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CLEANER HULLS FOR CLEANER SEAS

Many-faceted research project studies greener antifouling systems. By John van Haare, Dutch Polymer Institute.

Marine biofouling has huge economic and environmental impacts. A EU research project aims to advance the control of biofouling and reduce hydrodynamic drag by integrating many technology concepts such as surface structure, surface chemistry and bio-active/bio-based fouling controls. The current scope of this project is described.

Marine biofouling, the colonisation of unwanted marine organisms on surfaces immersed in seawater, has tremendous impacts on fisheries, offshore, marine based renewable energy and the marine shipping industry.

Although nowadays regarded as an oversimplification, the process of marine biofouling is often displayed as a linear successional model

Figure 1: Development processes of marine fouling.

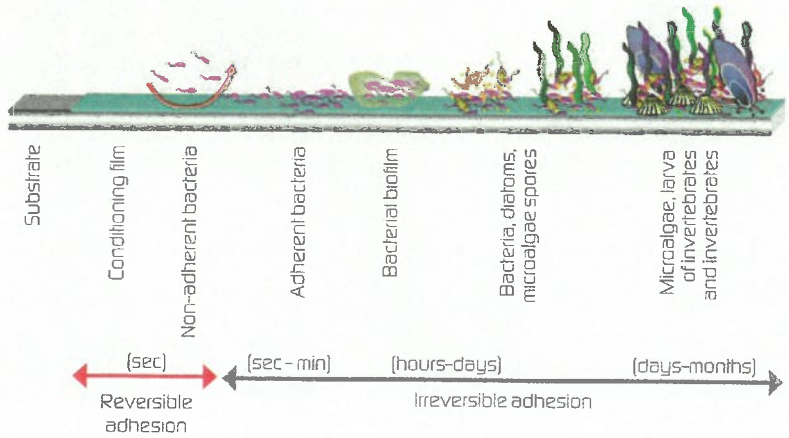
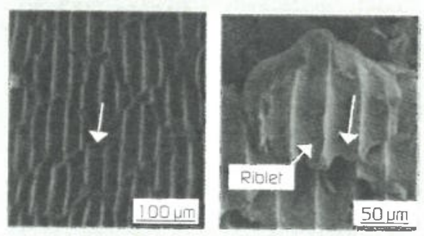


Figure 2: SEM images of riblet structures on shark skin.



RESULTS AT A GLANCE

→ Marine biofouling, the unwanted colonisation of marine organisms on surfaces immersed in seawater, has huge economic and environmental impacts in terms of maintenance, vessel fuel consumption, operating costs, greenhouse gas emissions and spread of non-indigenous species.

→ Following the ban on coatings containing TBT, most antifouling coatings are now copper-based. Low-adhesion coatings without active ingredients are used successfully, but only on faster-moving vessels.

→ The EU Seafront project aims to significantly advance control of biofouling and reduce hydrodynamic drag by integrating multiple technology concepts such as surface structure, surface chemistry and bio-active/bio-based fouling control methodologies into one environmentally benign and drag-reducing solution for mobile and stationary maritime applications. The current scope of this project is described.

comprising the following key steps (*Figure 1*):

- A conditioning film is formed by accumulation of adsorbed proteins, polysaccharides and glycopeptides;
- Bacteria adhere reversibly on the surface;
- Followed by irreversible adhesion via cellular appendages and exopolymers;
- Existing film provides food for spores of macroalgae, fungi and protozoa (microfouling), and larvae of invertebrates settle (macrofouling) [1].

The entire process occurs over times ranging from seconds to several weeks. Biofouling significantly reduces the energy efficiency of vessels by increasing the hydrodynamic drag, resulting in increased use of fuel and operational costs. A very large crude carrier (VLCC) consumes 100 metric tonnes of heavy fuel a day, and increased roughness on marine vessels can increase fuel consumption by 40% [2]. In addition, biofouling has a large environmental impact on marine ecosystems and other environments due to millions of tons of greenhouse gas emissions. Environmentally benign solutions for biofouling will thus have significant economic and environmental impacts.

