Novel Antifouling Coatings: A Multiconceptual Approach

D. Rittschof

Abstract The development of novel antifouling and foul release coatings must be considered in the context of business, government, and academic research. Existing antifouling technology is based upon the use of broad-spectrum biocides. Foul release technology is partially developed, has incompletely understood mechanisms and unknown long term fates and effects. Business is structured to register, generate, deliver, apply, and remove antifouling coatings based upon broad-spectrum biocides. Business is weak in biology and study of fates and effects beyond those required for registration. Government is structured to regulate, respond to, and support basic research. Government is not proactive or cooperative. Academics are highly competitive, still relatively isolated from reality, strong in basic research, and not well versed in business or government. Rapid progress in novel coatings technology is unlikely in this environment. Business responses to regulations and awareness of environmental responsibility will drive the process.

1 Introduction

The intent of this discourse is to provide a stationary target to promote conversations on how best to make substantial progress toward environmentally benign antifouling and foul release coatings. It is presented from the perspective of a researcher who has dedicated 25 years to the development of environmentally benign antifouling coatings. From that perspective, understanding four related topics is central to thinking and planning new approaches. The four topics are:

D. Rittschof
Duke University Marine Laboratory, Nicholas School of the Environment, 135 Duke Marine Lab Road, Beaufort, NC 28516, USA
e-mail: ritt@duke.edu

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1. Fouling, antifouling, and foul release concepts and technology (Costlow and Tipper 1984; Kavanagh et al. 2003)
2. The role of business models and issues as they relate to antifouling and foul release coatings(Champ 2000; Rittschof and Parker 2001)
3. The role of government and regulatory agencies and laws in novel coatings development (Champ 2000; Rittschof 2000; International Maritime Organization 2003)
4. The role of academic research in the process (Clare 1997; Rittschof and Holm 1997; Rittschof and Parker 2001)

I argue that progress requires that all four topics be addressed simultaneously. However, it is likely that other equally important yet to be conceived topics will be added to this list.

I will make the argument that progress in developing novel coatings is unlikely because the existing global, political, business, and research structures inhibit sharing of expertise and the necessary cooperation between business, government, and academia. Finally, although I am pessimistic about any hope of rapid progress due to my perception and growing cynicism of human nature, I will suggest ways to facilitate progress in assessing developing environmentally benign solutions to fouling.

2 Fouling

In our context, fouling is the attachment and/or growth of undesirable molecules and organisms to submerged surfaces. Fouling includes molecules, microbes, and macroorganisms and spans the spectrum from true temporal succession (each subsequent stage requiring a prior stage) to essentially random events determined by availability of foulers. The actual process of fouling ranges from passive mechanisms comparable to dust settling on a surface to highly specific mechanisms that require active behavior (Fig. 1; Clare et al. 1992; Hadfield 1998). Biological fouling impacts the esthetics, performance, and economics of stationary and mobile platforms.

3 Antifouling Coatings

Classically, antifouling is any of a large number of control measures that use broad spectrum biocides to control fouling (Fisher et al. 1984; Preiser et al. 1984). Antifouling coatings are coatings that control fouling by releasing broad-spectrum biocides. Antifouling coating technology is closely tied to anticorrosion coating technology. The two technologies are generally present on hulls in a multilayered coating system. Development of these systems preceded global awareness of environmental degradation due to build up and impact of biocides. Regulations have been in general reactive rather than proactive (Brancato et al. 1999; Champ 2000; International Maritime Organization 2003). Global business models, rules, regulations,

