Yearbook of Maritime Technology

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Hard fouling organisms in their natural environment.

New molecule protects ships against marine biofouling

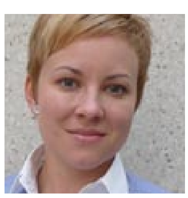
The present technologies to inhibit attachment and growth of marine fouling organisms rely on bioactive chemicals. Mostly, they are acting by being toxic and lethal. However, killing is not necessary when preventing settlement.

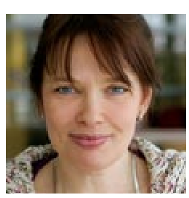
The need for new antifouling substances has been an issue for long and understanding the basic mechanisms behind fouling was expressed over fifty years ago by the world's largest shipowner, the US Navy:

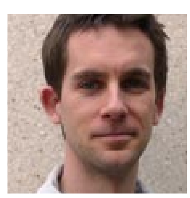
"Fouling is, however, a biological phenomenon. If it is to be dealt with effectively from an engineering point of view, it is important that the biological principles which determine its development be understood."

The present technologies to inhibit attachment and growth of marine fouling organisms rely on bioactive chemicals. Mostly, they are acting by being toxic and lethal. However, killing is not necessary when preventing settlement. It is possible to manipulate marine larvae to prevent from attaching to a surface. This can be achieved by altering behavioural keys or by preventing the gluing mechanisms that allow surface attachement. With knowledge in basic biology, it is possible to find solutions, based on fouling organism biology.

»Thousands of different species can be found on a fouled surface.«







Cecilia Ohlauson, M. Sc, Regulatory Affairs Specialist, I-Tech AB, +46 (0)706 03 42 36, cecilia.ohlauson@i-tech.se

Lena Lindblad, Assoc. Prof., R&D Manager, +46 (0)31 703 19 49, lena.lindblad@i-tech.se

Dan Isaksson, PhD, R&D Chemist, +46 (0)735 24 03 42, dan.isaksson@i-tech.se

Within the sea, hard surfaces are rare. Any surface is an attractive place for non swimming organisms providing a place for attachment and reproduction. The phenomenon is known as marine biofouling. Organisms that adhere could be anything from bacteria and algae to marine invertebrates. However, what they do have in common is a mechanism that allows them to attach to the surface and create a permanent habitat.

Yearbook of Maritime Technology

The process from a clean surface to a fouled surface goes quickly. Within a few weeks, when the circumstances are right, a layer of up to ten centimeters of biomass can be found on the surface.

Thousands of different species can be found on a fouled surface. Most of them are unicellular bacteria or diatoms (unicellular algae with a silica case) usually referred to as slime or biofilm. The multicellular organisms are divided into soft foulers and hard foulers. Soft foulers are those without shells, such as algae, sponges, tunicates or hydroids. Hard foulers have a calciferous shell and among those tube worms, mussels and perhaps the worst fouler of them all, barnacles, can be found. All the different organisms have evolved their specific means to adhere to surfaces and staying attached. From an evolutionary point of view, the ability to glue in a marine environment has been invented several times and each time with a new solution. The complexity of the problem from a biological point of view is therefore immense.

Before adhering to a surface, all organisms have been free swimming larvae. Adhering may occur passively, relying on physical parameters such as buoyancy or gravity, random processes due to surface vortices. However after attachment, a new phase starts when different biological cues become important to guide and start the process that will result in a permanent attachment. The most effective way to prevent fouling is to hinder attachment. That can be done by taking advantage of the natural behaviour of the fouling organisms.

The search for a new antifouling molecule has been in progress since the ban of tributyl tin (TBT) for leisure crafts were initiated in the 1980s and intensified with the adoption of the IMO International Convention on the Control of Harmful Anti-fouling Systems on Ships in 2001. The efficacy of the TBT paints are well known and so are the detrimental effects they caused in the marine environment. Banning them was a step in the right direction but it also lead to another environmental problem. The high efficacy of TBT kept fouling organisms off the ship hulls, minimizing the friction between hull and water keeping fuel consumption down. With a less effective antifouling system, fouling on the ship hull increased with the friction,resulting in increase in fuel consumption and emissions of green house gases.

From an environmental perspective there was therefore a need for new antifouling molecules with the ability to minimize emissions of green house gases and at the same time be as environmentally friendly as possible. To achieve this a molecule should be potent to maximize the antifouling efficacy while minimizing the release to the environment or it needs to be highly degradable to minimize pollution. A combination of potency and a high degree of degradation is of course the most favored properties for a new antifouling molecule. The antifouling molecules in use today all have their advantages and disadvantages but the optimal antifouling molecule, from an environmental perspective, has yet to reach the market.

The regulatory barriers for a new antifouling molecule to reach the market are vast and challenging in many parts of the world. Within the European Union, USA and Australia a new antifouling molecule must go by biocidal legislation and fulfill several criteria before it is allowed for use in biocidal products. These regulatory barriers are used to ensure that new biocidal products are not a threat to human health or to the environment.

