The development of foul-release coatings for seagoing vessels

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This paper is a record of the work of an informal, interdisciplinary group, which contributed to the development of what has come to be known as foul-release coatings. These 'non-stick', non-toxic, antifouling coatings are essentially low surface energy, silicone elastomeric materials, which can be applied by airless spray. The paper opens with an account of the development of antifouling provision, the nature of biofouling and a review of the adhesion mechanisms of diatom slimes, macroalgae and barnacles. The physics and chemistry of low surface energy coatings are then described, followed by the specific research evidence of the difficulty of settlement and adhesion of biofouling to these coatings. The development of a practical product as an applicable low surface energy antifouling, is outlined, followed by an account of ongoing research into the surface characteristics and fluid drag of these novel coatings, not only on ship hulls but also on propellers. The paper closes with some account of the world-wide environmental and economic advantages of foul-release coatings.

AUTHORS’ BIOGRAPHIES

Colin Anderson has worked for the Marine and Yacht divisions of International Coatings in Newcastle upon Tyne for over 26 years, initially in R&D, and latterly in marketing, where he is Business Manager - Antifoulings. He is also a Visiting Professor in the School of Marine Science and Technology at the University of Newcastle upon Tyne.

Mehmet Atlar completed a BSc and MSc in naval architecture and marine engineering from the Technical University of Istanbul, after which he obtained a PhD in naval architecture and ocean engineering from Glasgow University in 1985. He worked as principal research officer at British Maritime Technology before joining Newcastle University in 1994. He currently holds a personal chair in Ship Hydrodynamics and is also the Director of the Emerson Cavitation Tunnel at the School of Marine Science and Technology. His main interest lies in the field of hydrodynamics with specific emphasis on the powering and seakeeping of ships.

Maureen Callow graduated from the University of Sheffield with a BSc in Honours Botany in 1967, followed by a PhD in 1971. From 1971 – 1992 she was a research fellow funded by International Coatings, at the University of Leeds until 1982 and for the next ten years at the University of Birmingham. Since 1992, she has been a senior research fellow in the School of Biosciences at the University of Birmingham, working on various aspects of marine biofouling.

Maxim Candries obtained his Bachelor’s and Master’s Degrees at Ghent State University, Belgium. He completed his PhD at the Department of Marine Technology (now School of Marine Science and Technology), University of Newcastle upon Tyne under the supervision of Prof M Atlar. Dr Candries then worked as post doctoral researcher in the field of drag, boundary layer and roughness characteristics of marine coatings as the continuation of his PhD until leaving the school in summer 2002 to live in Belgium.

Alex Milne gained a BSc in mathematics and chemistry from St Andrew’s University before taking a post as a paint research chemist. After an initial spell with Red Hand Marine Coatings, Ripon, he moved to Newcastle upon Tyne, joining International Paint in 1968. Whilst there, he discovered and pioneered both self-polishing copolymer (SPC) antifouling and foul-release coating both of which are patented in his name. Subsequently, Alex Milne spent a few years with the Ship Performance Group at Newcastle University, where he authored and co-authored a number of papers developing the broader issues of ships’ outer bottom conditions. He returned to International, retired in 1990 and continues to act as a consultant.

Bob Townsin spent 45 years in Newcastle University as student and academic, becoming Head of the former Department of Naval Architecture and Shipbuilding in 1983. His PhD concerned low-drag hydrofoils and he was awarded his DSc in ‘theoretical and experimental hydrodynamics’, partly as a result of the research in his Ship Performance Group. He retired from the University in 1992, but continues his work as a consultant. He is a Fellow of IMarEST and has been a Vice President of RINA.
INTRODUCTION

From the earliest times, fouling of the outer bottoms of ships has been ameliorated by toxins (poisons) applied to the hull surface, ranging from copper to, most recently, tributyltin (TBT). This paper concerns the development of non-toxic, foul-release coatings for seagoing vessels. These products are also known as non-stick coatings. They are essentially low surface energy, silicone elastomer materials that can be applied conventionally, by airless spray. Whilst combating marine fouling without polluting the marine environment with virulent toxins, their effective longevity and inherent smoothness also contributes to the reduction in smoke stack emissions.

Marine biologists have been interested in the adhesion mechanisms of marine organisms for many years. In the late 1970s and early 1980s, marine organism adhesion research, in relation to certain silicone elastomer substrates, had developed to a promising pre-production phase. A classic statement of the position by Milne and Callow may be found in the IMarE Transactions. However, further development was put in abeyance by a quite different technology, stemming from a patent filed by Milne and Hails. This gave rise to the so-called self-polishing copolymer (SPC) antifoulings, which allowed a constant emission of a virulent toxin, tributyltin (TBT). The proven performance of five years of foul-free operation persuaded ship operators to extensively use SPC coatings. At this time, the Ship Performance Group at Newcastle University undertook extensive research to quantify the performance savings attributable to these new foul-free and smooth coatings, with their consequent reductions in smoke stack emissions.

The increasing use of organo-metallic biocides such as TBT on ships and the flushing of residues after coating and bottom maintenance in dry dock, led marine biologists to examine the effects of these toxins on marine life. As is well known, this gave rise in 2001 to the prohibition by the International Maritime Organization (IMO) of further application of TBT SPC after 2003, followed by a complete phase-out of their use by 2008. Meanwhile, the self-polishing technology is being continued, but with less virulent toxins, principally copper with booster biocides. An overview of all these developments was recently reported by Townsin.

The anticipation of these prohibitions reactivated the development of non-toxic, low surface energy coatings, which had been eclipsed by TBT SPC. An example of recent resurgent research is the work of Candries, and Candries et al., at the University of Newcastle upon Tyne, which explored the drag characteristics of these novel, low surface energy, foul-release coatings in comparison with the hitherto conventional self-polishing coatings. Marine coatings companies in this highly competitive industry are now marketing their own, variously effective versions of foul-release antifoulings.