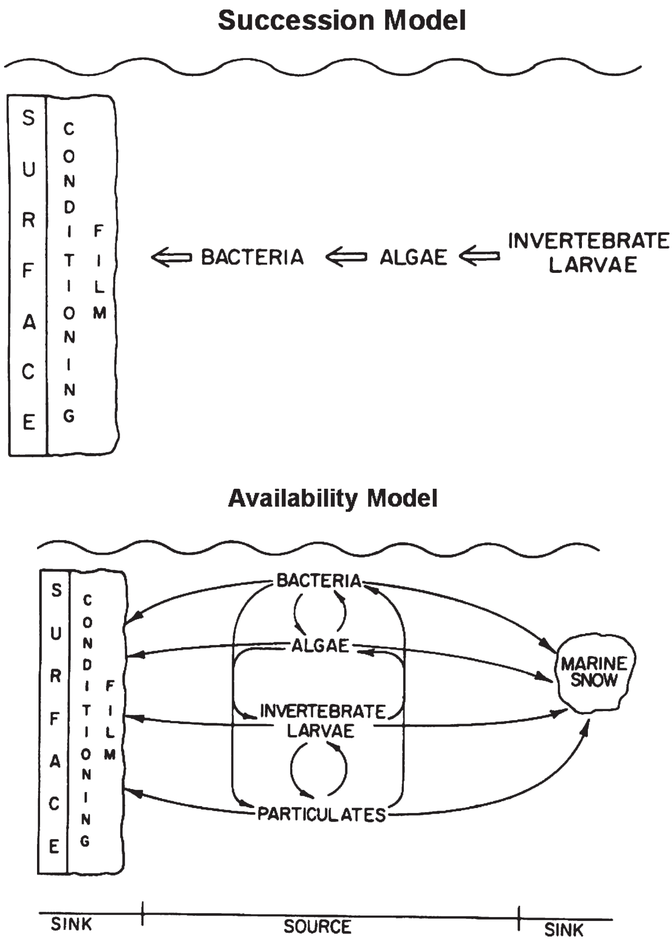

Fig. 1 The spectrum of biological fouling (from Clare et al. 1992). Classically, biofouling was thought to be an exclusively successional process (**a**). However, since the early 1990s evidence has accumulated that supports the availability model (**b**), especially for the majority of the cosmopolitan fouling organisms now found in the worlds ports. These foulers have been introduced through shipping and dominate because they are analogous to terrestrial weeds

and performance expectations are tied to economics and performance of toxic coatings (Champ 2000; Rittschof 2000).

4 Foul Release Coatings

The concept of developing foul release surfaces, surfaces that are easy to clean because biological adhesives adhere to them poorly, has been popular for over three decades. Originally, the concept was based upon fluoropolymers (Bultman et al. 1984).

In the last several decades foul release coatings have been based upon silicone polymers, which are much easier to clean than fluoropolymers (cf Brady 2000; Stein et al. 2003). The physical/chemical mechanisms resulting in low adhesion of silicones are incompletely understood. Poor physical properties of foul release coatings are a major stumbling block. When physical properties are improved, the ease of cleaning is reduced. Because foul release coatings are based upon coating technology that is different from antifouling coatings, facilities that can apply either kind of coating are unlikely at this time.

5 Antifouling–Foul Release Coatings

The notion of coatings that are hybrids of antifouling and foul release technology is beginning to be a popular one. The basic concept is to deliver antifoulants through foul release coatings. One popular idea is to improve the physical characteristics of the foul release coating and then to add antifoulants that target pernicious foulers that are hard to clean. The overall concept may be based upon observations that nontoxic silicone coatings containing organotin or other toxic catalysts and additives such as silicone oils (Kavanagh et al. 2003) alter macrofouling larval behavior (Afsar et al. 2003), inhibit fouling, and are routinely easy to clean. Some of these coatings release sufficient toxic species that they may perform as antifouling coatings for months (Rittschof and Holm 1997; Holm et al. 2005).

6 Business Models

Business approaches are harder to document. This section is based upon my experience in working with a variety of businesses for over 20 years. The antifouling coating industry has the mission of making money. Products are designed for specific performance niches within the broader market. For example, the small pleasure boat antifouling coating niche is for products that can be self-applied and that are effective for 3–6 months, while the niche for coatings for large ships is for products that are applied in specialized facilities and are expected to maintain physical and antifouling properties up to for 10 years. The yacht and intermediate-sized vessel market is for coatings with expectations that are intermediate to the extremes.