In general the biocidal legislation dictates the registration of the active molecule which is performed by submitting a dossier of information regarding the molecule to competent authorities. This dossiers include detailed chemical and physical data, proof of efficacy against intended target organisms, several toxicological studies on mammals and ecotoxicological studies on a number of species, both marine and terrestrial. This data set is then used for evaluating the effectiveness and safety of the molecule, human health effects, environmental effects and hazard identification for the active molecule. If all these properties are regarded as acceptable by the competent authority a new active molecule has a chance to reach the market.

This regulatory barrier may seem as quite an easy barrier to overcome but the amount of data needed for a registration dossier is massive and might take years to compile. After submission for registration all information is reviewed by the competent author-

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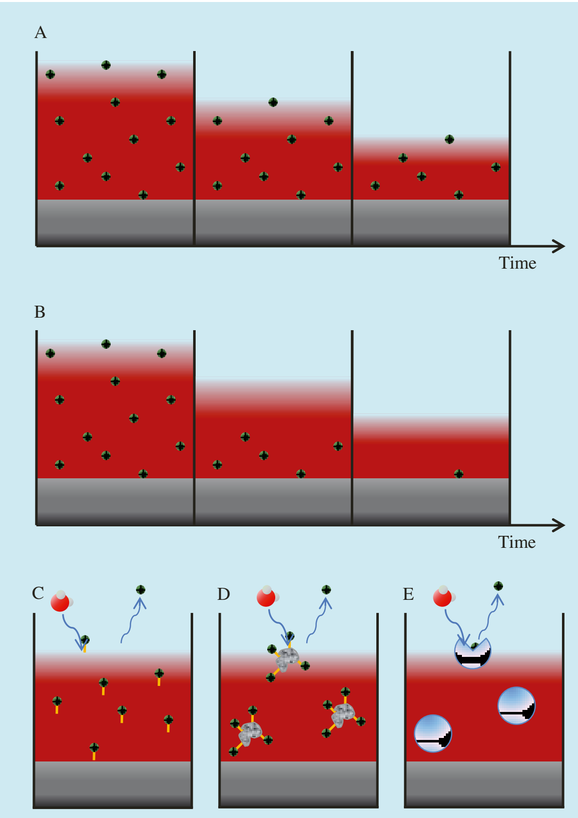
A solitary barnacle filtering surrounding waters for food.

Yearbook of Maritime Technology



Barnacles are regarded as the most problematic fouling organism and can colonize ship hulls in large numbers.

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ity and then a decision of approval or refusal is formed. This process takes at least one year and even though this might seem unnecessary to the consumer who is interested in a new better antifouling molecule, this process is performed to ensure the safety of the consumer and all other living organisms that might come in contact with the molecule.

Outside the European Union, USA and Australia the regulatory barriers concerning antifouling molecules differ from country to country. Japan employs a system with notification to the authorities. The demands for further information regarding the molecule depend on its properties and can be as demanding as the registration described previously. China also uses the notification system but has yet to reach the same regulatory barrier as the countries described here.

Today there are many different strategies being tested and a lot of efforts and research are done to find more environmental friendly solutions to the fouling problem.

There are a few main roads that are identified.

- The non sticky coating: The idea is that fouling organisms won't be able to attach to the surface or that the attachment is so weak that they will be washed away once the ship starts to move.
- The controlled depletion paint (CDP): Antifouling agents dispersed in the paints are released as the paint surface erodes.
- Self polishing coatings (SPC): The antifouling agent is bound to the polymer matrix in the paint and are released at the same rate as the paint surface is being polished (hydrolysed).

There are also hybrids between CDP and SPC which make use of both the systems.

As mentioned above the aim of a biocide containing CDP or SPC is that the release rate of biocide is the same as the rate of erosion of the coating, allowing for a constant release of biocide during the whole lifetime of the coating. See figure A.

In reality if the biocide is only dissolved in the CDP there is a great risk that the diffusion of the biocide from the painted layer is faster than the rate of erosion causing a depletion of the coating with regards to the biocide. See figure B. This means that the coating will loose its antifouling properties, at least partly before the end of the lifetime of the coating is reached.

How can a slow or controlled release of biocide be achieved?

In order to get around the problems given in figure B there are a number of strategies that can be used in CDPs and SPCs. The one used in SPC is to physically bind the biocide to the polymer matrix inside the coating. See figure C. The bond will secure that the biocide does not diffuse out prematurely. At the surface of the coating the bond between the biocide and the polymer is hydrolyzed and the biocide is set free.

A second approach would be to attach the biocide to a particle unable to move through the coating-film. See figure D. As the surface of the coating layer is eroded new particles are exposed at the surface where the attached biocide can be released by water aided hydrolysis.

In a third approach the biocide is encapsulated. When the capsule containing the biocide is exposed to water at the coatings surface it opens up and the biocide is released. See figure E. By the erosion of the paint new capsules are continually exposed at the surface.