This paper illustrates that developments such as that of a non-toxic coating to control fouling, must be the work of an interdisciplinary group. In this case the group included coating chemists, marine biologists, marine engineers and naval architects.

Again, developments of these types are likely to arise in more than one country, and with many scientists and engineers involved, but this paper contends that the leaders in the field of marine coatings technology are in the UK. A further localisation of the paper is the north of England, partly due to the presence of a world-wide leading marine coatings company in Tyne and Wear and also, in part, due to the presence of the School of Marine Science and Technology at the University of Newcastle upon Tyne with its strengths in marine engineering, naval architecture and marine biology. The pioneering work of the marine biologists started at Leeds University and the team is now located in Birmingham University. The juxtaposition of industry, academia, laboratores and the appropriate specialists, has resulted in creative dialogues. This community of interest led, originally, to the development of TBT-SPC and now has led to the commercial production of foul-release, low surface energy coatings.

SOME HISTORY

The deleterious effects of fouling on ship performance have been feared and recorded from as far back as the last few centuries BC. An interesting example is a quotation from a book by Captaine John Smith, (circa 1600), formertimes Governor of Virginia, and Admirlar of Navy, England. The title of his book is A Sea Grammar, with the plain exposition of Smith’s Accidence for young Sea men, enlarged. His definition of Graving (hence, ‘graving dock’ – a stepped dock, where the outer bottom of a ship could be easily got at): GRAVING is only (used) under water—a white mixture of Tallow, Sope and Brimstone, or Tallow-oil, Rosin and Brimstone boiled together, is the best to preserve her calling and make her glib or slippery to passe the water, and when it is decayed by weeds, or BARNACLES, which is a kind of fish like a long red worne (which) will eat throwe al the Planks if she be not SHEATHED, which is as casing the Hull under water with Tar and Haire, close covered over with thin boards fast nailed to the Hull, which though the Worne pierce, shee cannot endure the Tar.

So, fouling and associated problems have been written about from the earliest times. Between 1862 and 1904 there were 18 papers on corrosion and fouling issues read to the then Institution of Naval Architects in London. The two issues were often seen as one problem in those days, as iron was replacing wood as the shipbuilding material. Copper sheathing had protected wooden hulls from the depredations of the teredo worm, and, by serendipity, the copper kept fouling at bay. The efficacy of copper as an antifouulant led to attempts to clad iron ships with copper. The British Admiralty had to call upon the distinguished chemist, Sir Humphry Davy, to help with the inevitably accelerated corrosion of the iron and copper combination. An attempted solution at the time was to clad the iron ship hull with wood and then fix the copper sheets to the wood, without contact with the iron: clearly, fouling was recognised as a serious performance problem, requiring such a drastic solution.

The effect of fouling at these times is well illustrated by a quotation from one of the INA papers referred to earlier. In this, Lewes says, ‘of some protective and antifouling 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’.

As well as copper sheathing, many entrepreneurs were patenting and experimenting with various compositions with which to coat the outer bottoms of steel and iron ships. Indeed, the first record of an antifouling coating was in a British Patent of William Beale, as far back as 1625. As Bertram’ quotes, in his helpful WEGEMT lecture, ‘Until 1865, more than 300 such ‘patent paints’ were registered. All of them were quite ineffective’. Some exotic brews resulted from these attempts. One such was of fish scales pounded up with red lead. What transient antifouling benefit there was resulted...
more from the red lead than the fish scales.

The last of the 18 INA papers referred to earlier, was by Holzapfel. Holzapfel reports on test patches, keel to light waterline, of about 100 different compositions, which he applied to some 80 boats sailing from Genoa, principally in the Mediterranean trade. He also tested composition-coated plates immersed in Genoa harbour. He distinguished two types of antifouling composition current at the time, which he called ‘varnishes’ and ‘greases’. All his experiments were with ‘varnishes’. He found that the more successful of the ‘varnishes’ were those with substantial copper and mercury content; but, he writes, a successful composition must also be one ‘capable of being gradually dissolved in sea water’ which he called ‘primary disintegration’. Antifouling chemists subsequently discovered that rosin, a natural substance obtained from trees, could be used to partially achieve this ‘primary disintegration’ but it contains impurities which eventually leads to insolubility and it causes cracking and detachment if used excessively. The ‘greases’, which were much softer, and gave rise to greater surface friction and fuel consumption (we would now say they were ‘rougther’), were supposed to shed the fouling by what he called ‘secondary disintegration’ under fluid frictional shear. Professor Lewes used the word ‘exfoliation’ in his earlier support of ‘greases’. The industry went down the ‘hard varnishes’ road for the next 70 years and exfoliating greases were not pursued much further. However, in Holzapfel’s paper we may read the beginnings of ideas about what we now call ‘fully ablative coatings’.

Anyone interested in antifouling coatings and, to some extent, inboard anticorrosive coatings, would, no doubt, enjoy reading Holzapfel’s paper because of his clear understanding of the problems and his occasional prophetic passages. He could be thought of as the father of modern antifouling provision. The successor to the marine coatings company set up by the Holzapfel brothers, which has an international reputation, is still on the banks of the River Tyne and his house, with its oak apple motif worked into its iron gates, is close by the University of Newcastle upon Tyne.

The ‘hard varnishes’ road led eventually to inter-docking periods of 2–2.5 years, at best. It became evident that the leach rate of toxins was falling off with time, so that fresh coatings had an over-rich leach rate, whereas an older coating had an ineffective leach rate, even though biocide remained. Holzapfel’s ‘primary disintegration’ was not being achieved.

Self-polishing copolymers

All this changed with the British patents of Milne and especially Milne and Hails, based on their work at Felling–on–Tyne, which led to the so-called ‘self-polishing copolymers’ (SPC) loaded with tributyltin as the biocide. The chemistry of these new products provided an ablation rate that ensured a constant rate of leach of biocide. The effective life of these products depended solely on the coating thickness in relation to the ablation rate, and, in practice, could ensure a foul-free hull for up to five years, which coincides with the classification societies requirements for inter-docking survey periods.