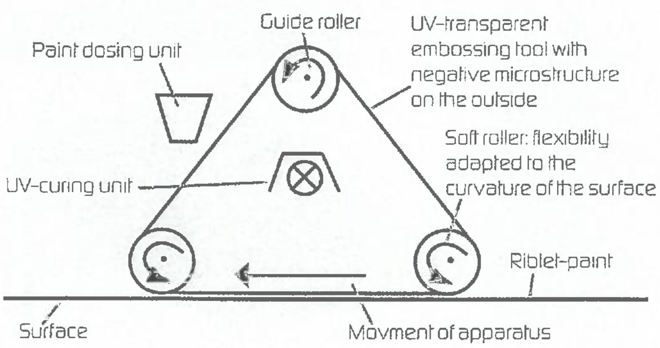
HOW ANTIFOULING COATINGS HAVE EVOLVED AFTER THE BAN ON TBT

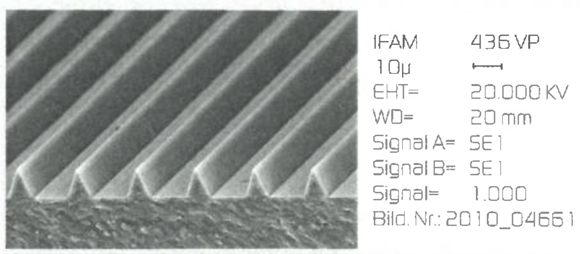
Following the worldwide ban on tributyltin based antifouling coatings by the International Marine Organisation (IMO) novel antifouling coatings have been introduced into the market which can be divided into two main technologies. Biocide-based coatings represent the majority of commercial antifouling coatings; these rely on the release of chemical actives in order to achieve inhibition of biofouling. The most advanced biocidal antifouling coatings are based on self or linear polishing polymer technologies which facilitate the sustained delivery of biocide by virtue of a seawater-mediated hydrolysis or ion exchange reaction.
Presently, the overwhelming majority of antifouling coatings are copper-based. However, as a consequence of their potential environmental impact [3, 4] such materials are the subject of an increasing level of regulatory scrutiny [5]. Fouling release coatings provide a biocide-free solution and are based on polymers which minimise molecular adhesive forces between the adhesives excreted by the marine organisms and the coating. As a result, adhered organisms are easily released by hydrodynamic shear forces on the vessel and cleaning by water jet.
However, fouling release coatings are often less mechanically robust and fouling release efficiency drops at low hydrodynamic shear (typically at flow speeds < 8 knots). As a result, the performance of these coatings is somewhat less effective when applied to stationary structures [6].
Environmentally benign marine fouling control coatings are urgently sought by the coatings industry and there is considerable interest in developing biocide-free coatings that rely on surface physico-chemical and bulk material properties to combat biofouling. However, current approaches tend to focus exclusively on evaluating individual technology-based solutions. The EU Seafront (Synergistic Fouling Control Technologies) project takes a different approach by combining multiple technologies into one coating solution. In parallel, considerable improvement of the fundamental understanding of biofouling mechanisms by development of advanced test methods is targeted.

SURFACE STRUCTURING AS AN ANTIFOULING CONCEPT

Hierarchical topologies of structures are commonly applied by nature to provide colour (reflection), antifouling and drag reduction proper-

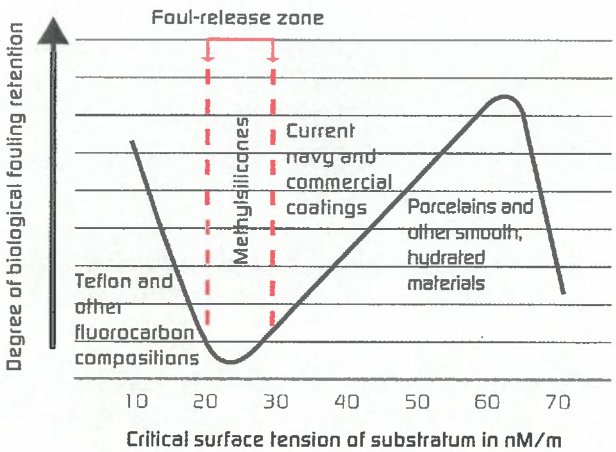
Figure 3: Schematic representation of the riblet application device (Patent: DE 103 46 124 B4). Photograph at the right shows an SEM picture of a cured synthetic riblet film.





ties. Though it is believed that every biofouling organism has its own length and timescale to settle on a surface, riblet structures are also known to reduce drag during fast swimming of sharks (*Figure 2*).
Attempting to mimic the biofouling prevention properties of natural systems in synthetically engineered analogues is an area that has received an increasing amount of attention [7, 8].
Recent work by Fraunhofer IFAM demonstrated that riblet technology based on synthetic analogues indeed results in drag reduction (*Figure 3*). [9]. The project combines riblet technology with surface functionalisation (e.g. hierarchical topology) for optimised fouling control and drag reduction.

Figure 4: Baier curve demonstrating the correlation between foul-release and surface tension of the substrate.



