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The challenge to find new sustainable antifouling approaches for shipping

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Abstract — Fouling of ships and its counter measure—antifouling—is receiving justified attention as a serious marine environmental problem. If the ship is fouled its fuel consumption will increase radically. If a ship is fouled its emissions to air will increase, its manoeuvrability will be affected and it will contribute to the spreading of aliens. The present antifouling strategies seem to be non-sustainable, either environmentally or technically/commercially. The large amounts of biocides used in antifouling paints constitute a marine pollution problem. Research for more sustainable solutions, biocidal as well as non-biocidal, is ongoing. Optimisation of new antifoulant combinations combined with microcapsule technology will afford the possibility to decrease the exposure of the marine environment to antifouling biocides.

Key words: Antifouling, fouling, biocides, microcapsules, combinations

Transport at sea —opportunities and challenges

Around 90% of world trade is carried by the international shipping industry. There are around 30000 vessels of over 1000 gross tonnes in the world merchant shipping fleet. Essentially shipping is a sustainable means of transport since it requires minimal infrastructure and a relatively low input of energy for the quantity of transported goods.

However, the shipping industry faces some serious environmental challenges: The emission of greenhouse gases, the emission of NOx and SOx, the use of non-sustainable, antifouling measures, oil discharges, contaminated bilge water, and the handling of ballast water. Leisure boats face some of the same challenges as those of the large tonnage. Hence, sustainable solutions for leisure boats is also a crucial step towards a healthier marine environment.

Fouling on surfaces —a natural phenomenon

When a surface comes into contact with seawater, it changes very rapidly. Dissolved organic compounds natural to the sea, adhere to the surface within minutes. Within a few hours, unicellular living organisms, such as bacteria and unicellular algae, colonise the surface, which becomes smooth and slimy. After a week or more, the surface will be colonised by a variety of microorganisms, algae and animals. There are some 4000 marine species which can and will colonise different surfaces in the marine environment. For organisms to adhere and grow on surfaces is an important survival strategy in the marine ecosystem. All submerged surfaces are affected—both natural and those introduced by man; ship hulls, offshore installations and other structures at sea.

The fouling problem

Fouling on ships increases the surface roughness of the hull, which in turn increases its frictional resistance when the vessel moves through water. The increased resistance leads to increased fuel consumption. The cost of increased fuel consumption is substantial—after six months, a ship without an appropriate antifouling coating can suffer a 40% increase in fuel consumption to maintain normal speed. Maintenance costs increase with fouling. The ship must be dry-docked more often, and will require extra surface treatment and painting. In addition, fouling has a negative effect on a ship's manoeuvrability.

To prevent fouling, over 80000 tonnes of antifouling paint is used globally every year with a total market value of €1 billion. The total cost of fouling protection is significantly higher. The US Navy faces annual costs resulting from fouling of its ships, including maintenance costs and increased fuel consumption, of over €1 billion.

The environmental problem is evident and serious. Increased fuel consumption leads to increased emissions of the greenhouse gas carbon dioxide, nitrogen oxides, sulphur oxides, hydrocarbons and particles. In addition, there is new data showing that fouling can play an important and undesirable role in spreading marine species from their natural areas of distribution to new areas where they can constitute a threat to the ecological balance, becoming what are called "alien species". There is a trade-off between the adverse effects of fouling and the adverse effects resulting from the use of antifouling paints that are toxic to the marine ecosystem.

The nature of fouling

The particular species adhering to and growing on a hull depend on the waters through which the vessel is sailing, the season, and how long the vessel spends in port. The initial colonisers are unicellular organisms. Bacteria, protozoa (unicellular animals) and diatoms (unicellular algae) are common species in the initial microfouling. Diatoms secrete large quantities of polymers, which contribute to the sliminess of the surface. Following the microfouling, a macrofouling community establishes itself, consisting of soft or hard fouling. Soft fouling includes higher algae, such as the green algae *Ulva intestinalis*. Ulva releases spores, which, on contact with a surface, secrete an adhesive consisting of glycoproteins to ensure they adhere to, and can grow attached to the surface. Soft fouling may also consist of sea squirts, anemones or soft corals. Hard fouling may involve mussels, tubeworms and barnacles, all of which have a highly developed ability to adhere firmly to the surface. The various adhesives used by the species differ chemically, but have the same function in allowing the species to attach themselves. Consequently, the fouling on a ship's hull becomes a unique ecosystem, but one that creates major problems for both commercial shipping and leisure boating.