With the advent of these TBT SPCs, suddenly, fouling became yesterday’s problem and interest then began to centre upon the fluid friction penalties due to the micro roughness of outer bottom coatings. The roughness of new ship coatings had always been of interest because of contractual speed and power trials at hand of a new ship. The renowned Lucy Ashton trials, in the Gare Loch, in Scotland, were conducted in the late 1940s and early 1950s with this in mind. But now, with the prospect of foul-free hulls, the through-life roughness of antifouled hulls became of interest to ship operators. The Ship Performance Group at Newcastle University, among others, pursued this work, (eg Townsin et al). The Group’s formulation for calculating the resistance penalty for a ship with a moderate and measurable roughness was subsequently adopted by the 19th International Towing Tank Conference (ITTC).

Whilst the ablation of these products and the consequent constant biocide leach rate was their prime raison d’être, it was also noted that any initial roughness due to application was smoothed out in service. The name ‘self-polishing’ for these products was therefore applied by the marine coatings industry to indicate smoothing properties, although, whilst the paint itself became smoother, the hull, overall, often became rougher due to surface damage. The added resistance due to paint surface damage was a problem recognised by Holzapfel.

The success of tributyltin was not to last. Marine biologists, world-wide, were able to assemble evidence of the effects of TBT on coastal marine life. The poisoning of oyster beds and imposex among dog whelks were among the effects observed. The passage of vessels with TBT antifouling in coastal waters was seen as the cause, but the prime reason may have been the flushing of dry docks where the coatings were applied or removed and where no filters were used. For these reasons, tributyltin is now banned, with various conditions and deadlines.

The present position is that the industry does not wish to lose the benefit of an ablative matrix containing a biocide. The chemistry is being reconstructed to accommodate different biocides, and copper returns as the major present candidate, supplemented with booster biocides. Marine coatings chemists are currently busy trying to improve these so-called tin-free, self-polishing copolymers to match the effectiveness of what is being banned. There is a little way yet to go before the confidence of ship operators returns completely.

Another candidate coating to control fouling, which is the subject of this paper, is already being applied successfully to the bottoms of ships, namely the low surface energy, foul-release coating. It is anticipated that the use of this non-biocidal coating will increase rapidly in the future and one may note the prophetic banning of copper biocides on some coastal stretches of Scandinavia. It is worth recalling that work on these non-toxic coatings was underway as TBT SPC was being developed. The success of the latter partially obscured the promise of the former.

BIOFOULING

Biofouling is the accumulation of micro-organisms, plants and animals on surfaces. The marine environment is unique because of the diversity of organisms that cause biofouling of man-made structures; more than 2500 organisms having been described in fouling communities world-wide.

Within minutes of immersing a clean surface in water it adsorbs a molecular ‘conditioning’ film consisting of dissolved organic material. Bacteria colonise within hours, as may unicellular algae, cyanobacteria (blue-green algae) protozoa and fungi. These early small colonisers form a biofilm, which is an assemblage of attached cells often referred to as ‘microfouling’ or ‘slime’. Macrofouling consists of higher algae and soft-bodied
invertebrates such as sponges and tunicates (soft macrofouling), and calcified invertebrates such as barnacles and tubeworms (hard macrofouling).

Fig 1: Adult barnacles, (Balanus amphitrite) settled on Perspex (Photograph courtesy of Dr AS Clare)

The specific organisms that develop in a fouling community depend primarily on the substratum, although factors such as geographical location, season, competition and predation are also important. On ships, most interest has focused on fouling by barnacles and all successful compositions must control barnacle fouling (Fig 1). Fouling by the green alga Enteromorpha (Fig 2), which is relatively resistant to copper, is once again becoming more important as copper-based antifouling paints replace the TBT copolymers.

Fig 2: Underwater photograph of Enteromorpha on a boat hull

Microfouling slimes are dominated by diatoms, which are brown pigmented unicellular algae enclosed in a silica wall (Fig 3). Cells range in size from a few to several hundred microns. Diatom biofilms are of interest because, as well as being highly resistant to biocidal antifouling paints, they are especially difficult to remove from non-toxic foul-release coatings.

Fig 3: Scanning electron micrograph of the surface of a diatom slime growing on an antifouling coating. The diatoms are approximately 20 µm in length and the ornamented ‘glass-house’, the silica cell wall, can be seen

ADHESION OF BIOFOULING ORGANISMS

Representatives of all the phyla living in the sea, from bacteria, through algae, to invertebrates, use sticky materials with permanent or temporary adhesive capabilities at some point in their life histories, to attach to substrata. Larvae of invertebrates and spores of algae need to quickly find and attach to a surface in order to complete their life history. This ‘first-kiss’ adhesion takes place often within minutes, under water, to a wide range of substrates, over a wide range of temperatures, salinities and conditions of turbulence. Adhesion may be permanent or reversible if the organism needs to move around on a surface to find the most appropriate settlement site. Controlling fouling without the use of toxins is essentially a problem of controlling adhesion, and nature, unlike technology, has very effectively conquered the problem of sticking to wet surfaces.

The mechanisms of attachment and detailed molecular characteristics of marine fouling organisms (or indeed any organisms) are largely unknown apart from the adhesives produced by adult mussels. Mussels produce threads to attach themselves to solid surfaces in the inter-tidal zone. These ‘byssus’ threads, secreted by the mussel foot are effectively biocomposites of collagen fibres embedded in a proteinaceous matrix. The protein glues of the blue mussel byssus apparatus have been extensively characterised as a dihydroxyphenylalanine (DOPA)-rich family of polypeptides, which cross-link through an oxidative phenolic tanning type process. Although mussels are extensive colonisers of static structures, they are rarely found on vessels.