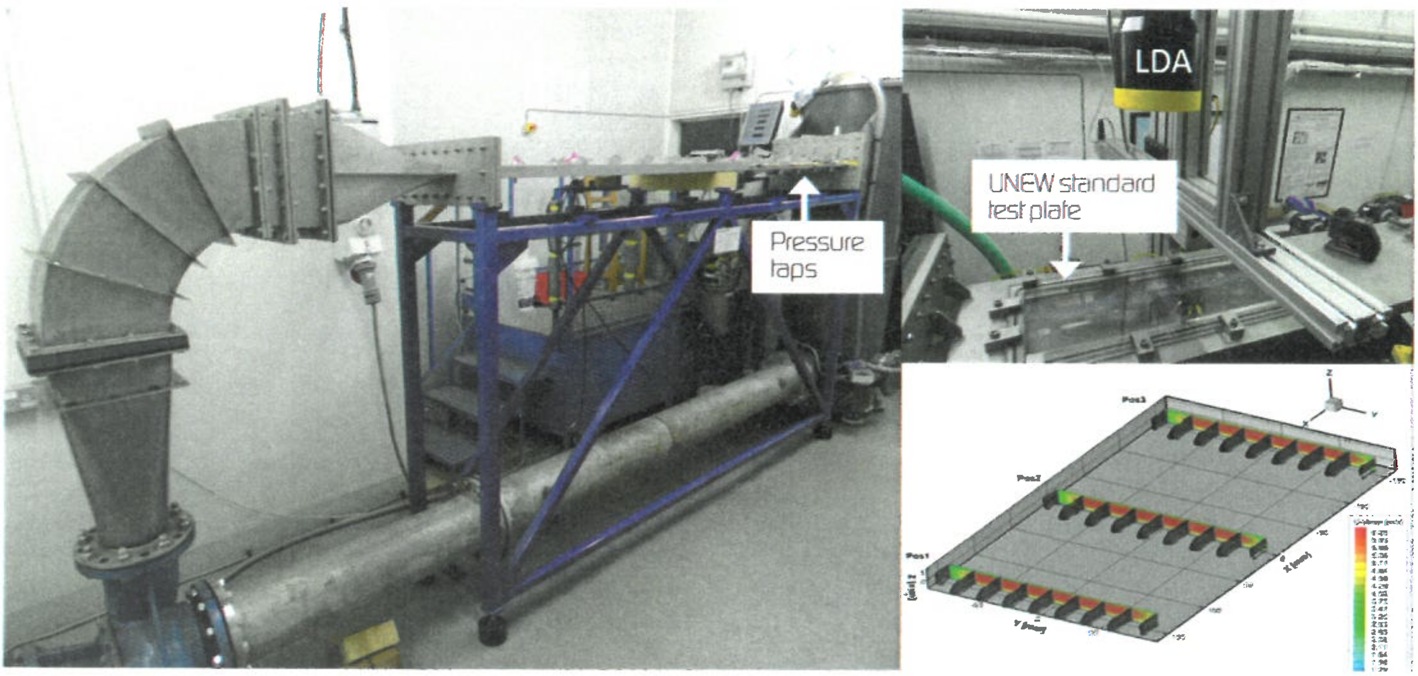
SURFACE CHEMISTRY AS AN ANTIFOULING CONCEPT

Foul release coatings are typically low modulus silicone and fluoropolymer paints which minimise the adhesion strength of attached organisms, allowing for easy removal under hydrodynamic shear or specialist cleaning (e.g. water jet). The work of Baier in the late 1960s demonstrated a correlation between the relative adhesion of fouling organisms and the energy of the surface (*Figure 4*) [10].
However, in order to be effective against the diverse and complex range of adhesion mechanisms exhibited by marine organisms, the ideal fouling control system should exhibit a range of hydrophilic and hydrophobic properties. Recently, effective amphiphilic foul-release coatings composed of hydrophilic and hydrophobic polymers have been launched on the market [11], which demonstrate typical surface tensions in the order of 55–60 mN/m.
The current commercially available fouling release coatings prevent the formation of biofilm to a certain extent, but have an operational window limited to vessels moving at more than 12-15 knots. The research project adheres to the current trend in the development of fouling release coatings by focussing on optimised fouling release at minimum hydrodynamic shear and reduced hydrodynamic drag whilst improving the mechanical robustness of the coating layer.

BIO-ACTIVE AND BIO-BASED FOULING CONTROL

The antifouling properties of naturally occurring bio-active materials have been the focus of consistent research attention for the last two decades. Over this time a multitude of natural products have been isolated and their antifouling properties investigated [12, 13].
Despite the fact that these materials are naturally derived, since they act specifically on the target organism they are considered to be a biocide under the terms and conditions of the Biocidal Products Directive [14].
The costs associated with the full package of regulatory studies including toxicity, release and environmental fate data required for registration of a new active are prohibitive, and as a result only two new active substances have been commercialised in recent years. The EU research project focuses on the immobilisation of actives onto formu-

Figure 5: The flow cell.



lation components such as binder material and pigment particles, in order to prevent any leaching during operation whilst maintaining activity. Also, bio-derived and bio-based polymeric binder materials are used to develop novel formulations for self-polishing or self-replenishing hydrophilic surfaces.

