of the surface by living organisms. Although the conditioning film is not readily visible to the eye, various surface analysis techniques can be used to characterise it, including X-ray photoelectron spectroscopy (XPS) (Cerca et al., 2005; Pradier et al., 2000), time-of-flight-selective-ion mass spectrometry (TOF-SIMS) (Compere et al., 2001; Pradier et al., 2000), Fourier transform infrared spectroscopy(FTIR) (Compere et al., 2001; Mafirad et al., 2011), atomic force microscopy (AFM) (Beech et al., 2002; Compere et al., 2001), scanning electron microscopy (Xu et al., 2013) and surface-energetic characteristic determination via contact angle measurements using liquid or vapour surface tension parameters (Compere et al., 2001). In a study in which stainless steel was immersed in natural seawater collected at Brest (France), a nitrogen-containing compound (possibly derived from proteins) and carbohydrate were detected on the surface after 5 h of immersion. After 24 h, an increase in the amount of adsorbed molecular species can be observed and the proportion of bound carbohydrate increased relative to protein, but no continuous film was revealed by the analytical techniques used (Compere et al., 2001).

After formation of the conditioning film, the subsequent onset of macrofouling may be preceded by the formation of a bacterial biofilm and such a biofilm may have a deleterious effect on the ability of a surface to remain free from larger fouling organisms. Different microorganisms have contrasting effects on the settlement of other fouling organisms and the nature of the underlying surface also plays an important role. For instance, the diatom (microscopic alga) *Achnanthes longipes* is a common fouler in shallow water, attaches preferentially to hydrophobic surfaces but is inhibited by live biofilms and bacterial extracellular polymeric substances (EPS) (Gawne et al., 1998). However, the presence of EPS can modify the surface of the substrate (in terms of surface energy and topography) in favour of *A. longipes* settlement (Gawne et al., 1998). Where the substrate surface was initially hydrophobic, the development of a bacterial biofilm increased attachment of *A. longipes* but where the substrate was initially hydrophilic, attachment was not increased. Various biofilm-forming bacteria produced biofilm surfaces with different propensities for subsequent attachment of *A. longipes* (Gawne et al., 1998). The properties of the surface, pre-existing biofilms and the presence of diffusible molecular signals are also important in determining the propensity of other macrofouling organisms, including crustacea and molluscs, to settle (Callow and Callow, 2000, 2002; Khandeparker and Kumar, 2011).

Microscopic foulers such as diatoms and bacteria can influence the settlement of much larger fouling organisms. For example, the polychaete, *Hydroides elegans* settles in response to cues from biofilms of diatoms (Lam et al., 2003). Some diatoms have an inductive effect, such as