Adhesion of diatom slimes

Diatoms are ubiquitous on all surfaces immersed in the marine environment that are illuminated and, as with bacteria, adhesion is through the production of copious amounts of mucilaginous extracellular polymeric substances (EPS). EPS moderates both attachment and motility, enabling diatoms to glide across surfaces. In some diatoms, the EPS may be modified into attachment pads, tubes or even stalks. Diatom EPS, like that produced by bacteria, is predominantly polysaccharide in composition although proteins or proteoglycans appear to be important in primary adhesion. Diatom trails are initially sticky and elastic but, with time, the EPS appears to be modified by secondary processes such as cross-linking. Accumulated EPS produced by bacteria and diatoms provides the gelatinous matrix that binds the cells into a compact biofilm.

Adhesion of Macroalgae (Enteromorpha)

Colonisation of new surfaces by Enteromorpha is mainly through the production of motile, pear-shaped spores, 5-8 µm in length, as shown in Fig 4a. Swimming spores attach rapidly once the spore has ‘detected’ a suitable surface for settlement. Secretion of adhesive(s) results in firm attachment to the substratum as can be seen in Fig 4b. The adhesive is present in membrane-bounded vesicles in the swimming spore, which on release forms a self-aggregating glycoprotein that forms an adhesive pad surrounding the spore. The adhesive then cures by some form of cross-linking as witnessed by increasing adhesion strength, progressive insolubility in detergents and insensitivity to proteolysis. Environmental scanning electron microscopy (ESEM) of newly settled hydrated ‘live’ spores shows the adhesive pad to be an expanding, hydrophilic gel-like material with a volume approximately 300 times that of the vesicles from which it is derived. Hydrodynamic studies have shown an increasing tenacity of spores to surfaces after
settlement. Spores evaluated four hours after settlement resist flow rates equivalent to a ship travelling at 40kts. A

Barnacles start life as larvae that feed on plankton and undergo a series of moults. The final larval stage is the cypris larva or ‘cyprid’ which is approximately 500µm in length, does not feed, but swims around freely in the water prior to settlement, as shown in Fig 5. In order to complete the transition to adult life, these cyprids must attach themselves to a hard substrate. During this exploration phase the cyprid ‘walks’ over the surface using a pair of attachment organs or ‘antennules’ that secrete a temporary adhesive from unicellular glands. Cyprids exploring a surface also have to be capable of detaching, leaving behind blebs of temporary adhesive ‘footprints’. The temporary adhesive does not disperse in water, is resistant to biodegradation and also operates as a signalling molecule to induce the settlement of additional cyprids, but its physical properties are unknown.

After selection of an appropriate site on which to settle, the cyprid stands on its head and releases a proteinaceous cement, from cement glands, onto the paired antennules. Initially fluid, this permanent cyprid cement flows around and embeds the antennules, curing within one to three hours to form a discrete matrix. The secretory products of two cell types, – and , comprise the ‘two-pack’ adhesive. The firmly attached juvenile subsequently metamorphoses into the calcified adult barnacle.

Adult cement has been partially characterised and appears to be a complex of hydrophobic proteins, unrelated to the blue mussel proteins, cross-linked through disulphide bonds.

PHYSICS AND CHEMISTRY OF LOW SURFACE ENERGY COATINGS

The free energy of a surface, which is commonly referred to as ‘surface energy’ or ‘surface tension’, is the excess energy of the molecules on the surface compared with the molecules in the thermodynamically homogeneous interior. The size of the surface energy represents the capability of the surface to interact spontaneously with other materials. The surface energy and the critical surface tension of a surface are determined by comprehensive contact angle analysis, using a variety of diagnostic liquids, measuring the angles that the liquid droplets make with the coated surface.

It is the surface tension of a polymer which is the property that has most commonly been correlated with resistance to biofouling. A generalised relationship between surface tension and the relative amount of bio adhesion has been established, and is shown in Fig 6. This is commonly known as the ‘Baier curve’. and 

Fig 6: The ‘Baier curve’
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shows the relationship between the Critical Surface Free Energy (\(\gamma\)) in mN/m (mJ/m\(^2\)) and Relative Adhesion (dimensionless). The key feature of this curve is that the minimum in relative adhesion, at 22-24 mN/m, (mJ/m\(^2\)), does not occur at the lowest surface energy. A variety of explanations have been given to account for this including the effects of elastic modulus (E), thickness and surface chemistry summarised in the following.

Elastic modulus

From a study of fracture mechanics it has been shown that elastic modulus is a key factor in bio-adhesion and hence the ability of organisms to ‘release’ from a coating, Brady and Singer\(^31\) and Berglin et al.\(^33\). The \(\gamma\) and E values and the calculated value for the square root of their product (\(\gamma E^{1/2}\)) for a range of polymers are shown in Table 1.

From these data, a direct relationship between relative adhesion and (\(\gamma E^{1/2}\)) has been established, as shown in Fig 7. Despite some scatter in the data, Fig 7 demonstrates that adhesion correlates better with (\(\gamma E^{1/2}\)) than with either surface energy or elastic modulus on their own.

Thickness

Thickness is another characteristic of low surface energy coatings that plays an important role in bioadhesion. It has been found that below \(\sim 100\mu m\) dry film thickness, barnacles can ‘cut through’ to the underlying coats and thus establish firm adhesion.