When a new active compound with a desirable effect is discovered, formulation work is necessary in order to reach an optimal product. The surrounding matrix has to be chosen so that suitable solubility of the active compound is achieved. The active substance should preferably be soluble in the paint matrix. Otherwise a phase separation will occur unless the substance is distributed as a stable emulsion within the paint. If the active substance is very water soluble problems may occur due to premature leakage of the active compound from the coating causing a depleted coating layer. Further, the way with which the release will be controlled (if any) has to be decided. This means to study the active compound and determine what functional groups are present and in what way they are possible to use for this purpose. Functional groups can interact with the polymer or other components in the paint as discussed and demonstrated above in figure C–E.

»A second approach would be to attach the biocide to a particle unable to move through the coating-film.«

As global trading increases as well as the concern for the marine environment, more and more interest is focused on shipping. Marine biofouling is a typical multifaceted problem that concerns the environment in more than one way and the solutions must take into account more than biofouling itself. Without proper hull protection, a dramatic increase in fuel consumption occurs, causing an increase of green house gases emission. On the other hand, protecting the hull from unwanted biomass can release toxic substances into the marine ecosystem.

For many years, the area of antifouling was not under regulatory scrutiny. This has dramatically changed. The first multinational regulatory decision is the TBT ban that was ratified in 2008. In Europe, there is a complete overview of the existing substances according to the Biocide Product Directive and there is an uncertainty regarding the future paints. Although the regulatory work is indeed wanted and necessary to prevent risks for human health and environment, it is a hindrance for innovation and future product development. The challenge ahead is not to find new substances that prevent biofouling, but to find molecules that are effective from the shipowners point of view and can be regulatory approved regarding risk assessments, both concerning human health and the environment. And all those demands must be within a reasonable economical frame.

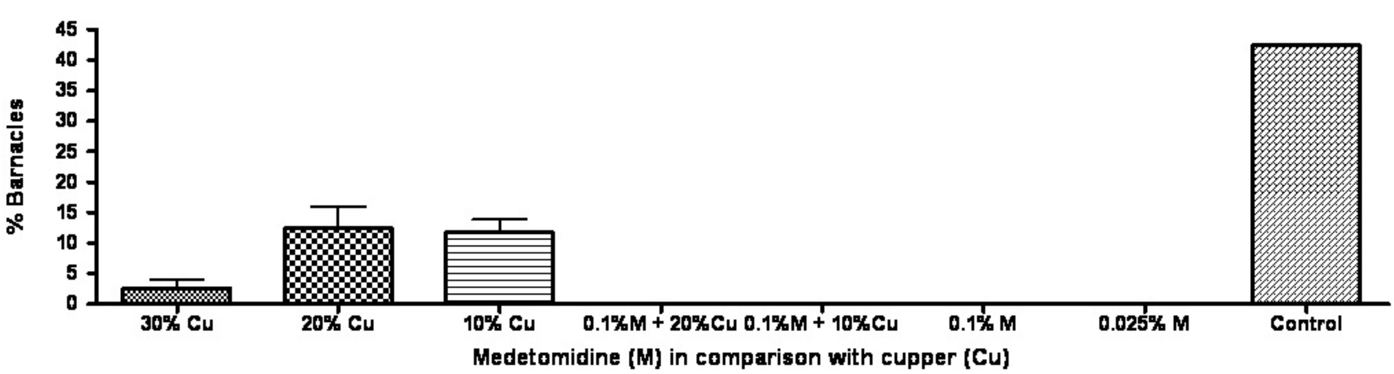
Throughout the years as we have worked with medetomidine, our perspective has always been that we have to know the biological effects both on target organisms as well as non-target species, including humans, control the release and thereby, reducing risks. We have now submitted medetomidine for regulatory approval in Europe. *

Medetomidine and its mode of action

Barnacle larvae have an exploratory surface behavior, necessary for settlement. A novel antifouling substance (Medetomidine), effectively prevents barnacles and other shell forming animals from adhering to ship hulls. This substance takes advantage of the natural behaviour of the organisms. When the larvae approach a surface coated with Medetomidine, the surface exploring behaviour that will result in permanent attachment is reversed into a swimming behaviour away from the surface. Instead of being lethal to barnacle larvae, a deterring behaviour is promoted and the attachment and permanent settlement is therefore inhibited. The effect of Medetomidine on the larvae is fully reversible and causes no permanent damage to the larval biology. Actually, any nearby surface can be colonized by the very same larvae.

Medetomidine represents a third generation of antifouling substances. The first generation used for thousands of years were characterized by being as toxic as possible. Substances such as mercury, arsenic or lead were used. During the second half of the 20th century, organic substances came into use. Many of them are still in use and the state of the art is to combine those with cuprous oxide in a self polishing paint matrix. The third generation, represented by Medetomidine, take advantage of the biology itself of the fouling organisms. Instead of being lethal, it is possible to shortcut a biological behaviour without causing any permanent harm. By doing so, it is also possible to reduce the amount of biocides used and thereby find more effective and more environmentally sound solutions.

However, a molecule can be very effective in the laboratory but not suitable on a ship's hull due to inborn incompabilities with paint matrices. An identified molecule must therefore always be followed by a suitable paint matrix that will allow release to secure the antifouling effect.



One year field study at the Swedish west coast.