The antifouling coatings business has three major components:

1. Antifouling additive suppliers, which develop and register biocides
2. Coatings manufacturers, which develop polymer systems, mix, deliver, and develop protocols for product application
3. Coatings appliers, which apply and remove anticorrosive and antifouling coatings

The technical infrastructure is strong in protection of intellectual property, polymer chemistry, anticorrosion chemistry, registration of toxic compounds, and customer support. It is relatively weak in fouling biology and in environmental stewardship.

The business of antifouling coatings is based upon coatings that control fouling with broad-spectrum biocides. The biocides are delivered either by coatings (resin–rosin systems) that act as slow release reservoirs from the bulk coating or by toxin release that is controlled hydrolysis of the polymer (usually acrylates), which expose and release new toxin over time. The highly effective but environmentally damaging organotinpolymer films, which were voluntarily removed from global markets in 2003, were of the ablative (hydrolytic) or self-polishing type. The base polymers used in commercial antifouling coatings meet a spectrum of important physical and anticorrosion characteristics (Preiser et al. 1984).

The coatings industry has a history of modifying its products when they are shown to have unacceptable environmental impacts. More recently, environmental concerns have resulted in regulatory pressure to reduce the release of copper from antifouling coatings. The industry response to restriction of use of copper has been to reduce amounts of copperand to supplement the coatings with broad-spectrum organic biocides(Gough 1994; Liu et al. 1999; Readman 1996; Tolosa et al. 1996; Rittschof 2000).

7 Government

The role of government in regulating antifouling technology is centered on registration of additives (national governments) and in making and enforcing laws and regulations (cf International Maritime Organization 2003). Governments are, in general, reactive and adversarial rather than proactive and cooperative. Even when government is well informed by stakeholders such as business, scientists, and environmental groups, political solutions are inadequate, expensive, and slow (cf Champ 2000). For example, US registration of a new compound for use as an antifouling biocide can take over a decade and cost over US$10,000,000 (Rittschof 2000).

However, governments also have a dramatic positive impact on fouling control technology. Due to defense and economic and environmental considerations, governments have a major role in supporting research in antifouling, foul release, and environmental impacts(cf. Exploratory Research for Advance Technology, ERATO, Biofouling Project Japan, 1990–1995; US Office of Naval Research Antifouling program, Alberte et al. 1992; Nordic Council of Ministers, Dahllöf et al. 2005; AMBIO 2006). Government involvement is central to funding of basic research; training of government, industry and academic researchers; and development of assessment techniques and concepts.

8 Academia

Academia and government researchers associated with antifouling are highly competitive, strong in basic research and relatively weak in applied research. Academic researchers are generally uninterested or uniformed about the workings of business and government. In general, academics are isolated from business and from government agencies charged with regulation. Historically, in the USA and many other developed countries, academics from upper tier research universities were encouraged to avoid interests in societally relevant research. More recently, there have been gradual changes in attitudes in major research universities, associated with changes in the scope of funding opportunities. Researchers have a role in initiating new avenues of research. As ideas mature, often over the course of several decades, potential productive avenues are identified and new research structures are generated to move the concepts toward products. In the case of antifouling, these changes and advances are on the horizon

9 Synopsis

Existing antifouling technology is based upon the use of broad-spectrum biocides. Foul release technology is partially developed, has incompletely understood mechanisms and unknown long-term fates and effects. Business is structured to protect intellectual property and to register, generate, deliver, apply, and remove antifouling coatings based upon broad spectrum biocides. Business is weak in biology and in the study of fates and effects beyond those required for registration. Government is structured to regulate broad spectrum biocides and to enforce laws such as the US Clean Water Act. Government is not proactive or cooperative. Academics are highly competitive, still relatively isolated from reality, strong in basic research, and not well versed in business or government. It is in this context that novel antifouling coatings development should be considered.