The attempts to prevent fouling

Over the years, a wide range of methods have been tried to protect ship hulls. The principal approach has been to make the hull toxic by painting it with tar or using iron or copper sheathing to protect the wood. When iron hulls came into use, it was no longer possible to protect these with copper sheathing, since the iron was then attacked by galvanic corrosion. The first patent for antifouling was filed in the seventeenth century. It was based on iron powder, copper and cement. The development of bottom paints really took off in the nineteenth century. They contained everything from lead and mercury to arsenic and tin compounds. These were the precursors of the paints used today.

Current technologies and the search for new solutions

Current antifouling technologies follow two routes, the chemical approach and the physical approach. The chemical methods involve coating the hull with a paint containing an active substance—a biocide—to prevent fouling. Formerly organic tin compounds were the most common biocides, but they are being phased out because their use is hazardous to the marine environment. Copper, often in combination with additional organic biocides, is the most commonly used biocide today. The coating formed after the paint has dried can be of several types:

- A matrix, which slowly dissolves in seawater and thereby releases the biocide
- An insoluble matrix through which the biocide moves freely by diffusion out into the water
- A self-polishing coating (SPC) producing a soluble micro layer on the surface, resulting in a continuous polishing of the surface and the release of biocide.

These three paints belong in the class of chemical approach to fouling protection. The physical methods rely on effects other than leakage of chemical/toxic substances. Fouling-release technologies involve protecting the hull by a coating with very low surface energy. Low surface energy means that the marine organisms that adhere to the hull have very low adhesion strength, and are dislodged by the hydrodynamic forces when the vessel moves through the water. Silicone is a suitable base for this type of coating. The coating is effective at high velocities through the water (over 20 knots), which generate the hydrodynamic forces necessary to scour off the fouling. Many excellent review articles and books on fouling and antifouling have been published. To mention a few: Almeida et al (2007), Chambers et al (2006), Flemming et al (2009), Hellio and Yebra (2009), Omae (2003), Railkin (2004), Wahl (1989) and Yebra et al (2004). An alternative to the methods mentioned above is to remove the fouling mechanically. Brush systems are now on the market that can clean the hull without requiring the boat or ship to be taken out of the water (www.boatwasher.nu and www.cleanhull.no)

There are many research initiatives to find new and better solutions to fouling. In the search for new biocides, substances produced by marine organisms have been identified, Fusetani and Clare (2006). These substances help organisms to avoid being fouled by other marine organisms. Research efforts are also underway to develop a technology that makes it possible to replace biocides with enzymes that interfere with the biological bonding mechanisms. This concept is now available on the market (www.biolocus.com). Another research initiative is investigating the possibility of controlling fouling by creating oxygen depletion on the hull surface and thereby decreasing the fouling by oxygen-requiring organisms, Lindgren et al (2009). Other physical approaches to inhibit fouling include micro- or nanostructures in the coating and on the surface of the coating. Microstructures in the order of several hundred micrometers have proved effective in preventing the adhesion of barnacles, Andersson et al (1999). AMBIO, an integrated project funded by the European Commission, focuses on modern molecular engineering of the surface to create nanostructures that prevent or reduce the adhesion of fouling organisms (www.ambio.bham.ac.uk).

The legislative pressure

The necessity to develop antifouling strategies with low environmental impact, has led to a substantial commitment from national and international authorities. The International Maritime Organization (IMO), a UN organ, agreed in 2001 to a ban on TBT (tributyltin) based paints. TBT has been shown to have severe ecotoxicological effects. As of 2003, applying new TBT-containing coatings has been forbidden, and there has been a ban on the presence of such paints on ship hulls since 2008. There are many lessons to be learned from the introduction and the subsequent ban of TBT. One such is the long process from the first warning signs to effective international sanctions—see table below.