Table 1: Physical properties of some polymers (Brady and Singer, 2000)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Relative Adhesion</th>
<th>Surface Energy ((\gamma)) mJ/m(^2)</th>
<th>Elastic Modulus GPa</th>
<th>((\gamma E^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-(hexafluoropropylene)</td>
<td>21</td>
<td>16.2</td>
<td>0.5</td>
<td>2.9</td>
</tr>
<tr>
<td>p-(tetrafluoroethylene) (PTFE)</td>
<td>16</td>
<td>18.6</td>
<td>0.5</td>
<td>3.1</td>
</tr>
<tr>
<td>p-(dimethylsiloxane) (PDMS)</td>
<td>6</td>
<td>23.0</td>
<td>0.002</td>
<td>0.2</td>
</tr>
<tr>
<td>p-(vinylidene fluoride)</td>
<td>18</td>
<td>25.0</td>
<td>1.2</td>
<td>5.5</td>
</tr>
<tr>
<td>p-(ethylene)</td>
<td>30</td>
<td>33.7</td>
<td>2.1</td>
<td>8.4</td>
</tr>
<tr>
<td>p-(styrene)</td>
<td>40</td>
<td>40.0</td>
<td>2.9</td>
<td>10.8</td>
</tr>
<tr>
<td>p-(methyl methacrylate)</td>
<td>48</td>
<td>41.2</td>
<td>2.8</td>
<td>10.7</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>52</td>
<td>45.9</td>
<td>3.1</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Above this thickness there is no marked increase in foul-release properties.

Surface chemistry

The polymer systems that have generally shown the lowest adhesion of biofouling are silicone polymers, based on a backbone of repeating (-Si – O –) units with saturated organic moieties attached to the two non-backbone valencies of the silicon. The Si – O bond is stronger than a C – C bond (108kcal/mole compared to 83kcal/mole) and is extremely durable. This means that silicone polymers have the capability to provide the long-term in-service duration – beyond five years – that is required by classification societies, in order to provide fouling control on ships.

The silicone polymers used in foul-release coatings are generally formed by a condensation mechanism in which OH-terminated telechelic silanol polymers are reacted at ambient temperature with a tetraalkoxyxilane cross-linking agent. The most commonly used silicone polymers are those based on polydimethylsiloxane (PDMS).

It has been found that incorporation of low molecular weight silicone polymers (‘oils’) can enhance foul-release properties of PDMS polymers.\(^34,35\) Oils, by their nature, are lubricants and therefore should decrease the coefficient of friction, but this is not the main reason for their efficacy. This is thought to be due to the surface tension and hydrophobicity changes that the oils effect during the curing process,\(^1\) and after immersion.\(^36\)

Fig 7: Relative Adhesion as a function of the square root of the product of critical surface free energy (\(\gamma\)) and elastic modulus (E) (Brady and Singer, 2000)

Fig 8: Tropic Lure (2563dwt ro-ro) in dry dock in Tampa, Florida, March 2003. After 10 years in service with a foul-release coating. This picture was taken prior to washing, and shows that there was only slime present on the intact foul-release coating, with no macroalgae or barnacles

It has been shown that foul-release coatings do not rely on leaching of the oils for their foul-release properties, both from laboratory studies using \(^{14}\)C-labelled laboratory studies which revealed minimal leaching of oil,\(^39\) and from ships’ trials which showed that performance was maintained for up to 10 years in-service. The foul-release coating, Intersleek, was first applied to Tropic Lure in April 1993. Intermediate dockings took place in 1995 (two years) and 1998 (five years) when the system was simply maintained by high pressure washing and repair to damaged areas, as shown in Fig 8.
SETTLEMENT AND ADHESION TO LOW ENERGY COATINGS

Experiments to quantify the properties of low energy (eg paraffin wax) and other materials were first reported by Crisp and colleagues at Bangor University. They measured the load required to detach mussel byssus threads from the substratum, the data being expressed as force per unit area for detachment, after correction for the area of byssus in contact with the surface.37 International Coatings’ laboratories used the same technique to measure the strength of attachment of mussel byssus threads to a range of silicone elastomers, and showed the superior non-stick properties of a room temperature vulcanised (RTV) silicone elastomer containing a small amount (5%) of methyl phenyl silicone fluid, the prototype of a later commercial product. These data and measurements of attachment strength of bacteria and diatoms were first reported at a meeting of the Institute of Marine Engineers in 1984 and published inMilne and Callow.1 In their paper, Milne and Callow concluded, ‘the possibility of interfering with the adhesive process exists, and if a suitably general mechanism could be developed, then an intrinsically non-hazardous, non-polluting long-life antifouling could be produced’.

Research on low energy surfaces including variously modified silicones continued throughout the 1980s and 1990s, see review by Callow and Fletcher.38 During the 1990s, interest in the deployment of foul-release coatings on US naval vessels increased and new methods to measure the strength of attachment of barnacles and soft foulers were developed. Much of the recent work on the attachment of soft foulers has been conducted in the UK at the University of Birmingham. Two main lines of investigation have been followed. The first has focused on the application of laboratory methods to evaluate the efficacy of antifouling and foul-release coatings with respect to attachment of diatoms and Enteromorpha spores. The second involved a detailed biochemical study of Enteromorpha spore adhesive and its interaction with surfaces.

Hydrodynamic adhesion strength assays have been applied, using either a flow channel or a water jet, to Enteromorpha spores or diatom biofilms settled on microscope slides. The operating principle of the former,19 is that of a high aspect ratio, turbulent or diatom biofilms settled on microscope slides. The operating

Fig 9: Percentage removal of Enteromorpha biofilm from glass and Veridian (foul-release coating) at a water shear stress of 56Pa. Biomass was measured as chlorophyll a. Percentage removal was calculated from three replicate slides exposed to flow compared to control slides not exposed to flow. Bars show 95% confidence limits from arc sine transformed data. From Schultz et al. (2003)

Experiments employing Veridian (a foul-release silicone coating from International Coatings for pleasure craft) showed that young sporelings (days after settlement) of Enteromorpha were more susceptible to detachment in the water channel than even newly settled spores (one hour). Moreover, there was an increase in susceptibility to detachment with increasing age of the sporelings compared to that for the glass controls. Whilst the shear stress on the biofilm most likely increased as it grew (up to approximately 100µm on both the glass and foul-release substrates), the adhesion strength decreased on the silicone, leading to increased removal over time. As shown in Fig 9, when the experimental results were used as inputs to three models, more than 60% removal of a four-to-six days-old Enteromorpha biofilm from a ship coated with Veridian could be expected at a downstream distance of 50m, at a ship velocity of between 9.1m/s (17.7kts) and 8.4m/s (16.4kts) depending on the model applied.41 These data suggest that if macroalgae do colonise a foul-release coating, they will detach after a few days-to-weeks of growth, from the surface of vessels operating at moderate speeds. In fact, this is borne out by the absence of macroalgae on foul-release coating applied to ships.