10 Goals of Environmentally Benign Antifouling Coatings

Environmentally benign antifouling is a possibility that could be efficiently approached if one could generate the necessary list of goals and their associated assumptions and prioritize them. Given the context provided I suggest the following list of goals and assumptions that all should be met by the first generation of environmentally benign coatings:

1. Coating should be compatible with existing business models
2. Coating should use existing polymers, production, delivery, application methods, and application facilities
3. Compatible with existing anticorrosion systems
4. Function comparably to coatings that are presently on the market
5. Deliver compounds with known minimal environmental impact

To make a long story short, in the context provided, the only solution that fits the context established is a short-lived broad spectrum biocide. If one looks at the more recent products on the market one can see that there are two business strategies that meet all but the assumption of known minimal environmental impact. Both strategies use organic toxins to enable reduction in the level of copper released by antifouling coatings:

1. Use of clearly long lived broad spectrum biocides such as Irgarol (Gough 1994; Liu et al. 1999; Readman 1996; Tolosa and Readman 1996; Tolosa et al. 1996; New York State Department of Environmental Conservation 1996) and Diuron (PAN 2008)
2. Use of shorter lived broad spectrum biocides, copper pyrithione (Dahllöf et al. 2005), and Sea 9–211 (Willingham and Jacobson 1996). These strategies are clearly in line with the argument developed that business models can tolerate only minor changes.

There are two related possibilities for the rationale of replacement of heavy metal biocideswith long lived organic biocides: (1) Following the classical business model to the letter by replacing one long lived biocide with another. Perhaps, it is possible that these businesses could claim ignorance as an excuse for lack of concern for environmental consequences. (2) Following the classical business model by replacing one long lived biocide with another with knowledge of consequences, but without legal, moral, or ethical responsibility for protecting the environment. Independent of which possibility is correct, the result is the same high potential for environmental degradation.

Similarly, using short lived broad spectrum biocides to replace long lived biocides, could be unintentional or it could be a carefully considered decision that reflects a company with a forward looking business model that includes responsibility for environmental impacts. In these case there is documentation that the environment was considered (cf. Callow and Willingham 1996; Galvin 1998; Willingham and Jacobson 1996; Harrington et al. 2000; Dahllöf et al. 2005). Independent of which option is correct, the end result is companies positioned to move more quickly away from the old business model. It is these companies that should have a competitive edge in a global community that will eventually recognize that business must take responsibility for the environmental impacts of its products (Rittschof 2000).

In addressing development of novel antifoulant compounds from this perhaps naive academic point of view, I came to understand one important concept. It is not the half-life of the toxin that is important, it is whether or not the toxin will build-up in the environment to deleterious levels. Although this kind of analysis is sufficiently well developed to be standard fare in environmental chemistry textbooks (cf Schwarzenbach et al. 2003), this kind of analysis is not to my knowledge part of the regulatory structure. My sense is that business (most easily because they track customer use and sales and know trade secrets) or academics could develop models that could be used to predict conditions of use where there would be environmental impacts. From an environmental perspective this would be a preferred alternative to reporting dangerous build-ups (Gough 1994; Liu et al. 1999; Readman 1996; Tolosa and Readman 1996; Tolosa et al. 1996) after the fact. Perhaps this will be the next step in the process of developing environmental responsibility.

One inevitable conclusion from this intellectual exercise is that in the existing global regulatory and business and research structure, novel antifouling technology will evolve slowly from small changes in existing art. If one asks the question, "Could the process be accelerated?" the answer is straightforward, but not easily implemented. That answer is restructure business, government, and academia to enable these sectors to work cooperatively by sharing expertise in working toward a common goal (Rittschof and Parker 2001).

Such utopian restructuring is unlikely at the national level, but might be possible at the level of an international organization such as the European Union or the United Nations. The EU has a research and development structure, the Advanced Nanostructured Surfaces for Control of Biofouling (AMBIO) project(AMBIO 2006), which meets many of these objectives. In reality, development of a multi-functional cooperative structure would be a novel infrastructure that could be charged with addressing a variety of global problems.

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