1880s	Organotins first synthesized
1950s	TBT developed
1960s	TBT first used as antifoulant
1976	TBT+SPC patent
1983	First report on marinas/malformation of oyster shells
1986	First report of imposex in molluscs
1989	EU ban on TBT on boats <25 m
2001	IMO Anti-fouling system convention re. TBT
2008	No ships may enter an EU port with TBT
2008	The IMO Anti-fouling system convention comes into force
2009	TBT is till used in several countries

When developing new antifouling substances, it is of the utmost importance to rigorously anticipate and assess the risk of long-term effects on the environment, Arai et al (2009) and Konstantinou (2006).

In the EU, the Biocidal Products Directive (BPD) was implemented in 2000. The EU is reviewing all biocidal products including antifouling paints. Of 46 notified antifouling substances in 2002, only ten have now entered the BPD registration process. At the moment it is not known how many of the ten biocides will be deemed acceptable. Unacceptable biocides will be removed from the EU market.

In addition, there are other national restrictions on antifouling paints. In Canada, antifouling paints containing copper must display a very low copper release rate, and in Sweden copper-based antifouling paints are banned for leisure crafts in the Baltic Sea. In the UK, two commonly used organic biocides, Irgarol and Diuron, have not been approved for leisure craft use.

The need for a multidisciplinary approach

Fouling is the establishment of complex ecosystems on submerged surfaces. To develop sustainable counter measures calls for multidisciplinary approaches, which many ongoing research initiatives show.

One of the larger research groups—Marine Paint—has been established in Gothenburg, Sweden at the University of Gothenburg and Chalmers University of Technology. Mistra, The Foundation for Strategic Environmental Research, supports the research. The research programme, Marine Paint, has focused on developing more environmentally friendly antifouling substances as well as concepts that will decrease the antifouling-biocide load and exposure to the marine environment (www.marinepaint.se).

A novel antifouling substance (medetomidine) has been developed, which effectively prevents shell forming fouling organisms such as barnacles, from adhering to ship hulls, Dahlström et al (2000, 2004) and Mårtensson Lindblad and Dahlbäck (2007). Medetomidine does not seem to endanger other marine organisms due to its efficacy in extremely low concentrations and non-lethal mode of action. The compound has been thoroughly tested in European as well as in tropical marine environments. Under the ownership and management of I-Tech, medetomidine is currently undergoing registration as a biocide in accordance with the European Biocide Directive (www.i-tech.se).

Mixtures of biocides and microcapsules

Medetomidine is effective against shell forming fouling organisms such as barnacles, and therefore needs to be combined with other antifoulants to produce coatings that successfully target the full spectrum of fouling organisms.

Analysing mixtures of chemicals has long standing in the optimisation of industrial processes and the development of chemical products. The idea of using chemical mixtures is especially tempting for biologically active chemical products such as antibiotics, pesticidal preparations, or in our case: antifouling substances. This is because unwanted side effects, such as resistance development, might potentially be minimised and at the same time the efficacy of the product might be increased, leading to less of the substance being used.

The aim is to find antifouling combinations with the highest efficacy and minimum environmental risk. Experimental testing of fouling organisms and antifouling compounds (approximately 35 pairs) produces a matrix of high-precision concentration/efficacy relationships. This data is used together with predictive mixture toxicity models to estimate the required concentrations of a huge number (> 100000) of antifouling mixtures, to prevent settling of all fouling model organisms. In this way the most efficient ways of combining medetomidine with other antifoulants will be identified. To select the minimum-risk combinations we will weight each of the 100000 combinations based on their respective concentration, mixture composition and risk values of the mixture components, in order to generate a ranking list of the optimal combinations. After experimental validation, recipes of optimised antifoulant combinations will be used as input to the ongoing development of microcapsules that can carry the biocides in a paint.

Microcapsules are small and robust particles capable of loading very large amounts of biocides. The main advantage of this technology is that it offers the same base technology for all the different biocides (7–10) of interest to the programme. Techniques have been developed for producing particles cost efficiently on a large scale and in a much more environmentally benign way compared to old production techniques, Nordstierna et al (2009). Alongside tests in paint films, the microencapsulation technique will be further developed to fully control the optimised release rates of the biocide components. This is the main challenge for the technology platform.

The Marine Paint research initiative will deliver an efficacy database, predictive mixture toxicity and hazard ranking tools, together forming a strong basis for optimisation of new antifoulant combinations. This, together with the microcapsule technology, will afford the possibility to decrease the exposure of the marine environment to antifouling substances.

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