Studies on model surfaces have allowed individual components of the physico-chemical properties of the surface to be studied. On surfaces that varied only with respect to wettability, Enteromorpha spores settled more readily on hydrophobic (low energy) than on the hydrophilic surfaces.42 However, the strength of attachment was much lower on the hydrophobic surfaces compared to the hydrophilic surfaces. Thus, for Enteromorpha fouling, low surface energy appears to be related to low strengths of adhesion. The situation is however, rather different for diatoms. There are a number of reports in the literature showing that diatom slimes stick tenaciously to
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Environmental scanning electron microscopy (ESEM) is proving to be a useful tool to understand interactions between the secreted adhesives of fouling organisms and the surface. ESEM allows the examination of fully hydrated ‘live’ specimens and has shown the Enteromorpha spore adhesive to be a swollen, hydrophobic gel-like material (Fig 4b), which is very different to the shown the secretion of different types of mucilage that result in rapid permanent and tenacious attachment.

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Permanent and tenacious attachment.

The development of foul-release coatings for seagoing vessels

DEVELOPMENT OF A PRACTICAL, APPLICABLE, LOW SURFACE ENERGY COATING

The discovery of the fouling control properties of silicone systems came about through observation of an unexpected result during a routine R&D experiment.1 Milne was investigating the antifouling properties of pre-cast elastomeric (usually neoprene) rubber panels in the early 1970s, into which biocides were incorporated. Since it was inconvenient to handle these panels in the laboratory as solid rubber sheets, Milne sought an alternative method of application, in liquid form. The only materials readily available to him were a limited number of ambient-temperature-curing liquid elastomers, amongst them urethane elastomers and room-temperature vulcanising (RTV) silicone rubbers. He then observed that the non-biodegradable containing control for this series was a better antifouling than the experimental material that contained biocides. He also noted that the slime fouling which the control accumulated was remarkably non-adherent.

Following Milne’s observation, a detailed laboratory development programme commenced, testing a series of commercially available silicone elastomers for foul-release properties, with different additives.44,45 It was found that the addition of a low molecular weight silicone polymer (often referred to as a ‘silicone oil’) greatly enhanced the foul-release properties, and this was the key invention incorporated into the 1977 Milne patent. This remains the basis of most silicone foul-release systems commercially available today. Shortly after this patent was taken out, the focus of antifouling research and development effort was redirected towards exploiting the newly introduced TBT SPC systems (which, co-incidentally, were also an invention of Milne’s), and which were proving very successful commercially. So progress on commercialisation of the foul-release technology was stalled.

In the early 1980s, when the environmental problems associated with TBT SPC antifoulings were starting to appear, International’s research and development programme on foul-release technology was restarted, and focused on finding solutions to the following ‘problems’:

- Suitable anti-corrosive priming systems, to which the ‘non-stick’ silicone elastomer finish would adhere.
- Toughness and durability for use in the marine environment.
- Practicality of application (Long pot-life and shelf-life).
- Prevention of sagging when applied on vertical surfaces.
- Maintenance and repair of damaged areas.
- Suitable market end-uses.

The first application by International Coatings of their resulting product, Intersleek, was on the company yacht Artemis, based in Southampton, in 1987. The application was carried out by roller, but this produced a relatively-rough surface, which rapidly succumbed to unsightly slime fouling. This slime fouling was quickly deemed unacceptable by the skipper of the yacht and the trial was terminated. Since then, little progress has been made with the technology in the yacht market.

The first deep sea vessel application of Intersleek was also carried out in 1987, as a test patch on Selendu, a US Military Sealift Command containership. When the vessel dry-docked again in 1990, this test patch was found to be in remarkably good condition. This gave encouragement to further trials on marine vessels.

The Intersleek development programme was transferred from Newcastle to Houston in the early 1990s. There was deemed to be a greater market requirement in the USA than in Europe for this novel and ‘green’ technology, and once a proven full scheme had been found (including the antifouling system), a good many aluminium vessels in the US Coast Guard fleet were subsequently coated with Intersleek. A particular benefit of Intersleek for aluminium vessels is the absence of copper (as used in most conventional antifoulings) meaning that there is no risk of galvanic corrosion.

In 1996, one of the variants of Intersleek was introduced for the rapidly expanding fast ferry market. The high speeds of these vessels (>30kts) made them ideal for ‘self-cleaning’ and in addition there were both speed increases and fuel savings reported.46 These vessels use large quantities of expensive fuel per tonne/mile and small improvements to hull smoothness and the prevention of fouling can have immediate beneficial effects on operating costs. Many of the world’s leading fast ferry operators now use a foul-release coating.

In 1996 the well-known cruise liner Norway (formerly the France), was fully re-blasted in Southampton and Intersleek applied. As with Tropic Lure this vessel was operating in the high fouling area around Florida, and the foul-release coating proved to be equally as successful on Norway as on Tropic Lure. Other successful scale-up trials were carried out on other vessel types and so, in March 1999, a new version was launched, targeted at the high activity, high speed scheduled ship market, such as containerships, gas carriers, vehicle carriers, reefer, cruise liners and large ro-ro vessels. Since then, sales have continued steadily, reaching over $2 million in 2002, and with over 30 full ship applications carried out.