PERFORMANCE BENCHMARKING AND FIELD TRIALS

Despite the fact that advanced surface analysis techniques have been developed to study the chemical and physical composition of coating surfaces with and without water immersion, a huge lack of fundamental understanding of biofouling-surface interactions exists. In addition, the initial screening of novel fouling control technologies is often limited to biological assays of a limited number of biofouling organisms in a static setup. However, the EU project is developing novel test methods and molecular biology techniques, including next generation DNA sequencing, to move beyond state-of-the-art mechanistic understanding of biofouling.
Newcastle University will make use of 3-D video tracking to investigate possible deterrent effects of certain coatings on pre-settlement behaviour of fouling organisms. It was previously shown in ONR sponsored research that barnacle cyprids tracked in two dimensions leave polyCBMA test surfaces significantly more quickly than polySMBA, whilst both surfaces showed no settlement even after 72 h incubation [15].

MOLECULAR BIOLOGY IS ALSO BEING STUDIED

In addition, the University of Gothenburg (Sweden) is conducting studies on gene and protein expression in relation to the various exploratory phases of cyprids. In this study the understanding of molecular biology of settlement should advance, aimed at identifying targets for fouling deterrence. Furthermore, microbial biota associated with different surfaces/coatings will be evaluated by analysis of the replicate samples collected across seasons and geographical locations by the University of Bristol, UK.
The DNA extraction and sequencing techniques should provide evidence to determine whether the composition of the early microbial community, the coating or the environment is the most important determinants of the final macrofouling community.

FLOW CELL STUDIES EXAMINE COATING RELEASE PROPERTIES

Finally, new hydrodynamic testing methods are being developed by using the direct method of measuring the boundary layer and hence evaluating the frictional drag characteristics of standard size flat plates. Slime release performance is determined by measuring the water flow speed at which the slime is removed/released from the fouled coatings using the hydrodynamic flow cell shown in *Figure 5*.
The slime-fouled slides are mounted in the flow cell testing section and fully turbulent water is passed across the surface, increasing in speed, step-wise from 0 to 13 knots, with the speed held for 60 seconds between each test interval.
Using computational fluid dynamics, the speed of the water flow inside the 1 cm high and 2.4 m long flow duct (water velocity) has been scaled to the same flow that is encountered by a 200 m ship (scaled ship speed).

WHY A BROAD-BASED AND COMPLEX STUDY IS NEEDED

The complex mechanism of biofouling and the fact that antifouling coatings have to be effective against a diverse range of more than

"Keeping shipping economically feasible even with the current low fuel prices."

3 questions to John van Haare

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How does hydrodynamic drag influence fuel consumption of vessels? *Biofouling significantly increases the roughness of the hull resulting in substantial drag increase. As a result, the fuel consumption can eventually increase up to 70% within six months when no biofouling coating or cleaning of the hull is applied. The coating should be kept very smooth and should have a long lifetime (>5 years) in order to keep shipping economically feasible even with the current low fuel prices.*

What are the most prominent species in biofouling? *Marine biofouling is typically referred to as 'hard fouling', 'soft fouling' and microbial fouling or 'slime'. The former comprises organisms with calcified structures such as shells. Members of this category include barnacles, mussels and tubeworms. Soft fouling organisms include hydroids, tunicates, sponges and algae. Slime comprises a multitude of organisms with bacteria and diatoms prominent.*

What institutes or companies are involved in the Seafront project? *Involved are: Dutch Polymer Institute, International Paint Marine & Protective Coatings, Fraunhofer-Gesellschaft zur Förderung der Angewandten Forschung e.V., I-Tech AB, University of Newcastle upon Tyne - School of Marine Science and Technology, University of Newcastle upon Tyne - School of Chemistry, Minesto AB, Solvay Specialty Polymer S.P.A., Delft University of Technology - Process and Energy, Delft University of Technology - Materials Science and Engineering, Eindhoven University of Technology, University of Bristol, Val FoU, Biotrend, BioLog Biotechnologie und Logistik GmbH, University of Gothenburg, Bio-On, Bluewater Energy Services, Smartcom Software, Solintel, Hapag Lloyd.*

4.000 fouling organisms suggests that a single fouling control technology will never offer the ultimate solution.
Therefore, the EU research project combines multiple approaches and technologies into one coating solution rather than considering single technologies in isolation. Preliminary results of combined technologies have been achieved, but need further investigations for down-selection into field trials.
In a parallel approach, improvements in fundamental understanding of biofouling-surface interactions are being made by developing novel testing methods and reducing frictional drag to save fuel and reduce greenhouse gas emissions.

ACKNOWLEDGEMENTS

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