Several other vessels, such as Norway and a number of fast ferries, have completed five years in-service periods successfully. Given this ‘proof of performance’ and given the almost universal concern for protection of the marine environment, it is very likely that foul-release technology will come to dominate antifouling
technology, especially as market forces and economies of scale bring down the prices of the foul-release coatings.

**FLUID DRAG OF A FOUL-RELEASE COATING COMPARED WITH A CONVENTIONAL ABLATIVE ANTI-FOULING**

When foul-release coatings were commercially introduced in the mid-1990s and applied to a high-speed catamaran ferry, replacing a toxic controlled depletion polymer (CDP) antifoul- ing, the recorded fuel consumption was lower at the same service speed, implying lower drag characteristics as reported by Millett and Anderson, as referred to above. As a consequence a research project was set up at the University of Newcastle upon Tyne with the objective of collecting data on the drag, boundary-layer and roughness characteristics of foul-release and tin-free SPC coatings, and to compare them systematically. The coatings used were a PDMS foul-release and a tin-free copper-pigmented acrylic SPC that contained zinc pyrithione as a booster biocide.

Drag measurements were carried out in towing tank experiments with two friction planes of different size (2.5 m and 6.3 m long), which showed that the foul-release system exhibits less drag than the tin-free SPC system when similarly applied. The difference in frictional resistance varied between about 2% and 23%, depending on the quality of application as reported by Candries et al. Rotor experiments were also carried out to measure the difference in torque between uncoated and variously coated cylinders. In addition to coatings applied by spraying, a foul-release surface applied by rolling was included because there were indications that this type of application might affect the drag characteristics. The measurements indicated an average 3.6% difference in local frictional resistance coefficient between the sprayed foul-release and the sprayed tin-free SPC, but the difference between the rolled foul-release and the sprayed tin-free SPC was only 2.2.

**Boundary layer characteristics**

The friction of a surface in fluid flow is caused by the viscous effects and turbulence production in the boundary layer close to the surface. A study of the boundary layer characteristics of the coatings was therefore carried out in two different water tunnels using laser-beam two-component laser Doppler velocimetry (LDV) and the coatings were applied on 1m-long test sections that were fitted in a 2.1m-long flat plate set-up. Velocity profiles were measured at five different streamwise locations and at five different free-stream velocities. A rolled surface and a sprayed foul-release surface were tested to investigate the effect of application method. A surface covered with sand grit was tested in order to have a very rough surface comparison. The velocity loss function, $SU' = SU'/U^*$, indicates the difference in frictional resistance between a rough and a smooth surface. (Experimental precision uncertainty over a surface comparison. The velocity loss function, $SU'/U^*$, is the difference between the rollered foul-release and the sprayed foul-release, and the sprayed tin-free SPC, but the difference between the rollered foul-release and the sprayed tin-free SPC was only 2.2).

Roughness characteristics were measured using the BMT hull roughness analyser, which is the stylus instrument in common use in dry-docks or underwater, for standardised hull roughness measurement. It measures $R_6$, which is the highest peak to lowest valley roughness height over a sampling length of 50mm. Successive values are averaged over a surface. It is clear from the rotor experiments and the large plate towing tank experiments that this single amplitude param-

![Fig 10: Boundary-layer velocity profiles in inner co-ordinates at $U_c = 5m/s$ and at a streamwise location $x = 1.607m$ from the leading edge](image)

The measurements show that the friction velocity for foul-release surfaces is significantly lower than for tin-free SPC surfaces, when similarly applied. This indicates that at the same streamwise Reynolds number the ratio of the inner layer to the outer layer is smaller for foul-release surfaces. The inner layer is that part of the boundary layer where major turbulence (and hence drag) production occurs.

Statistical analysis of the values of the roughness function obtained by means of multiple pairwise comparison, using Tukey’s test, indicated that the roughness function for foul-release surfaces is significantly lower than for tin-free SPC surfaces at a 95% confidence level. These findings are consistent with the drag characteristics measured in the water tunnel and rotor experiments, as reported in Candries et al. 1

**Roughness characteristics**

In addition to the difference in frictional resistance and the roughness function, the roughness characteristics of each of the surfaces were investigated. The average values of their roughness were measured using the BMT hull roughness analyser, which is the stylus instrument in common use in dry-docks or underwater, for standardised hull roughness measurement. It measures $R_6$ ($R_6$), which is the highest peak to lowest valley roughness height over a sampling length of 50mm. Successive values are averaged over a surface. It is clear from the rotor experiments and the large plate towing tank experiments that this single amplitude param-
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eter does not correlate with the measured drag increase for foul-release surfaces, as it does with SPC surfaces.

A detailed non-contact roughness analysis was carried out with an optical measurement system fitted with a 3mW laser. Measurements were taken on sample plates coated alongside the surfaces tested in the towing tank and water tunnel, and were thus assumed representative of the test surface characteristics. In the case of the cylinders used in the rotor experiments, sections were cut from the cylinders after testing, for use in the optical measurements. A moving average was applied to filter long-wavelength curvature.

![Figure 11: Pairs of typical roughness profiles of (from bottom to top respectively) a foul-release scheme applied by spraying, a tin-free SPC scheme applied by spraying and a foul-release scheme applied by rollering. The horizontal gridlines are separated by 25 µm.](image)

The upper bandwidth limit or cut-off length was set at 2.5 and 5mm, whereas the lower bandwidth limit or sampling interval was set at 50mm. Typical roughness profiles for each type of coating are shown in Fig 11.

The detailed roughness analysis revealed that when long-wavelength curvature has been filtered out, the amplitude parameters of the sprayed foul-release surfaces are, in general, lower than those of the rolled foul-release surfaces and the SPC surfaces. However, the rolled foul-release surfaces display a roughness height distribution which is considerably more leptokurtic (i.e., exhibits a larger number of sharp roughness peaks) than the sprayed foul-release surfaces. The greater number of high peaks on the rolled foul-release surfaces is expected to engender higher drag than sprayed foul-release surfaces.

![Figure 12a: Profilogram of a foul-release surface applied by spraying](image)

![Figure 12b: Profilogram of a tin-free SPC surface applied by spraying](image)

The main difference between the foul-release and the tin-free SPC systems lies in the texture characteristics, as shown in Figs 12a and 12b for two typical roughness profilograms of such coatings, applied by spraying. Whereas the tin-free SPC surface displays a spiky ‘closed’ texture, the wavy ‘open’ texture of the foul-release surface is characterised by a smaller proportion of short-wavelength roughness. This is particularly evident in texture parameters such as the mean absolute slope and the fractal dimension. There is relatively little data available in the literature of irregularly rough surfaces on the influence of texture only on drag. Grigson50 has mentioned explicitly that open textures have a beneficial effect on drag.

**Correlation between roughness characteristics and drag of marine coatings**

It is clear that in order to correlate with drag, the roughness of the generality of irregularly rough surfaces needs to take both amplitude and texture parameters into account, e.g., Musker,51 Townsin and Dey.52 Based on the experiments presented here, it is thought that the rheology of the paint, which is significantly different for foul-release and tin-free SPC coatings, has a direct effect on its texture, whereas amplitudes depend significantly on the application quality. A correlation analysis of the texture parameters with the amplitude parameters, however, has shown that the two are inter-related, so that bad application can be expected to have a knock-on effect on the texture parameters.

At present, the procedure adopted by the International Towing Tank Committee (ITTC) to correlate roughness with drag only accounts for a single roughness amplitude parameter.11 The procedure hinges on the use of a practical formula for the added ship resistance (or roughness correlation allowance), which was proposed by Townsin and Dey12 in terms of average hull roughness for the moderately-rough ship range where R(50) is less than 230 µm. Unfortunately, this procedure may not work for foul-release surfaces, unless a texture parameter is included in the roughness characterisation. For a selection of 41 different coated surfaces, including eight newly-applied foul-release surfaces, Candries4 found that the measured drag correlated best when the roughness is characterised by the product of the average roughness height, Ra, and the mean absolute slope, Ya.

**PROPELLER COATING**

An area where foul-release coatings can offer scope for increased propulsive efficiency is the coating of propellers, as reported by Atlar.53 The effect of the propeller surface condition may be less important than
the hull surface condition but is significantly more important in terms of energy loss per unit area. In economic terms, a high return from a relatively low investment may be obtained by appropriate propeller maintenance. Based upon this idea and the fact that foul-release technology performs best at high fluid shear, the number of foul-release coated propellers has been increasing recently (Fig 13). Consequently, a long term research programme into propeller coating has been set up at the University of Newcastle upon Tyne, supported by a number of oil companies and International Coatings.

**ADVANTAGES OF THE FOUL-RELEASE COATING**

Taking a balanced and holistic view, the now-banned TBT SPC, did have some environmental and economic advantages over the antifoulings which it supplanted. Milne,\(^5^6\) in a note to a workshop on marine roughness and drag, calculated the economic advantages to the world fleet per annum, under a number of headings, namely:

- Direct fuel savings of 4% due to improved smoothness and less fouling.
- Extended dry-docking intervals.
- Improved plant utilisation.
- Savings on the reduced transport of fuel to the bunkering ports.

Assuming that the world fleet was exclusively using TBT SPC, in place of the previous non-ablative antifoulings, he calculated a total annual saving of $22,49 x 10^6, using the then current figures for fuel, dry-docking costs, etc. The changes in roughness due to the introduction of TBT SPC, he took from a survey by Townsin et al.\(^5^7\)

The consequential environmental savings were equally dramatic. The saving of 7.2 x 10^6 tonnes of fuel per annum, and which has a carbon content of 85-86%, produces 3.1 to 3.2 tonnes of CO\(_2\) per tonne of carbon, yielding a reduction of nearly 20 x 10^6 tonnes of greenhouse gas per annum.

It cannot be expected that a foul-release coating can achieve savings compared with TBT SPC, similar to the success of the latter over its predecessors. If foul-release can achieve parity in terms of smoothness and fouling control, with TBT SPC, then it also has the supremacy of non-toxicity. At present, a disadvantage is the persistence of slime on foul-release coatings, causing some fuel penalty. On the other hand, an advantage is the lifetime nature of the coating, with reduced maintenance, and the avoidance of the problem of ‘ablative polish-through’ due to inadequate application. On balance, overall, the foul-release coating can be as economically effective as TBT SPC, whilst avoiding pollution by the world fleet of 2000t of tributyltin per annum.

**CONCLUSIONS**

The authors look forward to further development as experience of these coatings on ships in-service, is acquired. Increased hardness is required, better to resist in-service surface damage, with its consequential fuel penalty (and this is relevant for all outer bottom coatings of course). There are likely to be other, increasing uses for foul-release coatings: propeller coating has been discussed above and the coating of power station cooling water uses for foul-release coatings: propeller coating has been discussed above and the coating of power station cooling water ducting is another application being developed.

It has been a privilege for the authors, having different disciplines, to discover each other’s expertise, over the years, leading to a common goal. They share some satisfaction that the goal was to replace an annual deposit of 2000t of toxin into the world’s oceans by an innocuous coating, which itself is as effective an antifouling as its predecessors.

**REFERENCES**

The development of foul-release coatings for seagoing vessels


The development of foul-release coatings for seagoing vessels


This innovative new fuel saving fouling release coating has been developed in consultation with our customers to offer an additional choice for owners and yards and to deliver optimal fuel savings, said Henrik Dyrholm, Group Product Manager at Hempel. Due to its high efficiency, the Hempasil X3+ will significantly reduce the carbon footprint of a vessel making it the ideal choice for environmentally aware shipowners, who want the best for the environment and their business. Our innovative hydrogel technology gives an additional layer of protection that remains present and stable over time.